December 2013

Investigations of Cost-Effective Biodiesel Production from High FFA Feedstock

Lesly N. Lesmes Sanchez
The University of Western Ontario

Supervisor
Dr. Anand Prakash
The University of Western Ontario

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science

© Lesly N. Lesmes Sanchez 2013

Follow this and additional works at: https://ir.lib.uwo.ca/etd

Part of the Chemical Engineering Commons

Recommended Citation
https://ir.lib.uwo.ca/etd/1816

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact tadam@uwo.ca, wlswadmin@uwo.ca.
INVESTIGATIONS OF COST-EFFECTIVE BIODIESEL PRODUCTION FROM HIGH FFA FEEDSTOCK

(Thesis format: Integrated Article)

by

Lesly Natalia Lesmes Sanchez

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Engineering Science

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

© Lesly Natalia Lesmes Sanchez 2013
ABSTRACT

Commercial production of biodiesel from refined vegetable oils has been widely practiced. However, more economic raw materials are required in order to make biodiesel competitive in the fuel market. This is a challenge since low-cost lipid feedstock contains high concentrations of free fatty acids (FFA) and water, which inhibit transesterification. This work investigates new catalyst combinations and method configuration to develop a cost-effective and suitable process utilizing refined canola oil and canola oil with high oleic acid content. Results suggest that potassium carbonate is more tolerant to water in the feed and enhances phase separation when compared to traditional catalyst, potassium hydroxide. A semi-batch reactor operating mode was tested and compared to conventional batch in two-step esterification-transesterification process to investigate mixing effects. Based on experimental results, esterification conversion close to 99% is achieved by using sulphuric acid as catalyst and a biodiesel yield of 93.6% is obtained after transesterification employing a combination of potassium carbonate and potassium hydroxide as catalysts. Chemical characterization revealed that the two-step process is effective in the production of biodiesel from high FFA feedstock leading to an up to standard quality product.

Keywords: Biodiesel, transesterification, esterification, low-quality feedstock, semi-batch
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor Dr. Anand Prakash for his support, guidance, valuable contributions, and constructive comments during the course of my Master program. I am very thankful that I had the opportunity to work with him and learn from him.

I would like to express my gratitude to Caitlin Marshal for her time and training on the GC-MS. Without her help, I couldn’t have gotten an important piece of my research. I appreciate the time she spent fixing the equipment and answering my questions. Special thanks to Muhammad Amin for his suggestions and advice on analytical techniques. I would also like to thank Soheil Afara for allowing me to use his laboratory equipment.

My thanks are also extended to my friends, Juan Restrepo, Ana Aguirre, Gabriela Navarro, and Luis Luque for our coffee breaks, and for making this journey more enjoyable.

Finally, I would like to thank my parents, Alfredo Lesmes and Nubia Sanchez, for guiding me, and sharing my challenges and frustrations. Thanks to my sisters and best friends, Caterin Lesmes and Erika Lesmes, for being there for me in good and bad times. Most importantly, I thank my husband, Diego Cufiño, for providing me with love and continuous encouragement throughout this work. They all have always been a source of support and I am extremely lucky to have them in my life.
TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ ii

ACKNOWLEDGEMENTS ................................................................................................................. iii

TABLE OF CONTENTS ................................................................................................................ iv

LIST OF FIGURES .......................................................................................................................... viii

LIST OF TABLES ............................................................................................................................. x

LIST OF APPENDICES .................................................................................................................... xi

LIST OF ABBREVIATIONS .............................................................................................................. xii

CHAPTER 1 ....................................................................................................................................... 1

1 Introduction ................................................................................................................................. 1

1.1 Objectives .................................................................................................................................. 3

1.2 Thesis Format and Structure .................................................................................................... 4

1.3 References ............................................................................................................................... 6

CHAPTER 2 ....................................................................................................................................... 7

2 Literature Review ....................................................................................................................... 7

2.1 Background .............................................................................................................................. 7

2.2 Advantages and Disadvantages of Biodiesel ......................................................................... 9

2.3 Biodiesel Production ............................................................................................................... 10

2.4 Transesterification .................................................................................................................. 11

2.4.1 Alkaline-catalyzed System ................................................................................................. 14
2.4.2 Acid-catalyzed System ................................................................. 17

2.4.3 Non-catalyzed System ................................................................. 19

2.4.4 Reaction parameters ................................................................. 19

2.5 Esterification ................................................................................. 23

2.6 Two-step Process ........................................................................... 25

2.7 Feedstock for Biodiesel Production ................................................. 27

2.7.1 Non-edible oils ........................................................................... 28

2.7.2 Waste edible oils ......................................................................... 29

2.7.3 Algal oils .................................................................................. 29

2.8 Reaction Medium ........................................................................... 30

2.9 Biodiesel Properties and Standards ................................................. 31

2.10 Economics and Commercialization Issues ....................................... 33

2.11 Concluding Remarks .................................................................... 35

2.12 References .................................................................................. 36

CHAPTER 3 .......................................................................................... 41

3 Transesterification of Refined Canola Oil .............................................. 41

3.1 Introduction .................................................................................. 41

3.2 Experimental Details ....................................................................... 44

3.2.1 Materials and Chemicals ............................................................ 44
4.2.3 Reaction Procedure ................................................................. 87

4.2.4 Analysis of final product .......................................................... 92

4.3 Results and Discussion ............................................................... 93

4.3.1 Esterification Reaction .............................................................. 93

4.3.2 Purification of Esterified Oil ...................................................... 99

4.3.3 Transesterification Reaction ...................................................... 101

4.4 Conclusions .............................................................................. 105

4.5 References .............................................................................. 107

CHAPTER 5 ..................................................................................... 108

5 Conclusions and Recommendations ............................................. 108

5.1 Summary and Conclusions ......................................................... 108

5.2 Recommendations for Future Work .......................................... 109

APPENDICES ................................................................................. 111

CURRICULUM VITAE .................................................................... 116
LIST OF FIGURES

Figure 2.1 Fatty acid alkyl esters production through different routes (adjusted from [11]) ................................................................. 11

Figure 2.2 Mechanism of Fisher esterification reaction by methanol [47] .................... 25

Figure 2.3 Progression of biodiesel reaction over time using conventional base-catalyzed transesterification [62] ................................................................. 31

Figure 3.1 Experimental set up for transesterification .................................................. 45

Figure 3.2 Process flow diagram for transesterification .............................................. 48

Figure 3.3 Chromatogram of refined canola oil ......................................................... 53

Figure 3.4 Comparison of triglyceride conversion during transesterification A) Literature studies B) Operating modes used in this work ......................................................... 65

Figure 3.5 Methyl ester content during transesterification catalyzed by 1% KOH at 60°C ................................................................................................. 67

Figure 3.6 TG content using batch and semi-bach method ........................................ 68

Figure 3.7 Concentration profile for glycerides using semi-batch mode .................... 69

Figure 3.8 Concentration profile for glycerides using batch mode ........................... 69

Figure 3.9 Effect of temperature on product and by-product yield using 1% KOH under semi-batch mode .............................................................. 73

Figure 3.10 Glycerides concentration profile for KOH-catalyzed transesterification at 30°C ........................................................................................................... 74

Figure 3.11 Glycerides concentration profile for KOH-catalyzed transesterification at 60°C ........................................................................................................... 75
Figure 3.12 Methyl ester content for KOH-catalyzed transesterification at different temperatures ................................................................. 76
Figure 3.13 Density and viscosity measurements for different types of alcohols ........ 79
Figure 3.14 Glycerol and biodiesel yield for different types of alcohol ................. 79
Figure 4.1 Experimental setup for biodiesel synthesis ........................................ 87
Figure 4.2 Block flow diagram for esterification step ....................................... 89
Figure 4.3 Block flow diagram of purification steps for esterified oil .................. 91
Figure 4.4 Block flow diagram for transesterification process ......................... 92
Figure 4.5 Comparison of batch and semi-batch method based on reaction progress (Initial FFA:6%) ................................................................................................................... 95
Figure 4.6 Comparison of esterification reaction progress obtained with the two methods for high initial FFA and increased agitation ......................................................... 96
Figure 4.7 Change in FFA content with time for different initial FFA values ......... 97
Figure 4.8 Comparison between 5% and 10% catalyst concentration ................. 98
LIST OF TABLES

Table 2.1 Recommended FFA level for homogeneous alkali-catalyzed transesterification [51] ............................................................................................................................................................... 27

Table 2.2 Estimated oil yield of non-edible oils [58] .................................................................................................................. 28

Table 2.3 American and European biodiesel standards for vehicle use (from [65]) ............ 32

Table 3.1 Operating conditions during transesterification of vegetable oils .................... 66

Table 3.2 Biodiesel GC Report for Semi-batch and Batch. Conditions: 60oC, 6:1 MeOH to oil molar ratio, 1%KOH .................................................................................................................................................. 70

Table 3.3 Final product analysis using Semi-batch and Batch mode ............................. 71

Table 4.1 Mass percentage of methyl ester, bound and free glycerol in purified biodiesel samples .................................................................................................................................................. 104
LIST OF APPENDICES

Appendix A – Biodiesel and Diesel Properties ................................................................. 111
Appendix B – Material Balances ....................................................................................... 112
Appendix C – Esterification Reaction Calculations ......................................................... 113
Appendix D – GC Analysis ................................................................................................. 114
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American Standards for Testing and Materials</td>
</tr>
<tr>
<td>B</td>
<td>Batch</td>
</tr>
<tr>
<td>BD</td>
<td>Biodiesel</td>
</tr>
<tr>
<td>CEN</td>
<td>European Committee for Standardization</td>
</tr>
<tr>
<td>DG</td>
<td>Diglycerides</td>
</tr>
<tr>
<td>FAAE</td>
<td>Fatty Acid Alkyl Ester</td>
</tr>
<tr>
<td>FAEE</td>
<td>Fatty Acid Ethyl Ester</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty Acid Methyl Ester</td>
</tr>
<tr>
<td>FFA</td>
<td>Free Fatty Acid</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>GL</td>
<td>Free Glycerol</td>
</tr>
<tr>
<td>IS</td>
<td>Internal Standard</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium Hydroxide</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>Potassium Bicarbonate</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>Potassium Carbonate</td>
</tr>
<tr>
<td>ME</td>
<td>Methyl Ester</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MG</td>
<td>Monoglycerides</td>
</tr>
<tr>
<td>MSTFA</td>
<td>N-methyl-N-trimethylsilyl trifluoracetamide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl tert-butyl ether</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>SB</td>
<td>Semi-Batch</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Sulphuric Acid</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TG</td>
<td>Triglycerides</td>
</tr>
<tr>
<td>VO</td>
<td>Vegetable Oil</td>
</tr>
</tbody>
</table>

**Greek Letters**

<table>
<thead>
<tr>
<th>Greek Letter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$</td>
<td>Dynamic Viscosity (Pa·s)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density (g/ml)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Kinematic Viscosity (mm$^2$/s)</td>
</tr>
</tbody>
</table>
CHAPTER 1

1 Introduction

Demands for energy and fuel are rapidly growing due to increases in population, industrialization and economic development. Currently, their supply is highly dependent on non-renewable sources such as oil, natural gas, and coal. In 2010 and 2011, global energy consumption increased 5.1% and 2.5% respectively, with fossil fuels representing 87% of market share [1]. Meeting future energy demands with continued limited resources has been acknowledged to be unsustainable. Additionally, the over consumption of these fuels has raised concerns on energy security, depletion of reserves, environmental pollution, and negative human health impact. To assess some of these issues, extensive research on renewable energy has been conducted on different areas including hydro, wind, solar, geothermal, and biomass. One of the most viable alternatives is the use of fuels derived from biomass as they provide a convenient mean for distribution due to their liquid state. Biodiesel is one such biofuels considered to be the only renewable energy source as a substitute for fossil diesel [2]. It can be easily implemented and used directly in existing compression-ignition engines with little or no modification [3, 4]. Among its various environmental advantages are: reduction of carbon monoxide, hydrocarbon, particulate matter, and sulphur oxides emissions; its biodegradable and non-toxic properties, and its contribution to rural development. For these reasons, there is a growing interest in expanding the biodiesel industry worldwide.
Biodiesel, defined as a mixture of mono-alkyl esters of long-chain fatty acids, is derived from a lipid source through transesterification or also referred as alcoholysis. The chemical reaction occurs between a triglyceride (TG) and a short chain alcohol in the presence of a catalyst in three consecutive steps, producing monoglycerides (MG) and diglycerides (DG) as intermediates. Suitable alcohols include methanol, ethanol, propanol, and butanol with methanol being commonly employed due to low cost and wide availability [4]. Generally, a catalyst is required when conducting transesterification at mild operating conditions. Alkaline and acidic materials have been widely investigated and found to be efficient in assisting alcoholysis. However, alkali-catalyzed reactions are characterized by having a high reaction rate under mild operating conditions [5, 6]. Nonetheless, this is subjected to highly refined vegetable oils. As a result, researchers have recommended the use of alkali metals in the carbonate form to conduct alcoholysis of low quality oils in the presence of free fatty acids [7]. Other studies have focused on the development of heterogeneous acid and alkaline catalyst to simplify purification steps [8-10].

Nowadays, refined edible oils are widely used as the primary raw material in the biodiesel industry. The use of high value food-grade vegetable oil in transesterification often results in high purity biodiesel but limits its commercialization as production costs are high. It has been reported that the cost of feedstock constitutes 60-80% of the overall cost in the production process [11]. To develop an economically convenient process, animal fats, algal oils, waste oils, non-edible oils have been proposed as alternative feedstock. However, their high free fatty acid and moisture content promote side reactions such as hydrolysis and saponification; thereby decreasing product yield.
Extensive research has been conducted on different approaches for improving biodiesel production from high-acid number oils [12-14]. One of the most viable alternatives is an integrated two-step process in which an acid pre-esterification treatment is carried out followed by transesterification using an alkaline catalyst.

Even though commercialization of biodiesel has expanded around the world, the production process still faces some challenges, especially when low grade raw materials are used. Emulsion formation, soap formation, incomplete reactions, and product purification are some aspects that need to be considered in order to optimize biodiesel synthesis. Attempts have been made to overcome mass transfer limitations by different ways such as increasing mixing intensity, by changing reactor mode of operation or using co-solvents [15-17]. Problems of emulsion and soap formation can be avoided by appropriate feed pretreatment to reduce free fatty acid (FFA) and moisture contents to acceptable levels [11, 12].

1.1 Objectives

This report aims to investigate cost effective methods to produce biodiesel from feedstock with high free fatty acid content. A main objective is to reduce processing steps to lower cost of operation and improve yield by appropriate selection of low cost catalysts (and their combination), low operating temperature and low power consumption for reactants mixing. The improvements will be monitored by comparing the results with conventional approaches reported in literature.
1.2 Thesis Format and Structure

This thesis is presented in the format of integrated-article as specified by the School of Postdoctoral Studies of the University of Western Ontario. The body of this work is written as technical papers without an abstract. Individual chapters have their own bibliographic section.

The contents of this work have been organized in five chapters. Chapter 1 includes a general introduction. In Chapter 2, Literature Review, main advantages of disadvantages of using biodiesel as a substitute of conventional diesel are described. This chapter discusses biodiesel production processes used at a commercial scale including transesterification and esterification as well as the reaction mechanisms and reaction parameters. Furthermore, economic regulations and fuel characteristics are presented to understand the penetration of biodiesel in the fuel market.

In Chapter 3, Transesterification of Refined Canola Oil, the effect of reaction parameters on biodiesel and glycerol yield is investigated under two operating reactor modes: batch and semi-batch. Additionally, the catalytic activity of traditional potassium hydroxide and non-conventional potassium carbonate is studied with the aid of GC analysis. Other transesterification processes are tested including the use of inert co-solvent, and use of ethanol.

In Chapter 4, Esterification and Two-Step Process, acid pre-treatment of oil with 6% and 15% FFA with sulphuric acid under batch and semi-batch is investigated. Results show that semi-batch is a better method when compared to conventional batch achieving high conversion. Then, an integrated process is recommended for biodiesel production from
raw materials with 15% FFA employing sulphuric acid in the first step and a combination of potassium hydroxide and potassium carbonate in the latter step. The experiments are assessed based on biodiesel and glycerol yield, density, and viscosity of the final product.

In Chapter 5, *Conclusions and Recommendations*, major findings are presented outlining contributions of this work. Finally, recommendations for future work are discussed.
1.3 References

CHAPTER 2

2 Literature Review

2.1 Background

The utilization of vegetable oils in combustion engines originated in the 19th century by Rudolph Diesel. The inventor of the compression-ignition engine used straight peanut oil as a fuel in a demonstration in Paris. During Second World War, Germany, Japan, Italy, France, China, and United Kingdom tested different types of vegetable oils as biofuels from time to time [1]. However, due to low cost and unlimited supply of petroleum, the biofuel industry did not evolve. In addition, technological advancements led to the creation of smaller diesel engines, which required low viscosity fuels [2]. Later on, the oil crisis in 1970s and the Gulf war in 1991 revived the interest on renewable sources to reduce dependence on mineral oil. More recently, concerns on global warming, energy security, shortages in petroleum supply and environmental degradation have led to extensive research on alternative fuels. Animal fats, vegetable oils (VO) and its derivatives have gained importance as substitutes for conventional diesel.

