THE PRODUCTION OF METHYL ESTERS FROM
VEGETABLE OIL/FATTY ACID MIXTURES

by

Lirong Chi

A thesis submitted in conformity with the requirements
for the degree of Master of Applied Science
Graduate Department of Chemical Engineering and Applied Chemistry
University of Toronto

© Copyright by Lirong Chi (1999)
The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author’s permission.

L’auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L’auteur conserve la propriété du droit d’auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-45896-2
ABSTRACT

The one-phase acid- and base-catalyzed methanolysis of soybean oil and palmitic acid/soybean oil mixtures has been investigated. Methyl tert-butyl ether (MTBE) was used as cosolvent to form the single phase. A two-step method employing acid and base catalysis sequentially has been developed for producing methyl ester from oils which have significant fatty acid content.

One-phase methanolysis of pure soybean oil at room temperature using 1.0 wt.% sodium hydroxide (27:1 methanol/oil molar ratio) resulted in a 99.6% methyl ester content of the product in only 8 minutes. In contrast, one-phase methanolysis of soybean oil (30:1 methanol/oil molar ratio) with 2.0 wt.% concentrated sulfuric acid at 57°C resulted in a 96.6% methyl ester content of the product in 10 hours. In addition, one-phase acid catalyzed methanolysis of soybean oil/palmitic acid mixtures of different compositions produced a maximum 97.5% methyl ester content of the product in 10 hours. One-phase methanolysis of pure palmitic acid yielded product containing 99.8% ester after 10 hours; more importantly only 1.4% of palmitic acid was unreacted after 33 minutes*.

A two-step methanolysis batch process in which an acid-catalyzed step was followed by a base-catalyzed step, converted a 50/50 by weight palmitic acid/soybean oil mixture to a 95.1% yield of 99.9% purity product in approximately 3.5 hours.

* Dr. Samir Konar- private communication.
Acknowledgments

This thesis would never have happened without the help, suggestion, encouragement, evaluation, support, insight, and patience of many great people. I wish to express my heartfelt appreciation and gratitude especially to the following people:

First and foremost, I wish to express my gratitude to my supervisor, Professor D.G.B. Boocock, for his invaluable and enthusiastic guidance, inspirational insight and for making this thesis possible.

I would like to acknowledge and thank Dr. S.K. Konar for his endless help throughout my graduate studies at University of Toronto.

My sincerest appreciation goes to Dr. F. H. Chang for his ceaseless encouragement, moral and technical support; for his direction during the period of my endless thesis write-up.

I deeply owe a gratitude to my whole family for their understanding, boundless support and encouragement during my graduate studies at University of Toronto.

I am grateful to my friends Dr. Haiyong Cai, Xudong Cao, Kecheng Li and my colleagues in the Boo’s Lab: George, Wei-yang for their help, friendship, support and smiles.
# Table of Contents

## Abstract .......................... ii

## Acknowledgments .................. iii

## Table of Contents .................. iv

## List of Figures .................... viii

## List of Tables ..................... ix

## List of Symbols ................... xi

## Chapter 1: Introduction ............. 1

## Chapter 2: Literature Review ......... 5

2.1 The Current Status of Biodiesel .. 5
2.2 Production of Biodiesel .......... 7
2.3 Chemistry of Transesterification . 9
   2.3.1 Base-Catalyzed Transesterification 12
   2.3.2 Acid-Catalyzed Transesterification 15
   2.3.3 Analysis of Transesterification Products 17
2.4 Process Variables Affecting Transesterification 18
   2.4.1 Temperature .................. 18
   2.4.2 Catalysts .................... 20
      ( a ) Acid Catalyst ............... 20
      ( b ) Base Catalyst .............. 24
   2.4.3 Molar Ratio .................. 29
   2.4.4 Type of Alcohol .............. 31
   2.4.5 Effect of Moisture Content, Quality of Fat and Oil 32
   2.4.6 Glycerol Separation .......... 33
2.5 Feedstocks for Biodiesel ........... 33
2.6 Fuel Properties of Biodiesel and Engine Testing 34
2.7 Environmental Aspects 35

**Chapter 3: Background Information** 37
3.1 Overview of Two-Phase Transesterification 37
3.2 Overview of One-Phase Transesterification 39
3.3 Cosolvents 41

**Chapter 4: Experimental** 44
4.1 Materials and Chemicals 44
4.2 Base-Catalyzed Transesterification Procedure 46
   4.2.1 Preparation of Base-Catalyst Solution 46
   4.2.2 Method of Base-Catalyzed Transesterification 46
4.3 Acid-Catalyzed Transesterification Procedure 47
   4.3.1 Method of Acid-Catalyzed Transesterification 47
   4.3.2 Minimum Cosolvent Requirement 48
4.4 Two-Step Transesterification Process 50
   4.4.1 Determination of Fatty Acid Content after First-Step Methanolysis 50
   4.4.2 Method of Two-Step Transesterification 51
      ( a ) First Step: Acid-Catalyzed Methanolysis 52
      ( b ) Second Step: Base-Catalyzed Methanolysis 52
4.5 Product Purification 53
4.6 Investigation of Cosolvent ( MTBE ) Degradation 53
4.7 Analysis of Ester Product 54
   4.7.1 Sample Preparation for Gas Chromatography 54
   4.7.2 Determination of the Standard Material Retention Time 54
   4.7.3 Instrumentation and Operating Condition 55
Chapter 5: Results & Discussion 56

Part I: Analysis by Gas Chromatography 56
5.1 Results 56
5.2 Discussion 57

Part II: One-Phase Base-Catalyzed Transesterification 58
5.3 Results 58
5.4 Discussion 59

Part III: One-Phase Acid-Catalyzed Transesterification 64
5.5 Results 64
  5.5.1 One-Phase Acid-Catalyzed Methanolysis of Neat Vegetable Oil 64
  5.5.2 One-Phase Acid-Catalyzed Methanolysis of The Vegetable Oil/Palmitic Acid Mixtures 68
  5.5.3 One-Phase Acid-Catalyzed Methanolysis of Palmitic Acid 76
  5.5.4 Investigation of Cosolvent (MTBE) Degradation 76
5.6 Discussion 77
  5.6.1 One-Phase Acid-Catalyzed Transesterification of Neat Vegetable Oil 77
  5.6.2 One-Phase Acid-Catalyzed Methanolysis of The Vegetable Oil/Palmitic Acid Mixtures 79
  5.6.3 One-Phase Acid-Catalyzed Methanolysis of Palmitic Acid 85
  5.6.4 Investigation of Cosolvent (MTBE) Degradation 86

Part IV: One-Phase Two-Step Transesterification Process 86
5.7 Results 86
5.8 Discussion 88

Chapter 6: Conclusions 91

Chapter 7: Recommendations 94

References 95
Appendices

Appendix A
1. Theoretical Amount of Methyl Ester Calculation
2. The Theoretical Amount of Methyl Palmitate Amount Calculation
3. The Amount of Na₂CO₃ Required to Neutralize the Sulfuric Acid

Appendix B Kinetic Data from the Literature

Appendix C-1 Data for Base-Catalyzed MTBE-Assisted One-Phase Methanolysis of SBO (Figure 5.3.1)

Appendix C-2 Data for Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis of SBO/PA mixtures (Figure 5.5.2-1)

Appendix D-1 Gas Chromatograms of Residues Remaining after Products from Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis of SBO Were Distilled

Appendix D-2 Gas Chromatograms of Residues Remaining after Products from Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis of SBO/PA Mixtures Were Distilled

Appendix D-3 Gas Chromatograms of Residues Remaining after products from MTBE-Assisted One-Phase Two-Step Methanolysis of SBO/PA Mixtures were distilled
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.1-1</td>
<td>The procedure for a typical base-catalyzed transesterification</td>
<td>14</td>
</tr>
<tr>
<td>2.3.2-1</td>
<td>The typical acid-catalyzed transesterification.</td>
<td>16</td>
</tr>
<tr>
<td>2.4.1-1</td>
<td>Temperature effect on the methanolysis of soybean oil with NaOH catalyst</td>
<td>20</td>
</tr>
<tr>
<td>2.4.2-1</td>
<td>Comparison of methanolysis of soybean oil using 1.0 wt.% H₂SO₄ and 2.0 wt. % H₂SO₄ as catalyst.</td>
<td>23</td>
</tr>
<tr>
<td>2.4.2-2</td>
<td>A summary of possible reaction routes.</td>
<td>27</td>
</tr>
<tr>
<td>2.5.1</td>
<td>Effect of methanol/sunflower oil molar ratio on ester production.</td>
<td>30</td>
</tr>
<tr>
<td>5.3-1</td>
<td>One phase methanolysis of SBO: change of composition of the product with time for molar ratio of methanolysis/SBO (27:1) 1 wt.% NaOH catalyst using MTBE as cosolvent</td>
<td>58</td>
</tr>
<tr>
<td>5.3-2</td>
<td>Comparison of one-phase THF-assisted methanolysis of SBO, molar ratio of methanol/oil 8:1; with one-phase MTBE-assisted methanolysis, molar ratio methanol/oil 27:1. (Both in 1 wt.% NaOH catalyst)</td>
<td>59</td>
</tr>
<tr>
<td>5.3-3</td>
<td>Gas chromatogram of one-phase base-catalyzed reaction.</td>
<td>60</td>
</tr>
<tr>
<td>5.5.1-1</td>
<td>The relation between methyl ester composition and reaction time.</td>
<td>65</td>
</tr>
<tr>
<td>5.5.1-2</td>
<td>Comparison of MTBE-assisted one-phase methanolysis of SBO at 57°C, 2 wt% H₂SO₄ catalyst with butanolysis of SBO at 77°C and 1 wt.% H₂SO₄ catalyst.</td>
<td>66</td>
</tr>
<tr>
<td>5.5.1-3</td>
<td>Comparison of THF-assisted one-phase methanolysis of SBO at 70°C, 2 wt.% H₂SO₄ as catalyst with MTBE-assisted one-phase methanolysis of SBO at 57°C, 2 wt.% H₂SO₄ as catalyst.</td>
<td>66</td>
</tr>
<tr>
<td>5.5.1-4</td>
<td>The typical gas chromatograms of distilled product from methanolysis of SBO</td>
<td>67</td>
</tr>
<tr>
<td>5.5.2-1</td>
<td>The relationship between methyl ester yields and palmitic acid content in the substrates.</td>
<td>70</td>
</tr>
<tr>
<td>5.5.2-2</td>
<td>The typical gas chromatogram of distilled methanolysis product from SBO/palmitic acid mixture.</td>
<td>74</td>
</tr>
<tr>
<td>5.5.2-3</td>
<td>The typical gas chromatogram of residue remaining after distillation of methanolysis product from SBO/palmitic acid mixture</td>
<td>75</td>
</tr>
</tbody>
</table>
List of Tables

2.5-1 Effect of methanol/soybean oil molar ratio on methyl ester content for one phase transesterification (Boocock et al., 1998) 31

2.6-1 ASTM fuel properties of NO. 2 diesel fuel, methyl soyate and ethyl soyate 34

2.7-1 Allowable amount of minor component in biodiesel 36

3.1-1 Reaction condition of one-phase acid-catalyzed methanolysis of soybean oil 40

3.2-1 Physical properties of potential cosolvents 42

4.1-1 Fatty acid composition of SBO 45

4.2-1 Experimental conditions for base-catalyzed methanolysis of SBO 46

4.3-1 The reaction condition for the acid-catalyzed methanolysis 48

4.3.2-1 Composition of the mixtures 50

4.4-1 Reaction conditions for two-step transesterification process 52

5.1-1 Gas chromatographic retention times for the standards 57

5.5.1-1 Results of the MTBE-assisted one-phase acid-catalyzed methanolysis of SBO 65

5.5.2-1 Minimum amount of cosolvent (MTBE) required to produce one-phase transesterification system for SBO, the SBO/palmitic acid mixture (30:1 methanol/SBO; 10:1 methanol/PA) 69

5.5.2-2 Methanolysis of the SBO/palmitic acid mixture, using 30:1 methanol/oil; 10:1 methanol/PA molar ratio, 2 wt. % concentrated H$_2$SO$_4$ catalyst in 10 hour reaction time 71

5.5.2-3 Residue analysis results for methanolysis of the SBO/palmitic acid mixture, using 30:1 methanol/oil; 10:1 methanol/PA molar ratio, 2 wt.% concentrated H$_2$SO$_4$ catalyst in 10 hour reaction time 72

5.5.2-4 Relation between the minimum reaction temperature required for good reflux and the content of palmitic acid 72

5.5.2-5 Relation between the recoverable amount of the MTBE/MeOH mixture after 10 hour methanolysis and the content of palmitic acid 73
5.5.3-1 Comparison of (a) one-phase methanolysis of palmitic acid, and (b) two-phase methanolysis of palmitic acid (10:1 methanol/PA molar ratio, 2 wt.% concentrated H₂SO₄ Catalyst in 10 hour reaction time)

5.7-1 Comparison of methyl ester yield from: (a) acid-catalyzed MTBE-assisted one-phase methanolysis in 10 hours; (b) two-step MTBE-assisted methanolysis substrate in 3.5 hours (50/50 SBO/palmitic acid mixture)

5.7-2 The composition of residues from two-step methanolysis and from acid-catalyzed methanolysis
# List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American standard testing materials</td>
</tr>
<tr>
<td>BSTFA</td>
<td>N,O-bis(trimethylsilyl)-trifluoroacetimide</td>
</tr>
<tr>
<td>BuOH</td>
<td>Butanol</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>ME</td>
<td>Methyl ester</td>
</tr>
<tr>
<td>ML</td>
<td>Methyl linoleate</td>
</tr>
<tr>
<td>MP</td>
<td>Methyl palmitate</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl tert-butyl ether</td>
</tr>
<tr>
<td>NaOBu</td>
<td>Sodium butoxide</td>
</tr>
<tr>
<td>NaOCH$_3$</td>
<td>Sodium methoxide</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>Sodium carbonate</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>Sodium sulphate</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium chloride</td>
</tr>
<tr>
<td>PA</td>
<td>Palmitic acid</td>
</tr>
<tr>
<td>SBO</td>
<td>Soybean oil</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
</tbody>
</table>
CHAPTER 1

Introduction

With the rise in concern for pollution caused by fossil fuels such as petroleum, coal and natural gas, and the realization that energy supplies are not infinite, alternative fuels and renewable sources of energy such as biodiesel are being considered worldwide.

In the United States and Europe, the requirement for transportation fuel has increased; this trend will continue. In developing countries, such as India, Malaysia, South Africa, Vietnam and China, energy use will continue to increase for economic growth and improved standards of living. With the increasing reliance on imported petroleum, these countries are extremely vulnerable to fuel price fluctuations and supply disruption.
Fossil fuel use in transportation is the leading contributor to urban air pollution and to global warming. In recent years, new sulfur and aromatic compound limits give the petroleum producers a new challenge to lower the sulfur and aromatic content of traditional fuel. As a result, the cost associated with fuel-production and engine-modification will increase in order to meet the more stringent environmental legislation. People throughout the world are looking for effective, cost-competitive technologies to comply with current and pending regulations. Renewable fuel sources such as biodiesel and ethanol can play a modest role in reducing greenhouse gases and other potentially hazardous emission related to fossil fuels.