Direct use of plant oils in diesel engines seems attractive due to its biodegradability, non-toxic nature, and relatively high heat content (80% of diesel fuel) [3] but it is impractical due to high viscosity values (10-20 times higher than No. 2 diesel fuel) and low volatilities [4]. Issues such as deposit formation in injection systems from poor atomization in the combustion chamber, oil ring sticking and thickening, and gelling of the engine lubricant oil are problematic and affect the performance of engines as well as
their durability. Several methods for low-viscosity formulations have been developed to improve the combustion characteristics of VO. Pyrolysis, transesterification, dilution, and microemulsification are some examples that can be employed to produce fuels [2].

Dilution of plant oils can be accomplished by using diesel fuels or ethanol up to 25% by volume to reduce viscosity to an acceptable range. It does not affect the chemical composition of the raw material but it is not recommended for long term usage due to lubricant thickening [4]. Pyrolysis, a thermochemical conversion process in the absence of oxygen, has shown to be effective in reducing the viscosity of vegetable oils. However, the process requires large amounts of energy and leads to the production of a variety of compounds due to low selectivity. In addition, pyrolitic oil has a high content of ashes, carbon deposits, and high pour point [4]. Microemulsions are thermodynamically stable dispersions of oil, water, surfactant and a co-surfactant [5]. Microemulsification does not alter the chemical composition of the oil; nonetheless, the use of emulsions has shown lower energy content, lower cetane number, heavy carbon deposits, and incomplete combustion. Finally, transesterification is an equilibrium chemical reaction that reduces the viscosity of vegetable oils 10 times by using an aliphatic alcohol. To date, transesterification has been the most common method employed to produce high quality biodiesel due to its simplicity and low cost [3].

With the implementation of new energy policies and governments ambitious energy goals, biofuel production and consumption has grown rapidly over the years. In September 2005, Minnesota became the first U.S. state to require all 5% biodiesel content in conventional petro-diesel. Moreover, the European Union aimed for voluntary biodiesel inclusion by 2010 and intends to make it mandatory by 2020 [2]. The Canadian
government has also announced the addition of 2% biodiesel content in diesel distillates by 2015 and plans to invest $2 billion to build up renewable fuels production capacity. In order to satisfy Canadian mandates, without significant imports, production of biodiesel must increase 450% [6]. In addition, second and third generation feedstock have been taken into account as edible oils cannot realistically satisfy biodiesel demand.

### 2.2 Advantages and Disadvantages of Biodiesel

Biodiesel possess many environmental benefits over petroleum diesel fuel. In terms of emissions levels, it reduces carbon monoxide by 48%, particulate matter by 47%, unburned hydrocarbons by 67%, polycyclic aromatic hydrocarbons by 80%, nitrated polycyclic aromatic hydrocarbons by 90%, and sulphur oxide by 100% [7]. Life cycle analysis of 100% biodiesel has reported zero carbon dioxide emissions considering carbon dioxide life cycle during cultivation, production, and conversion of oil [7]. Biodiesel also reduces petroleum dependency and enhances energy security. Oilseed crops can be grown in both developed and developing countries; therefore, it can be produced domestically decreasing petroleum imports from politically unstable regions.

The risks associated with handling, storing, and transporting biodiesel are lower due to its higher flash point and higher biodegradability; it degrades about four times faster than diesel [8]. This makes biodiesel even a more attractive alternative as petroleum oil spills have become a major source of contamination and have led to loss of animal life. Biodiesel can be blended with conventional diesel and used in compression ignition engines with minimum or no modifications depending on the proportion of biofuel added. Furthermore, it has a greater lubricity than petro-diesel which reduces corrosion in
engines and increases durability [9]. Finally, due to oxygen content in the chemical structure, combustion properties are better.

Major drawbacks associated with biodiesel include higher cloud point and pour point, lower energy content (10% less than diesel), higher NOx emissions, and higher viscosity [8]. More importantly, high production cost limits its commercialization. Industrial biodiesel production is not profitable without government supportive tax incentives and subsidies at current petroleum prices. This is mainly due to heavy start-up costs and high feedstock price, which accounts for almost 80% of total production costs [10]. The utilization of alternative low-quality raw materials could make biodiesel more economically viable.

2.3 Biodiesel Production

There are different chemical routes to produce biodiesel (alkyl esters) as shown in Figure 2.1. However, commercial synthesis of FAAE only occurs from direct esterification of FFA or transesterification of TG [2]. Feedstock quality, type of catalyst, and operating conditions dictate the process and technologies used. Generally, the path followed using refined edible vegetable oils involves transesterification, recovery of excess alcohol, separation of glycerol from ester-rich phase, neutralization of catalyst, and purification of FAAE. Extensive research has been carried out to optimize the overall process, but transesterification reaction has been a priority in many studies.
Biodiesel production has had a significant impact worldwide especially in Europe, and North America. The European Union has been the leader in production of alkyl esters creating an industry that has grown and succeed over the years. Agricultural subsidies and tax-exemption on biodiesel are major drivers for its commercialization. In addition, high taxes on gasoline and diesel are incentives to produce more renewable fuels. On the other hand, industrial production of biodiesel in North America is still not economically viable due to low taxes on petroleum-based fuels and high raw material cost. However, the implementation of Clean Air Act in 1990 and the Energy Policy Act of 1992 has driven more attention towards the manufacturing of biodiesel.

### 2.4 Transesterification

Transesterification or alcoholysis is a reversible chemical reaction of a vegetable oil, animal fat, or algal oil (mainly composed by triglycerides) with an aliphatic alcohol generally conducted in the presence of a catalyst to form fatty acid alkyl esters and
glycerol. Triglycerides are esters of three long chain fatty acids link to a glycerol backbone. Oils from different sources vary in their fatty acid profile in relation to carbon chain length and number of double bonds in the molecule. In this context, transesterification does not alter the composition of fatty acid of the raw material; thus, the FAAE produced reflects the composition of the parent oil. The overall reaction is illustrated in Reaction 2.1.

Stoichiometric coefficients indicate that the reaction requires 3 moles of alcohol for every mole of TG; however, the process is carried out with excess alcohol to drive the equilibrium towards the products side. Transesterification occurs in a three consecutive reversible reactions in which monoglycerides (MG) and diglycerides (DG) are formed as intermediates and glycerol as a by-product. In each step, a mole of fatty acid alkyl ester is produced, as shown in Reaction 2.2, 2.3 and 2.4. It is important to note, that intermediates are considered as contaminants in the final product.
A catalyst is often required during transesterification to increase the reaction rate. Different types have been investigated including homogeneous [12-15], heterogeneous [16-18], enzymes [19-22] and in some cases no catalyst at extreme operating conditions.
Most commercial processes use acid and alkali catalysts with the latter being preferred due to low reaction times, mild operating conditions, and higher conversions. However the selection of catalyst is dependent on the amount of FFA and water in the feed. Alkaline-catalyzed reactions are inhibited by FFA due to saponification as shown in Reactions 2.5 and 2.6. Soap formation can also result from hydrolysis of esters including TG, DG, MG and FAAE.

\[
\begin{align*}
R_1COOR + H_2O & \rightleftharpoons R_1COOH + ROH & \text{(R2.5)} \\
R_1COOH + M-OH & \rightleftharpoons R_1COONa^+ + H_2O & \text{(R2.6)} \\
M = \text{Alkali metal (i.e. Na, K)}
\end{align*}
\]

### 2.4.1 Alkaline-catalyzed System

Producing biodiesel with a strong homogeneous basic catalyst is the oldest and most common method used in industry. The main advantage of this type of catalysts is that transesterification proceeds almost to completion at short reaction times and under mild conditions, usually at temperatures between 40 and 65°C and atmospheric pressure [4]. In addition, bases are less corrosive than acidic catalysts. Some examples include sodium and potassium alkoxides, their corresponding hydroxides, carbonates, amides and hydrides [2]. While, sodium and potassium alkoxides have been found to be the most effective, hydroxides have been predominant due to their low cost and ease of use.

The major disadvantage associated with this type of catalysts is that they are sensitive to the quality of the reactants used. Moisture and FFA content in the feed strongly
influences the rate of reaction due to unwanted side reactions as previously discussed. The formation of soap not only lowers the yield of esters but also increases viscosity, promotes gel formation and creates emulsions, making the separation of glycerol and biodiesel difficult. To overcome these problems, an acid catalyst can be used, especially if the FFA content is greater than 1%. Acid catalysts are also capable of performing simultaneous transesterification and esterification. However, the reaction is about 4000 times slower \[25\], a higher ratio of alcohol to oil is often required, and the temperature and pressure conditions are generally higher when compared to the alkaline catalytic process.

Base alcoholysis proceeds in a sequence of 4 steps. First, metal hydroxide or carbonate ionizes to some extent in pure state alcohols leading to the formation of active species (i.e. methoxide, ethoxide) and protonated catalyst as follows:

\[
MOH + ROH \leftrightarrow RO^- + M^+ + H_2O \quad (R2.7)
\]

\[
M_2CO_3 + ROH \leftrightarrow RO^- + M^+ + HMCO_3 \quad (R2.8)
\]

Then, a nucleophilic attack of the RO⁻ on the carbonyl group of the TG molecule takes place leading to the formation of a tetrahedral intermediate. The third step involves the formation of FAAE and a DG anion. Finally, proton transfer from the alcohol to the ion occurs producing a DG molecule and regenerating the active species. Likewise, DG and MG are converted into a mixture of FAAE and glycerol. The mechanism is illustrated in Figure 2.1.
Figure 2.1 Mechanism of alkali-catalyzed transesterification of triglyceride with methanol

Transesterification of vegetable oils under the presence of a homogeneous base catalyst has been extensively reported. Freedman et al. found conversions of 98% using 1% sodium hydroxide for 1 hour reaction time [26]. However the shortcomings of base-catalyzed systems are well known: high energy demand, water intensive due to downstream treatment to remove the catalyst from the ester-rich phase, difficulty in glycerol recovery, and unwanted side reactions. Development on heterogeneous system might alleviate some of these issues; nonetheless, the economic viability of biodiesel production is affected by high operating costs [27].
2.4.2 Acid-catalyzed System

Transesterification can also be carried out under the presence of an acid catalyst. It is a relatively inexpensive choice and it has been gaining great importance in the last years due to the wide resources and characteristics of feedstock available. Brønsted acids such as hydrochloric acid, sulphuric acid, phosphoric acid, and sulphonic acids are preferred. Although transesterification reaction using acid catalyst is considerably slower with respect to alkaline catalyst, this can be remedied if more alcohol is added and operating conditions are changed to higher temperatures and pressures, though it may increase the production cost. Typical temperature conditions for an acid-catalyzed system are above 100°C with reaction times longer than 3 hours to reach complete conversion [28]. Moreover, biodiesel production using acid-catalyzed reactions do not produce soap as a by-product despite the FFA content of the lipid raw materials. This system is also capable of conducting both transesterification of TG and esterification of FFA to enhance alkyl ester formation. This property of the acid catalysts makes it a viable option for feedstock with a high FFA content (3-20%); as not as much equipment and energy are required. It should be noted, that moisture also inhibits production of biodiesel under acidic conditions. Water content in the starting feedstock or alcohol rapidly deactivates the catalyst hindering the production of active species.

Major drawbacks of homogeneous acid-catalyzed system are long reaction times; acid catalysts are corrosive and tend to attack double bonds in the triglycerides leading to the formation of unwanted products such as dialkyl ethers and glycerol ethers [11]; neutralization processes are required leading to large amounts waste water.
The chemical pathway for acid-catalyzed transesterification, shown in Figure 2.4, occurs in sequence of steps. The first step involves protonation of the carbonyl oxygen, which increases the electrophilicity of the carbon atom making it more susceptible to a nucleophilic attack [29]. Then, the alcohol attacks the carbonyl and loses a proton forming an intermediate. DG molecule and a protonated FAAE are formed in the splitting process. Finally, the ester loses a proton and leads to the final FAAE molecule. The sequence is repeated on the DG and MG molecules to obtain a mixture of FAAE and glycerol.

Figure 2.2 Mechanism for acid-catalyzed transesterification of triglycerides with methanol
2.4.3 Non-catalyzed System

Transesterification can be conducted in a free-catalyst environment via co-solvent-assisted or supercritical alcohol processes [30]. The use of inert co-solvents was first proposed by Boocock and his team at the University of Toronto to promote one-phase methanolysis of vegetable oils [31]. Mass transfer resistances between alcohol and oil are eliminated resulting in high purity biodiesel. BIOX corporation has developed a process in which tetrahydrofuran (THF) and methyl tert-butyl ether (MTBE) are used as co-solvents in a non-catalyzed system eliminating the need for water washing and filtration for both glycerol and ester rich phases [30].

Supercritical transesterification using different alcohols in non-catalytic systems have been reported [32-34]. Saka and co-workers [35] were pioneers in producing methyl esters from rapeseed oil in a supercritical process without any catalyst. Their experimental work showed that almost complete conversion was achieved in 240s at 1:42 oil to methanol molar ratio and 350°C. Warabi et al. [36] studied the transesterification of triglycerides and esterification of fatty acids in rapeseed oil under supercritical conditions employing methanol, ethanol, 1-propanol, 1-butanol, and 1-octanol. The highest yield (almost 100%) was obtained after 15 min using methanol as the alcohol at 300°C. Although non-catalytic processes are attractive, it is not economically viable due to harsh operating conditions.

2.4.4 Reaction parameters

Nowadays, most industrial transesterification processes are carried out in a batch or a continuous stirred tank reactors at temperatures between 60°C and 200°C using a homogeneous alkali or acid catalysts. The operating conditions are directly related to the
nature of the feedstock, alcohol and catalyst type. The reaction parameters affecting the extent and rate of completion are as follows:

2.4.4.1 Alcohol type

The use of methanol, ethanol, propanol, and butanol in transesterification of vegetable oils has been well documented [37-41]. However, production of alkyl esters from longer chain alcohols is possible but uneconomical as their price is higher and production processes are more complex and energy intensive. In addition, as the number of carbon atoms increases in a molecule, the hydroxyl group loses importance in relation to the alkyl group making it less reactive. [11] Generally, linear short chain alcohols are preferred as they react faster than the corresponding branched types. Of those, methanol is predominantly used due to its low cost and wide availability. Though, it is toxic, hygroscopic, and it is produced from non-renewable sources. Ethanol, on the other hand, has low toxicity and can be generated from renewable resources, which makes the manufacturing of biodiesel more environmentally friendly. Major shortcomings of ethyl ester production involve the need for anhydrous alcohol to obtain high yields and formation of very stable emulsions that inhibit phase separation [42]. Ethanol is more hygroscopic than methanol and thus, more susceptible to soap formation. Drying the alcohol before transesterification requires the need for expensive and sophisticated equipment leading to a significant increase in costs. With this in mind, methanolysis of vegetable oils is more advantageous than ethanolysis from an economic and technical perspective.
2.4.4.2 Alcohol to oil ratio

Alcohol to molar oil ratio is among the most important parameters that affect the yield of fatty acid alkyl esters. As previously mentioned, transesterification, as a reversible reaction, should be carried out with excess of alcohol to displace the equilibrium towards the products side. In general, at higher molar ratios higher TG conversions are achieved. However, there is an upper limit to alcohol concentration as large amounts can delay the glycerine/methyl ester separation and increase production costs. Optimum alcohol to oil molar ratios should be determined experimentally for specific raw materials and catalyst employed in the process. Typical molar ratios for alkali-assisted methanolysis vary between 4.5:1 – 8:1, and for acid-catalyzed process up to 30:1 [26].

2.4.4.3 Catalyst type and concentration

Catalyst type and concentration are critical in determining the rate of reaction, conversion, purity of alkyl esters, and downstream processing steps. Alkaline homogeneous catalysts are efficient and widely employed in industrial processes mainly due to fast reaction rates. However, their primary limitation is the need for high quality raw materials and the anhydrous nature of both oil and alcohols. The high cost associated with alkali-transesterification, limits the commerciality of biodiesel. For this reason, other types of catalysts have been studied (i.e. acid, enzymes). Removal of acid and base homogeneous catalyst is technically difficult and results in large amounts of wastewater produced [43]. Research has been carried out in the development of heterogeneous systems. Some examples of solid basic catalysts include sodium and potassium carbonates, bicarbonates, phosphates; calcium and magnesium oxides, and their corresponding carbonates, and zinc oxide. Arzamendi et al. [44] investigated the catalytic
activity of some of the above compounds in the methanolysis of sunflower oil and found that most of them have lower reactivity when compared to their corresponding hydroxides. However, potassium carbonate showed high reactivity whereas and sodium carbonate and sodium sulphate resulted in moderate catalytic activity. Solubility in methanol and strong basicity of surface sites are key variables in formation of methyl esters. Regarding solid acid catalyst, numerous compounds have been tested including a variety of zeolites, ion exchange resins, superacid solids as WO$_3$ on zirconia, and sulphated oxides [44].

Typical concentration for homogeneous base-catalyzed process vary between 0.5%-1.0% (based on the weight of oil) [26]. However, when FFA content is higher than 1%, more catalyst should be added to neutralize the acids and obtain relatively high conversions. This has a negative impact on glycerol phase and yield of esters due to soap formation. Increasing catalysts loadings adds extra cost and complicates to purification of alkyl esters.

2.4.4.4 Reaction temperature

The rate of reaction is strongly affected by reaction temperature. Given enough time, alcoholysis of triglycerides under basic conditions can proceed to near completion even at ambient temperatures [2]. There is usually a trade-off between reaction time and reaction temperature. With this in mind, in order to reduce production costs, most commercial processes are conducted between 50°C and 70°C within one hour. The temperature is limited to the boiling point of the alcohol for atmosphere-pressure base catalyzed reactions. For instance, methanolysis above 60°C accelerates evaporation of alcohol and increases saponification reaction at a much higher rate, which is undesirable. Acid-
catalyzed systems are often carried out at higher temperatures (100°C – 120°C) and higher pressures. Under these conditions transesterification and esterification can occur simultaneously for low quality raw materials. In a catalyst-free system, reaction temperatures are about 350°C.

2.4.4.5 Mixing and mass transfer

Transesterification of triglycerides by methanol and ethanol take place as a two-phase reaction, as oils or fats are immiscible with these alcohols at mild operating conditions. Therefore, mixing is critical at a stage in which there is poor diffusion between the two liquid phases. Mixing intensity was investigated by Noureddini and his research group. Their findings concluded that higher mixing intensities favour the formation of alkyl esters. At 600rpm mass transfer limitations were almost non-existent [45]. Mass transfer resistances are predominant in the first stage of the transesterification, but once alkyl esters are formed the reaction medium transforms into an emulsion that leads to a one-phase reaction. This is also promoted by the appearance of mono- and di-glycerides, which are emulsifying agents [11]. At this point mixing intensity is no longer a critical parameter for methyl ester formation. Zhou et al. [46] noticed that emulsions produced from ethanolysis of vegetable oils are more stable than those produced from methanolysis. This can be beneficial to the mass transfer process during transesterification but disadvantageous to phase separation.

2.5 Esterification

Esterification, also known as Fischer esterification, has played a significant role in the chemical industry in the production of esters for plasticizers, fragrances, adhesives, and lubricants [47]. It is also an alternative chemical route to produce FAME from FFA as
previously shown in Figure 2.1. This process is generally conducted under the presence of an acid catalyst and low molecular weight alcohols. The chemical reaction is shown in Reaction 2.9.

\[ FFA + ALCOHOL^{cat} \leftrightarrow FAAE + WATER \quad \text{(R2.9)} \]

Formation of alkyl esters is favored by the continuous removal of water from the system, as it is a reversible reaction. A variety of catalyst can be used but inorganic acids such as H\(_2\)SO\(_4\), HCl, and, H\(_3\)PO\(_4\) are preferred due to high catalytic activity, efficiency, and low cost. In the same way, various alcohols can esterify carboxylic acids; however, straight-chain alcohols are primarily used due to a higher reaction rates when compared to branched-chain structures [47]. The mechanism for fisher esterification is a variant of acid-catalyzed transesterification and occurs in a sequence of 4 steps as shown below.
Esterification can be used as a pretreatment, prior to transesterification, to convert fatty acid oil contaminants to biodiesel to avoid saponification. By doing this, biodiesel yield would be considerably increased when low-quality oils are used as feedstock. When producing alkyl esters at drastic operating conditions, esterification is capable of converting both TG and FFA into FAAE simultaneously.

### 2.6 Two-step Process

Different approaches have been considered to produce biodiesel from low quality feedstock. As previously mentioned, base-catalyzed systems are greatly affected by impurities in the feed, especially FFA and water, reducing product yield and obstructing
phase separation. On the other hand, acid catalyzed systems are more tolerant to the presence of FFA but still the reaction rate is hindered by moisture. Moreover, high operating conditions and reaction times are required in order to obtain a fuel that meets ASTM and EN standards. One approach is to conduct a two-step esterification transesterification process to take advantages of both types of catalysts and avoid soap formation and slow reaction times. In the first step, low quality oils are pretreated using an acid catalyst to convert FFA into FAAE under mild operating conditions. Subsequently, pretreated oil is transesterified under the presence of a strong base to complete the formation of FAAE from TG. This approach has been suggested by various researches. For instance, Ramadhas et al. [48] produced biodiesel from high FFA rubber seed oil by esterifying the oil using 0.5% sulphuric acid to obtain a final FFA content of less 2%. Then, transesterification was carried out under the presence of NaOH leading to a product that met ASTM standards. Canakci and Gerpen [49] adopted the same technique to produce FAAE from a synthetic mixture of soybean oil and palmitic acid representing a 20% and 40% FFA feedstock. Their findings suggested that a two-stage pretreatment process was necessary in order to decrease the acidity of the oil to less than 1%. Following esterification, fuel-grade biodiesel was produced by completing transesterification with an alkaline catalyst. The production of biodiesel using *Jatropha Curcas* L. seed oil was studied by Berchmans and his research group [50]. In this work, FFA was reduced from 15% to less than 1% in the first step. Then the oil was further transesterified using a solution of sodium hydroxide and methanol to obtain a 90% product yield in 2 hours.
Recommended FFA levels after esterification vary in literature studies. Table 2.1 presents some suggested values.

<table>
<thead>
<tr>
<th>Author and Reference</th>
<th>Recommended FFA level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ma and Hanna [3]</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ramadhas et al. [48]</td>
<td>≤2</td>
</tr>
<tr>
<td>Zhang et al. [52]</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Freedman et al. [53]</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Kumar Tiwari et al. [54]</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Sahoo et al. [55]</td>
<td>≤2</td>
</tr>
</tbody>
</table>

The integrated two-step technique offers the possibility of using low quality feedstock without increasing operating conditions. This opens up an opportunity for biodiesel to be competitive in the fuel market.

### 2.7 Feedstock for Biodiesel Production

A wide range of feedstock are available for biodiesel production including plant oils, animal fats, waste greases, by-products from the food processing industry, and algal oils. According to published studies there are more than 350 oil-bearing crops that are recognized as potential sources for biodiesel production [56]. The main type of feedstock currently used in industry is virgin oil, with soybean and rapeseed/canola being the largest sources available in Europe and the US respectively. However, the used of refined oil increases significantly the cost of biodiesel as it accounts for almost 80% of the total production costs [10]. In addition, the use of food crops as a primary raw material in the
production of biofuels have led to debates since it compromises the availability of food sources. To overcome this, researches have opted to look for alternative low quality feedstock such as animal fat, waste cooking oil and greases, inedible oils, which contain high amounts of FFA and water. The use of low-grade raw materials has attracted the attention of biodiesel producers not only due to lower production costs but to avoid competition with the food industry.

2.7.1 Non-edible oils

There are numerous non-food crops that are promising substitutes to edible oil in the synthesis of biodiesel. Jatropha curcas, castor, mahua, soapnut, sea mango and rubber seed oil are some examples. The presence of toxic compounds in their seeds, fruits and sap makes them unsuitable for human consumption [57]. The potential of non-edible oil seed crop species as raw materials for biodiesel production depends mainly on oil yield; the higher the yield, the lower the cost of production. Other important factors to consider include cultivation requirements, properties of biodiesel, and oil composition. Table 2.2 shows some examples of non-edible oils with corresponding oil yield.

<table>
<thead>
<tr>
<th>Scientific Name (Common Name)</th>
<th>Oil Yield (kg/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Azadirachta Indica</em> (Neem)</td>
<td>2670</td>
</tr>
<tr>
<td><em>Calophyllum Inophyllum</em> (Polanga)</td>
<td>4680</td>
</tr>
<tr>
<td><em>Hevea Brasiliensis</em> (Rubber)</td>
<td>40-50</td>
</tr>
<tr>
<td><em>Jatropha Curcas</em> (Phusic nut)</td>
<td>1900-2500</td>
</tr>
<tr>
<td><em>Pongamia</em> (Millettia) <em>Pinnata/Pongamia glabra</em> (Koroch, Karanja)</td>
<td>225-2250</td>
</tr>
<tr>
<td>Plant Name</td>
<td>Number of Seeds</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td><em>Ricinus Communis</em> (Castor)</td>
<td>450</td>
</tr>
<tr>
<td><em>Simarouba Glauca</em> (Paradise Tree)</td>
<td>900-1200</td>
</tr>
<tr>
<td><em>Thevetta Peruviana</em> (Yellow Oleander)</td>
<td>1575</td>
</tr>
</tbody>
</table>

The production costs for non-edible oil is substantially lower than the cost of producing oil food crops as lower inputs of fertilizers, pesticides, land and water are required. Some of the above species can be grown in waste lands.

### 2.7.2 Waste edible oils

Waste cooking oils are substances that result from food processing and services facilities and are no longer suitable for human consumption [57]. Large amounts of waste cooking oil are produced worldwide. In some countries a fraction of these sources are devoted to animal feed and soap production and a significant portion is discharge into drains and sewers. The disposal of these substances is problematic as they could contaminate water sources and increase costs in water treatment facilities. During the frying process, the presence of heat and moisture in food accelerates hydrolysis of triglycerides given rise to FFA. Waste frying oils and greases are categorized into two types: yellow greases (FFA level <15%) and brown greases (FFA level >15%). The use of waste cooking oil as a raw material for biodiesel production alleviates the issues associated with improper disposal and provides an alternative to reduce the overall biofuel manufacturing cost. The price of waste cooking oil has been estimated to be half of that of refined oil [59].

### 2.7.3 Algal oils

Microalgae have been recognized as a potential source for biofuel production due to its high oil content and high growth rates. It is the only source capable of satisfying global
demand on transportation fuels [60]. Microalgae have oil content of 50% by weight of dry mass.

Currently, biodiesel production from microalgae is not economically viable due to extensive upstream and downstream processing making it substantially expensive. There are several factors that influence the economic feasibility of microalgae in biofuel production: 1) high cost in algal biomass production, 2) high energy consumption for oil extraction and conversion 3) utilization of residual biomass [61]. In order to make biodiesel from microalgae viable, the cost of algal biomass production must be reduced by a factor of 7 [61].

2.8 Reaction Medium

Transesterification is a two-phase reaction process limited by mass transfer, reaction kinetics, and reactant solubility. They occur at different stages during the reaction. Short-chain alcohol such as methanol and ethanol are immiscible in oils. Therefore, intensive mixing is required to minimize mass transfer resistances; thereby, promoting product formation. Some studies have analyzed the used of different reactor systems to achieve high conversions in short periods of time. Transesterification transits from a multiphase mixture to a two-phase medium as the reaction progresses through a pseudo-single phase emulsion. Polar compounds (methanol, glycerol and catalyst) are immiscible in non-polar species (VO and FAME). As mixing is provided, methanol droplets, which contain the liquid catalyst, are dispersed in the oil phase. To explain this further, Figure 2.3 shows how the reaction takes place in three different stages [45].
During the first stage of the reaction, the concentration of oil in methanol is rather low due to the relative large size of methanol droplets. In this case, mass transfer is the limiting factor. In the second stage, the droplet size decreases and mass transfer occurs rapidly. At this stage the medium has been described a pseudo-single phase emulsion [63]. In the third stage a drop in the reaction rate can be observed; two new liquid-liquid phases are formed, a dense phase mainly composed by glycerol and a nonpolar phase mainly composed by FAME. The catalyst, due to its polar nature, gets mostly dissolved in the glycerol phase and the unreacted MG, DG and TG are dissolved in the FAME phase. In this case the solubility of components limits the reaction rate [13].

2.9 Biodiesel Properties and Standards

Introduction and commercialization of biodiesel in the fuel market is regulated by a variety of standards to ensure high quality and guarantee engine performance. Guidelines have been developed in many countries around the world including Germany, Italy,
France, United States, Czech Republic, and Austria, with the latter being the pioneer in establishing a set of specifications for biodiesel derived from rapeseed oil [64]. The two most common standards, shown in Table 2.3, are given by the American Society for Testing and Materials in ASTM D6751 and European Standard EN 14214. As can be seen, biodiesel is characterized based on physical and chemical properties including viscosity, density, acid value, cloud point, pour point, iodine value, total glycerine, and methyl ester content.

Table 2.3 American and European biodiesel standards for vehicle use (from [65])

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM D-6751 Limits</th>
<th>Test Method</th>
<th>Units</th>
<th>EN 14214 Limits</th>
<th>Test Method</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity (40°C)</td>
<td>1.9-6.0</td>
<td>D445</td>
<td>mm2/s</td>
<td>3.5-5.0</td>
<td>EN ISO 3104</td>
<td>mm2/s</td>
</tr>
<tr>
<td>Density (15°C)</td>
<td>860-900</td>
<td>EN ISO 3675</td>
<td>kg/m³</td>
<td>96.5</td>
<td>EN 14103</td>
<td>mass %</td>
</tr>
<tr>
<td>Ester content</td>
<td>47 min.</td>
<td>D613</td>
<td>-</td>
<td>51 min.</td>
<td>EN ISO 5168</td>
<td>-</td>
</tr>
<tr>
<td>Cetane number</td>
<td>130 min.</td>
<td>D 93</td>
<td>°C</td>
<td>120 min.</td>
<td>ISO/CD 3679</td>
<td>°C</td>
</tr>
<tr>
<td>Flash point</td>
<td>Report</td>
<td>D2500</td>
<td>°C</td>
<td>500 max.</td>
<td>ENISO12937</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Water</td>
<td>0.050 max.</td>
<td>D2709</td>
<td>vol. %</td>
<td>0.02 max.</td>
<td>ISO3987</td>
<td>mass%</td>
</tr>
<tr>
<td>Sulphated ash</td>
<td>0.020 max.</td>
<td>D 874</td>
<td>mass%</td>
<td>0.02 max.</td>
<td>DIN 51680</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.05 max.</td>
<td>D 5453</td>
<td>mass%</td>
<td>100 max.</td>
<td>DIN 51680</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>No.3 max.</td>
<td>D 130</td>
<td>-</td>
<td>No.1(3h at 50°C)</td>
<td>EN ISO2160</td>
<td>-</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>0.050 max.</td>
<td>D 4530</td>
<td>mass%</td>
<td>0.3 max</td>
<td>ENISO10370</td>
<td>mass%</td>
</tr>
<tr>
<td>Acid number</td>
<td>0.80 max.</td>
<td>D 664</td>
<td>mgKOH/g</td>
<td>0.5 max.</td>
<td>prEN14104</td>
<td>mgKOH/g</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>0.020 max.</td>
<td>D 6584</td>
<td>mass%</td>
<td>0.02</td>
<td>prEN 14105</td>
<td>mass%</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>0.240 max.</td>
<td>D 6584</td>
<td>mass%</td>
<td>0.25</td>
<td>prEN 14105</td>
<td>mass%</td>
</tr>
<tr>
<td>Phosphorous content</td>
<td>0.001 max.</td>
<td>D 6584</td>
<td>mass%</td>
<td>10 max.</td>
<td>prEN 14107</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Iodine number</td>
<td>120 max.</td>
<td>D 6584</td>
<td>-</td>
<td>prEN 14111</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
### Oxidative stability

<table>
<thead>
<tr>
<th>Oxidative stability (110°C)</th>
<th>6 min.</th>
<th>prEN14112</th>
<th>h</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Monoacylglycerols</th>
<th>0.8 max.</th>
<th>prEN 14105</th>
<th>mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diacylglycerols</td>
<td>0.2 max.</td>
<td>prEN 14105</td>
<td>mass%</td>
</tr>
<tr>
<td>Triacylglycerols</td>
<td>0.2 max.</td>
<td>prEN 14105</td>
<td>mass%</td>
</tr>
</tbody>
</table>

| Distillation temperature | 360°max. | D 1160 | °C |

*a Including sediment, b 100% of the sample, c 10% of the sample, d 90% recovered*

While biodiesel can be derived from various sources implying that its chemical structure is dependent on the fatty acid profile of the parent oil, the final product should meet the above criteria regardless of the feedstock. Physical properties are strongly related to the degree of unsaturation and distribution within the fatty acid molecules [66].

### 2.10 Economics and Commercialization Issues

The major obstacle for commercialization of biodiesel is the cost of production. Raw material costs, operating costs, tax levels, and energy prices are dominating factors that could impede its industrial production. Currently, refined edible oils are predominant as feedstock with soybean oil being common in the US, rapeseed oil in Europe. The cost of raw material from food sources accounts for approximately 80% of the cost of the product [67]. With this is mind, biodiesel could become more economically attractive by using lower cost feedstock and simplifying oil production steps and transesterification process. Animal fat and recycled frying oil are attractive alternative raw materials that could reduce the price of the final product making it lower than that of conventional petro-diesel [68]. However, these sources are available in restricted quantities as they are used in other industries. More sustainable low quality sources such as non-edible oils including Jatropha Curcas L. oil, Karanja oil, Castor oil, Madhuca Indica oil, Rubber seed oil, etc. [69] constitute a large portion of potential raw materials for biodiesel production.
without compromising food sources. Additionally, most of these plant oils reduce water consumption and can be grown in less fertile land.

Biodiesel production technologies and methods could also be further explored to reduce operating costs. This is particularly important when non-conventional raw materials are used as they might contain a high concentration of contaminants including water and free fatty acids. Traditional base-catalyzed reactions are not the best option in this case as FFA lead to soap formation reducing alkyl esters yield and obstructing separation of products. This problem can be reduced to a large extent by utilizing a two-step esterification and transesterification process as previously discussed.

The majority of biodiesel synthesis occurs in stirred tank reactors, operated under a batch mode, due to their technical maturity. However, this process has four main challenges: 1) reaction rate can be limited by mass transfer, and 2) reversibility of reaction can decrease FAME yield 3) equipment productivity is low 4) operating costs are high. Scientists have addressed the mass transport obstacle by increasing mixing intensity; however the energy requirement can be relatively high. Moreover, the product quality is affected by the reaction reversibility as glycerol reacts with methyl esters or intermediates to produced TG, DG, and MG. This implies that to achieve higher conversion, it is necessary to constantly remove glycerol to shift the equilibrium towards the biodiesel side. For batch reactors this is not possible and generally the biodiesel produced does not meet ASTM standards due to high concentration of contaminants. Researchers have proposed and documented novel reactors to produce biodiesel to overcome the limitations of conventional batch reactors. Some of the technologies include: reactive distillation, supercritical reactors, micro-structured reactors, bubble reactors, microwave reactors,
oscillatory flow reactors, cavitational reactors, and rotating packed beds. All of the above reactor types can be operated in a continuous mode. However, most of these processes involve high operating and capital costs. The recovery of high quality glycerol would further contribute to reduce the overall biodiesel production cost.