Renewable fuels such as biodiesel are potential contributors to solving the energy problem. Biodiesel, which consists of fatty acid esters derived from vegetable oil, waste oils or animal fat in a process called transesterification, is a renewable energy source. It not only reduces the demands placed on our finite natural resources, but also enhances our energy security. Biodiesel contains no sulfur or aromatic compounds and its use results in lower emissions of carbon monoxides, hydrocarbons, and particulates. The agriculture sector also benefits from the use of biomass derived fuel.

In the past decade, vegetable oil and animal fat have been investigated for their potential as alternative fuels (Sharma & Bakhshi, 1991a). In 1916, castor oil was tested on the first diesel engine imported into Argentina as an alternative fuel (Gutierrez, 1916). In the 1930’s and 1940’s, vegetable oils were used as diesel fuel substitutes on a short term or emergency basis.

Reports from engine tests show that most of the problem associated with the use of vegetable oil in diesel engine are directly related to its high viscosity and to its unsaturated fatty acid components (Pryde, 1983). High viscosity oil leads to poor atomization of the fuel,
uneven and incomplete combustion, coking of the fuel injectors and ring carbonation (Mao, 1995). In the early 1980's, investigators indicated that a chemical reduction of viscosity can be achieved by a process called "transesterification". Biodiesel, a lower alcohol fatty acid ester such as methyl or ethyl ester is the product resulting from this process.

Biodiesel is an excellent diesel fuel substitute with the advantage that it generates fewer emissions upon combustion. Biodiesel in more than 50 tests done world-wide matched regular diesel performance in terms of power, fuel mileage and engine wear (Lau, 1996; INFORM, 1993; INFORM, 1994). Moreover, biodiesel is safer than other alternative fuels such as methanol and natural gas. It has a high flash point and does not produce explosive air/fuel vapors; it has low mammalian toxicity if ingested and it is biodegradable.

Unfortunately, biodiesel costs almost twice as much to produce as diesel fuel (Culshaw, 1993) due to the vegetable oil being more expensive than petroleum as a raw material for fuels. With the use of waste oils and fats, biodiesel products will be more attractive economically.

Since vegetable oils and methanol are immiscible, two-phase transesterification of vegetable oil, employing both base and acid catalyst, has been used to produce methyl esters. Reaction times were long and reactions did not go to completion. Researchers under the guidance of D.G.B.Boocock at the University of Toronto have employed one-phase transesterification of vegetable oil to speed the process.

Previous studies conducted by Boocock et al. have shown that one-phase base-catalyzed methanolysis of soybean oil using tetrahydrofuran as cosolvent is much faster than the two-phase process and goes essentially to completion. Unfortunately, waste oil or animal
fat often contains a high percentage of free fatty acid, which cause soap formation with the base catalyst. In this case, an acid catalyst must be used.

Two-phase acid-catalyzed methanolysis of vegetable oil has been reported. Sixty nine hours were required to achieve conversions to 93 wt.% of methyl ester (Freedman et al., 1984). One-phase acid-catalyzed transesterification process of vegetable oil tetrahydrofuran as cosolvent has been developed in which 97.9% methyl ester can be produced in about 10 hours (Boocock et al., 1996). The purpose of this research work described in this thesis was to further study this method for the substrates which contain large amounts of free fatty acids. The scope includes:

1) investigating one-phase base-catalyzed methanolysis of neat vegetable oil using methyl tert-butyl ether (MTBE) as cosolvent.

2) investigating one-phase acid-catalyzed methanolysis of neat vegetable oil using methyl tert-butyl ether (MTBE) as cosolvent.

3) investigating one-phases acid-catalyzed methanolysis of the vegetable oil/fatty acid mixtures using methyl tert-butyl ether (MTBE) as cosolvent.

4) developing and optimizing a reaction sequence which combines both acid and base catalyzed reactions to form methyl esters from mixtures of fatty acid and triglycerides.

Soybean oil and palmitic acid mixtures were used as substrates for waste fats and oils in this study. It was hoped that the results would provide significant information concerning the methanolysis of used vegetable oil, waste oil and animal fats, as well as information for developing a process that could be implemented in industry.
CHAPTER 2

Literature Review

2.1 The Current Status of Biodiesel

Biodiesel consists of methyl or ethyl esters derived from vegetable oil, animal fat, waste oil, and microalgal oil through the process of “transesterification”.

In the early literature, there are several terminologies for these ester-forming reactions, namely: alcoholysis, acidolysis and ester interchange; but recently, it is more common to use the term “transesterification” to describe the ester reaction, which when carried out with an alcohol in the presence of an acid or base catalyst is known as alcoholysis. Depending on the specific alcohol used, alcoholysis is referred to as methanolysis, ethanolysis, propanolysis, and butanolysis, etc.. In this study, these terminologies: transesterification, alcoholysis and methanolysis will be adhered to throughout this whole work.
Transesterification has been widely used in the manufacture of cosmetics since the 1940's (USP, 1945). The patent by Bradshaw and Meuly (Bradshaw and Meuly, 1942) was to make soap through methylation of fats accompanied by high water-free glycerine recovery. The patent reported that a methanolysis of dry neutral fats was carried out at 80°C in the presence of sodium or potassium hydroxide as catalyst (0.1-0.5 wt. % based on the weight of oil). The methyl esters produced from this reaction were further processed into soap. The glycerine resulting from soap making process was recovered in an aqueous solution.

Many researchers reviewed and investigated the methods for transesterification. Hatman (Hatman, 1956) has examined experimentally different methods for the methanolysis of fats and oils. He found that it is more convenient, rapid and economical to produce methyl ester from fats and oils using the method suggested by Bradshaw and Meuly rather than the conventional method. The latter method, which consists of saponifying the fats (hydrolysis of fats), decomposing the soaps into fatty acids by acidification and esterifying the fatty acids with methanol to prepare methyl ester, is not only time-consuming but also requires a large amount of solvent.

Since the worldwide energy shortage and oil crisis in the late 1970's and early 1980's, vegetable oils and waste oil have attracted attention as a potential renewable resource for the production of an alternative to petroleum-based diesel fuel. Various products from vegetable oils and waste cooking oils have been proposed as an alternative fuel for diesel engines. The use of neat vegetable oil, mixtures of vegetable oil and other components and alcohol esters of vegetable oils as fuel has been studied at the University of Idaho since 1979. Peterson and his co-workers (Peterson, 1986) have given a complete description of the process for the production of the methyl and ethyl ester of winter rape. Methyl ester of winter rape has been
manufactured in a 756-liter batch pilot plant using potassium hydroxide as a catalyst (Roger A. Korus. et al., 1993). The interdisciplinary team at Idaho identified, developed, evaluated and optimized the fuel production process. Researchers from the Colorado School of Mines produced fatty acid methyl ester from waste cooking oil using base-catalyst. It contains up to 10% free fatty acid which also reacted with catalyst. In this case it is necessary to remove the excess free fatty acid during or before the reaction (Reed, 1991).

Researchers also studied the biodiesel made from free fatty acids. This reaction is catalyzed by acid at elevated pressure (Swerm, 1981).

M. O. Bagby, B. Freedman, E. H. Pryde and their research group from the U.S. Department of Agricultural in Peoria investigated vegetable oils as fuel in the early 1980’s. They have actively been involved in the different areas of biodiesel for more than one decade. Recently, they have focused on other alternative diesel substitutes such as microemulsion formulations (Mao, 1995).

The United States Department of Commerce (biofuels, 1992-1996) and European Commission (Chemical Market Reporter, 1992) have presented comprehensive reviews on the status and opportunities for the production and use of different types of biofuel including biodiesel in the U.S. and Europe. They also established the fuel and emission standard for biodiesel in various blends with standard diesel fuel.

**2.2 Production of Biodiesel**

In the United States, batch pilot plants (under 1,000 gal/batch) were built at various universities: the University of North Dakota produced sunflower methyl ester (Hassett et al., 1988); the University of Idaho produced methyl ester of rapeseed (Caringal, 1989) and the
Colorado School of Mines produced Biodiesel from waste cooking oil (Reed, 1991 ). Interchem Industries Inc. (Leawood, Kansas City) contracted Proctor and Gamble Co. to produce up to 15 million gallons/y of methyl ester at plants in Massachusetts and California since 1992 (Chowdhury et al. 1993; Caruana et al. 1992; Interchem, 1992). The Sunrider Expedition, a 24-foot Zodiac boat circling the world to raise global environmental awareness, was powered by Interchem's biodiesel fuel. The Gratech division of Stratco Inc. in Kansas city began construction of a continuous plant that produced 3 to 12 million gallon/y of methyl ester of vegetable oil (Chemical Engineering, 1992a).

As reported by Chowdhury in 1992, there were more than 20 large and small scale plants in Europe producing biodiesel commercially with more than 200,000 metric ton (m.t.)/y of production capacity (Chowdhury et al. 1992). A further increase to 500,000 m.t./y was planned for 1995. The world's first industrial plant with a capacity of 60,000 m.t./y of biodiesel at Livorno, Italy was started up by Milan-based Novamount in 1992 (Chemical Engineering, 1992b, c). With the second plant, the annual biodiesel capacity was increased from 100,000m.t. to 160,000m.t./y. The German taxi federation planned to have 40,000 cabs running on Novamount's fuel by 1995.

A two-step, two-phase process was developed for the conversion of acidic oils to methyl ester (Societe Annon., 1965). It was suggested that fatty acids be first esterified uncatalyzed with added glycerol at 210°C-230°C at 5-10 mm Hg and then interesterified with methanol and alkaline catalyst to afford a yield of totally available fatty acid components from the acidic oil of well over 90%.

New processes are being developed to make biodiesel more economical. A patented German semicontinuous ATT-process was reported in 1988 (H. Stage, 1988). The raw oil
was first purified by removing up to 15% free fatty acids. The purified oil was then transesrerified with methanol at 80°C to produce methyl ester. The process also included methods such as purification and recovery of by-products glycerine, free fatty acid and methanol as pure compounds. Another patented process called ‘esterfip’ was developed by Institut Francais du Petrole to produce ‘diester’ (Stern, et al. 1986; 1987). The process involves several steps including transesterification, esterification and purification. The substrates were raw oils ranging from neutral oil to oil containing 60% free fatty acid. Reaction time and temperature are 10-12 hours and 100-120°C respectively. The alcohol to oil molar ratio employed was 4.8 to 6. The purity of ester was 93-99 wt.% depending on the quality of the oil, and the yield on oil was 95-103 wt.% depending on the alcohol.

Boocock and his co-workers in the Department of Chemical Engineering and Applied Chemistry at University of Toronto developed the one-phase transesterification process, which added an inert co-solvent to the acid and base catalyzed methanolysis of vegetable oil to speed up the reaction. The addition of cosolvent such as tetrahydrofuran (THF) (1.25 volumes per volume of methanol at 6:1 methanol/oil molar ratio) produces an oil-dominant one-phase system in which methanolysis rates are fast at room temperature and atmospheric pressure. A 98% methyl ester content of the product resulted after only 3 minutes using a 2 wt.% sodium hydroxide level. Therefore, the process could be run in a continuous mode.

2.3 Chemistry of Transesterification

Vegetable oils and animal fats have remarkably similar chemical structures, although they may have different flavor and color. Generally, they are the esters of glycerol in which all three hydroxyl groups are esterified by saturated or unsaturated (C12 to C20) long chain fatty
acids. These triglycerides can be transesterified to lower the high viscosity of the oil or fat which otherwise may cause the coking of the injectors, oil ring sticking and thickening of lubricating oil. The high viscosity results from the high molar masses of the oils. The transesterification of vegetable oil or fat lowers the molar mass to one third that of triglyceride. Typically, the cleavage of the oil or fat reduces the molar mass from about 900 to 300 and the viscosity from 20cSt to 3-5cSt.

The reaction can be catalyzed by either base or acid. The overall chemistry of transesterification with methanol is represented in equation 2.1. Overall it involves the interchange of the alkoxide group between an ester and an alcohol to give a new ester and a new alcohol. The overall reaction in equation 2.1 consists of a number of consecutive and reversible reactions as follows:

a) the formation of diglycerides (equation 2.2)

b) the formation of monoglycerides (equation 2.3)

c) the formation of glycerol (equation 2.4)

\[
\text{Triglyceride (oil)} + 3 \text{CH}_3\text{OH} \rightleftharpoons \text{Methyl ester mixture} + 3 \text{CH}_2\text{O}-\text{H}
\]

\[
\text{Catalyst} \quad \text{Acid/Base}
\]

(2.1) \( R = C12 \) to \( C20 \) straight saturated or unsaturated hydrocarbon chain
\[
\begin{align*}
\text{Triglyceride} + \text{Methanol} & \xrightleftharpoons[k_4]{k_1} \text{Diglyceride} + \text{Methyl esters} \\
\text{Diglyceride} + \text{Methanol} & \xrightleftharpoons[k_5]{k_2} \text{Monoglyceride} + \text{Methyl esters} \\
\text{Monoglyceride} + \text{Methanol} & \xrightleftharpoons[k_6]{k_3} \text{Glycerol} + \text{Methyl esters}
\end{align*}
\]
The stoichiometry of the reaction requires a 3:1 molar ratio of alcohol to triglyceride. Because esters and alcohols appear on both sides of the equation it might be expected that equilibrium contents would be close to unity. However, the glycerol moiety is usually not such a good nucleophile as the alcohol and typically only a 6:1 molar ratio is required to drive the transesterification to >95% completion. Therefore, the presence of mono- and diglycerides at the end of the reaction must be anticipated.

For fatty acid esterification, which is known as Fischer esterification, the overall equation is as follows:

\[
\begin{align*}
\text{Acid catalyst} & \\
\text{RCOOH} + \text{CH}_3\text{OH} & \rightleftharpoons \text{RCOCH}_3 \cdot \text{H}_2\text{O} \\
\text{Fatty Acid} & \quad \text{Methanol} \quad \text{Methyl Ester} \quad \text{Water}
\end{align*}
\]

(2.5)

Typical equilibrium constants are close to unity. The esterification may be driven to the right either by using a significant excess of one of the reactants or by removing one of the products. Water may be removed either by distillation or by the addition of a dehydrating agent such as magnesium sulfate or molecular sieves (dehydrated zeolite crystals that adsorb water). This is commonly used in industry (Wade, 1991).

2.3.1 Base-Catalyzed Transesterification

The base-catalyzed transesterification of vegetable oils and fats to form alkyl ester is faster than the acid-catalyzed reaction. The base-catalyzed reaction proceeds rapidly at ambient temperature, whereas the acid-catalyzed reaction commonly uses temperature above 100°C, depending on the boiling point of the alcohol. This base-catalyzed reaction normally
works well when the substrates contain low free fatty acids and are substantially anhydrous; that is, the starting material should have free acid content less than 0.5% (acid value less than 1)(Wright et al., 1944) and water content less than 0.3%. Metal hydroxides and alkoxides are both employed for base-catalysis and are known to be effective. Being relatively cheap, they are widely used for commercial processes.