Even though, the cost of biodiesel is still rather high and non-competitive with conventional petro diesel, the demand for biofuel production is expected to increase rapidly due to the introduction of ambitious government legislations for renewable content in diesel and gasoline fuels. The impact of biodiesel on the transportation sector will be tremendous as it is considered to be the only viable alternative as a substitute for conventional diesel [44].

2.11 Concluding Remarks

Biodiesel is an attractive alternative renewable fuel that has had a significant impact in various regions of the world as it alleviates some environmental concerns. Its chemical and physical properties make it suitable to be used in compression ignition engines in pure form or blended with conventional petroleum diesel with minimum or no modifications. Biodiesel produced from vegetable oils and animal fats will not be sufficient to replace completely diesel demands due to limited availability of raw materials and high competition with other industries. However, extensive research is being conducted to implement non-traditional feedstock such as waste frying oils, inedible oils, and algal oils. Improvements on production technologies are also being investigated to reduce chemical consumption, energy requirements, and product losses. These improvements would lead to lower productions costs and make biodiesel more competitive in the existing fuel market.
2.12 References


CHAPTER 3

3 Transesterification of Refined Canola Oil

3.1 Introduction

It is evident that fossil fuels no longer constitute reliable and inexpensive energy sources as they are finite materials. Moreover, environmental damage including pollution of air, water, and soil resulting from the production and consumption of these fuels has been significant. Despite the negative impacts, more than 80% of global energy supply is still derived from coal, natural gas, and oil [1]. Therefore, in order to suppress our dependence on fossil fuels and reduce environmental destruction, new forms of energy from renewables need to be evaluated and implemented in large proportions. Out of various alternatives, bioethanol and biodiesel have gained considerable attention in North America, Europe, and emerging countries due to their positive contribution to agriculture and energy security. Biodiesel, a substitute for petro-diesel, can be derived from any lipid sources, generally vegetable oils and animal fats. Canola oil is a promising source due to improved fuel properties (pour point, cloud point, and stability) when compared to other edible oils [2].

Biodiesel is defined as a mixture of mono alkyl esters of long chain fatty acids that is predominantly produced by transesterification of triglycerides (TG). These molecules are comprised of three long chain fatty acids linked to a glycerol backbone. Transesterification is an equilibrium chemical reaction, between TG and low molecular weight alcohols, consisting of a three consecutive reversible reactions in which a
molecule of fatty acid alkyl ester (FAAE) is produced in each step as seen in Reaction 3.1, 3.2, and 3.3. Diglycerides (DG) and monoglycerides (MG) are intermediates and glycerol (GL) is the side product.

\[
\text{Triglyceride (TG) + Alcohol} \leftrightarrow \text{Diglyceride (DG) + Alkyl Ester (FAAE)} \quad (R3.1)
\]

\[
\text{Diglyceride (DG) + Alcohol} \leftrightarrow \text{Monoglyceride (MG) + Alkyl Ester (FAAE)} \quad (R3.2)
\]

\[
\text{Monoglyceride (MG) + Alcohol} \leftrightarrow \text{Glycerol (GL) + Alkyl Ester (FAAE)} \quad (R3.3)
\]

Transesterification is a mass transfer limited reaction as oil and short chain alcohols form two immiscible phases. The reaction is biphasic in the initial and final stage and becomes homogeneous as intermediates appear in the reaction mixture. Different approaches have been proposed to overcome mass resistances encountered by the low solubility of reactants. For instance, high mixing speed from mechanical agitation in batch stirred reactors, promotes a pseudo-homogeneous phase; however, the mechanism of mass transfer-controlled region followed by kinetically-controlled region is generally proposed [3]. Also, the use of inert co-solvents such as tetrahydrofuran (THF), 1,4-dioxane, acetone, diethyl ether, generates one-phase alcoholysis producing high quality fuel in short periods of time [4, 5]. Primary concerns with this method are possible hazards and toxicity and recovery and recycling of co-solvents [6]. A novel technique was developed by Pal and Prakash, which allows the oil to enter the system gradually with an even dispersion in the liquid phase. This approach, facilitates early formation of ME, MG and DG in a large pool of methanol/catalyst solution leading to a homogeneous mixture and thus, pushing the reaction towards the product side [7].
Alcoholysis is usually catalyzed by acids or bases depending on the characteristics of feedstock. Sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide are common examples of efficient catalysts. However, researchers have studied a wide range of homogeneous and heterogeneous catalysts in order to optimize the overall production process. Recently, potassium carbonate has been suggested in literature publications as a chemical with moderate catalytic activity. It brings benefits to the process when low-grade oil is used as the lipid source since it is more tolerant to the presence of FFA [8].

This work compares different configuration methods, namely semi-batch and batch as well as two alkaline catalysts, KOH and K$_2$CO$_3$, in the production of biodiesel from refined canola oil. Optimum process variables including reaction temperature, reaction time, type of alcohol, and catalyst loadings are studied and proposed.
3.2 Experimental Details

3.2.1 Materials and Chemicals

Anhydrous grade methanol (>99.8%), concentrated hydrochloric acid, anhydrous reagent grade potassium carbonate (99%), potassium hydroxide (85%), anhydrous grade sodium sulfate, sodium hydroxide, and anhydrous acetone (99.5%) were supplied by Caledon Laboratories Ltd. Anhydrous grade ethyl alcohol was obtained from Commercial Alcohols. Refined canola oil used in the experiments was the Messina Brands marketed by Costco grocery stores (Canada). Phenolphthalein indicator solution (1%/50% alcohol) was provided by VWR (Canada). The following calibration standards and chemicals were purchased from Sigma Aldrich (Canada) for GC analysis: glycerin solution, monolein solution, 1,3-diolein solution, triolein solution, tricaprin solution, reagent grade N-methyl-N-trimethylsilyl trifluoracetamide (MSTFA) and n-Heptane (HPLC grade, >99%).

3.2.2 Equipment

All experiments were conducted in a one liter jacketed glass reactor equipped with a reflux condenser, an impeller of 63.5mm in diameter with three pitched blades (45°) of 5mm width, placed concentrically at 36mm from the bottom. Four baffles were attached to the lid of the reactor to provide better mixing of reactants and products. A schematic of experimental set up can be seen in Figure 3.1. The vessel was connected to a water bath capable of maintaining a desired temperature to within ±1°C. A thermocouple was used to monitor the reaction temperature. Three ports were accessible from the lid of the vessel, one was used to connect the condenser to the system, the other one was the inlet of the rod of the impeller, and the third was employed to feed the reactants into the
reactor and to take intermittent samples for analysis. Additionally, a drain valve was installed to empty the contents of the reactor at the end of transesterification. Other equipment used during experiments included: a Buchi vaporizer, a centrifuge, and separatory funnels.

![Experimental set up for transesterification](image)

**Figure 3.1 Experimental set up for transesterification**

### 3.2.3 Experimental Procedure

The reactor was operated in batch or semi-batch mode to investigate mixing effects. While most literature studies have used batch mode, a semi-batch method based on gradual feeding of oil into a pool of alcohol was presented by Pal and Prakash [7]. This approach allowed good dispersion of oil into alcohol phase from start of the reaction, minimizing mass transfer limitations. Initial reaction parameters including alcohol to oil molar ratio, mixing speed, and temperature range were established based on literature studies. Reaction conditions selection was guided by considerations of inherent safety i.e.
mild reaction temperature and pressure and low catalyst concentration. A 6:1 alcohol to oil molar ratio was used as it has been found to be sufficient in transesterifying vegetable oil at mild temperature conditions and atmospheric pressure while obtaining high yields (>95%) [9-11]. Excess methanol is required in order to drive the reversible reaction towards the products side. Also, mixing intensity of 600 rpm has been proposed as an optimum value to improve diffusion between the two liquid phases [3, 12]. Finally, a temperature range of 30 – 60°C has been widely used and found to be efficient in producing high purity biodiesel [10, 13, 14].

Two alkaline catalysts were selected for transesterification reactions based on their environmental advantages over other type catalysts. For instance, wastewater resulted from synthesis of biodiesel using KOH and K$_2$CO$_3$ can be neutralized using phosphoric acid to produce potassium phosphate, a widely used fertilizer. It has been documented that KOH is one of the most common catalyst used in the biodiesel industry. On the other hand, K$_2$CO$_3$ is not a traditional base catalyst but it is beneficial to the whole production process. It produces the least amount of soaps when compared to NaOH, and KOH; especially when dealing with low quality feedstock. It has also been reported that glycerol containing potassium carbonate can be an environmentally friendly deicing or anti-icing fluid [15].

Transesterification reactions were conducted employing methanol and ethanol as alcohols and KOH and K$_2$CO$_3$ as catalysts. In batch mode, the oil was added to the reactor and preheated to the desired temperature. Then the catalyst was dissolved in the alcohol and fed into the vessel. Reaction was carried out for 1 hour using various catalyst loadings. In semi-batch mode, the alcohol and the catalyst were initially poured into the reactor and
preheated to the established temperature. Following this, preheated oil was slowly added to the reactor using a metering pump at a flow rate of 18ml/min. The determination of flow rate was based on the amount of feedstock used. The reaction was timed as soon as the first droplet fell into a pool of alcohol/catalyst solution and conducted for preselected duration. When half of the oil was pumped into the reactor, an agitation speed of 300 rpm was used. As the contents of the reactor increased with time, the speed of the impeller was adjusted to 400 rpm to reduce mass transfer resistances. The controlled feeding process was carried out in 30 min followed by a batch mode for another 30 min. At the end of transesterification, for both methods, agitation was stopped and the water bath was turned off. The contents were transferred to a separatory funnel in which the reaction mixture was allowed to stand overnight to ensure complete separation. Due to the difference in densities of biodiesel and glycerol, two phases were observed; an alkyl ester-rich phase was obtained at the top and a viscous glycerol-rich phase at the bottom. Excess alcohol and the catalyst were dispersed throughout both layers. The upper phase also contained TG, DG, and MG, depending on the conversion achieved. After separation was complete, alcohol was removed from both layers using a rotary evaporator at 60°C for 40 min. Then the alkyl ester-rich phase was further purified using a washing process to remove impurities such as, traces of glycerol, traces of alcohol, soaps and residual catalyst. The first wash was intended to neutralize most of the remaining catalyst with 1N HCl solution. Then, two washes using distilled water were employed to ensure proper contaminants removal. The volume of water and acidic solution was calculated based on 28% volume of the ester phase. The pH of wastewater was measured constantly obtaining a value between 7 and 8 for the final wash. Usually 3 to 6 washes were needed
to completely remove impurities. The washed alkyl phase was dried using a rotary evaporator at 100°C for 40 minutes. Finally, the purified product was filtered using a micro-filter with a pore size of 45µm, stored in a dark place and prepared for quality analyses. The following figure shows a process flow diagram of the entire process.

![Process Flow Diagram](image-url)

**Figure 3.2 Process flow diagram for transesterification**

### 3.3 Analytical Methods

The quality of final biodiesel should be monitored to ensure the fuel meets ASTM or EN standards. The established parameters in North America are given by ASTM D 6751: Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distilled Fuels. Specific chemical and physical properties should be met before biodiesel can be commercialized.
3.3.1 Physical Characterization

Density and viscosity measurements are usually the first analyses performed in biodiesel samples as they provide a rapid method for predicting the conversion of vegetable oils to methyl esters. Determination of both parameters is ideal for process control due to its simplicity. Density and viscosity were measured after each run to ensure the values obtained were within the range given by ASTM standards: 0.88 max g/ml and 1.9-6.0 mm²/s for density and viscosity respectively. These parameters help predict the performance of biodiesel fuel in engines. They dictate the amount of mass injected in pumps, and other equipment as well as the design of pipe and fittings in a production plant [16].

Viscosity

Dynamic viscosity was measured by using a Brookfield Digital Viscometer Model DV-II+ Pro. 16ml of sample was poured into a sample cup. Then a spindle was immersed in the test fluid and rotated at different speeds; sufficient time was allowed for the display reading to stabilize. The values detected by the viscometer were constant regardless of the spindle speed or shear rate. This indicated that the fluid being tested was Newtonian as expected. Dynamic viscosity were recorded and converted into kinematic viscosity values using the density values measured at the same temperature. For comparison purposes kinematic viscosity values were predicted at 40°C using Equation 3.1 given by Tat and Van Gerpen [17].

\[ Ln(\nu) = A + \frac{B}{T} + \frac{C}{T^2} \]  \hspace{1cm} (3.1)

\[ \nu = \text{kinematic viscosity (mm}^2/\text{s}) \]
\[ T = \text{Temperature (K)} \]

\[ A = 0.7883; B = -1.638 \times 10^3; C = 5.825 \times 10^5 \]

**Density**

Product density was measured by using an analytical balance with a precision of 0.001g in a 10ml calibrated flask. Product transfer was done by using a micropipette for better accuracy. For comparison purposes, density values were corrected for temperature by using a correlation from EN14214 (2008) \[18\].

\[ \rho_{15} = \rho_T + 0.723 \ (T - 15) \tag{3.2} \]

\( \rho = \text{Density (kg/m}^3\) \]

\( T = \text{Temperature (°C)} \)

**Biodiesel and Glycerol Yield**

The commercial viability of the fuel can be assessed in part by measuring biodiesel and glycerol yield. Processes that do not result in product yields higher than 90\% are not of commercial interest \[1\]. To calculate by-product yield, the total amount of catalyst used in alcoholysis was assumed to remain in the glycerol-rich phase due to its polar nature. An alternative and more precise method involves the purification of glycerol. However, this process results in large amounts of waste water from catalyst neutralization, and it is not cost-effective. For biodiesel yield, the calculated values were in relation to weight of oil. Equations 3.3 and 3.4 were used to determine percentage yields.
\[ GL\ Yield = \frac{\text{Weight of Crude Glycerol}(g) - \text{Weight of Catalyst}(g) - \text{Weight of Oil}(g)}{\text{Molecular Weight of Glycerol}(\frac{g}{\text{mol}})} \times 100\% \quad (3.3) \]

\[ BD\ Yield = \frac{\text{Weight of Final Product}(g)}{\text{Weight of Oil}(g)} \times 100\% \quad (3.4) \]

3.3.2 Chemical Characterization

Purified biodiesel was characterized by the chemical properties including acid value and glycerol and glycerides compositions.

3.3.2.1 Gas Chromatographic Analysis

Instrumentation and Operating Method

Samples were analyzed by gas chromatography (GC-2010 Schimadzu) using a capillary column (15 meters length, 0.32mm internal diameter, and 0.1µm film thickness.) and a flame ionization detector (FID). Volume samples of 1µl were injected on-column by an AOC 20s auto sampler at an oven temperature of 50°C and an injector temperature of 250°C with helium as the carrier gas at a flow rate of 3ml/min. The temperature program followed was in accordance with ASTM D 6584 to determine free glycerol and total glycerol in biodiesel samples: temperature of 50°C was held for 1 min; then, it was increased at a rate of 15°C/min to 180°C; followed by a rate of 7°C/min to 230°C. Finally, the temperature was increased at a rate of 30°C/min to 380°C and held for 10 min. The total operating time was 31.84 min. The FID temperature was kept constant at 380°C.

Sample Preparation

A sample taken from the final product was filtered to remove any solid impurities. Then, the sample was centrifuge at 4000rpm for 15 min and further dried using anhydrous sodium sulphate. Once water was completely removed from the sample, a measured
amount of biodiesel was accurately weighted, using an analytical balance of an accuracy of 0.0001g, and added to a 3ml glass vial. Derivatization was carried out by adding MSTFA to the sample to improve the chromatographic properties of hydroxylated materials [19]. The mixture was occasionally shaken to ensure proper glycerides derivatization. After 20 minutes, 2ml of n-Heptane was added to each vial to dilute the sample. Finally, 1ml of resulting mixture was transferred to a 1.5ml auto sampler vial for GC analysis.

**Determination of Standard Retention Time**

An accurate amount of standard glycerin solution, monolein solution, 1,3-diolein solution, triolein solution, tricaprin solution was weighted in a 3ml vial. Samples were sylilated using MSTFA and allowed to stand for 20 min at room temperature. n-heptane was then added to dilute the mixture. Each sample was analyzed by GC-FID and specific retention times were obtained. A blank sample containing only n-heptane, was analyzed through the unit in order to discard peaks generated from external sources and contaminants. Also, a sample of canola oil was analyzed to verify retention times of triglycerides and to identify compound peaks that do not take place in the reaction i.e. sterols. A chromatogram from a canola oil sample is observed in Figure 3.3.
3.4 Results and Discussions

Process variables including catalyst type and concentration, reactor operating mode, type of alcohol, reaction time, reaction temperature, mixing intensity, and use of co-solvent, were investigated to optimize biodiesel production from canola oil. Experiments were conducted in triplicates.

3.4.1 Effects of Catalyst Type and Concentration

Two alkali catalysts namely, KOH and K$_2$CO$_3$ were chosen for this study. Potassium hydroxide has been extensively studied and proven to be efficient in carrying out methanolysis of refined vegetable oils. It is one of the most common types of catalyst used in industry due to its high catalytic activity and low cost, along with sodium hydroxide. In this work, KOH was selected as it is more soluble in methanol and ethanol than NaOH [20]. On the other hand, potassium carbonate was selected based on its potential as an effective catalyst when using a both refined and low quality feedstock [8, 21]. Various runs were conducted to determine the effect of KOH and K$_2$CO$_3$
concentration on transesterification. The amount of catalyst was varied from 0.5%-1.5wt.% for potassium hydroxide and 1%-4wt.% for potassium carbonate, expressed as weight percentage of oil. Concentrations were selected based on preliminary experiments and review of literature publications [8, 10, 22, 23]. Experiments were conducted at 50°C under semi-batch mode using 6:1 methanol to oil molar ratio. The catalyst was added to methanol prior to transesterification with the purpose of initiating the production of methoxide ions. In case of KOH, the mixing process lasted approximately 5 minutes in which all the alkali pellets were dissolved in the alcohol liquid phase. On the other hand, methanol and K2CO3 were mixed for longer periods to obtain a homogeneous solution. For catalyst loading of 1%, 2% and 3%, it was observed that the catalyst was mostly dissolved in the methanol phase after 30 minutes. However, as the amount of potassium carbonate was increased, the solubility of potassium carbonate in methanol decreased. Therefore, higher portions of catalyst were lost during transfer. The efficiency of both catalysts was evaluated based on biodiesel yield and purity. Figure 3.4 shows a comparison of biodiesel yield obtained from using KOH and K2CO3 as catalyst.
As can be seen from the figure, potassium hydroxide exhibits a better performance on biodiesel yield at lower catalyst concentrations. However, high yields were also obtained when using potassium carbonate at loadings of 2% and higher. In general, biodiesel yield increases with an increase in amount of alkali up to 3% $\text{K}_2\text{CO}_3$ and 1% $\text{KOH}$. The last two concentrations showed a decrease in final product weight due to soap formation. In case of 4% potassium carbonate, it was observed that a gel-like material formed during the washing step. Therefore, more washes (6-7) were required in order to completely remove impurities from the final product. On the other hand, the use of higher KOH concentrations promotes water formation and leads to hydrolysis of esters present in the system (TG, DG, MG, and ME) followed by saponification as shown by Reaction 3.6.

![Figure 3.4 Biodiesel yields obtained with two alkaline catalysts](image-url)
Based on these experiments, optimum catalyst concentration were selected as 1%KOH and 3%K$_2$CO$_3$ for the following reasons: 1) Excessive catalyst loadings have a negative effect on downstream processes such as phase separation and purification, 2) At 4%K$_2$CO$_3$, a large portion of potassium carbonate is lost during transfer since it does not completely dissolve in the liquid phase, and 3) Soap formation during washing step is more predominant at higher alkali loadings.

Biodiesel purity from alkaline transesterification was determined according to ASTM D6584 from GC analysis. Chromatograms obtained for final product using KOH and K$_2$CO$_3$ as catalyst are presented in Figure 3.5 and Figure 3.6.

\[
\text{RCOOR'} + \text{KOH} \overset{\text{H}_2\text{O}}{\leftrightarrow} \text{RCOOK} + \text{R'OH}
\]

(R3.4)

Figure 3.5 Chromatogram obtained for a purified biodiesel sample from KOH-catalyzed transesterification
The resulting chromatograms are similar; a slightly higher concentration of DG can be seen around 21.5 min for KOH. Also, MG appears to be higher in the same sample around 18.2 min. Finally, a very small glycerol peak can be seen on the chromatograms around 6.9 min in Figure 3.6. GC reports indicates that both sample meet ASTM standards with total glycerol contents of: 0.124 for KOH and 0.083 for K$_2$CO$_3$.

The progress of the reaction was further monitored by removing approximately 2ml samples from the reactor. Bound glycerol content at a given time is presented in the next plot.
It can be observed that $K_2CO_3$ catalyzes effectively transesterification to a greater extent when compared to KOH. The recurrent sampling affects TG conversion with time, affecting the final glyceride content. However, GC analysis of purified biodiesel in a process without sampling shows that under the experimental conditions ASTM specifications are met.

**Formation of Active Catalyst Species**

Methoxide ions resulted from interactions between methanol and potassium hydroxide and methanol and potassium carbonate, are responsible for initiating transesterification as it attacks the carbonyl group of the tri-, di-, and monoglyceride molecules. The amount produced is dependent on the catalyst concentration and the alkali dissociation constant. As potassium hydroxide is a very strong base, its dissociation constant is high. On the contrary, potassium carbonate is a less strong base and therefore its dissociation constant
is lower than for KOH. In this sense, the catalyst amount needed to produce a methoxide anion is higher for K$_2$CO$_3$ than for KOH. However, a portion of potassium carbonate remains as solid the reaction also occur in its basic surface sites, enhancing methyl ester formation.

**KOH/CH$_3$OH system**

When potassium hydroxide is dissolved in methanol the following reaction occurs:

\[
KOH + CH_3OH \leftrightarrow CH_3OK + H_2O \tag{R3.5}
\]

Platonov et al. [24] studied the composition in the vapor and liquid phase of the four-component system at room temperature. It was found that methanol solution of KOH using a molar ratio of 0.018 (KOH/CH$_3$OH) is mainly composed by CH$_3$OK, H$_2$O, and minor quantities of unreacted KOH, represented in a 96.7% yield. An increase in the molar ratio results in a conversion decrease as equilibrium is shifted towards the reactants side. Potassium hydroxide to methanol molar ratio used in this work varied from 0.013 - 0.038. This would result is a yield of approximately 96-89%. Therefore the system is primarily constituted by potassium methoxide and water. The amount of active species generated when using 1% KOH (by weight of oil) in methanol during transesterification was determined to be 6g/110g of methanol.

High solubility of potassium hydroxide in methanol results from the strong basicity of the KOH. Dissociation of KOH occurs rapidly in a polar medium leading to a highly alkaline solution.
The solubility of anhydrous potassium carbonate in methanol at room temperature was previously studied by Platonov et. al. [26]. The acid-base interaction is represented by the following reversible reaction:

\[ CH_3OH + K_2CO_3 \rightleftharpoons CH_3OK + KHCO_3 \quad (R3.6) \]

Equilibrium concentration of both potassium carbonate and potassium bicarbonate in methanol were determined using titrimetric method. The above reaction occurs as a heterogeneous system; a solid phase composed by KHCO₃ and unreacted K₂CO₃, and a liquid phase constituted by CH₃OK and CH₃OH, and KHCO₃. In the study it was found that 99% of the total generated KHCO₃ remained in the solid phase shifting the equilibrium towards the formation of products. However, this is affected by a temperature rise due to an increased in the solubility of KHCO₃ in the liquid medium. In order to stimulate the formation of potassium methoxide, it is important to carry out the mixing process at room temperature. At 25°C, the concentration of K₂CO₃ and CH₃OK in methanol averages 6.43g/100g of methanol. The amount of potassium carbonate used in the reaction is critical to obtain a methyl ester yield that meets ASTM and EN standards. Even though the solubility of potassium carbonate is low in methanol, the solubility of potassium methoxide is much higher and sufficient to initiate alcoholysis of canola oil at a 3% concentration based on weight of feedstock.

The behavior of potassium carbonate as a catalyst is dependent on its homogeneous or heterogeneous character. This is important to consider since the reaction pathways are different in both cases. A liquid catalyst in transesterification leads to the formation of
catalytic species, methoxide ions. Consequently, the reaction takes place in the liquid phase. On the contrary, when a heterogeneous catalyst is employed the reaction occurs at the basic surface sites of the solid. Parameters like internal and external diffusion of reactants and products, adsorption, surface reaction, and desorption need to be taken into account in a heterogeneous catalytic reaction.

**Gravity Separation of Glycerol**

Separation of glycerol from biodiesel by gravity settling was studied in this work by conducting various experiments and recording the time required for the reaction mixture to separate out. The following diagram shows phase separation in terms of crude glycerol yield at different time intervals.

![Crude glycerol yield at different time intervals](image)

**Figure 3.8** Crude glycerol yield at different time intervals

Phase separation was achieved much faster when using K$_2$CO$_3$. As soon as the reaction mixture was poured into a calibrated flask the denser phase settled at the bottom of the
cylinder almost instantly. Around 90% of phase separation occurred within the first 8 minutes for K$_2$CO$_3$ and within 15 minutes for KOH. This is due to the difference in densities of both catalysts; K$_2$CO$_3$ has a density of 2.29g/ml compared to 2.04g/ml for KOH. Another factor that influences separation is the presence of solid particles in the medium. It is important to note that a portion of K$_2$CO$_3$ remains in solid state.

Glycerol yield obtained with KOH and K$_2$CO$_3$ are presented in Figures 3.9 for different catalyst concentrations.

![Figure 3.9](image-url)

**Figure 3.9 Effect of alkali concentration on glycerol yield**

In both cases, glycerol yield increases with catalyst concentrations; therefore, a higher conversion is achieved. Glycerol values obtained for 1% and 1.5% KOH and 4% K$_2$CO$_3$ overcome the 100% limit. This is explained by the presence of soaps, glycerides, dissolved esters, and water in the bottom layer after phase separation. Excessive use of alkali leads to an increase in solubility of methyl esters in the glycerol phase, allowing
them to be carried out in the glycerol phase during decantation [1]. This observation is supported by Noureddini et al. who also reported a high loss of product yield at higher catalyst loadings [27]. A higher solubility of biodiesel in glycerol can be accounted to an increased in polarity of the reaction system and to the presence and formation of soaps. It should be pointed out that soap formation is more predominant with metal hydroxides due to the presence of water in the system from interaction between the alcohol and potassium hydroxide as explained by Equation 3.7. Soaps tend to emulsify unreacted vegetable oil and esters and allow them to be carried out in the glycerol phase [28]. These drawbacks are not associated with the use of metal carbonates as water is not produced during base dissolution in alcohol.

### 3.4.2 Comparison and Evaluation of Semi-batch and Batch Mode

Mixing effects are of significant importance for the methanolsysis of triglycerides [29]. In the present study, the reactor was operated under batch and semi-batch mode to investigate these effects on biodiesel yield and purity while keeping other parameters constant: 6:1 MeOH to oil molar ratio, 60°C, 1 hour reaction time, and 1% KOH. A comparison from a gas chromatographic evaluation of TG conversion over the course of reaction under batch mode from this work and reported scientific literature is plotted in Figure 3.10 followed by a direct comparison between semi-batch and batch in Figure 3.10 B. TG conversion is calculated by the expression below:

\[
TG = \frac{TG_i - TG_f}{TG_i} * 100
\]
The initial weight of feed was 500g and it was assumed that 96% of oil was constituted by TG. Molecular weight of canola oil (TG) used in this study is 882.1g/mol based on fatty acid composition of oil.

**TG Conversion – Semi-batch**

\[
TG = \frac{TG_i - TG_t}{TG_i} \times 100
\]

TG = TG conversion (%)

TG = Moles of TG in the system

TG_{i} = Moles of TG in the system at time t

The amount of oil in the system at time t is determined as follows:

\[
w_{t, oil} = t (min) \times 18 \frac{ml}{min} \times 0.91 \frac{g}{ml}
\]
Figure 3.4 Comparison of triglyceride conversion during transesterification A) Literature studies B) Operating modes used in this work.
Table 3.1 Operating conditions during transesterification of vegetable oils

<table>
<thead>
<tr>
<th>Reference</th>
<th>Cat., Conc.</th>
<th>Oil</th>
<th>FFA$_i$ (wt.%)</th>
<th>T (°C)</th>
<th>Mixing Speed (rpm)</th>
<th>MeOH:Oil molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vicente et al. [12]</td>
<td>KOH,1%</td>
<td>Sunflower</td>
<td>0.02</td>
<td>65</td>
<td>600</td>
<td>6:1</td>
</tr>
<tr>
<td>Issariyakul [30]</td>
<td>KOH,1%</td>
<td>Palm</td>
<td>0.10</td>
<td>60</td>
<td>600</td>
<td>6:1</td>
</tr>
<tr>
<td>Kumar et al. [31]</td>
<td>NaOH,1%</td>
<td>Linseed</td>
<td>2.40</td>
<td>60</td>
<td>750</td>
<td>6:1</td>
</tr>
<tr>
<td>Batch (This work)</td>
<td>KOH,1%</td>
<td>Canola</td>
<td>0.14</td>
<td>60</td>
<td>600</td>
<td>6:1</td>
</tr>
<tr>
<td>Semi-batch (This work)</td>
<td>KOH,1%</td>
<td>Canola</td>
<td>0.14</td>
<td>60</td>
<td>300, 400, 600</td>
<td>6:1</td>
</tr>
</tbody>
</table>

Data presented in Figure 3.10A shows a similar trend despite the different fatty acid composition of vegetable oil used in each study. Lower TG conversions were reported by Kumar et al. since the FFA content in the feed was higher when compared to other references. The presence of FFA hinders transesterification by consuming the catalyst in a neutralization reaction. In batch mode, there is no apparent lag period when 600 rpm is used as mixing speed. The TG conversion to ME occurs rapidly in the early stage achieving more than 85% conversion in 10 min; these results are also confirmed by Freedman et al. [32]. Then, the rate decreases and finally it reaches equilibrium due to reversibility of the reaction. On the other hand, methanolysis of canola under semi-batch mode reaches a higher TG conversion up to 15 min. Initial mass transfer-controlled region in non-existent in this case. The controlled feeding process allows the raw oil to enter the system with a large excess methanol increasing the solubility of reactants and thereby pushing the reaction towards the products side. However, as oil is added to the system, the concentration of TG in the vessel builds up reducing rate of reaction. The lowest TG conversion occurs at 30 minutes when the feeding process stops. From this
point forward, the reaction occurs rapidly assisted by an increase in agitation speed. Methyl ester content in biodiesel samples in the course of transesterification using batch and semi-batch can be seen in Figure 3.11.

![Figure 3.5 Methyl ester content during transesterification catalyzed by 1% KOH at 60°C](image)

Evaluation of Figure 3.11 confirms the benefits of semi-batch at the beginning of the reaction. It facilitates the formation of ME esters in the first 15 minutes even though the impeller rotation speed is set to 300rpm. However, as methanolysis progressed, the rate of reaction decreased. Early formation of ME molecules is followed by an increase in GL concentration as it is released from TG molecules. The reacting media can turn into a stable emulsion at the initial stage of the transesterification; however, the presence of GL produces the opposite effect: separation of non-polar TG-ME-rich phase from GL-MeOH-rich phase. This is accompanied by an increase in viscosity of the liquid media. With this in mind, adding oil into the system under the presence of GL molecules aids the
separation of two distinct layers. This will be predominant if agitation speed is not sufficient to promote homogenization of the reactants and products.

**TG and intermediate content profile**

TG content in biodiesel samples was monitored and plotted against time in Figure 3.12.

The difference in both modes is better appreciated in the above diagram. The content profile demonstrates the advantages of using semi-batch mode in the initial stage of transesterification as compared to conventional batch. The presence of excess methanol facilitates the formation of biodiesel without excessive reactant mixing.

Samples were analyzed for DG, MG, and GL content. However, GL molecules were not detected since they were removed along with alkali in the water washing process prior to
analysis, Concentration profiles are illustrated in Figure 3.12 and Figure 3.13 for semi-batch and batch respectively.

Figure 3.7 Concentration profile for glycerides using semi-batch mode

Figure 3.8 Concentration profile for glycerides using batch mode
Concentration of methanol in semi-bath systems is reduced faster than in batch due its consumption during transesterification and the addition of fresh oil, the reaction rate decreases. TG, DG, and MG content are at the highest value around 30 minutes, as previously mentioned. These results suggest that methoxide species available in the system decrease rapidly with time. Additionally, mixing speed of 400rpm between 15 minutes and 30 minutes is not sufficient to overcome mass transfer limitations. This is clearly observed after the gradual feeding of oil stops and the impeller speed is adjusted to 600rpm. The reaction rate increases and thus, methyl ester formation occurs faster. However, impurity content does not reach an acceptable value. The total glycerol content for batch and semi-batch was found to be 0.180 and 0.362 respectively. The latter value is well above ASTM requirements (0.24max). This is due to the intermittent sampling which affects the conversion mode since the first couple withdrawn samples contain mostly methanol and catalyst contributing to a reduction of active species. The continuous sampling during batch does impact final conversion significantly. The following table shows the final content of MG, DG, and TG in purified biodiesel samples for runs that were not interrupted by sampling procedures.

<table>
<thead>
<tr>
<th>Operating Mode</th>
<th>MG</th>
<th>DG</th>
<th>TG</th>
<th>Total Glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.272</td>
<td>0.051</td>
<td>0.151</td>
<td>0.110</td>
</tr>
<tr>
<td>SB</td>
<td>0.344</td>
<td>0.080</td>
<td>0.220</td>
<td>0.124</td>
</tr>
</tbody>
</table>
The values are in agreement with previous results. Batch leads to a high quality product in terms of purity when compared to semi-batch. However, it can be seen that the difference in values is much smaller than before and that both methods meet ASTM specifications. Semi-batch can be further improved by increasing mixing intensity towards the end of the gradual feeding process to decrease diffusional limitations. An alternative option would be to add methanol along with fresh oil to compensate for losses during evaporation and sampling. It should be noted that semi-batch achieves an up to standard level biodiesel while utilizing lower mixing intensity.