For typical base catalyzed alcoholysis of oils and fats, the catalyst is first dissolved in the alcohol such as methanol or ethanol and then mixed with oil. The solubility of alcohol in oil varies depending on the size of the alkyl group of the alcohol and the reaction temperature. The solubility of methanol in oil is fairly low at room temperature, even at moderate temperature such as 60°C (Mao, 1995). Therefore, very vigorous mixing is employed to initiate the first phase of the reaction. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally to glycerol. The glycerol starts to form after the addition of alcohol and slowly settles at the bottom of the reaction vessel by gravity. The lower glycerol-rich phase containing a small amount of alcohol and probably some monoglyceride is separated for purification. The upper fatty ester-rich phase contains the remainder of glycerol, most of the unreacted alcohol, catalyst, and mono-, di-, and triglycerides. The excess alcohol is removed by distillation, and the ester-rich phase is washed with water to pH=7. Soap is usually a by-product. This base-catalyzed transesterification is exothermic (Feuge and Gros, 1949). They reported that a rise of 1 to 2°C above the reaction temperature occurs immediately after the addition of catalyst solution to the oil. After about 4 or 5 minutes, the temperature returns to the original reaction temperature and then remains constant throughout the reaction. Figure 2.3.1-1 presents the procedure of typical base-catalyzed transesterification.
Figure 2.3.1-1 The procedure of typical base-catalyzed transesterification
2.3.2 Acid-Catalyzed Transesterification

Acid-catalyzed transesterification is slower than base-catalyzed transesterification. The reaction temperature is usually above 100°C and reaction time is 3 to 48 hours except when the reaction is conducted under high temperature and pressure (Taylor et al. 1927; Allen et al. 1945). The procedure of acid-catalyzed transesterification is different from base-catalyzed one. The reaction is refluxed at or near the boiling point of the mixture of cosolvent and alcohol. Sulfuric acid and hydrochloric acid are usually employed as catalyst. Glycerol settles down at the bottom of the reaction vessel by gravity. Glycerol is separated and excess methanol removed by distillation. The organic phase is washed with water and dried by an evaporator. The procedure described above is shown in Figure 2.3.2-1.

Acid-catalyzed transesterification is very useful when the starting materials are low-grade fats or have a large amount of free fatty acid content. The fatty acids neutralize alkaline catalyst and form soaps. Although the amount of base catalyst may be adjusted for the acid values of the substrate, the resulting soap will cause an increase in viscosity or formation of gels and interfere with separation of glycerol.

The transesterification of soybean oil with methanol, ethanol and butanol using 1 wt.% concentrated sulfuric acid based on the weight of oil has been studied (Freedman et al. 1984). Each alcoholysis was conducted with a molar ratio of 30:1(alcohol/oil) and near the boiling point of the alcohol. After 69 hours high conversion to 93% of fatty ester was reported.
Add alcohol, acid catalyst oils or fats.

Reflux

Recovered alcohol for recycle

Immediately cool and add base to neutralize the acid catalyst to the system.

Distillation

Glycerol (can be further refined)

Organic layer

Wash organic layer with water. Allow to separate.

Aqueous layer (waste)

Vacuum Distillation if necessary

Organic layer

Purified Product Ester

Water (waste)

High m.w. carbon chains (waste)

Figure 2.3.2-1 Typical acid-catalyzed transesterification process
2.3.3 Analysis of Transesterification Products

Many analytical methods have been reported to quantitatively determine the composition of the transesterification reaction products. The extent of the reaction can be monitored by the amount of glycerol being formed (Feuge and Gros, 1949). For the determination of glycerides in the transesterification products, several chromatographic methods have been proven to be applicable. Namely, thin-layer chromatography/flame ionization detection (TLC/FID) with an Iactrosan instrument (Freedman et al., 1984); separation of transesterification mixtures by HPLC with light scattering detection (Bruns, 1988 ) and density detection (Trathnigg and Mittelbach, 1990 ). The major disadvantage of these methods is the lower accuracy and precision compared to gas chromatography. However, they are excellent for the crude rapid analysis of the reaction mixture during the transesterification process.

For analyzing the main components: methyl ester, mono-, di-, and triglycerides in the reaction products, gas chromatographic methods have been developed. The method includes derivatization of the products with a silylating reagent and separation on capillary column (Freedman et al., 1986; Mariani et al., 1991). This method was further developed and made more reliable. ( Plank and Lorbeer, 1992 ).

For biodiesel analysis ( Plank and Lorbeer, 1992 ), only gas chromatography meets all demands as an analytical method for the determination of low contents of mono-, di-, and triglycerides in biodiesel. Plank and Lorbeer in Austria have developed a rapid gas chromatographic procedure to determine the components in the esters for quality control of biodiesel. Besides the four major components: methyl ester, mono-, di-, and triglycerides, the analysis for sterols and free glycerol were also included. ( Mittelbach, 1994 ).
2.4 Process Variables Affecting Transesterification

The important process variables affecting the rate of alcoholysis, and the yield and purity of fatty ester from transesterification process include: 1) temperature, 2) type and amount of catalyst, 3) molar ratio of alcohol to vegetable oil, 4) type of alcohol, 5) quality of the oil such as moisture and free fatty acid content, 6) glycerol separation.

The completion of the transesterification reaction can be measured in terms of ester composition (or content) of the product, percentage ester yield, and compositional yield (purity), which are defined as follows:

1. Ester composition (or content) of the products is obtained from gas chromatographic analysis.
2. Actual amount of ester = distilled product x ester content of the product % + residue remaining after distillation x ester content of residue %
3. Ester yield = (actual amount of ester / theoretical amount of ester) x 100 %
4. Actual total product amount = distilled product mass + residue mass after distillation
5. Compositional yield (purity) = (actual amount of ester / actual total product Amount) x 100%

These definitions are used throughout this study.

2.4.1 Temperature

Acid-catalyzed reactions were first conducted under high temperature and pressure (Taylor and Clarke, 1927). They commonly require temperatures above 100°C (Markey, 1961). Freedman et al. studied the effect of temperature on ester formation for the reaction of
1-butanol with SBO at a molar ratio of 30:1 catalyzed by 1 wt.% H₂SO₄. Five temperatures ranging from 77-117°C were examined. The results of this study showed that ester formation is essentially complete in 3 hours at 117.0°C, compared to 20 hours at 77.0°C. The transesterification of soybean oil with methanol, ethanol and butanol using 1 wt.% concentrated sulfuric acid based on the weight of oil, 30:1 molar ratio of alcohol to oil was investigated (Freedman et al., 1984). Each alcoholysis was conducted near the boiling point of the alcohol. The researchers indicated that reaction temperature appeared to control the time of completion. The times needed to obtain ester conversions of 93% were 3, 22, and 69 hours, respectively, for the butyl, ethyl, and methyl alcohols. The final ester conversion of 93% was similar for all three alcohols after 69 hours at about 65°C.

Base-catalyzed alcoholysis of fats or oil is usually performed near the boiling point of the alcohol or at elevated temperature in order to improve the rate of reaction. However, room temperature is considered to be the optimum due to safety and energy consumption cost. Nye and Southwell (Nye et. al. 1984) conducted methanolysis and ethanolysis of rapeseed oil with 1 wt.% NaOH at 6:1 methanol/oil molar ratio and 24°C. They successfully produced "substantial" amounts of methyl and ethyl ester of rapeseed oil in an hour.

Methanolysis of soybean oil with 1 wt.% NaOH and 6:1 methanol/oil molar ratio at 32°C, 45°C, 60°C was studied by Freedman et al.. The results are summarized in Figure 2.4.1-1 and indicate that the strong temperature effect on the reaction rate, showing that methanolysis rate was accelerated dramatically at 60°C.
Fig. 2.4.1-1 Temperature effect on the methanolysis of soybean oil with NaOH catalyst (Data adapted from Freedman et al. JAOCS, 1984 Figure 6.)

2.4.2 Catalysts

There are two types of catalysts for transesterification: acid catalysts and base catalysts. Sulfuric acid and hydrochloric acid are usually employed for acid catalysis and metal hydroxides and alkoxides for base catalysis. The amount of catalyst used in the reaction is usually quoted based on the weight of the oil or fat.

The mechanism of acid-catalyzed transesterification and base-catalyzed transesterification are analogous to acid and base-catalyzed ester hydrolysis.

(a) Acid Catalyst

The mechanism of Fischer esterification involves an acid-catalyzed nucleophilic acyl substitution. An alcohol is not a strong enough nucleophile to attack the carbonyl group of a carboxylic acid; however, the acid catalyst protonates the carbonyl group and activates it
toward nucleophilic attack. Loss of a proton gives the hydrate of an ester. Protonation of the alkoxy group allows it to leave as water, this protonated ester then loses a proton, giving the ester. The mechanism of Fischer esterification of fatty acid by methanol is illustrated below:

\[
\begin{align*}
\ce{\text{Protonated carboxylic acid}} & \quad \ce{\text{Hydrate of an ester}} \\
\ce{R-C-\overset{\text{H}}{\overset{\text{O}}{\backslash}}-\overset{\text{H}}{\backslash}} + \ce{H^+} & \rightleftharpoons \ce{R-C-\overset{\text{O}}{\backslash}}-\overset{\text{H}}{\backslash} + \ce{H^+} \\
\ce{R-C-\overset{\text{O}}{\backslash}}-\overset{\text{H}}{\backslash} + \ce{H^+} & \rightleftharpoons \ce{R-C-\overset{\text{O}}{\backslash}}-\overset{\text{H}}{\backslash} + \ce{H^+}
\end{align*}
\]

Acid-catalyzed transesterification is a variant of the Fischer esterification. Protonation of the ester carbonyl activates it toward nucleophilic attack by methanol. Methanol attacks and loses a proton, giving an intermediate that has both a \(-\ce{CH_2-O-}\) group and a methoxy group. Protonation of the alkoxy group allows C-O bond to cleave, giving the protonated methyl ester. This protonated ester loses a proton, giving the final product methyl ester. The

\[
\ce{R-C-O-CH_3 + H_3O^+} \rightarrow \ce{\text{Ester}} \quad (2.6)
\]
mechanism of transesterification of triglycerides or fats by methanol is illustrated below (equation 2.7):

![Chemical reaction diagram]

The formation of monoglyceride and glycerol follow the same mechanism.
Concentrated sulfuric acid, H$_2$SO$_4$ is widely used as catalyst in Fischer esterification and acid-catalyzed transesterification. Freedman et al. studied the methanolysis of soybean oil using 1 wt% concentrated sulfuric acid, 30:1 methanol to oil molar ratio, under temperature 65°C. the final conversion of methyl ester is 93% after 69 hours (Freedman et al. 1984).

Boocock et al. investigated one-phase methanolysis of soybean oil using both 1.0% concentrated sulfuric acid and 2.0% concentrated sulfuric acid as catalyst, and THF as co-solvent. The reaction was carried out by refluxing the oil with methanol (molar ratio of methanol to oil is 30:1) at a temperature of 70°C. The results of this study are shown in Figure 2.4.2-1. The initial rate of reaction using 2 wt.% H$_2$SO$_4$ was approximately double that when 1 wt. % was used. After 10 hour reflux in the presence of 2.0 % acid catalyst the reaction yielded 97.9% methyl ester. More studies on one-phase methanolysis of soybean oil, palmitic acid, and high free acid content soybean oil, using MTBE as co-solvent, and 2.0 wt. % concentrated sulfuric acid catalyst will be presented in the next Chapter.

![Graph](image-url)  
*Fig. 2.4.2-1 Comparison of methanolysis of soybean oil using 1.0 wt.% H$_2$SO$_4$ and 2.0 wt.% H$_2$SO$_4$ as catalyst (Boocock et al., Private Communication)*
(b) **Base Catalyst**

Transesterification occurs under basic conditions, catalyzed by a small amount of alkoxide ion. The mechanism of base-catalyzed transesterification begins with the attack on the ester by an alkoxide. The mechanism (in the presence of a methoxide ion) is shown below (equation 2.8):

\[
\begin{align*}
\text{CH}_2\text{-O-C-R} & \text{ CH}_2\text{-O-C-R} \overset{\text{Exothermic}}{\rightleftharpoons} \text{CH}_2\text{-O-C-R} + \text{CH}_3\text{-O-C-R} \\
\text{CH}_2\text{-O-C-R} & \text{ CH}_2\text{-O-C-R} \overset{\Delta}{\rightarrow} \text{CH}_2\text{-O-C-R} \\
\text{CH}_3\text{-O-H} & \text{CH}_2\text{-O-C-R} \\
\end{align*}
\]

Methoxide ion

Diglyceride anion

Methyl ester

(2.8)

The resultant diglyceride anion equilibrates with the methanol to produce more methoxide ion (equation 2.9).

\[
\begin{align*}
\text{CH}_2\text{-O-C-R} & \text{ CH}_2\text{-O-C-R} \rightarrow \text{CH}_2\text{-O-C-R} + \text{CH}_3\text{-O-H} \\
\text{CH}_2\text{-O-C-R} & \text{ CH}_2\text{-O-C-R} \\
\text{CH}_3\text{-O-H} & \text{CH}_2\text{-O-C-R} \\
\end{align*}
\]

Diglyceride

Methoxide ion

(2.9) The formation of monoglyceride and glycerol follow the same mechanism.
Metal alkoxides were concluded to be more effective than hydroxides particularly in promoting virtually complete alcoholysis. Sodium or potassium alkoxide of the specific alcohol used in the reaction is preferred. Equation (2.10) illustrates the ionization of sodium methoxide in methanol releasing the methoxide ion for the reaction.

\[
\text{NaOCH}_3 \quad \xrightarrow{\text{\text{Sodium methoxide}}} \quad \text{Na}^+ + \text{OCH}_3^- \quad \text{Methoxide ion}
\]

Equation (2.10)

However, the use of alkoxide is not convenient, usually requiring the reaction of the metal and the alcohol. The methanol on equation 2.11 reacts rapidly with sodium to form sodium salt of methoxide. Hydrogen gas is formed and bubbles out of the solution.

\[
\text{CH}_3\text{OH} + \text{Na} \quad \rightarrow \quad \text{CH}_3\text{O}^-\text{Na}^+ + \text{1/2 H}_2
\]

Sodium methoxide

Equation (2.11)

In this case, the lower cost of metal hydroxide and its ease of use has attracted its wide use in industrial application. In the presence of metal hydroxide, the mechanism is the same. The actual catalyst is the methoxide ion formed as follows:

\[
\text{NaOH} \quad \xrightarrow{\text{\text{Water}}} \quad \text{Na}^+ \text{OH}^- \quad \xrightarrow{\text{\text{Water}}} \quad \text{H-O-H} + \text{CH}_3\text{O}^-\text{H}^- \quad \text{Methoxide ion}
\]

Equation (2.12)
Like water, alcohols can act as weak acids and lose a proton; however, in pure state, alcohols ionize to a lesser extent than does water. This is due to the lower acidity of pure alcohols. For example, the acid dissociation constant of pure methanol is 17 whereas for water it is 15.7. Sodium hydroxide ionizes completely in water, but in methanol, the ionization is only favored to some extent as shown in equation 2.12. The position of this equilibrium is not certain; however, since methanol is only slightly less acidic than water, it can be assumed that the equilibrium lies further to the methoxide ion. Both methoxide and hydroxide ions are strong nucleophiles. The amount of these ions present and the relative rates at which these ions attack the esters are very important. This is because the hydroxide could irreversibly attack all forms of esters (tri-, di-, monoglycerides and methyl esters) to form soap, as well as lower the total amount of base present for the reaction (equation 2.13). Leaving the hydroxide ions in the reaction mixture at the end of reaction would allow them to gradually attack the methyl esters thus forming soap and further reducing the final yield. Theoretically, soaps can be re-esterified to the methyl esters but this reaction is difficult at ordinary temperatures. A summary of these possible reaction routes is shown in Figure 2.4.2-2.

\[
\begin{align*}
\text{CH}_3\text{O}^- + \text{H}^+ & \rightleftharpoons \text{CH}_3\text{OH} \\
\text{Na}^+ + \text{CH}_3\text{O}^- & \rightarrow \text{CH}_3\text{ONa}^+ \\
\text{CH}_3\text{ONa}^+ + \text{H}^- & \rightarrow \text{CH}_3\text{ONa}^+ \\
\text{Na}^+ + \text{CH}_3\text{OH} & \rightarrow \text{CH}_3\text{ONa}^+ \\
\text{CH}_3\text{ONa}^+ + \text{H}^- & \rightarrow \text{CH}_3\text{ONa}^+ \\
\text{CH}_3\text{OH} & \rightleftharpoons \text{CH}_3\text{O}^- + \text{H}^+
\end{align*}
\]

\text{e.g. Methyl ester}

\[
\text{CH}_3\text{OH} + \text{Na}^+ \cdot \text{O}^- \text{C}^- \text{R} \rightarrow \text{Soaps}
\]

(2.13)
Figure 2.4.2-2 A summary of possible reaction routes

Water is formed by equilibration of hydroxide with the alcohol but it is too weak to act as a nucleophile to attack the ester. However, the presence of water favors the hydroxide which would significantly reduce the amount of methoxide ions available for transesterification. Ideally the reaction should be catalyzed by methoxide in a water-free environment. Although transesterification rates increase at a higher base concentration, it is also known that soap production becomes progressively more dominant when higher concentrations of hydroxide are used.