Semi-batch and batch modes were evaluated using various operating conditions. Results from eight different runs are summarized in Table 3.1.

Table 3.3 Final product analysis using Semi-batch and Batch mode

<table>
<thead>
<tr>
<th>Mode</th>
<th>Mixing Speed (RPM)</th>
<th>Temp. (°C)</th>
<th>Catalyst, Conc. (wt.%</th>
<th>ME Content (wt.%</th>
<th>BD Yield (%)</th>
<th>GL Yield (%)</th>
<th>Kinematic Viscosity (mm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>600</td>
<td>30</td>
<td>KOH, 1</td>
<td>97.2</td>
<td>88.69</td>
<td>89.201</td>
<td>5.23</td>
</tr>
<tr>
<td>SB</td>
<td>300, 400, 600</td>
<td>30</td>
<td>KOH, 1</td>
<td>94.1</td>
<td>85.47</td>
<td>92.93</td>
<td>5.08</td>
</tr>
<tr>
<td>B</td>
<td>600</td>
<td>60</td>
<td>KOH, 1</td>
<td>98.7</td>
<td>92.58</td>
<td>101.71</td>
<td>4.71</td>
</tr>
<tr>
<td>SB</td>
<td>300, 400, 600</td>
<td>60</td>
<td>KOH, 1</td>
<td>97.5</td>
<td>90.18</td>
<td>109.58</td>
<td>4.52</td>
</tr>
<tr>
<td>B</td>
<td>600</td>
<td>40</td>
<td>K₂CO₃, 1</td>
<td>-</td>
<td>82.05</td>
<td>64.86</td>
<td>7.10</td>
</tr>
<tr>
<td>SB</td>
<td>300, 400</td>
<td>40</td>
<td>K₂CO₃, 1</td>
<td>-</td>
<td>81.26</td>
<td>66.78</td>
<td>6.91</td>
</tr>
<tr>
<td>B</td>
<td>600</td>
<td>60</td>
<td>K₂CO₃, 3</td>
<td>99</td>
<td>91.13</td>
<td>87.95</td>
<td>4.94</td>
</tr>
<tr>
<td>SB</td>
<td>300, 400, 600</td>
<td>60</td>
<td>K₂CO₃, 3</td>
<td>98.1</td>
<td>90.67</td>
<td>90.78</td>
<td>4.77</td>
</tr>
</tbody>
</table>
Conventional batch results in higher conversions and improved product yield when compared to semi-batch. Biodiesel production in literature studies is often conducted in batch systems with mechanical mixing speeds of 600rpm or higher to enhance mass transfer between methanol and oil, though, it is an energy intensive process. Semi-batch, on the other hand, resulted in slightly lower yields. However, overall energy requirement from reactants mixing is lower in the latter mode. It is, therefore, a promising method to reduce operating costs and energy requirements in the manufacturing of biodiesel thus making it more economically competitive in the existing fuel market. It is also seen from Table 3.1 that glycerol yield is always higher in semi-batch. This is explained by the dispersion of reactants and products in the system towards the end of the reaction. In the first case, Batch, all species are well dispersed in the reaction medium and therefore phase separation takes longer. This represents an issue for production of biodiesel at an industrial scale.

Semi-batch aids the formation of methyl esters at the beginning of the reaction as small oil droplets get easily dispersed in the liquid media using a large methanol to oil molar ratio. The rapid formation of ME in the system, allows transesterification to be carried out in a single phase as it acts as solvents along with methanol. However, it was observed that the liquid medium for runs conducted at 30°C and 40°C were initially heterogeneous. Oil droplets accumulated rapidly in reactor stagnant regions (above the drain port). It was not until the contents reached a certain level (approximately after 5 minutes of feeding oil) that the mixture became homogeneous. During Batch, mass transfer limitations were also evident at the beginning of transesterification. The
formation of small droplets in the system took approximately 2 minutes before the mass transport process was initiated.

3.4.3 Effect of Reaction Temperature

Runs were conducted at temperatures from 30 to 60°C in order to select optimum reaction temperature. It has been reported that solubility of vegetable oils in methanol increases at a rate of 2±3% (w/w) per 10°C as temperature is increased [13]. At higher temperatures, methanol and triglyceride molecules are more active as their collision probability increases leading to higher reaction rates. However, upper temperature was limited to 60°C since at higher temperatures lead to a decrease in conversion as methanol is removed from the system by evaporation. Figure 3.15 presents final yields in a KOH catalyzed system.

![Figure 3.9 Effect of temperature on product and by-product yield using 1% KOH under semi-batch mode](image)

Figure 3.9 Effect of temperature on product and by-product yield using 1% KOH under semi-batch mode
Form Figure 3.15 it can be seen that biodiesel yield increases with a rise in temperature. Though, product and by-product yield remained at a nearly constant level after 50°C. A slight increase in glycerol yield suggests that transesterification proceeded further. The influence of temperature on reaction kinetics is significant, equilibrium conversions are achieved faster at higher temperature values [33].

Additionally, GC analysis was performed on runs with KOH at 30 and 60 to evaluate how temperature affects the course of reaction. Intermediates and TG concentrations with respect to time are presented in Figures 3.16 and 3.17. As observed MG, DG and TG content is higher when operating at lower temperatures.

![Figure 3.10 Glycerides concentration profile for KOH-catalyzed transesterification at 30°C](image-url)
Reactions at 30° C do not proceed to completion as reflected by high bound glycerol content. As temperature increases the solubility of reactants is improved and thus increasing contact between oil and methanol. The following diagram shows ME content in the course of transesterification conducted at different temperatures.
Rate of reaction is strongly influenced by temperature as previously mentioned. The maximum biodiesel yield is observed at 60°C for both alkaline catalysts. Higher reaction temperatures at atmospheric pressures should be avoided as methanol evaporation could hinder the formation of methyl esters. In addition, saponification is enhanced at higher temperature conditions. Therefore, 60°C is recommended as the optimum reaction temperature.

### 3.4.4 Acetone as a co-solvent

Transesterification starts as a two phase reaction system. The solubility of oils, fats and greases in aliphatic alcohols is limited at mild operating conditions. Usually, vigorous mixing is necessary to generate a homogeneous mixture. However, the addition of a co-solvent promotes one phase reaction overcoming mass transfer limitations. Literature studies have proposed the use of different co-solvents to assist the formation of FAAE. Boocock and his research group [34] conducted base-catalyzed alcoholysis of soybean oil.
using tetrahydrofuran as a co-solvent and obtained high purity biodiesel. Chi [35] used methyl-tert-butyl ether (MTBE) as co-solvent in a base-catalyzed transesterification of refined edible soybean oil and obtained a final product with 99.8% methyl ester content in only 8 minutes. Maeda et al. [36] proposed acetone as an effective co-solvent for transesterification using a low quality feedstock, Jatropha Curcas seed oil. Conversions of 99% using ambient temperature and atmospheric pressure were reported. One of the advantages of using acetone is its relatively low boiling point, similar to boiling point of methanol. Its removal could be achieved along with methanol during recovery process.

An experiment was conducted based on the information provided on the study conducted by Maeda et al. A 6:1 MeOH to oil molar ratio, 1.22:1 acetone to oil mass ratio, and 3% potassium carbonate were used. Initially, it was observed that the catalyst did not dissolve completely in the liquid phase and agglomerates were formed at the bottom of the reactor vessel. The mixture turned yellow as it proceeded, and then a brown single phase was observed due to the presence of glycerol. The procedure followed was the same as in previous runs. After 1 hour, the motor was turned off and the reaction mixture was transferred to a rotary evaporator for acetone and methanol removal. This process was conducted at 70°C under vacuum for 90 min. Following this, the resulting liquid phase was allowed to stand for 1 day for product separation. Glycerol and methyl esters were partially separated; only 5g of glycerol were recovered (expected value was about 30g). The lighter phase was a brown/orange liquid indicating that there was some co-solvent and glycerol remaining in the methyl ester rich phase. Rotary evaporation was carried out one more time under vacuum for 90 min to complete acetone removal. Unfortunately, not much was collected even though the temperature was increased to
85°C. The process of separation was repeated without acceptable results. During washing, emulsions were formed leading to a one phase mixture. Separation was again difficult and therefore purification of methyl esters could not be completed.

### 3.4.5 Effect of Alcohol Type

The effect of alcohol type on transesterification was analyzed by conducting runs with alcohols widely used in the biodiesel industry, methanol and ethanol. Also, a combination of alcohols was employed for one experiment to take advantage of the high reactivity given by methanol and better reactant solubility provided by ethanol.

The reactivity of aliphatic alcohols decreases as the number of carbons in the chain increases. The use of different alcohols including methanol, ethanol, propanol, and butanol has been a topic of interest in many literature studies. To date, methanol has been the preferred alcohol for transesterification due to its high reactivity, wide availability, and low cost. However, most methanol industrial production comes from fossil fuels. This has been controversial as biodiesel is an environmentally friendly alternative fuel. For this reason, ethanol has gained importance in the past years as it is derived from green processes. Another advantage is that some of the physical properties of ethyl esters are better than those of methyl esters. To mention a few, calorific value and centane number of ethyl esters are slightly higher and cloud point is lower. Even tough, ethanol is a more environmentally friendly than methanol, it is more sensitive to water content in the feed and it requires higher temperature conditions. Additionally, it acts as a better co-solvent between methyl esters and glycerol and therefore the separation of products is more difficult.
Runs were conducted using ethanol, methanol and a mixture of 50% methanol and 50% ethanol, while keeping other parameters constant: 6:1 alcohol to oil molar ratio, 50°C, 1 hour reaction time, and 3% potassium carbonate. The collected data is presented in Figure 3.16 and Figure 3.17.

Figure 3.13 Density and viscosity measurements for different types of alcohols

Figure 3.14 Glycerol and biodiesel yield for different types of alcohol
Experimental results show that final product using only methanol and a mixture of methanol and ethanol met the standards specified the CEN and ASTM. The density value for 100% ethanol exceeds the 0.88g/ml limit and well as the viscosity limit of 6mm²/s. This is due to the large portion of free and total glycerol present in the final biodiesel sample. It was observed during the experimental procedure, the separation of products was very slow when ethanol was used in both form (100% and 50%). This can be confirmed by the results presented in Figure 3.17, where the glycerol yield is less than 10%. In addition, separation took place in two stages for both samples with ethanol. Right after transesterification the reaction mixture was poured in a separatory funnel, and allowed to stand overnight; separation was not completed. Therefore, the alcohols were removed and then separation was allowed to take place for one extra day. The suspended glycerol in the ester phase resulted in a viscous product. Ethanol plays a role as solvent, increasing the mutual solubility of glycerides and methyl esters. As a result, it negatively impacts separation and purification of methyl esters after transesterification, as it assists the dissolution of methyl esters molecules in the glycerol rich phase and vice versa.

When analyzing the methyl ester yield presented in Figure 3.17, it can be seen that all three runs resulted in high yields. However the extent of reaction conversion is difficult to be assumed, especially in these runs, because ethanol acts as a better solvent for both product phases.

3.5 Conclusions

Suitability of K₂CO₃ in transesterification was studied and compared with KOH, a commonly used catalyst. At concentrations of 3%, potassium carbonate was found to
have moderate catalytic activity mainly due to its both homogenous and heterogeneous behavior. Formation of active species in the liquid media was found to be sufficient in promoting generation of methyl esters. The advantages of using $K_2CO_3$ over KOH are: faster glycerol separation which is essential in continuous biodiesel processing at an industrial scale; higher tolerance to moisture content in the feed; and higher methyl ester content in final product. Investigations of ethanolysis of canola oil were also conducted. However, due to poor solubility of potassium carbonate and higher solvent properties of ethanol, products separation was slow and incomplete.

Semi-batch as reactor operating mode can reduce energy requirements and operating costs from lower reactant mixing as compared to conventional batch. Further studies are needed to improve processing by semi-batch mode by either increasing mixing speed from 15 to 30 minutes reaction time or by adding extra alcohol to compensate for sampling losses and rapid consumption effects.

The use of acetone as inert co-solvent, allowed the reaction to be carried out in one homogeneous phase. However, phase separation was extremely complex leading major shortcomings in purification steps. The addition of pure glycerol could enhance removal of by-product prior to neutralization of alkali.
3.6 References


CHAPTER 4

4 Esterification and Two-Step Process

4.1 Introduction

Environmental concerns due to fossil fuels combustion have led to extensive research on renewable energy sources including geothermal, solar, wind, and biomass. Biodiesel, derived from plant oils and animal fats is an attractive alternative fuel to fossil-based diesel as it is biodegradable, non-toxic, renewable, and has a low emission profile. It consists of a mixture of mono-alkyl esters of long-chain fatty acids chemically produced by transesterification of triglycerides (TG) or esterification of free fatty acids (FFA). A catalyst is generally required to speed up the reaction and improve yield [1, 2]. Industrial production of biodiesel faces major challenges including limited supply of raw material due to the utilization of high quality refined vegetable oils; and, the cost of feedstock, which accounts for 60-80% of total production cost [3]. At present, biodiesel is not economically feasible and competitive with petroleum based-fuels. In order to overcome some of these issues, the use of inexpensive raw materials such as waste frying oils, inedible oils, and animal fats have attracted attention of biodiesel producers. However, one main obstacle is that low quality feedstock contains significant amounts of free fatty acid (FFA) and water. FFA molecules react with a base to produce soap and water hindering conventional alkaline transesterification. To address this problem, low cost feedstock can be treated before proceeding to alcoholsysis of TG.
The pretreatment of high acidity materials can be achieved by various methods: steam distillation, extraction using an alcohol, and esterification. The first two methods are impractical since they involve high energy requirements and large amount of solvents due to a limited solubility between FFA and alcohols. Esterification, on the other hand, provides an efficient method to remove fatty acids from the feedstock and at the same time leads to improved product yield. In the present study, a two-step process is conducted in which FFA are converted to methyl esters by acid catalyzed esterification, followed by base catalyzed transesterification to process TG into methyl esters. Several authors have noted the importance of a two-step process when dealing with high FFA feedstock with acceptable product yields. However, biodiesel commercialization using this technique is limited as optimum operating conditions are not well established, and a cost-effective process has not been proposed.
4.2 Experimental Details

4.2.1 Materials and Chemicals

Anhydrous grade methanol (>99.8%), anhydrous reagent grade potassium carbonate (99%), potassium hydroxide (85%), concentrated sulphuric acid (95-98%), and anhydrous grade sodium sulfate were supplied by Caledon Laboratories Ltd. Anhydrous grade ethyl alcohol was obtained from Commercial Alcohols, oleic acid (90%) from Alfa Aesar and concentrated hydrochloric was supplied by Fisher Scientific. Canola Oil used in experiments was the Messina Brands marketed by Costco grocery stores (Canada). 1% Phenolphthalein indicator solution in 50% alcohol, and methyl orange indicator 0.1% aqueous solution were obtained from VWR (Canada). The following calibration standards and chemicals were purchased from Sigma Aldrich (Canada) for GC analysis: glycerin solution, monolein solution, 1,3-diolein solution, triolein solution, tricaprin solution, reagent grade N-methyl-N-(trimethylsilyl) trifluoracetamide (MSTFA), and n-Heptane (HPLC grade, >99%).

4.2.2 Equipment

All experiments were conducted in a one liter jacketed glass reactor equipped with a reflux condenser, an impeller and four baffles evenly distributed to provide a better mixing of reactants and products. A schematic set up can be seen in Figure 4.1. The vessel was connected to a water bath capable of maintaining a desired temperature to within ±1°C. A thermocouple was used to monitor the reaction temperature. Three ports were accessible from the lid of the vessel, one was used to connect the condenser to the system, the other one was the inlet of the rod of the impeller, and the third was employed to feed the reactants into the reactor and to take intermittent samples for analysis. The
impeller diameter was 63.5mm and it had three pitched blades (45°) of 5mm width, placed concentrically at 36mm from the bottom. Additionally, a drain valve was installed to empty the contents of the reactor at the end of reaction. Other equipment used during experiments included: a Brookfield viscometer, a Buchi vaporizer, a centrifuge, and separatory funnels.

![Figure 4.1 Experimental setup for biodiesel synthesis](image)

### 4.2.3 Reaction Procedure

#### 4.2.3.1 Esterification Reaction

High FFA feedstock was modeled by adding a known amount of oleic acid to refined canola oil. Oleic acid was selected as it is found in abundance in several plant oils such as canola, soybean, mahua, karanja and marula oil. Acidity was varied from 12mgKOH/g to 30mgKOH/g corresponding to 6% and 15% FFA content by weight respectively. Methanol was used as alcohol due to its low cost, wide availability and extensive used in
the biodiesel industry. Methanol to FFA molar ratio of 20:1 was employed for all experiments, based on previous literature studies [4]. The reactor was operated under batch and semi-batch mode to investigate mixing effects. For batch mode, acidified oil was first added to the reactor and heated until the desired temperature was reached. Then, the methanol/sulphuric acid mixture was poured into the reaction system and a mixing speed of 600rpm was adjusted. The reaction was conducted for 1 hour and intermittent samples were collected for analysis.

For the semi-batch mode, methanol and sulphuric acid were initially transferred into the reactor and heated to the desired temperature at a mixing speed of 300rpm. In a separate flask, a mixture of canola oil and oleic acid was mixed and pre-heated to 60°C. A metering pump was used to add this mixture to the reactor vessel at a constant flow rate of 18 ml/min. By using this feeding rate, the reaction was allowed to proceed under a semi-batch mode in which oil was added in the first 25 minutes of esterification and then the reaction proceeded under batch mode for the remaining 35 minutes. Impeller speed was varied over the course of the reaction from 300 to 600 rpm for different runs. These variations in rpm allowed investigations of mixing intensity to overcome mass transfer limitations. During esterification, samples were withdrawn from the vessel at regular intervals to analyze progress of the reaction.