The base-catalyzed reaction is considerably faster than acid-catalyzed reaction and ambient temperatures may be used. Moreover, base-catalysts are less corrosive to reaction equipment than acid-catalysts. The base-catalyzed process is preferred in commercial practices.

Freedman et al. investigated the alcoholysis of vegetable oil using different base catalysts. They compared 1 wt.% sodium hydroxide and 0.5 wt.% sodium methoxide at methanol/oil molar ration of 3:1 and 6:1 methanolysis of sunflower and soybean oil at 60°C
(Freedman et al. 1984). At the 6:1 molar ratio, the initial ester conversion for 0.5 wt.% NaOCH₃ reaction was lower than that for 1 wt.% NaOH reaction but was very similar (ester content of about 97-98%) after 1 hour. At a 3:1 methanol/oil molar ratio, however, methoxide-catalyzed reaction was clearly superior to the hydroxide reaction; the ester contents were 80% and 60% respectively after 1 hour (Freedman et al., 1984).

Nye and Southwell investigated the alcoholysis of rapeseed oil using a variety of catalysts: Magnesium and calcium oxide, sodium and potassium hydroxide and alkoxides; phase transfer catalysts; sulfuric acid; p-toluensulfonic acid. However, metal hydroxide were the cheapest and effective at room temperature. Sodium hydroxide is widely used in industrial process. The results indicate that the reaction with 1 wt.% NaOH gave the best result in an hour (Nye and Southwell, 1984).

Researchers at University of Toronto (Mao, 1995) investigated one-phase base-catalyzed methanolysis of soybean oil using tetrahydrofuran as co-solvent at room temperature. They compared the methanolysis of soybean oil at room temperature with 0.5 wt.%, 1.0 wt.% 2.0 wt.% NaOH, 0.5 wt.%, 1.0 wt.% 1.35 wt.% NaOCH₃, and 1 wt.% KOH at different methanol/oil molar ratio. A 98% methyl ester content of the product resulted after only three minutes at a 2.0wt% NaOH level, accompanied with some soap.

Boocock et al. (Qazi, 1997) have studied one-phase base catalyzed methanolysis of crude canola oil using 1.0 wt.% of NaOH as base catalyst. The reaction was carried out with 27:1 methanol/oil, under room temperature, using THF as co-solvent, 1.0wt.% NaOH plus an extra amount of NaOH to adjust for the free fatty acid in the crude canola oil. A 99.0% of methyl ester conversion was achieved in 7 minutes.
2.4.3 Molar Ratio

The stoichiometry of transesterification requires a 3:1 molar ratio of alcohol to triglyceride. Because this reaction involves the conversion of an ester and an alcohol to another ester and another alcohol, an excess of alcohol is used to drive the reaction close to completion.

Freedman et al. investigated the acid-catalyzed methanolysis of soybean oil with 6:1 and 20:1 molar ratios of methanol to oil for 3 and 18 hours respectively. Conversion to ester was unsatisfactory. A molar ratio of 30:1 (methanol / oil) resulted in high conversion to the methyl ester using 1wt.% concentrated sulfuric acid. This same molar ratio was also employed for studies using ethanol and butanol (Freedman et al., 1986). These reactions were conducted near the boiling point of the alcohol, using 1wt.% concentrated sulfuric acid. High conversions to ester were obtained after 3, 22, and 69 hours, respectively, for the butyl, ethyl, and methyl esters.

For base-catalyzed transesterification, previous researchers conducted alcoholysis with a variety of molar ratios. At a 4.8:1 molar ratio of methanol to dry neutral fats (Bradshaw and Meuly, 1942) the use of 0.1 wt.% to 0.5 wt.% NaOH or KOH at 80°C resulted in a 98% methyl ester conversion in an hour. In a study of the methanolysis of sunflower oil at 60°C using 0.5 wt.% NaOCH₃ catalyst, the methanol/oil molar ratio was varied from 1:1 to 6:1 (Freedman et al., 1984). Results in Figure 2.5-1 show the effect of the molar ratio on ester production after 1 hour. As shown in the results, the ester content at 6:1 molar ratio after 1 hour is 98%.
Figure 2.5-1 Effect of methanol/sunflower oil molar ratio on ester production (60°C, 1hr, 0.5wt.% NaOCH₃ catalyst). (Data adapted from Freedman et al. JAOC, 1984)

One-phase transesterification of vegetable oil was performed by Boocock et al. at the University of Toronto (Boocock et al. 1998). They investigated the methanolysis of soybean oil employing THF as cosolvent with various molar ratios of methanol to oil using 1.0 wt.% NaOH catalyst. The results are outlined in Table 2.5-1. They indicate that increasing the polarity of the reaction mixture by the addition of more methanol will improve reaction rates. However, the highest methyl ester content after 5 minutes occurred at a molar ratio of approximately 27:1. Above a molar ratio of 28:1, a dilution effect resulted in lower yields. A methyl ester content which reached the Austrian Biodiesel standard of 99.4% was reached after 7 minutes at 27:1 molar ratio.
Table 2.5-1 Effect of methanol/soybean oil molar ratio on methyl ester content for one-phase transesterification (Boocock et al., 1998)

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>25:1</th>
<th>27:1</th>
<th>28:1</th>
<th>35:1</th>
<th>40:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>83.3</td>
<td>82.0</td>
<td>80.6</td>
<td>75.6</td>
<td>63.7</td>
</tr>
<tr>
<td>2</td>
<td>89.3</td>
<td>90.9</td>
<td>89.5</td>
<td>88.2</td>
<td>79.7</td>
</tr>
<tr>
<td>3</td>
<td>90.2</td>
<td>95.3</td>
<td>95.1</td>
<td>91.8</td>
<td>86.2</td>
</tr>
<tr>
<td>4</td>
<td>91.3</td>
<td>98.2</td>
<td>97.1</td>
<td>95.7</td>
<td>95.5</td>
</tr>
<tr>
<td>5</td>
<td>94.7</td>
<td>98.3</td>
<td>98.0</td>
<td>96.2</td>
<td>95.0</td>
</tr>
<tr>
<td>7</td>
<td>NA</td>
<td>99.4</td>
<td>99.2</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA = not available.

2.4.4 Type of Alcohol

Methanol and ethanol are the alcohols most commonly used for transesterification. Both can also be produced from biomass. Methanol has an economic advantage over ethanol. It is also an important raw material for lots of chemical process. Methanol can be produced in many ways from a variety of feedstocks. These include natural gas and coal. Ethanol may be obtained from sugarcane, wheat, coke-oven gas, and via ethylene from petroleum. Gauglitz and Lehman studied the activity of straight and branch chain alcohols in the alcoholysis of menhaden oil (60°C, 3.8/1 molar ratio of alcohol/oil) (Gauglitz and Lehman, 1963). Branched-chain alcohols were less reactive than the corresponding straight-chain compounds. The degree of oil conversion to fatty ester was found to be inversely proportional to the number of carbon atoms in the alcohol. The reaction time doubled with an increase of one ethylene group in the alcohol. The phenomenon is different from that described above when butanolysis and methanolysis take place at 6:1 molar ratio (Freedman et al., 1986). Butanolysis occurs faster than methanolysis due to the formation of one phase.
2.4.5 Effect of Moisture Content, Quality of Fat and Oil

Wright et al. noted that the starting materials used for alkali-catalyzed alcoholysis of triglycerides should meet certain specifications (Wright et al., 1944). The alkali-catalyzed alcoholysis is completely successful only if the fat is almost neutral and the reaction mixture is substantially anhydrous. Failure to comply with either of these conditions causes soap formation, which leads to a loss of alkalinity and also the building up of a gel structure that prevents or retards separation and settling of the glycerol. As little as 0.3% water in the reaction mixture significantly reduced glycerol yields by consuming catalyst. When the free acid content of oil exceeds about 0.5%, the alcoholysis becomes difficult because of deactivation of the base catalyst (Swern, 1979).

The effect of moisture may be partially compensated by use of additional base-catalyst or alcohol. The water tolerance of this mixture is increased to 0.5-0.6% if the amount of catalyst is doubled (Swern, 1979).

As mentioned earlier, acid catalysis is suitable for oil with a high free fatty acid in which case the alkaline catalyst would be deactivated. Refined oils which contain the least amount of moisture and free fatty acids (acid value < 1) are the most suitable feedstock for transesterification. Sprules and Price in 1950 found that the use of a large excess of alcohol coupled with alkaline and acid catalysis can accommodate low quality and unrefined fats and oils. Freeman et al. investigated methanolysis of crude and refined vegetable oils. They found that considerable conversion to ester could be obtained with crude oil by adjusting the amount of catalysts according to the acidity of the oil. However, the yields were always much lower in the case of crude oil compared to refined oil. The reason of the reduced yield was the formation of soap and the presence of solid and extraneous material present in the crude oil.
2.4.6 Glycerol Separation

Glycerol is the by-product of the alcoholysis of fat and vegetable oil. It is an important chemical product and has many industrial uses such as application in cosmetics and medicine. It was estimated that the cost of the transesterification processing could be paid for if suitable markets can be found for the glycerol. Glycerol produced by alcoholysis of refined fat is anhydrous and can be used directly in many processes without much refining. The formation of soap might interfere with the glycerol recovery. Part of the glycerol produced from the reaction dissolves in the upper ester-rich layer which contains most of the unreacted alcohol, mono-, di, and triglycerides. In one-phase transesterification reaction, due to the addition of inert cosolvent, there is no physical separation of glycerol during reaction. However, the glycerol can be separated after the excess alcohol and cosolvent has been removed by distillation.

Some researchers suggested that the phase separation of glycerol has no significant effect on the rate and completeness of the reaction (Feuge and Gros, 1949). This may be the result of the glycerol and its anion being inferior nucleophiles respectively compared to the alcohol and its anion.

2.5 Feedstock for Biodiesel

Due to the cost of crude and refined vegetable oil, cheaper waste fats and oils available from restaurants and households attracted attention as possible feedstocks. Researchers (Nye et al. 1983; Pudel et al. 1993) have developed processes to produce biodiesel from used frying oils. A feasibility study on the production, processing and conversion of beef tallow to
biodiesel have also been reported (Nelson et al. 1993). Unfortunately, no experimental data are reported.

2.6 Fuel Properties of Biodiesel and Engine Tests

Engine and emission tests with the use of biodiesel as fuel have been reported (Kloopenstein et al., 1983; Clark et al., 1984; Geyer et al., 1984; Prye, 1982; Reece and Peterson, 1993; Mittelbach et al., 1988). Many researchers and companies have produced high quality ester for testing in conventional diesel engines. Extensive testing on fleets and buses in more than 50 cities has been carried out. The ASTM fuel properties for No. 2 diesel fuel, methyl soya and ethyl soya are shown in Table 2.6-1 (Clark, Wager et al., 1983).

At 40°C, the viscosity of soybean oil (32.6 cst) is nearly 10-15 times that of No.2 diesel, whereas the viscosity of methyl ester is only about twice that of the diesel. The heat of combustion of the ester is about 90% that of diesel on a weight basis (95% on a volume basis). The esters have higher cetane numbers of 46 to 80 in comparison to diesel which has a cetane of about 45. Both methyl soyate and ethyl soyate have higher flashpoints than No.2 Diesel. This make them safer to handle than diesel fuel.

Table 2.6-1 ASTM fuel properties of No. 2 diesel fuel, methyl soya and ethyl soya

<table>
<thead>
<tr>
<th>Properties</th>
<th>ASTM NO.</th>
<th>No.2 Diesel Fuel</th>
<th>Methyl soyate</th>
<th>Ethyl soyate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane rating</td>
<td>D613</td>
<td>45.8</td>
<td>46.2</td>
<td>48.2</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>D93</td>
<td>78</td>
<td>141</td>
<td>160</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>D2500</td>
<td>-19</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>---</td>
<td>0.847</td>
<td>0.884</td>
<td>0.881</td>
</tr>
<tr>
<td>Gross heating value (MJ/KG)</td>
<td>D240</td>
<td>45.2</td>
<td>39.8</td>
<td>40.0</td>
</tr>
<tr>
<td>Sulfur (% mass)</td>
<td>D129</td>
<td>0.25</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Viscosity at 40° (cst)</td>
<td>D445</td>
<td>2.39</td>
<td>4.08</td>
<td>4.54</td>
</tr>
</tbody>
</table>
Klopfenstein (1983) studied the relationship between cetane number and fatty ester structure. The results indicate that the greater the degree of unsaturation, the lower will be the cetane number. High cetane ester could be used to upgrade poorer quality diesel fuel. Conventional fuel additives for petroleum diesel were found to work well in biodiesel.

The cloud point of the esters is higher than that of No.2 diesel, which causes problems for low temperature operation. Esters will congeal below their freezing points. However, if biodiesel is blended with regular diesel, the above problem may be alleviated.

2.7 Environmental Aspects

A major driving force for the use of biodiesel is its potential to burn with less emission than conventional diesel fuel. Test results indicate that gaseous hydrocarbons and carbon monoxide emissions are slightly lower when burning biodiesel either in blend (10-30%) or neat. The reductions in smoke and particulate emissions are very significant. Reed et al. (1991) reported that only a 30% blend with diesel reduced smoke opacity to 60% of that for diesel. Vegetable oil esters contain virtually no sulfur, and thus emission of sulfur oxides is eliminated. However, the emission of NOx and aldehydes from biodiesel was found to be slightly higher than that from conventional diesel fuel. Comparisons between biodiesel and fossil-based diesel have shown biodiesel to be effective in protecting environment. Production of an agriculture derived substitute diesel has the potential to partially ease our dependence on fossil-base fuel sources, and alleviate some of the environmental concerns affiliated with petroleum combustion (Nelson and Schrock, 1994). Biodiesel is also more environmentally friendly in the case of a spill. The fuel is biodegradable and will quickly break down to non-toxic compounds, thus preventing long-term damage to soil and water. Both Europe and the
United States are proposing national biodiesel standards which will strictly limit the glycerol, mono-, di, and triglycerides content in the fuel. In some European countries, the maximum allowable concentration of glycerol, monoglycerides, diglycerides and triglycerides in biodiesel has already been set. Table 2.7-1 outlines the maximum allowable amount of these minor component in biodiesel (Plank and Lorbeer, 1994).