Following esterification, the contents of the reactor, for both modes, were transferred to a separatory funnel and allowed to stand overnight to ensure complete separation of the phases (see Figure 4.2). The system was biphasic: a top layer was constituted by excess methanol, water and most of the catalyst and an organic layer mainly composed of
FAME, unreacted TG and FFA. Excess methanol and traces of water were removed from the bottom layer by vacuum evaporation at 100°C.

**Acid Content Analysis**

An acid-base titration method was used to quantify FFA content in the samples collected at specific intervals. Sodium hydroxide solution was initially standardized with dehydrated oxalic acid to accurately determine the normality of the solution. Values used were approximately 0.09, 0.031, and 0.013N. About 1g samples were withdrawn from the reactor and washed with distilled water to remove sulphuric acid and methanol from the organic phase. Subsequently, the vials were placed in the fridge to completely stop the reaction. At last, the organic layers were removed from the vials using a micropipette and centrifuged for 20 min at 3000 rpm to improve the separation of both phases.

The titration process followed in this work is a modified method of AOCS Ca 5a-40 in which smaller quantities of sample can be used as described by Rukunudin et al. [5] In the titration analyses, ethyl alcohol was used as the solvent and phenolphthalein as
indicator. The FFA content as oleic acid in the sample was calculated by the following equation.

\[ \text{FFA} = \frac{V_{NaOH \text{ used}} \cdot N_{NaOH} \cdot 282}{W_{\text{sample}}} \cdot 100 \]  \hspace{2cm} (4.1)

**FFA**: Free acidity as oleic acid (%)

**\(V_{NaOH}\)**: Volume of NaOH solution used during titration (ml)

**\(N_{NaOH}\)**: Exact normality of alkaline solution (mol/L)

**\(W_{\text{sample}}\)**: Weight of titrated sample (g)

282: Molecular weight of oleic acid (g/mol)

Conversion of esterification reaction was calculated by as follows:

\[ \text{Conversion}(\%) = \frac{\text{FFA}_i - \text{FFA}_t}{\text{FFA}_i} \cdot 100\% \] \hspace{2cm} (4.2)

**FFA\(_i\)**: Initial FFA content

**FFA\(_t\)**: FFA content at a given time

### 4.2.3.2 Two-Step Esterification and Transesterification Process

This approach facilitates the conversion of both FFA and TG to desired methyl esters. As discussed earlier esterification step first reduces the acidity of oil to an acceptable level in the presence of an acid catalyst. The esterified oil after decantation was prepared for transesterification by evaluating different combinations of purification steps shown in Figure 4.3. It contained residual amounts of methanol, sulphuric acid and water which could affect transesterification reaction.
Attempts were made to determine most effective combination(s) of steps 103 to 105 and their operating conditions in order to achieve maximum product yield while minimizing production costs. For example, methanol recovery was conducted at 60°C when it was followed by neutralization or at 100°C when both methanol and water were removed together and neutralization step was avoided.

Subsequently, transesterification was conducted in presence of alkali catalyst to convert triglyceride molecules into FAME. Two types of alkali catalysts namely potassium hydroxide and potassium carbonate, and their combination were employed. Weighed amounts of catalysts were dissolved in methanol using a molar ratio of alcohol to oil of 6:1. The selected catalyst concentrations were based on preliminary laboratory experiments. While most literature studies have used batch mode for transesterification reaction, this study also tested semi-batch mode of operation. Transesterification was carried out for 1 hour at a constant temperature of 60°C followed by product separation and purification (see Figure 4.4). Once the reaction was completed the mixture was allowed to stand overnight in a separatory funnel. Methanol was then removed from both
phases by evaporation for later reuse. Crude methyl esters were washed once with 28vol.% (based on product) 1N HCl, to neutralize any remaining catalyst, and then with distilled water until a pH close to 7 was reached. The washed product was dried in a rotary evaporator for 20 minutes and filtered to remove any solid impurities using a micro-filter with a pore size of 45µm.

4.2.4 Analysis of final product

Density was measured at room temperature by accurately weighing 10 product samples of known volume in a digital balance with an accuracy of +/-1mg. Viscosity was measured by using a Brookfield viscometer.

Acid-base titration was used to quantify the acidity of esterified oil and transesterified oil as described in Section 4.2.3.

Biodiesel was analyzed by using gas chromatography (GC Schimadzu 2010) equipped with a flame ionization detector (FID) and a capillary column with dimensions of 15 meters in length, 0.32mm internal diameter, and 0.1µm film thickness. 1µl was injected.
on-column by an AOC 20s auto sampler at an oven temperature of 50°C and an injector temperature of 250°C. High purity helium was used as the carrier gas. The temperature program followed was in accordance with ASTM D6584 to determine free glycerol and total glycerol in biodiesel samples: temperature of 50°C was held for 1 min, and then it was increased at a rate of 15°C/min to 180°C; followed by a rate of 7°C/min to 230°C. Finally the temperature was increased at a rate of 30°C/min to 380°C and held for 10 min. The total operating time was 31.84 min. The FID temperature was fixed at 380°C. Glycerol, monoolein, diolein and triolein were used as standards to quantify glycerides. Calibration curves were generated from the above four standards and 1,2,3-tricaproylglycerol (tricaprin) as an internal standard. A silylating agent, N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) was added to each GC sample to improve chromatographic properties of glycerides. Samples were prepared as per ASTM D6584 specifications.

4.3 Results and Discussion

4.3.1 Esterification Reaction

Esterification was carried out in order to reduce the FFA content in oil to an acceptable level (<2mgKOH/g) before proceeding with alkali transesterification to produce biodiesel. In this reaction, a fatty acid molecule reacts with an alcohol molecule to produce a methyl ester and a water molecule in the presence of an acid catalyst as illustrated bellow.
As previously mentioned, two types of mixing were studied, namely batch and semi-batch. While, batch is commonly used in industry its mixing effects can be limited especially at the beginning of the reaction between two immiscible liquids. Mixing process can be improved and initial mass transfer limitations can be overcome by gradually feeding the oil into previously added methanol and catalyst solution in the reactor. This technique was previously proposed by Pal and Prakash [6] for methanolysis of TG to overcome mass transfer limitations commonly encountered with batch mode.

As droplets of oil fall into a pool of methanol and catalyst solution, they easily get dispersed uniformly throughout the reaction system. By adding oil into the system at 18ml/min, the methanol to FFA molar ratio was enhanced specially in the early stages of the reaction with values of: 100:1 at 5min, 50:1 at 10min, 25:1 at 20min and finally a 20:1 from 25min to 60min.

The two methods were compared based on FFA conversion under different conditions. Figure 4.5 compares reaction progress obtained with the two methods for initial FFA of 6wt.% It can be observed from the figure that FFA conversions obtained with the semi-batch method are higher initially. The conversions obtained with the two methods are nearly the same between 20 to 40 minutes interval. For higher reaction durations, conversions are higher with the batch method. It seems any advantage of semi-batch method is lost after 30 minutes which is the end of feed flow. The reactor now operated in batch mode for another 30 minutes and agitator mixing speed remained at 400 rpm. In
case of batch mode, however, the mixing speed of 600 rpm was kept constant from beginning to end. Higher conversions obtained with the batch method in the second half of reaction indicate that mixing intensity is important to facilitate the reaction.

The role of mixing intensity was further investigated by adjusting the rpm as follows for semi-batch mode: 300 in first 15 minutes, 400 for the next 15 minutes and 600 for the remaining 30 minutes. The FFA content in the feed was raised to 15 wt% which is more representative of the value in most nonedible oils. Moreover, the higher FFA in oil feed was also expected to show clear difference between the two methods. The progress of the reaction with the above changes is shown in Figure 4.6 for batch and semi-batch. It can be observed that conversions obtained with the two methods are similar in the second half thus confirming the importance of agitation intensity to achieve high conversions in the reaction system. Final conversions of 94.6% and 96.0% were obtained for batch and semi-batch respectively.

Figure 4.5 Comparison of batch and semi-batch method based on reaction progress (Initial FFA:6%)
A comparison of remaining FFA in the reaction mixture as a function of time is presented in Figure 4.7 for low and high initial FFA. It can be seen that rate of drop in FFA content is faster with high initial FFA value. This is explained by the higher amount of catalyst added to the system. Even though the concentration of H$_2$SO$_4$ with respect to FFA content was the same in both cases (5%), the amount of active species is higher in the latter experiment. In addition, higher conversions are achieved, due to an increase in reactants concentration. Methanol loadings were higher when 15% FFA was employed. This facilitated the formation of methyl esters by increasing the solubility of the alcohol in the non-polar phase. This finding is supported by recent studies conducted by Lin et al. [7] and Marchetti et al. [8].
Further investigations were conducted to assess the effect of catalyst concentration of FFA conversion. Sulphuric acid concentration was increased to 10% (based on wt. of FFA), while keeping other parameters constant: 20:1 FFA to MeOH molar ratio, 60°C, 1 hour reaction time, semi-batch operating mode. The following diagram presents the results obtained for two runs.
Reaction conversion was improved by adding more catalyst to the system. The highest conversion achieved was 98.62% for 10% H$_2$SO$_4$. Using a low catalyst concentration improves the process as it reduces the chemical usage. However, it should be noted that the lower the acidity the less soap formation during alkali transesterification. The presence of soaps can be problematic as they are emulsifiers. Nowadays, commercial processes use food-grade vegetable oils due to its low FFA content regardless of the their high cost to avoid downstream problems [10]. Therefore, a high esterification conversion is required to minimize soap formation, yield losses, and facilitate purification process. For this reason, 10% sulphuric acid was selected as the optimum catalyst concentration for esterification.
4.3.2 Purification of Esterified Oil

After the reaction the esterified reaction mixture gets separated into a methanol-rich layer and an oil-rich phase – step 102 in Figure 4.2. Sulphuric acid being a homogeneous catalyst is distributed between the two phases although most of it is expected to be in methanol-rich phase due to its polar nature. In order to determine the exact catalyst distribution, alkaline titrations were performed using three samples from each phase. It was found that $1.6 \pm 0.005\%$ of the top phase was composed by sulphuric acid in semi-batch mode and $2.0 \pm 0.06\%$ in batch mode. The difference in values is explained by the mixing process conducted in each method. In batch, the agitation process was conducted at room temperature, whereas in semi-batch the mixture was heated up to $60^\circ\text{C}$ prior to esterification. It is believed that an increase in temperature favoured alkylation of sulphuric acid, thus, formation of mono- and dialkylsulphates (see R4.2). This finding suggests that lower active species were present in esterification conducted under semi-batch. Nevertheless, the approach resulted in higher conversions when compared to batch.

The same titration procedure was followed to determine the acid content in the bottom layer. However, since there is a small amount of unreacted oleic acid in the oil phase, an accurate value could not be obtained. An attempt to calculate sulphuric acid in the organic layer was made by using two indicators: methyl orange and phenolphthalein indicator, the first change in color, from yellow to red, would indicate the first equivalence point due to neutralization of the strongest acid present in the sample, sulphuric acid. Then the second change in color, from red to pale pink, would indicate neutralization of fatty acids. However, when three drops of methyl orange were added to
the sample solution, the mixture turned red, implying that negligible amounts of sulphuric acid were present in the organic phase. Therefore, a mass balance was performed to establish the level of acid in the product layer. It was found that about 45% of total sulphuric acid used in esterification was not accounted for. A review of literature studies showed that very little work has been done in this area to look at possible reaction(s) taking place; authors could locate only one such study [11]. Pisarello et al. show that alkylation of sulphuric acid given by the following reactions could take place prior to the esterification reaction.

\[
H_2SO_4 + CH_3OH \leftrightarrow CH_3HSO_4 + H_2O \tag{R4.2}
\]

\[
CH_3HSO_4 + CH_3OH \leftrightarrow (CH_3O)_2SO_4 + H_2O \tag{R4.3}
\]

The water molecules produced by the above reactions can aid in TG hydrolysis while inhibiting tranesterification of the glycerides. While most of the products and unspent sulphuric acid will be removed with decanted methanol layer, residual amounts of these impurities will leave with esterified oil as well.

The oil phase containing residual amounts of methanol, sulphuric acid and water was treated further before transesterification. Three possible steps considered were methanol recovery (103), neutralization (104) and drying (105) as shown in Figure 4.3. Attempts were made to determine most effective combination(s) of these steps and their operating conditions in order to achieve maximum product yield and minimize production costs. For example, methanol recovery was conducted at 60 °C when it was followed by neutralization or at 100°C when both methanol and water were removed together and neutralization step was avoided. The objective was to remove impurities which could
lead to lower product yield. A set of ten experiments were conducted whose details are given in Table 4.1.

### 4.3.3 Transesterification Reaction

The purified oil was subjected to transesterification reaction conducted at 60°C in presence of alkali catalysts. The loadings of catalysts potassium hydroxide, potassium carbonate or their combination were determined based on their optimum concentrations determined earlier and need for any acid neutralization. Additionally, two reactor operating modes were further investigated. Product yields reported in Table 4.1 were calculated based on the weight of oil initially fed into the system (i.e. high acidity oil). On the other hand, glycerol yields were based on esterified oil weight only. This followed the assumption that transesterification in the first step was negligible. Although, acidic catalysts are capable of conducting both reactions, the rate of methanolysis of TG is well known to be low at temperatures below 100°C, low methanol to oil molar ratio, and short reaction times (<3hr) [12, 13].

### Table 4.1 Product analysis after transesterification conducted on esterified oils.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Methanol Recovery</th>
<th>H₂SO₄ Removal</th>
<th>Drying</th>
<th>Operating Mode</th>
<th>Catalyst Type</th>
<th>Catalyst wt. (g)</th>
<th>BD Yield (%)</th>
<th>GL Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>B</td>
<td>K₂CO₃</td>
<td>15.7⁺</td>
<td>68.0</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>SB</td>
<td>K₂CO₃</td>
<td>15.7⁺</td>
<td>78.7</td>
<td>87.6</td>
</tr>
<tr>
<td>3</td>
<td>YES (60°C)</td>
<td>NO</td>
<td>NO</td>
<td>SB</td>
<td>KOH/K₂CO₃</td>
<td>2.4/8.8⁺</td>
<td>83.5</td>
<td>103.0</td>
</tr>
<tr>
<td>4</td>
<td>YES (100°C)</td>
<td>NO</td>
<td>NO</td>
<td>SB</td>
<td>KOH</td>
<td>5.74⁺</td>
<td>89.7</td>
<td>124.0</td>
</tr>
<tr>
<td>5</td>
<td>YES (100°C)</td>
<td>NO</td>
<td>NO</td>
<td>SB</td>
<td>K₂CO₃</td>
<td>15.82⁺</td>
<td>89.8</td>
<td>91.0</td>
</tr>
</tbody>
</table>
It can be seen from Table 4.1 that lowest yields are obtained with run 1 and 2 which were conducted without any pre-treatment. For these runs, the oil layer after phase separation from esterification was directly injected into the transesterification reactor. It can be seen that biodiesel yield is greatly affected by impurities in the feed. During these runs, it was observed that a layer of soap-like material formed after the alkaline reaction and became more obvious in the washing step. The resulting soap layer was removed from the product after 1 hour of settling. The product yield was greatly affected by this separation as a substantial amount of FAME was lost. It is evident that side reactions including hydrolysis of esters, saponification, and neutralization of acidic catalyst by alkali lead to a decrease in product yield. The presence of water has a negative impact on alcoholysis reaction as it participates in the hydrolysis of esters and glycerides and saponification of carboxylic acids (FFA) as shown below. It has been reported that as a moisture content of 0.06% is sufficient to considerably reduce ester yield [14].

\[
\begin{align*}
R \times \text{CO} \times \text{OH} + \text{H}_2\text{O} & \rightarrow R \times \text{CO} \times \text{OH} + \text{HO} \times \text{R} \\
\text{Ester} \quad \text{Water} \quad \text{Fatty Acid} \quad \text{Alcohol}
\end{align*}
\]
Soap gives rise to formation of gels, increase in viscosity, and hinders purification of biodiesel [15]. When excess of alkali is used to neutralize acid, there is also the possibility of more water production from neutralization reactions as shown below.

\[
\text{R}_4.5 \quad \text{Fatty Acid Base Soap Water (or Potassium Bicarbonate)}
\]

\[
\text{H}_2\text{SO}_4 + 2\text{KOH} \leftrightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \quad (\text{R4.6})
\]

\[
\text{H}_2\text{SO}_4 + \text{K}_2\text{CO}_3 \leftrightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2 \quad (\text{R4.7})
\]

Moreover, the refining of glycerol tends to be more complex and expensive as alkali and salts need to be removed from the bottom layer. More importantly, side reaction might occur during transesterification with an increase of species in the reacting media.

For run # 3, methanol recovery step (103) was conducted at 60°C under vacuum. While most of methanol would have been removed under these conditions, some amount of associated water would also be removed. For this run, a combination of KOH and K\(_2\)CO\(_3\) catalysts were used to reduce total weight of alkali catalyst. Higher yield obtained with run could be attributed to use of lower catalyst and slightly lower moisture in feed. For runs 4 to 6 methanol recovery was conducted at 100°C which would have removed both methanol and associated water from esterified oil. Higher product yield (~ 90%) obtained with these runs compared to run # 3 can be attributed to absence of water in the feed.