Table 2.7-1 Allowable amount of minor component in biodiesel

<table>
<thead>
<tr>
<th>Species of glycerides</th>
<th>Maximum concentration (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoglyceride</td>
<td>0.2-0.3</td>
</tr>
<tr>
<td>Diglyceride</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>Triglyceride</td>
<td>0.1</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.2-0.3</td>
</tr>
</tbody>
</table>
CHAPTER 3

Background Information

3.1 Overview of Kinetics for Two-Phase Transesterification

Transesterification of SBO and other triglycerides with alcohols in the presence of a catalyst was studied by Freedman et. al.. The kinetics studies of the methanolysis of SBO and the butanolysis of SBO under both acidic and basic condition showed that the reactions are consecutive and reversible. The forward reactions appear to be pseudo-first order or second order depending on the conditions used. The reverse reactions appear to be second order. Butanolysis carried out employing a 30:1 molar ratio of butanol to SBO and 1 wt.% H₂SO₄ indicates that the forward reaction follows pseudo-first order kinetics as expected. The reason is the large molar excess of alcohol used to favor the forward reaction.
Methanolysis of SBO with 6:1 methanol/SBO molar ratio and 0.5% NaOCH₃ was studied by Freedman et al.. A “shunt-reaction” scheme involving the simultaneous attack of three methanol molecules on triglyceride was proposed to give a better explanation for the reaction kinetics. Such a mechanism is however unlikely.

The reaction parameters affecting the yields of fatty esters from transesterification of SBO include: type and amount of catalyst, molar ratio of alcohol to vegetable oil, type of alcohol, and the reaction temperature. However, butanolysis is much faster than methanolysis even under the same condition. The reason is that the transesterification of SBO with butanol occurs in a homogenous one-phase system whereas the methanol/SBO system has two distinct phases. It was unfortunate that this physical problem was not recognized in the kinetic study described above. Impossible conclusions were drawn to explain the deviation from second order kinetics for methanolysis. In fact, the solubility of oil in the methanol where the catalyst is located is low which limits reaction rates. Vigorous stirring could improve the reaction rate but the latter is ultimately limited by mass transfer between the oil and methanol. Even under a vigorously stirred condition, the reactants appear only in a stable emulsion and never appear as a single homogeneous phase (Korus et al., 1993). The di- and monoglyceride once formed in the methanol phase, do not easily transfer back to the soybean oil phase. These intermediates therefore preferentially react further in the methanol and never build up to the concentrations predicted by the second order kinetics. As the reaction proceeds, the mixture eventually becomes an emulsion before separating into a major ester/alcohol phase and a minor glycerol phase.
3.2 Overview of One-Phase Transesterification

The most significant contribution to the acceleration of the conversion of vegetable oils to methyl esters has been made by Boocock et al. in 1995. The principal aim of the study was to show the superiority of a one-phase transesterification reaction system over the two-phase system. They investigated one-phase base-catalyzed methanolysis of soybean oil by using tetrahydrofuran as cosolvent. The results allowed a new interpretation of kinetic data for base-catalyzed methanolysis (Boocock et al., 1995). They found that both the rate of reaction and gravity separation of glycerol improved significantly in the one-phase THF-assisted methanolysis of SBO. The rate is even faster than the one-phase colsovent-free butanolysis; the glycerol separated from the reaction mixture four to five times faster in the THF system than in the THF-free system at a 6:1 methanol to SBO molar ratio and room temperature. At a 2 wt.% NaOH catalyst level, a 98% ester content resulted in only 3 minutes (Mao, 1995).

In 1996, Boocock's group studied the kinetics of the methanolysis of soybean oil using an acid catalyst and THF as a cosolvent in a one-phase system. They compared the results with the methanolysis of soybean oil in a two-phase system. The results showed that when 2.0 wt.% sulfuric acid was used the product reached a maximum methyl ester content of 97.9 wt.% after 10 hours whereas, the two-phase methanolysis resulted in only 93 wt.% methyl ester after 69 hours. The reaction conditions for one-phase acid-catalyzed methanolysis of soybean oil are summarized as shown in Table 3.2-1.
Table 3.2-1 Reaction condition of one-phase acid-catalyzed methanolysis of soybean oil

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio of methanol/oil</td>
<td>30:1</td>
</tr>
<tr>
<td>Catalyst (98% sulfuric acid)</td>
<td>2 wt.%</td>
</tr>
<tr>
<td>Temperature</td>
<td>70°C</td>
</tr>
<tr>
<td>Cosolvent</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>Time</td>
<td>10h</td>
</tr>
</tbody>
</table>

Unfortunately, few reports are available on the methanolysis of a substrate containing a large amount of saturated fatty acid. And no reports are available on such a system with methyl tert-butyl ether (MTBE) employed as cosolvent, which is well-known fuel additive and widely used to improve the gasoline properties.

In this study, MTBE-assisted one-phase base-catalyzed methanolysis of SBO employing a molar ratio of 27:1 (methanol/SBO) was first studied to gain a understanding in the reaction kinetics. MTBE-assisted one-phase acid-catalyzed methanolysis of SBO employing a molar ratio of 30:1 (methanol/SBO) was investigated to find out the relation between the methyl ester yields and reaction time. In addition, MTBE-assisted one-phase acid-catalyzed methanolysis of SBO/palmitic acid mixtures, which contain different contents of fatty acid, employing a molar ratio of 30:1 (methanol/SBO), was carried out to obtain the optimum process condition. Finally, a one-phase two-step process which combines the optimum reaction conditions of both base-catalyzed and acid-catalyzed methanolyses of substrates containing a large content of fatty acid has been developed. This process is simpler, more convenient and less time-consuming in industrial application.
3.3 Cosolvent

One-phase transesterification of SBO using a cosolvent is superior to two-phase system under both basic and acidic catalyst condition in terms of the reaction rate and methyl eater content.

The cosolvent selected to produce one-phase system must be able to dissolve both the polar methanol and essentially non-polar triglyceride, and remain inert during the reaction. Ethers are ideally suited as solvents for many organic reactions. They dissolve a wide range of polar and nonpolar substances, and their relatively low boiling points simplify their recovery from the reaction products. Ethers are nonhydroxylic and thus can not form hydrogen bonds in the pure state. However, if a hydrogen bond donor is present, ethers can serve as hydrogen bond acceptors. Non-polar substrates tend to be more soluble in ethers than in the low molecular weight alcohol because ethers have no hydrogen-bonding network to be broken by the non-polar substances. Ethers are also normally unreactive toward strong bases. Cyclic ethers with small molar masses are miscible with water in most if not all proportions, and were considered good candidates as cosolvent in the methanol/oil system. Methanol like water, has considerable polar and hydrophilic character; therefore, it was reasoned that the cyclic ethers could also behave with it as cosolvents. Two readily available cyclic ethers: Tetrahydrofuran (THF) (I) and 1,4-dioxane (II) were tested first. THF was preferred, because it has nearly the same boiling point as methanol and therefore can be co-distilled and recovered at the end of the reaction.

Acyclic cosolvents such as diethyl ether (III), methyl tert-butyl ether (MTBE) (IV), and diisopropyl ether (V) were also studied. Diethyl ether is not quite miscible with water in all proportions, but is miscible with methanol. In the cyclic ethers the lone pairs of electrons
are more accessible for hydrogen bonding than those of acyclic. It is reasoned that the bulky alkyl group in acyclic ethers acts as whirling propeller blades and present a hindrance to hydrogen bonding by the water molecules hereby lowing the miscibility. Table 3-2-1 shows the physical properties of potential cosolvents.

\[
\begin{align*}
\text{CH}_2\text{-} & \text{-CH}_2 \\
| \quad | \\
\text{CH}_2 & \text{-O-CH}_2\text{-CH}_2
\end{align*}
\]

Tetrahydrofuran (THF) (I)

\[
\begin{align*}
\text{CH}_2\text{-} & \text{-CH}_2 \\
\text{CH}_2 & \text{-O-CH}_2\text{-CH}_2
\end{align*}
\]

1,4-dioxane (II)

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3 & \quad (\text{CH}_3)_3\text{-C-O-CH}_3 \\
(\text{CH}_3)_2\text{CH-O-CH(CH}_3)_2 & \quad \text{diethyl ether (III) \quad methyl t-butyl ether (IV) \quad diisopropyl ether (V)}
\end{align*}
\]

Table 3.2-1 Physical properties of potential cosolvents

<table>
<thead>
<tr>
<th>Cosolvent</th>
<th>Boiling Point (°C)</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrofuran</td>
<td>67</td>
<td>72</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>101</td>
<td>88</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>35</td>
<td>74</td>
</tr>
<tr>
<td>Diisopropyl ether</td>
<td>68</td>
<td>102</td>
</tr>
<tr>
<td>Methyl t-butyl ether</td>
<td>53</td>
<td>88</td>
</tr>
</tbody>
</table>

The choice of cosolvent depends on availability, cost, implication for solvent recovery, recycle, and the possible hazards during its use. Diethyl ether is a very common solvent but it has a boiling point of about 10°C above typical room temperatures which present a potential operational hazard. Methyl t-butyl ether (MTBE) is normally used as octane enhancer in
gasoline to improve the fuel properties. MTBE is conveniently available and relatively safe. It is easily distilled and recycled with methanol. In this study, MTBE was employed as cosolvent to make the 30:1 methanol/ oil molar ratio mixture into a one-phase system.

In 1937, Kurz investigated the rate of methanolysis and ethanolysis of a series of vegetable oils such as olive, sesame, linseed and tung. A 50 mL solution of oil and diethyl ether in a volume ratio of 1:4 were reacted with 35mL of methanol (approximately 86:1 molar ratio to the oil) in the presence of potassium hydroxide (0.3%). The reaction under these conditions resulted in the liberation of 98% of glycerol in 24 hours. This reaction which was carried out in one phase was unexpectedly slow, and the reaction rate did not show any significant difference when compared to two-phase methanolysis studied by Freedman et al. mainly because the reaction mixture was highly diluted by the large amounts of diethyl ether and alcohol.

In this study, the minimum amount of MTBE was used in a 30:1 methanol/SBO molar ratio mixture. In this case the total volume of the reaction mixture was minimized and the reaction rate was improved.

The amount of cosolvent required to produce a one-phase system depends on the type of substrate as well as the cosolvent itself. In the next chapter, the procedure for determining the minimum amount of MTBE to achieve one-phase system will be outlined.
CHAPTER 4

Experimental

4.1 Materials and Chemicals

The following chemicals were supplied by Aldrich Chemical Company (Milwaukee, WI, U.S.A.): palmitic acid (99% pure); anhydrous grade methanol and methyl tert-butyl ether (purity > 99% and water content < 0.005%); analytical grade potassium hydroxide (99.99%); analytical grade sodium hydroxide (98% pure with 1% carbonate); anhydrous pyridine (purity > 99% and water content < 0.005%); N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA); concentrated hydrochloric acid. Concentrated sulfuric acid 998% pure; anhydrous grade sodium carbonate (98%) and anhydrous grade sodium sulfate were purchased from BDH Chemicals (Toronto, Ontario, Canada). Sodium chloride (ACS
certified) was supplied by ACP Chemical Inc. (Montreal, Quebec, Canada). Calcium chloride was purchased from J. T. Baker Chemical Company (Phillipsburg, NJ). The reference standards were chromatographically pure (>99%) and were purchased from Sigma Chemical Company (St. Louis, MO); these standards included: methyl palmitate, methyl oleate, methyl linoleate, methyl stearate, 1-monopalmitin, 1-monolinolein, 1,3-dipalmitin (1% 1,2 isomer), 1,3-dilinolein (1% 1,2 isomer), tricaprin, tripalmitin, trilinolein and tristearin. Edible grade Soybean oil (SBO) (President’s Choice) was purchased from Loblaws Supercentre in Toronto, Canada.

The average molecular weight of SBO was taken as 872.4 g/mol and density as 0.89 g/mL at 20°C. The typical composition of SBO is presented in Table 4.1-1 (Sontag, 1979). These values are known to vary slightly due to seed development process and source of seeds. Natural tocopherols and sterols (<1.5%) are known to be present in the oil.

The molecular weight of palmitic acid is 256.4 g/mol and its melting point is 61-64°C.

Table 4.1-1. Fatty acid composition of SBO

<table>
<thead>
<tr>
<th>Saturated acids composition</th>
<th>Unsaturated acid composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(15 wt.%)</td>
<td>(85 wt.%)</td>
</tr>
<tr>
<td>C14 and lower</td>
<td>trace</td>
</tr>
<tr>
<td>Palmitic acid (C16:0)</td>
<td>11</td>
</tr>
<tr>
<td>Stearic (C18:0)</td>
<td>4</td>
</tr>
<tr>
<td>C20 and higher</td>
<td>trace</td>
</tr>
<tr>
<td></td>
<td>C16 and lower</td>
</tr>
<tr>
<td></td>
<td>trace</td>
</tr>
<tr>
<td></td>
<td>Oleic (C18:1)</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Linoleic (18:2)</td>
</tr>
<tr>
<td></td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>Linolenic (18:3)</td>
</tr>
<tr>
<td></td>
<td>9*</td>
</tr>
</tbody>
</table>

* could be lower in some edible grades SBO
4.2 Base-Catalyzed Transesterification Procedure

Base-catalyzed transesterification was carried out in a moisture-free environment at room temperature (~23°C) and atmospheric pressure. Table 4.2-1 outlines the reaction condition.

Table 4.2-1 Experimental conditions for base-catalyzed methanolysis of SBO:

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Amount required</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBO</td>
<td>20.0g</td>
</tr>
<tr>
<td>MeOH (molar ratio of MeOH to SBO=27:1)</td>
<td>25.1mL (22.3 + 2.8 mL)</td>
</tr>
<tr>
<td>NaOH 1wt. % based on the weight of SBO in 2.8 ml MeOH</td>
<td>0.20g</td>
</tr>
<tr>
<td>MTBE</td>
<td>27.7mL</td>
</tr>
<tr>
<td>1M HCl solution</td>
<td>10mL</td>
</tr>
</tbody>
</table>

4.2.1 Preparation of Base Catalyst Solution

Sodium hydroxide (0.2 g) was accurately weighed, gently shaken and stirred with methanol (2.8mL) until it was dissolved. The homogeneous solution was used to perform the base-catalyzed reaction as described in the next section.

4.2.2 Method of Base-Catalyzed Transesterification

All glassware was oven-dried and then cooled to room temperature. SBO, MeOH and MTBE were added to a 200 mL flat-bottom flask equipped with a magnetic stirrer. The freshly prepared catalyst solution in MeOH was added into the reaction mixture, which invoked the start of the reaction. The mixture was vigorously stirred for the first 20 seconds.
Samples were taken out by pipette (approximately 0.5mL aliquots) at different time interval up to 1 hour. The samples were quickly quenched in 0.5 mL of 1M HCL solution to neutralize the base catalyst and stop the reaction.

4.3 Acid-Catalyzed Transesterification Procedure

The reactions were carried out with MeOH, the appropriate volume of MTBE as cosolvent, and the following substrates: soybean oil, mixture of soybean oil and palmitic acid with different contents of palmitic acid, 2 wt % of concentrated sulfuric acid (based on the weight of oil) is the catalyst in the reaction. With different substrates, the reaction temperature was slightly changed in order to keep good reflux condition (detailed reaction conditions will be presented in the table 4.3-1).

4.3.1 Method of Acid-Catalyzed Transesterification

All glassware was dried in the oven and then cooled to room temperature. In each case, substrate was mixed with anhydrous MeOH, the appropriate volume of anhydrous MTBE and 2 wt.% H₂SO₄, in a 200 ml flask equipped with a condenser and a calcium chloride guard tube. The mixture was refluxed on the water-bath at 57°C - 64°C (bath temperature: 64-70°C). For SBO, the 1hr, 3hr, 5hr, 7hr, and 10 hr methanolysis was conducted; for substrate containing different amount of palmitic acid, 10 hr methanolysis was conducted. After the reaction time, the flask was immediately cooled with ice and the equivalent amount of sodium carbonate was added to neutralize the sulfuric acid. The excess amount of methanol and MTBE were distilled and collected in a round-bottom flask, which could be recycled. The remaining solution comprised an organic layer and the mixture of
glycerol and NaCO₃ powder. Organic layer was washed by a hot distilled water (45°C). Small amount of NaCl was added to give a better phase separation. The aqueous phase was discarded and the organic layer was collected and dried in the rotary evaporator followed by vacuum distillation.

Table 4.3-1 The reaction conditions for the acid-catalyzed methanolysis

<table>
<thead>
<tr>
<th>Comp. of substrates</th>
<th>Subs. Mass (g)</th>
<th>2 wt.% H₂SO₄ (g)</th>
<th>MeOH 30:1 (MeOH/SBO) (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99% PA</td>
<td>20.0</td>
<td>0.4</td>
<td>31.6</td>
</tr>
<tr>
<td>90% PA, 10% SBO</td>
<td>18.0 PA 2.0 SBO</td>
<td>0.4</td>
<td>31.2</td>
</tr>
<tr>
<td>80% PA, 20% SBO</td>
<td>16.0 PA 4.0 SBO</td>
<td>0.4</td>
<td>30.9</td>
</tr>
<tr>
<td>70% PA, 30% SBO</td>
<td>14.0 PA 6.0 SBO</td>
<td>0.4</td>
<td>30.5</td>
</tr>
<tr>
<td>60% PA, 40% SBO</td>
<td>12.0 PA 8.0 SBO</td>
<td>0.4</td>
<td>30.1</td>
</tr>
<tr>
<td>50% PA, 50% SBO</td>
<td>10.0 PA 10.0 SBO</td>
<td>0.4</td>
<td>29.8</td>
</tr>
<tr>
<td>40% PA, 60% SBO</td>
<td>8.0 PA 12.0 SBO</td>
<td>0.4</td>
<td>29.4</td>
</tr>
<tr>
<td>30% PA, 70% SBO</td>
<td>6.0 PA 14.0 SBO</td>
<td>0.4</td>
<td>29.1</td>
</tr>
<tr>
<td>20% PA, 80% SBO</td>
<td>4.0 PA 16.0 SBO</td>
<td>0.4</td>
<td>28.7</td>
</tr>
<tr>
<td>10% PA, 90% SBO</td>
<td>2.0 PA 18.0 SBO</td>
<td>0.4</td>
<td>28.3</td>
</tr>
<tr>
<td>SBO</td>
<td>20.0</td>
<td>0.4</td>
<td>28.0</td>
</tr>
</tbody>
</table>

4.3.2 Minimum Cosolvent Requirement

The minimum amount of cosolvent required to produce one-phase acid-catalyzed transesterification is determined by the following procedure:
All the glassware was dried in the oven and removed to cool down to room temperature. In the case of substrates containing high amount of palmitic acid (from 99+%PA to 50% PA), the substrate was mixed with anhydrous MeOH, 2 wt.% H$_2$SO$_4$ catalyst in a 200 mL two-necked flask equipped with a condenser and a CaCl$_2$ guard tube. The mixture was refluxed on the water-bath at 64°C. The mixture varied from clear and homogeneous one phase to “milky” in appearance. After 40 minutes, the mixture contained two phases. Methyl tert-butyl ether (MTBE) was added slowly to make the system clear homogenous one phase again. The minimum amount of MBTE required to produce the one-phase system was recorded. For the substrates containing less palmitic acid (from pure SBO to 40%PA content), the whole procedure is the same as described above except that in the beginning, 2 wt.% H$_2$SO$_4$ catalyst was not added. Table 4.3.2-1 outlines the various mixtures of substrates and methanol.
### 4.4 Two-Step Transesterification Process

Based on both base-catalyzed and acid-catalyzed process investigated above, a two-step methanolysis process involving both procedures was developed.

#### 4.4.1 Determination of Fatty Acid Content after First-Step Methanolysis

All glassware was oven-dried and cooled to room temperature. The substrate containing 50% PA and 50% SBO was mixed with anhydrous MeOH, the appropriate volume of anhydrous MTBE and 2wt.% H$_2$SO$_4$, in a 200 mL round-bottom flask equipped with a condenser and a CaCl$_2$ guard tube. The mixture was refluxed at 59.5°C. After 3hr, the reflux
was stopped by cooling the flask with ice. An equivalent amount of Na$_2$CO$_3$ was added to neutralize H$_2$SO$_4$. The excess of MeOH and MTBE was removal by distillation. Hot distilled water 50 mL (68°C) was added to the remaining solution. The organic layer was separated into a 200 mL flask. Sodium hydroxide (50 mL, 1M) was added to it. The mixture was stirred and the pH of the aqueous solution was recorded (pH~11). The whole mixture was then transferred quantitatively to a 250mL separatory funnel and extracted three times with diethyl ether (3x300mL). The ether extracts was collected to a 500 ml flask. The aqueous phase was acidified with 6N HCl to liberate any palmitic acid (pH in the aqueous solution ~1). The solution was transferred quantitatively to another separatory funnel and extracted three times with diethyl ether (3x300 mL). The ether layer was separated and washed three times with distilled water (3x50 mL). The ether layer was collected in a round-bottom flask and aqueous fraction was discarded. The ether was removed by a Buchi rotary evaporator under vacuum condition and water-bath at 45°C. The content of fatty acid was analyzed by GC.

4.4.2 Method of Two-Step Transesterification

In the first-step, acid-catalyzed methanolysis was carried out by refluxing at 59.5°C for 3 hours. In the second-step, base-catalyzed methanolysis was conducted at room temperature. Both steps were carried out at the atmospheric pressure. The reaction conditions are reported in Table 4.4-1
Table 4.4-1 Reaction conditions for two-step transesterification process

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Amount required</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% PA, 50% SBO</td>
<td>20g</td>
</tr>
<tr>
<td>MeOH</td>
<td>29.8 mL</td>
</tr>
<tr>
<td>MTBE</td>
<td>19 mL</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$ 2 wt.% based on substrate mass</td>
<td>0.4g</td>
</tr>
<tr>
<td>NaOH 1 wt.% based on SBO mass plus the excess* of NaOH</td>
<td>0.1437g</td>
</tr>
</tbody>
</table>

* For neutralization of unreacted palmitic acid.

(a) First Step: Acid-Catalyzed Methanolysis

The reaction in this stage was carried out in 3 hours and the procedure is the same as the one described in Section 4.3.1. After the reaction was stopped by cooling the flask with ice, the equivalent amount of Na$_2$CO$_3$ was added to the reaction solution. The mixture was shaken followed by the addition of 2.0 g anhydrous Na$_2$SO$_4$ powder. The whole mixture was filtered through filter with glass wool. A small amount of MTBE was added to compensate the volatile MTBE loss during the filtering. The solid material was discarded and the solution was collected in a 250 mL flat-bottom flask equipped with magnetic stirrer for the second step: base-catalyzed methanolysis.

(b) Second Step: Base-Catalyzed Methanolysis

Base catalyst was prepared before this stage. The method to produce the sodium methoxide solution is as described in Section 4.2.1. The freshly prepared catalyst (0.1437g in 1.4 mL MeOH) was added to the mixture prepared in the acid-catalyzed reaction above. Agitation was stopped after 20 seconds. After 10 minutes, 50 mL of distilled water was added
to stop the reaction. The mixture was quantitatively transferred to a separatory funnel (small amount of distilled water was used for quantitative transfer). The aqueous fraction was discarded and the organic layer was washed 3 times (3x150 mL) with distilled water. The organic layer was collected in a 150 mL round bottom flask and the aqueous part was discarded. The small amount of MTBE and MeOH was removed using a rotary evaporator under reduced pressure and a water bath at 70°C. The solution then was distilled under vacuum 10mm Hg.

4.5 Product Purification

Since the acid-catalyzed methanolysis products from substrates containing FFA contain significant amounts of mono-, di-, and triglycerides, vacuum distillation is essential in order to meet the transportation fuel specification. The method of vacuum distillation was as follows:

All the glassware was dried in the oven and removed to cool down to room temperature. The methanolysis product was added to a 100 mL round-bottom two-neck flask equipped with a distillation head, thermometer, capillary, and condenser. An adapter and small receivers were used to obtain the various fractions. To protect the vacuum pump, an ice water cooled trap was used. The methyl ester mixture was usually collected on the temperature range of 170-175°C at the pressure of 10 mm Hg.

4.6 Investigation of Cosolvent Degradation

The method of investigating the possible formation of isobutene from methyl tert-butyl ether (TBME) under acid-catalysis was as follows:
All glassware was oven-dried and cooled to room temperature. Hexane (20g) was mixed with anhydrous MeOH (28.0 mL), anhydrous MTBE (25.6 ml) and 98% concentrated H$_2$SO$_4$ (0.4g) in a 200 mL flask equipped with a condenser and a CaCl$_2$ guard tube. The mixture was refluxed on a water-bath at 68°C. after 5 hours, the flask was cooled with ice. The total weight of the mixture was weighed before and after reflux.

4.7 Analysis of Ester Product

4.7.1 Sample Preparation for Gas Chromatographic Analysis

The sample taken from the transesterification product was accurately weighed (~100mg). Pyridine 0.4 mL and BSTFA 0.2 mL were added to prepare the silyl derivative of mono- and diglycerides. The mixture was heated at 65°C on a water-bath and was occasionally shaken during heating. After 20 minutes, the mixture was taken out from the water-bath and allowed to cool to the room temperature. THF 4.4 mL was then added to dilute the mixture for the GC analysis.

4.7.2 Determination of The Standard Material Retention Time

An accurate amount of methyl palmitate, methyl linoleate, methyl oleate, methyl stearate, Monolinolein, dilinolein, trilinolein, monopalmitin, and palmitic acid was weighed (~50 mg). For determining palmitic acid, Monolinolein, dilinolein, trilinolein, monopalmitin retention time, the preparation procedure was as described in Section 4.7.1, except that the amounts of pyridine, BSTFA, and THF were reducing by half. For determining other standard material retention times, only 2.5 mL THF was required to dilute the solution for GC analysis.
4.7.3 Instrumentation and Operating Condition

Analyses were carried out on a Hewlett Packard series 5880A gas chromatography equipped with an on-column injector, a flame ionization detector (FID) and a DB-1 fused silica capillary column (2m x 0.25 mm id) coated with 0.25μ film of 100% polymethyl siloxane (J&W). The operating condition were as follows:

Injector temperature: 350°C; Detector temperature: 320°C.

Helium carrier gas flow rate: 3 mL with make-up gas to a total 55mL/min.

Air flow rate: 310 mL/min; Hydrogen flow rate: 34 mL/min.

The sample (0.3 μL) were manually injected into the column. The oven temperature was held at 130°C for 2 minutes, and then increased at rate of 15°C/min to 350°C and held for 10 minutes. The total operating time was 26.6 minutes.
CHAPTER 5

Results & Discussion

Part I: Analysis by Gas Chromatography

5.1 Results

A gas chromatographic procedure was employed to determine the components in the transesterified SBO/fatty acid mixtures. The reference standards (methyl linoleate, methyl palmitate, 1-monolinolein, 1,3-dilinolein, and trilinolein etc. listed in Table 5.1-1) were chosen for this study to represent the major compound classes (methyl ester, mono-, di-, and triglycerides) in the SBO/fatty acid mixtures. The gas chromatographic retention times for several standard compounds are shown in Table 5.1-1.
Table 5.1-1  Gas chromatographic retention times for the standards

<table>
<thead>
<tr>
<th>Standards</th>
<th>Retention Times (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Palmitate (C16:0)</td>
<td>3.69</td>
</tr>
<tr>
<td>Methyl Stearate (C18:0)</td>
<td>5.06</td>
</tr>
<tr>
<td>Methyl Oleate (C18:1)</td>
<td>4.88</td>
</tr>
<tr>
<td>Methyl Linoleate (18:2)</td>
<td>4.76</td>
</tr>
<tr>
<td>Methyl Linolenate (18:3)</td>
<td>5.04</td>
</tr>
<tr>
<td>Palmitic Acid (C16:0)</td>
<td>4.84</td>
</tr>
<tr>
<td>Monopalmitin (C16:0)</td>
<td>6.84</td>
</tr>
<tr>
<td>Monolinolein (18:2)</td>
<td>7.40, 7.67*</td>
</tr>
<tr>
<td>Dipalmitin (C16:0)</td>
<td>12.15, 12.29*</td>
</tr>
<tr>
<td>Dilinolein (C18:0)</td>
<td>13.03, 13.23*</td>
</tr>
<tr>
<td>Tripalmitin (C16:0)</td>
<td>16.47</td>
</tr>
<tr>
<td>Trilinolein (18:2)</td>
<td>16.91</td>
</tr>
<tr>
<td>Tristearin (C18:0)</td>
<td>18.18</td>
</tr>
</tbody>
</table>

* monoglycerides contain 1 and 2 isomers, diglycerides contain 1,2 and 1,3 isomers

5.2 Discussion

The results from Table 5.1-1 indicate that the unsaturated compounds elute before the saturated compounds with the same carbon number and have retention times very close to those of the latter which made separation difficult. In fact, for fuel purpose, only the identification of methyl esters, monoglycerides, diglycerides, and triglycerides are more important. Detailed separations of the components within a class are not necessary.
Part II: One-Phase Base-Catalyzed Transesterification

5.3 Results

One-phase transesterification of SBO, employing a 27:1 methanol/SBO molar ratio 1 wt.% sodium hydroxide and MTBE as cosolvent under room temperature and atmospheric pressure condition, resulted in product containing 99.6% methyl ester in 8 minutes. The change of product composition with time is shown in Figure 5.3-1. The comparison of one-phase THF-assisted methanolysis of SBO at 8:1 molar ratio of methanol/SBO and one-phase MTBE-assisted methanolysis at 27:1 molar ratio of methanol/SBO both under 1 wt.% NaOH catalyst is presented in Fig. 5.3-2. The gas chromatogram of the product is shown in Fig.5.3-3.