Although product yield increased to about 90% with runs 4 to 6, generally product yields higher than 90% are desirable for economic reasons [16]. The only impurity remaining in
the feed was residual amount of sulphuric acid. For previous runs, excess alkali was used to neutralize remaining acid in feed but for run # 7, acid was removed by washing. After washing, most of the water settled out by decantation as water is immiscible in oil and methyl esters. Only trace amounts of water would enter the reacting medium in step two. In order to neutralize, the effects of any remaining water in the feed, a combination of KOH and K$_2$CO$_3$ catalysts was used. As seen in Table 4.1, highest product yield was obtained with this run. Potassium carbonate can react with available water molecules to produce more KOH as shown by reaction below.

$$K_2CO_3 + H_2O \leftrightarrow KOH + KHCO_3$$  \hspace{1cm} (R4.8)

As a result of this reaction, more catalytic species would be available for transesterification to occur. Thus potassium carbonate can be used as a drying agent to remove traces amount of water while generating potassium hydroxide in situ.

Final product quality was further assessed by gas chromatography to ensure ASTM requirements were met. Two purified biodiesel samples form run#4 and run#5 were injected into column for quantification of MG, DG, TG, and ME. The following GC report was obtained from analysis.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>ME</th>
<th>Free GL</th>
<th>MG</th>
<th>DG</th>
<th>TG</th>
<th>Total GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>99.18</td>
<td>0.016</td>
<td>0.272</td>
<td>0.051</td>
<td>0.151</td>
<td>0.109</td>
</tr>
<tr>
<td>5</td>
<td>99.11</td>
<td>nd$^+$</td>
<td>0.208</td>
<td>0.059</td>
<td>0.177</td>
<td>0.081</td>
</tr>
</tbody>
</table>

$^*$Not detectable
The level of free glycerol in run#4 is in accordance with specifications by ASTM and EN (0.02max). This was expected as most of the by-product present in the biodiesel phase is removed during washing process. Moreover, mass percentages of glycerides are also below the maximum allowable content established by CEN: 0.8max for MG, 0.2max for DG, and 0.2max for TG.

4.4 Conclusions

Esterification of FFA in the oily feedstock increased to about 99% under appropriate operating conditions determined in this study. Esterification reaction was investigated with batch and semi-batch reactor operating modes. While both methods are effective in reducing oil acidity to an acceptable level, results suggest that semi-batch mode enhances production of methyl esters, especially at the early stage of reaction, by providing excess alcohol. However, mixing speed should be gradually increased from 300 to 400 to 600rpm in order to overcome mass transfer limitations.

It was also found that pre-treatment of esterified oil to remove associated water and acid catalyst is required to achieve high biodiesel yield from transesterification reaction. Presence of water generated from esterification step can hydrolyze ester and glycerides followed by saponification of FFA. This leads to a decrease in purity as well as hinders biodiesel purification. Finally, removal of acid catalyst by water washing is recommended in order to decrease alkali consumption while achieving high product yields. Traces of water remaining after water washing and decantation can be removed by the use of potassium carbonate in transesterification.
An integrated process was proposed to convert both FFA and TG to FAME. The two-step approach is a simple and economic technique to produce biodiesel from high FFA feedstock. GC analysis confirmed that final product met ASTM standards for both KOH and K$_2$CO$_3$-catalyzed systems.
4.5 References

CHAPTER 5

5 Conclusions and Recommendations

5.1 Summary and Conclusions

A two-step process is developed to handle high FFA feedstock in biodiesel production by using a combination of catalysts. During the first step the acidity of oil is reduced by 98.6% using sulphuric acid as a catalyst. Subsequently, triglycerides are further converted into FAAE by using a combination of potassium hydroxide and potassium carbonate to obtain a final biodiesel yield of 93.6%. Series of experiments are conducted to analyze mixing effects during transesterification and esterification employing batch and semi-batch as reactor operating modes. Mass transfer limitations encountered in the initial stage of reactions by conventional batch are non-existent in semi-batch for the first 15 minutes. During this period, the conversion is enhanced by improving reactant mixing at a lower impeller speed.

A direct comparison between two alkaline catalysts, potassium hydroxide and potassium carbonate is made. Potassium carbonate and potassium hydroxide are active base catalysts capable of conducting transesterification with high TG conversions. Potassium carbonate is not as a strong base as potassium hydroxide and therefore higher concentrations are required. $K_2CO_3$ behaves both as a homogeneous and a heterogeneous catalyst. Its partial solubility in methanol allows the formation of methoxide species which have been recognized as the actual catalyst. On the other hand, the adsorption of methanol on undissolved $K_2CO_3$ also promotes methyl ester formation. The reaction
between potassium carbonate and methanol and potassium hydroxide and methanol explains the differences in soap formation. While the metal hydroxide produces water, the carbonate produces bicarbonate instead, and delays the hydrolysis of esters in the reacting media. Therefore soap formation is less likely to occur when potassium carbonate is used. Final biodiesel produced from KOH and K₂CO₃-assisted transesterification meets ASTM specifications.

The yield of biodiesel is highly dependent on the quality of feedstock. If raw materials with high FFA content are used, then esterification should be conducted in order to avoid side reactions. A systematic study of steps to pretreat esterified oil is conducted. The presence of water leads to hydrolysis of all forms of esters favoring saponification during alkaline-transesterification. In a two-step process, it is essential to remove excess methanol, and sulphuric acid from esterified oil to maximize conversion and biodiesel yield. Based on GC results, biodiesel produced using a two-step method results in up to standard quality product.

5.2 Recommendations for Future Work

- Experimental work with variations in temperature can be conducted to determine kinetic parameters for esterification reaction.

- A systematic study to determine the maximum amount of water in feedstock that can be tolerated by K₂CO₃ during transesterification is recommended.

- Two-stage process for transesterification and esterification in which by-products are removed after the first stage from the system by employing semi-batch approach is recommended to achieve higher yields.
• Washing procedure can be further investigated to reduce wastewater streams or utilize them in environmentally benign ways.
APPENDICES

Appendix A – Biodiesel and Diesel Properties

Table A. 1 ASTM standards of maximum allowed quantities in diesel and biodiesel fuel

<table>
<thead>
<tr>
<th>Property</th>
<th>Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>ASTM D975</td>
<td>ASTM D6751</td>
</tr>
<tr>
<td>Composition</td>
<td>HC (C10-C21)</td>
<td>FAME (C12-C22)</td>
</tr>
<tr>
<td>Kinematic Viscosity at 40°C (mm²/s)</td>
<td>1.9 – 4.1</td>
<td>1.9 – 6.0</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>188 – 343</td>
<td>182 – 338</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>60 – 80</td>
<td>100 – 170</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-35 to -15</td>
<td>-15 to 16</td>
</tr>
<tr>
<td>Water (vol %)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon (wt %)</td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td>Hydrogen (wt %)</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Oxygen (wt %)</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Sulphur (wt %)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>40 – 55</td>
<td>48 – 60</td>
</tr>
<tr>
<td>Stoichiometric air/fuel ratio (AFR)</td>
<td>15</td>
<td>13.8</td>
</tr>
</tbody>
</table>
## Appendix B – Material Balances

### Table B.1 Transesterification mass balance

<table>
<thead>
<tr>
<th>RUN</th>
<th>Mode</th>
<th>Canola Oil</th>
<th>MeOH</th>
<th>Catalyst, Conc.</th>
<th>Total</th>
<th>BD</th>
<th>Crude GL</th>
<th>Excess MeOH</th>
<th>Total</th>
<th>Losses (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B</td>
<td>499</td>
<td>110.15</td>
<td>K$_2$CO$_3$, 15.05</td>
<td>624.20</td>
<td>455</td>
<td>60.15</td>
<td>27.94</td>
<td>541.83</td>
<td>82.37</td>
</tr>
<tr>
<td>2</td>
<td>SB</td>
<td>500</td>
<td>110.21</td>
<td>K$_2$CO$_3$, 15.182</td>
<td>625.252</td>
<td>446</td>
<td>62.03</td>
<td>25.47</td>
<td>533.5</td>
<td>91.75</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>500</td>
<td>108.94</td>
<td>KOH, 5.091</td>
<td>614.031</td>
<td>459</td>
<td>58.38</td>
<td>25.22</td>
<td>518.6</td>
<td>71.431</td>
</tr>
<tr>
<td>4</td>
<td>SB</td>
<td>499</td>
<td>108.992</td>
<td>KOH, 5.098</td>
<td>613.681</td>
<td>447</td>
<td>60.02</td>
<td>22.593</td>
<td>522.61</td>
<td>83.47</td>
</tr>
</tbody>
</table>

### Table B.2 Esterification mass balance

<table>
<thead>
<tr>
<th>RUN</th>
<th>Mode</th>
<th>Canola Oil</th>
<th>Oleic Acid</th>
<th>MeOH</th>
<th>H$_2$SO$_4$</th>
<th>Total</th>
<th>BD/TG</th>
<th>Acidic MeOH</th>
<th>Excess MeOH</th>
<th>Total</th>
<th>Losses (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B</td>
<td>518</td>
<td>33.13</td>
<td>74.52</td>
<td>1.66</td>
<td>627.31</td>
<td>549</td>
<td>29.35</td>
<td>22.04</td>
<td>600.39</td>
<td>29.92</td>
</tr>
<tr>
<td>2</td>
<td>SB</td>
<td>519</td>
<td>33.18</td>
<td>76.83</td>
<td>1.69</td>
<td>630.70</td>
<td>549</td>
<td>29.51</td>
<td>19.88</td>
<td>598.38</td>
<td>32.32</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>382</td>
<td>67.55</td>
<td>152.86</td>
<td>3.426</td>
<td>605.83</td>
<td>443</td>
<td>117.77</td>
<td>13.62</td>
<td>574.39</td>
<td>31.44</td>
</tr>
<tr>
<td>4</td>
<td>SB</td>
<td>382</td>
<td>67.712</td>
<td>153.45</td>
<td>3.391</td>
<td>606.55</td>
<td>443</td>
<td>121.36</td>
<td>15.08</td>
<td>579.44</td>
<td>27.11</td>
</tr>
</tbody>
</table>
Appendix C – Esterification Reaction Calculations

Table C.1 Comparison between input requirements for 6% and 15% FFA esterification

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Units</th>
<th>Variable</th>
<th>Value</th>
<th>Units</th>
<th>Variable</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH to FFA molar ratio</td>
<td>20</td>
<td></td>
<td>MeOH to FFA molar ratio</td>
<td>20</td>
<td></td>
<td>MeOH to FFA molar ratio</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>5wt% H2SO4 (wt. of FFA)</td>
<td>555</td>
<td>g</td>
<td>5wt% H2SO4 (wt. of FFA)</td>
<td>460</td>
<td>g</td>
<td>10wt% H2SO4 (wt. of FFA)</td>
<td>69</td>
<td>g</td>
</tr>
<tr>
<td>Weight of Oil (Acid Oil)</td>
<td>522</td>
<td>g</td>
<td>Weight of Oil (Acid Oil)</td>
<td>391</td>
<td>g</td>
<td>Weight of Canola</td>
<td>391</td>
<td>g</td>
</tr>
<tr>
<td>Weight of Canola</td>
<td>33</td>
<td>g</td>
<td>Weight of FFA</td>
<td>69</td>
<td>g</td>
<td>Weight of FFA</td>
<td>69</td>
<td>g</td>
</tr>
<tr>
<td>Weight of Methanol</td>
<td>75</td>
<td>g</td>
<td>Weight of Methanol</td>
<td>156.54</td>
<td>g</td>
<td>Weight of Methanol</td>
<td>156.54</td>
<td>g</td>
</tr>
<tr>
<td>Weight of H2SO4</td>
<td>1.65</td>
<td>g</td>
<td>Weight of H2SO4</td>
<td>3.45</td>
<td>g</td>
<td>Weight of H2SO4</td>
<td>6.9</td>
<td>g</td>
</tr>
<tr>
<td>MW Canola</td>
<td>882.1</td>
<td>g/mol</td>
<td>MW Canola</td>
<td>882.1</td>
<td>g/mol</td>
<td>MW Canola</td>
<td>882.1</td>
<td>g/mol</td>
</tr>
<tr>
<td>MW FFA</td>
<td>282.46</td>
<td>g/mol</td>
<td>MW FFA</td>
<td>282.46</td>
<td>g/mol</td>
<td>MW FFA</td>
<td>282.46</td>
<td>g/mol</td>
</tr>
<tr>
<td>MW MeOH</td>
<td>32.04</td>
<td>g/mol</td>
<td>MW MeOH</td>
<td>32.04</td>
<td>g/mol</td>
<td>MW MeOH</td>
<td>32.04</td>
<td>g/mol</td>
</tr>
<tr>
<td>MW H2SO4</td>
<td>98.079</td>
<td>g/mol</td>
<td>MW H2SO4</td>
<td>98.079</td>
<td>g/mol</td>
<td>MW H2SO4</td>
<td>98.079</td>
<td>g/mol</td>
</tr>
<tr>
<td>Moles of AO</td>
<td>0.6559</td>
<td>mol</td>
<td>Moles of AO</td>
<td>0.5807</td>
<td>mol</td>
<td>Moles of AO</td>
<td>0.5807</td>
<td>mol</td>
</tr>
<tr>
<td>Moles of Canola</td>
<td>0.5918</td>
<td>mol</td>
<td>Moles of Canola</td>
<td>0.4433</td>
<td>mol</td>
<td>Moles of Canola</td>
<td>0.4433</td>
<td>mol</td>
</tr>
<tr>
<td>Moles of FFA</td>
<td>0.1168</td>
<td>mol</td>
<td>Moles of FFA</td>
<td>0.2443</td>
<td>mol</td>
<td>Moles of FFA</td>
<td>0.2443</td>
<td>mol</td>
</tr>
<tr>
<td>Moles of MeOH</td>
<td>2.3366</td>
<td>mol</td>
<td>Moles of MeOH</td>
<td>4.8856</td>
<td>mol</td>
<td>Moles of MeOH</td>
<td>4.8856</td>
<td>mol</td>
</tr>
<tr>
<td>Moles of H2SO4</td>
<td>0.0168</td>
<td>mol</td>
<td>Moles of H2SO4</td>
<td>0.0352</td>
<td>mol</td>
<td>Moles of H2SO4</td>
<td>0.0704</td>
<td>mol</td>
</tr>
<tr>
<td>Molar ratio H2SO4/FFA</td>
<td>0.144</td>
<td></td>
<td>Molar ratio H2SO4/FFA</td>
<td>0.144</td>
<td></td>
<td>Molar ratio H2SO4/FFA</td>
<td>0.288</td>
<td></td>
</tr>
<tr>
<td>Mass ratio H2SO4/AO</td>
<td>0.2973</td>
<td></td>
<td>Mass ratio H2SO4/AO</td>
<td>0.75</td>
<td></td>
<td>Mass ratio H2SO4/AO</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Molar ratio MeOH/AO</td>
<td>3.2975</td>
<td></td>
<td>Molar ratio MeOH/AO</td>
<td>7.106</td>
<td></td>
<td>Molar ratio MeOH/AO</td>
<td>7.106</td>
<td></td>
</tr>
</tbody>
</table>
Appendix D – GC Analysis

1. Calibration Curves

Figure D. 1 Monolein calibration curve

Figure D. 2 Diolein calibration curve
2. GC Analysis Report

Table D. 1 Sample of peak area report of biodiesel samples

<table>
<thead>
<tr>
<th>RUN</th>
<th>Mode</th>
<th>T (°C)</th>
<th>Cat. Conc. (wt.%)</th>
<th>Remarks</th>
<th>MG</th>
<th>DG</th>
<th>TG</th>
<th>IS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SB</td>
<td>60</td>
<td>K₂CO₃, 3</td>
<td>1-Step</td>
<td>26564.4</td>
<td>1809.4</td>
<td>15851.6</td>
<td>60470.7</td>
</tr>
<tr>
<td>2</td>
<td>SB</td>
<td>60</td>
<td>KOH, 1</td>
<td>1-Step</td>
<td>35898.6</td>
<td>8395.7</td>
<td>22888.2</td>
<td>60892.5</td>
</tr>
<tr>
<td>3</td>
<td>SB</td>
<td>60</td>
<td>KOH, 1</td>
<td>2-Step</td>
<td>31075.7</td>
<td>5793.6</td>
<td>17232.2</td>
<td>63324.4</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>60</td>
<td>K₂CO₃, 3</td>
<td>2-Step</td>
<td>25057.5</td>
<td>3233.5</td>
<td>12976.6</td>
<td>60641.0</td>
</tr>
</tbody>
</table>

Figure D. 3 Triolein calibration curve

y = 1.6648x + 0.011229, R² = 0.99951.
CURRICULUM VITAE

LESLEY NATALIA LESMES SANCHEZ

Education

2011-2013 Master of Engineering Science Candidate
Department of Chemical and Biochemical Engineering
Western University, London, ON, Canada

2006-2010 Bachelor of Engineering Science in Chemical Engineering
Western University, London, ON, Canada

Honors and Awards

July 2013 Oral Presentation Award Second Place, Presented at Sarnia Research Bridges Symposium

March 2011 Oral Presentation Award Third Place, Presented at the London City Hall for the Mayor's Sustainable Energy Council

Work Experience

2011-2013 Research Assistant
Western University, London, ON, Canada

2011-2013 Teaching Assistant
Western University, London, ON, Canada