[Figure 5.3-1 One-phase methanolysis of SBO: Change of composition of the product with time for a molar ratio of methanol/SBO (27:1), 1 wt.% NaOH catalyst, using MTBE as cosolvent.]
Figure 5.3-2 Comparison of one-phase THF-assisted methanolysis of SBO, molar ratio of methanol/oil 8:1 (data adapted from Mao, 1995); with one-phase MTBE-assisted methanolysis, molar ratio methanol/oil 27:1. (Both in 1 wt.% NaOH catalyst)

5.4 Discussion

Figure 5.3-1 exhibits the change in composition of methyl ester and monoglyceride in the reaction mixture with time for the one-phase MTBE-assisted methanolysis with 1wt.% NaOH catalyst at room temperature. The majority of the triglycerides disappeared almost immediately after the reaction had started. In fact, the reaction is too fast to obtain reproducible kinetic data within one minute because at least 15 seconds were required for mixing the reactants. The monoglyceride content was 7.8% after 1 minute. The actual maximum monoglyceride content must have occurred somewhere in the first 1 minute because the methyl ester content increases rapidly reaching 96.9% in only 3 minutes and 99.6% in 8 minutes.
Figure 5.3-3 Gas chromatogram of one-phase base-catalyzed reaction
Boocock et al. (Mao, 1995) compared THF-assisted one-phase methanolysis of SBO (molar ratio of methanol/SBO: 6:1), 1 wt.% NaOH as catalyst at room temperature with two-phase methanolysis of SBO at 32°C using 1 wt.% NaOH catalyst (Freedman et al., 1984). A 97% methyl ester content resulted in 4 hours in two-phase methanolysis; whereas, the same methyl ester content resulted after 2 hours in the one-phase cosolvent-assisted methanolysis. In fact, the one-phase methanolysis is initially much faster than the two-phase reaction but then slows suddenly. For example, when 1 wt.% sodium hydroxide and 6:1 molar ratio of methanol to SBO were employed in the one-phase THF-assisted methanolysis of SBO, an 80% methyl ester content was obtained in the first 3 minutes, but only a further 2.0% in the next minute. The reaction was characterized by an initial very fast period followed by a sluggish second phase. In order to further improve the reaction time, attention was focused on the deceleration phenomenon. One possible reason for this is a polarity effect.

The ionization of hydroxide and methoxide, which determines the amount of catalyst available for transesterification, is an important factor that affects the rate of reaction. The position of the equilibrium in equation 2.10 and 2.12 depends upon the identity of the alcohol as well as the polarity of the reacting media. The latter is a measure of the ability of a solvent to solvate or stabilize charged species. Transesterification is carried out in a mixed solvent of which the composition as well as the polarity changes during the course of the reaction. For a 6:1 molar ratio of methanol to SBO and THF as cosolvent methanolysis system, the oil, which accounted for 61% by volume in the starting mixture, acted as the major solvent. When the catalyst dissolved in methanol, which is highly polar, is added to the essentially non-polar solution of oil and THF, the polarity drops, as does the ionization of the catalysts. In addition, when methanol is consumed the polarity of the reaction mixture falls. As a result, the degree
of ionization of the catalyst drops and consequently the speed of the reaction is immediately affected. In the one-phase THF-assisted methanolysis which started off with a 6:1 methanol/SBO molar ratio, the methanol accounts for 14.9 vol.% of the mixture at the start of the reaction; if there is no significant change in the total reaction volume as the reaction proceeds, the methanol will fall to 8.9 vol.% when the transesterification is 80% complete. In order to counteract the effect of falling polarity and hence keep the catalyst active, more methanol should be used at the beginning of the reaction. Therefore, a 27:1 molar ratio of methanol to oil was used in this study.

The results in Figure 5.3-2 show the effect of increasing the polarity by raising the methanol/oil molar ratio to 27:1. The results are compared to these for an 8:1 molar ratio. As can been seen, the ester content of methanolysis in the 8:1 methanol/oil system is 74.9% after 2 minutes; whereas methanolysis in the 27:1 methanol/oil system resulted in 93.3% after the same time. The results also show that in the methanolysis of SBO at a 27:1 molar ratio of methanol/oil and an 8:1 molar ratio of methanol/oil, the content of ester reached 99.6% in 8 minutes and 98.5% in 4 hours, respectively.

It is obvious that the rate of methanolysis at a 27:1 methanol/SBO molar ratio is much faster than that at an 8:1. Therefore, the high molar ratio of methanol to SBO prevents a significant fall in polarity of the system, which drives the reaction to better completion.

Other researchers (Feuge et al. 1949) also observed the dramatic decrease in rate in the one-phase hydroxide-catalyzed ethanolysis of peanut oil at 50°C. They suggested the cause to be the combined effect of two factors: the decrease in the concentration of the reactants and the disappearance of base hydroxide through saponification.
Moreover, a similar kinetic trend was noticed in the butoxide-catalysis of SBO (Freedman et al., 1986). It was concluded that this reaction followed second order kinetics by assuming a significantly larger first rate constant for the conversion of triglycerides to diglycerides than for the subsequent steps; however, there seemed to be no explanation based on molecular structure for the large difference in rate constants. In fact, the nucleophilic attack of methoxide ion on tri-, di-, and monoglycerides follows the same mechanism. Thus, theoretically, the rate constants for the consecutive forward steps in the transesterification should not differ significantly.

It should be noted that although this transesterification reaction is simple to carry out, the presence of several process variables and the difference in the physical properties of the reactants, intermediates, and products complicate the study of the reaction. It is difficult to isolate one parameter and study the others. Overall, other possible factors to explain the sudden deceleration of the methanolysis could be a cumulative effect. Namely, the cumulative effect of hydroxide depletion, polarity effect, formation of cyclic intermediates, and glycerol separation.

No soap was observed during the entire reaction period when 1 wt.% NaOH catalyst was used. This is important for the high yield of methyl ester. Using 2 wt.% NaOH catalyst, a high conversion of SBO is probably achieved at the expense of a lower ester yield because of the soap formation. Moreover, the presence of soap would also complicate the washing step which could further lower the practical yield of the esters. As soon as the reaction was complete, dilute HCl was used to neutralize the base and prevent the formation of soap from the methyl ester.
5.5 Results

5.5.1 One-Phase Acid-Catalyzed Methanolysis of Neat Vegetable Oil

The results obtained from the investigation of acid-catalyzed MTBE-assisted one-phase methanolysis of SBO employing a 30:1 molar ratio of methanol to SBO, 2 wt.% $\text{H}_2\text{SO}_4$ as catalyst at 57°C and atmospheric pressure are presented in Table 5.5.1-1. The relationship between methyl ester yields and reaction time is reported in Figure 5.5.1-1. Figure 5.5.1-2 compares one-phase methanolysis of SBO at reaction conditions described above with butanolysis of SBO at 77°C using 1 wt.% $\text{H}_2\text{SO}_4$ catalyst. The comparison of THF-assisted one-phase methanolysis of SBO at 70°C, 2 wt.% $\text{H}_2\text{SO}_4$ as catalyst with one-phase MTBE-assisted methanolysis of SBO at 57°C, 2 wt.% $\text{H}_2\text{SO}_4$ as catalyst is presented in Figure 5.5.1-3. The typical gas chromatograms of distilled products from the methanolysis of SBO are shown in Figure 5.5.1-4. The gas chromatograms of residues remaining after methanolysis products were distilled are presented in Appendix D-1.
Table 5.5.1-1 Results of the MTBE-assisted one-phase acid-catalyzed methanolation of SBO

<table>
<thead>
<tr>
<th>SBO mass (g)</th>
<th>Time (hr)</th>
<th>Distilled Product mass (g)</th>
<th>ME Content in product (%)</th>
<th>Residue mass (g)</th>
<th>ME Content in residue (%)</th>
<th>ME yield* (%)</th>
<th>comp. yield+ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>6.4</td>
<td>99.3</td>
<td>12.5</td>
<td>19.6</td>
<td>43.8</td>
<td>46.6</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>12.4</td>
<td>99.8</td>
<td>7.3</td>
<td>13.1</td>
<td>66.3</td>
<td>67.7</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>16.8</td>
<td>99.7</td>
<td>2.5</td>
<td>6.1</td>
<td>84.1</td>
<td>87.6</td>
</tr>
<tr>
<td>20</td>
<td>7</td>
<td>17.1</td>
<td>99.7</td>
<td>2.3</td>
<td>66.7</td>
<td>92.5</td>
<td>95.8</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>18.3</td>
<td>99.7</td>
<td>1.1</td>
<td>44.9</td>
<td>93.2</td>
<td>96.6</td>
</tr>
</tbody>
</table>

Theoretical methyl ester amount: 20.1 g.
* ME in both distilled product and residue/20.1 g.
+ ME in both distilled product and residue/actual total product amount.

Figure 5.5.1-1. The relation between methyl ester composition and reaction time
Figure 5.5.1-2 Comparison of MTBE-assisted one-phase methanolysis of SBO at 57°C, 2wt.% H₂SO₄ catalyst with butanolysis of SBO at 77°C and 1wt.% H₂SO₄ catalyst (Data adapted from Freedman et al., 1986 Fig. 2)

Figure 5.5.1-3 Comparison of THF-assisted one-phase methanolysis of SBO at 70°C, 2 wt.% H₂SO₄ as catalyst with MTBE-assisted one-phase methanolysis of SBO at 57°C, 2wt.% H₂SO₄ as catalyst.
Figure 5.5.1-4 The typical gas chromatograms of distilled product from methanolysis of SBO
5.5.2 One-Phase Acid-Catalyzed Methanolysis of The Vegetable Oil/Palmitic Acid Mixtures

One-phase methanolysis of SBO/palmitic acid mixtures containing 10 to 90 wt.% palmitic acid, and employing 2.0 wt.% concentrated sulfuric acid as catalyst, and the necessary amounts of TBME as cosolvent, resulted in different methyl ester yields. The substrates containing 50-90 % palmitic acid are miscible with methanol, without the cosolvent, in the beginning of methanolysis. However, the cosolvent-free one-phase reaction systems became cloudy after 10 minutes and gradually two phases appeared after 40 minute of reflux. Cosolvent MTBE was therefore added at the beginning of the reaction. For substrates containing less than 50 % palmitic acid, cosolvent is required to produce one-phase at the beginning of reaction.

The minimum amount of cosolvent ( MTBE ) which is required to produce one-phase transesterification system for SBO, the SBO/palmitic acid mixtures is given in Table 5.5.2-1. The amount of distilled products and residues as well as the weight percentage of methyl ester content are shown in Table 5.5.2-2. The relation between methyl ester yields and palmitic acid content in the substrates is depicted in Figure 5.5.2-1. The typical gas chromatogram of distilled methanolysis product is illustrated in Figure 5.5.2-2. The typical gas chromatogram of residue remaining after distillation of methanolysis products is shown in Figure 5.5.2-3. Table 5.5.2-3 lists the analysis results of residues. Table 5.5.2-4 illustrates the relation between the minimum reaction temperature required for one-phase good reflux and the content of palmitic acid. Relation between the recoverable amount of the MTBE/MeOH mixture after 10 hr methanolysis and the content of palmitic acid is presented in Table 5.5.2-5.
The gas chromatograms of residues after methanolysis products distilled are presented in Appendix D-2.

Table 5.5.2-1 Minimum amount of cosolvent (MTBE) required to produce one-phase transesterification system for SBO, the SBO/palmitic acid mixtures (30:1 methanol/SBO; 10:1 methanol/PA)

<table>
<thead>
<tr>
<th>Methanolysis system (20 g)</th>
<th>Amount of methyl tert-butyl ether (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99% PA</td>
<td>4.5</td>
</tr>
<tr>
<td>90% PA, 10% SBO</td>
<td>8.5</td>
</tr>
<tr>
<td>80% PA, 20% SBO</td>
<td>12.5</td>
</tr>
<tr>
<td>70% PA, 30% SBO</td>
<td>13.5</td>
</tr>
<tr>
<td>60% PA, 40% SBO</td>
<td>18.0</td>
</tr>
<tr>
<td>50% PA, 50% SBO</td>
<td>19.0</td>
</tr>
<tr>
<td>40% PA, 60% SBO</td>
<td>20.8</td>
</tr>
<tr>
<td>30% PA, 70% SBO</td>
<td>22.0</td>
</tr>
<tr>
<td>20% PA, 80% SBO</td>
<td>23.0</td>
</tr>
<tr>
<td>10% PA, 90% SBO</td>
<td>24.6</td>
</tr>
<tr>
<td>SBO</td>
<td>25.0</td>
</tr>
</tbody>
</table>
The relationship between methyl ester yields (based on distilled products and residues) and palmitic acid content in the substrates (Data in Appendix C-2)

* Methyl ester yield = actual amount of methyl ester / theoretical amount of methyl ester
Table 5.5.2-2 Methanolysis of the SBO/palmitic acid mixtures, using 30:1 methanol/oil; 10:1 methanol/PA molar ratio, 2 wt.% concentrated H$_2$SO$_4$ catalyst in 10 hour reaction time

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Subs. Mass</th>
<th>Distilled Product Mass (g)</th>
<th>Content of ME in the distilled product (%)</th>
<th>Residue Mass (g)</th>
<th>Content of ME in residue (%)</th>
<th>Actual amount of ME (g)</th>
<th>Theoretical amount of ME (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90% PA 10% SBO</td>
<td>18.0 PA 2.0 SBO</td>
<td>19.7</td>
<td>99.8</td>
<td>1.1</td>
<td>59.0</td>
<td>20.3</td>
<td>20.8</td>
</tr>
<tr>
<td>80% PA 20% SBO</td>
<td>16.0 PA 4.0 SBO</td>
<td>19.5</td>
<td>99.9</td>
<td>1.1</td>
<td>5.7</td>
<td>19.5</td>
<td>20.7</td>
</tr>
<tr>
<td>70% PA 30% SBO</td>
<td>14.0 PA 6.0 SBO</td>
<td>18.5</td>
<td>99.4</td>
<td>1.9</td>
<td>48.7</td>
<td>19.3</td>
<td>20.6</td>
</tr>
<tr>
<td>60% PA 40% SBO</td>
<td>12.0 PA 8.0 SBO</td>
<td>18.4</td>
<td>99.0</td>
<td>2.1</td>
<td>5.9</td>
<td>18.4</td>
<td>20.6</td>
</tr>
<tr>
<td>50% PA 50% SBO</td>
<td>10.0 PA 10.0 SBO</td>
<td>17.4</td>
<td>99.0</td>
<td>3.1</td>
<td>27.3</td>
<td>18.1</td>
<td>20.5</td>
</tr>
<tr>
<td>40% PA 60% SBO</td>
<td>8.0 PA 12.0 SBO</td>
<td>16.7</td>
<td>99.5</td>
<td>3.6</td>
<td>16.7</td>
<td>17.2</td>
<td>20.4</td>
</tr>
<tr>
<td>30% PA 70% SBO</td>
<td>6.0 PA 14.0 SBO</td>
<td>17.0</td>
<td>99.6</td>
<td>3.3</td>
<td>18.6</td>
<td>17.5</td>
<td>20.3</td>
</tr>
<tr>
<td>20% PA 80% SBO</td>
<td>4.0 PA 16.0 SBO</td>
<td>17.3</td>
<td>99.5</td>
<td>3.0</td>
<td>18.8</td>
<td>17.8</td>
<td>20.3</td>
</tr>
<tr>
<td>10% PA 90% SBO</td>
<td>2.0 PA 18.0 SBO</td>
<td>17.8</td>
<td>99.8</td>
<td>2.2</td>
<td>25.4</td>
<td>18.3</td>
<td>20.1</td>
</tr>
</tbody>
</table>
Table 5.5.2-3 Residue analysis results for methanolysis of the SBO/palmitic acid mixture, using 30:1 methanol/oil; 10:1 methanol/PA molar ratio, 2wt.% concentrated H₂SO₄ catalyst in 10 hour reaction time

<table>
<thead>
<tr>
<th>Residues from mixtures of SBO/palmitic acid</th>
<th>Methyl ester %</th>
<th>Monoglyceride %</th>
<th>Diglyceride %</th>
<th>Triglyceride %</th>
<th>Unreacted SBO % (based on SBO weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%SBO 90%PA</td>
<td>59.0</td>
<td>3.0</td>
<td>11.7</td>
<td>26.3</td>
<td>15</td>
</tr>
<tr>
<td>20%SBO 80%PA</td>
<td>5.7</td>
<td>5.3</td>
<td>33.3</td>
<td>55.8</td>
<td>15</td>
</tr>
<tr>
<td>30%SBO 70%PA</td>
<td>48.7</td>
<td>4.3</td>
<td>15.4</td>
<td>31.6</td>
<td>10</td>
</tr>
<tr>
<td>40%SBO 60%PA</td>
<td>5.9</td>
<td>6.8</td>
<td>37.3</td>
<td>50.0</td>
<td>13</td>
</tr>
<tr>
<td>50%SBO 50%PA</td>
<td>27.3</td>
<td>11.6</td>
<td>22.1</td>
<td>39.0</td>
<td>12</td>
</tr>
<tr>
<td>60%SBO 40%PA</td>
<td>16.7</td>
<td>7.0</td>
<td>26.7</td>
<td>49.6</td>
<td>15</td>
</tr>
<tr>
<td>70%SBO 30%PA</td>
<td>18.6</td>
<td>12.9</td>
<td>28.8</td>
<td>39.7</td>
<td>9</td>
</tr>
<tr>
<td>80%SBO 20%PA</td>
<td>18.8</td>
<td>9.2</td>
<td>27.9</td>
<td>44.1</td>
<td>8</td>
</tr>
<tr>
<td>90%SBO 10%PA</td>
<td>25.4</td>
<td>7.0</td>
<td>27.7</td>
<td>39.9</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 5.5.2-4 Relation between the minimum reaction temperature required for good reflux and the content of palmitic acid

<table>
<thead>
<tr>
<th>Content of palmitic acid</th>
<th>Minimum temperature required for good reflux °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>99% PA</td>
<td>64.0</td>
</tr>
<tr>
<td>90% PA, 10% SBO</td>
<td>63.0</td>
</tr>
<tr>
<td>80% PA, 20% SBO</td>
<td>62.0</td>
</tr>
<tr>
<td>70% PA, 30% SBO</td>
<td>61.0</td>
</tr>
<tr>
<td>60% PA, 40% SBO</td>
<td>60.0</td>
</tr>
<tr>
<td>50% PA, 50% SBO</td>
<td>59.5</td>
</tr>
<tr>
<td>40% PA, 60% SBO</td>
<td>59.0</td>
</tr>
<tr>
<td>30% PA, 70% SBO</td>
<td>58.5</td>
</tr>
<tr>
<td>20% PA, 80% SBO</td>
<td>58.0</td>
</tr>
<tr>
<td>10% PA, 90% SBO</td>
<td>57.5</td>
</tr>
<tr>
<td>SBO</td>
<td>57</td>
</tr>
</tbody>
</table>
Table 5.5.2-5  Relation between the recoverable amount of the MTBE/MeOH mixture after 10 hour methanolysis and the content of palmitic acid

<table>
<thead>
<tr>
<th>Content of palmitic acid</th>
<th>The amount of MTBE and MeOH put in before reaction ML</th>
<th>The recoverable amount of MTBE and MeOH after 10 hr Methanolysis ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>99% PA</td>
<td>36.1</td>
<td>25.6</td>
</tr>
<tr>
<td>90% PA, 10% SBO</td>
<td>39.7</td>
<td>31.7</td>
</tr>
<tr>
<td>80% PA, 20% SBO</td>
<td>43.4</td>
<td>35.4</td>
</tr>
<tr>
<td>70% PA, 30% SBO</td>
<td>44.0</td>
<td>35.0</td>
</tr>
<tr>
<td>60% PA, 40% SBO</td>
<td>48.1</td>
<td>38.1</td>
</tr>
<tr>
<td>50% PA, 50% SBO</td>
<td>48.8</td>
<td>39.0</td>
</tr>
<tr>
<td>40% PA, 60% SBO</td>
<td>50.2</td>
<td>40.4</td>
</tr>
<tr>
<td>30% PA, 70% SBO</td>
<td>51.1</td>
<td>40.8</td>
</tr>
<tr>
<td>20% PA, 80% SBO</td>
<td>51.7</td>
<td>44.0</td>
</tr>
<tr>
<td>10% PA, 90% SBO</td>
<td>52.9</td>
<td>45.0</td>
</tr>
<tr>
<td>SBO</td>
<td>53.0</td>
<td>45.0</td>
</tr>
</tbody>
</table>
Figure 5.5.2-2 The typical gas chromatogram of distilled methanolysis product from SBO/palmitic acid mixture.
Figure 5.5.2-3 The typical gas chromatogram of residue remaining after distillation of methanolysis product from SBO/palmitic acid mixture.
5.5.3 One-Phase Acid-Catalyzed Methanolysis of Palmitic Acid

The results from MTBE-assisted (4.5 mL) one phase methanolysis of palmitic acid, using 2 wt.% H$_2$SO$_4$ catalyst together with those obtained from MTBE-free acid-catalyzed “two-phase” methanolysis of palmitic acid, using 2 wt.% H$_2$SO$_4$ catalyst are shown in Table 5.5.3-1.

Table 5.5.3-1 Comparison of (a) one-phase methanolysis of palmitic acid, and (b) “two-phase” methanolysis of palmitic acid (10:1 methanol/PA molar ratio, 2 wt.% concentrated H$_2$SO$_4$ catalyst in 10 hour reaction time)

<table>
<thead>
<tr>
<th>Methanolysis of PA</th>
<th>Substrate</th>
<th>Subs. Mass (g)</th>
<th>Product (g)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Two-phase” reaction</td>
<td>Palmitic Acid</td>
<td>20.0</td>
<td>20.6</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>99.0%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>One-phase reaction</td>
<td>Palmitic Acid</td>
<td>20.0</td>
<td>20.7</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>99.0%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Theoretical amount of methyl palmitate: 20.9g

5.5.4 Investigation of Cosolvent (MTBE) Degradation

The reaction system mass was weighed before and after a 5 hour reflux. Thus, the possibility of producing isobutylene from MTBE can be determined. The results were as follows:

The reaction system weights before and after the 5 hour reflux were 62.0g and 61.6g respectively.
5.6 Discussion

5.6.1 One-Phase Acid-Catalyzed Transesterification of Neat Vegetable Oil

MTBE was employed as cosolvent in the acid-catalyzed transesterification of SBO and SBO/PA mixtures. There are two reasons for this choice: first, MTBE is widely used as an octane enhancer in gasoline. Secondly, MTBE has a low boiling point and can be recovered and recycled by distillation. For a 30:1 molar ratio of methanol and SBO, the minimum MTBE/methanol volumetric ratio that was required for miscibility was 0.89; compared to THF for which the value is 0.79.

The results in Table 5.5.1-1 show that the recoverable distilled methyl ester product increases from 6.4g after 1 hour to 18.3g after 10 hours. The methyl ester yields (based on the methyl ester in both the distilled product and residue) also exhibit the same trend. They increased from 43.8% to 93.2% in the same period. As expected the compositional yields (based on isolated products) of methyl ester increase from 46.6% to 96.9%. The results displayed in Figure 5.5.1-1 show that the reaction may not be inconsistent with pseudo first order kinetics, particularly if experimental errors are taken into account.

Clearly, the one-phase methanolysis is much faster than the two-phase methanolysis. MTBE-assisted one-phase methanolysis of SBO employing a 30:1 molar ratio of methanol to SBO, 1 wt.% H₂SO₄, at 57°C resulted in 96.9% methyl ester in 10 hours. Two-phase acid-catalyzed methanolysis of soybean oil has been studied by Freedman et. al.. the results show that 93% methyl ester is obtained after 69 hours of reflux using 1 wt.% sulfuric acid catalyst at 65°C. As mentioned earlier, this is interpreted as the result of a two-phase reaction in which methanolysis occurs only in the methanol phase. Low oil concentration in methanol causes the
slow reaction rate. The addition of a cosolvent MTBE produces a one-phase system in which mass transport is not the limiting factor.

The methanolysis reaction rate in the MTBE-assisted one-phase reaction is also faster than one-phase butanolysis. Figure 5.5.1-2 compares the reaction of one-phase MTBE-assisted acid-catalyzed methanolysis of SBO using 2wt.% H$_2$SO$_4$ catalyst at 57°C to one-phase butanolysis of SBO at 77°C 1wt.% H$_2$SO$_4$ catalyst (Freedman et al., 1984). It is obvious that the rate of methanolysis of SBO in a cosolvent-assisted one-phase system at 57°C is much faster than the rate of butanolysis at 77°C. Methanolysis in a one-phase system resulted in 95.8% methyl ester in 7 hours, whereas butanolysis yielded 62 % butyl ester in the same time. When the butanolysis of SBO was performed at 65°C, as mentioned in Chapter 2, it produce 93% butyl ester after 69 hours. Whereas, at 57°C, the methanolysis of SBO gave 96.9% methyl ester in 10 hours. Several possible reasons could account for the difference. First, the use of twice the amount of catalyst could cause a faster reaction.; however, the initial rates are apparently too different to be explained solely by the concentration of catalyst, particularly as the butanolysis was performed at higher temperature. A second factor is that the methanol molecules are much smaller than those of butanol which would make their attack on the triglycerides easier. Finally, the polarity of methanol is much higher than that of butanol which might favor the polar entities involved in the mechanism.

The superiority of the 2 wt.% sulfuric acid over 1 wt.% sulfuric acid was also supported by the results of Boocock et al. when they conducted one-phase methanolysis of soybean oil using both 1 wt.% and 2 wt.% concentrated sulfuric acid as catalyst, and THF as co-solvent at 70°C. Reaction rate were approximately doubled in the first hour when 2 wt.% catalyst was used instead of 1 wt.. After 7 hour reaction, the methyl ester contents for 1wt.%
The amount of MTBE which is required to produce a one-phase reaction system depends on the type of substrate being transesterified. As can be seen from Table 5.5.2-1, the minimum amount of MTBE required to produce one-phase is decreased as the palmitic acid content in the substrate increased. For example, the minimum amount of MTBE required to make one-phase in the methanolysis of a pure palmitic acid system is only 4.5 mL (base on 20g substrate), whereas, the corresponding amount of MTBE required to produce one-phase in the methanolysis of pure SBO system is 25 mL. The minimum amount of MTBE required producing one-phase for other substrates with palmitic acid contents from 10% to 90% lies within this range.
The SBO/palmitic acid mixtures which contain different content of palmitic acid have different physical properties. For example, the solubility of the mixture in methanol is different. The solubility of SBO in methanol is fairly low even at 60°C. Boocock et al. (Mao, 1995) measured the solubility of SBO in methanol at 6:1 methanol/SBO molar ratio, and found that with continuous vigorous stirring, the value at 60°C was 9.8g/L. As the molar ratio increases, the solubility of SBO in methanol increases slightly. The reason is the high molar mass (approximately 870D) and long chain lengths (C16 and C18) of SBO which behaves essentially as a non-polar substrate. The hydrogen-bonded network in methanol effectively excludes the larger SBO molecules. Palmitic acid can dissolve freely in methanol at 60°C. As the palmitic acid content (more than 50%) increases, SBO in the SBO/palmitic acid mixture becomes more soluble in the palmitic acid-rich system. This is why the initial one phase reaction systems occur when methanolyses of the mixtures of SBO/PA containing 50% to 90% palmitic acid are carried out. The palmitic acid therefore becomes a surrogate for the cosolvent.

In the case of the substrates containing 50-90% palmitic acid, two phases are usually seen after 40 minutes. This is because most of palmitic acid reacts with methanol and produces methyl palmitate which is sparingly soluble in methanol and therefore does not function as a cosolvent. Thus, methyl palmitate separates out of the reaction system, as does SBO. MTBE is therefore added to the methanolysis of palmitic acid dominant systems in order to maintain the one-phase system throughout the whole reaction period.

MTBE is a good solvent for most of the components in the transesterification reaction mixture. Since MTBE has bulky alkyl group, palmitic acid has small molecules compared to SBO; consequently, MTBE presents more hindrance to form hydrogen bond with SBO during
dissolution than with palmitic acid. This accounts for the decreasing trend in the minimum amount of MTBE required to produce one-phase methanolysis system as palmitic acid content in the substrate increases.

Since the acid-catalyzed methanolysis products from the substrates containing large amounts of FFA contain significant amounts of mono-, di-, and tryglycerides, vacuum distillation is necessary to produce a final product that meets the transportation fuel specification. However, these methyl esters in their undistilled form could be directly used in many of the gas generators on market.

Results obtained for the 10 hour methanolysis of substrate containing different amounts of palmitic acid, and employing a 30:1 molar ratio of methanol to oil, 10:1 molar ratio of methanol to palmitic acid (2 wt.% H₂SO₄ as catalyst), are summarized in Table 5.5.2-2. As can be seen, the distillable product mass decreases from 20.3g to 17.2g as the palmitic acid content in the substrate decreases from 90% to 40%. But on further decreasing of palmitic acid content from 40% to 10%, the distillable product mass increases from 17.2g to 18.3g. The yields of methyl ester (based on the content of methyl ester in both distilled product and residue) have the same trend as shown in Figure 5.5.2-1. The substrate which contains 40% PA and 60% SBO is the worst substrate for methanolysis, because the methyl ester produced from this substrate is the lowest for any of the substrates.

Acid-catalyzed methanolysis of neat SBO performed better than that of SBO in the palmitic acid / SBO mixture. The results obtained from Section 5.5.2 show that the methyl ester production from pure SBO reached 96.9% after 10 hours with only 1.4% of SBO remaining. In contrast, the methyl ester production from SBO in SBO/palmitic acid mixture (60/40) in the same time was 72.5% (Figure 5.5.2-1), and the unreacted SBO was 15% (Table
5.5.2-3). Obviously, the palmitic acid somehow interferes with the methanolysis of SBO in the reaction mixture. Results from Boocock et al. (Dr. S.K. Konar private communication 1998) showed that only 1.4% palmitic acid was unreacted after 33 minutes. Namely, palmitic acid methylates much faster than SBO. This reaction produces some water (see equation 2.5, Chapter 2). As mentioned earlier, the reaction rate of the methanolysis of SBO is reduced significantly when as little as 0.3% water is present in the reaction mixture. Water can act as an nucleophile to attack the ester. As the palmitic acid content increases in the SBO/PA mixture, so does the amount of water produced. As the results, the unreacted SBO content increase and conversion of SBO in the SBO/PA mixture decrease. For example, the methanolysis of substrates which contain 50/50 SBO/PA and 40/60 SBO/PA produced 0.7g and 0.84g water respectively, (provided that the palmitic acid is completely converted to methyl palmitate) which would represent 3.5% and 4.2% water respectively in the reaction mixtures. It should be possible to maintain the methanolysis rate of SBO in the mixtures by removing water through the addition of dehydrating agents such as magnesium sulfate, sodium sulfate, or molecular sieves. The addition of dehydrating agent could not only improve the rate of methanolysis of SBO, it could also facilitate the conversion of palmitic acid to methyl palmitate by removing the by product-water formed, hereby shifting the equilibrium.

Since the esterification of palmitic acid is almost complete in 10 hours and the methyl palmitate makes up a large fraction of the products from methanolysis of substrates containing 50-90% palmitic acid, the overall methyl ester yields range from 88.2% to 97.5%. although the methyl ester conversion from the SBO is low. The lowest yield of methanolysis of SBO/PA mixtures is from methanolysis of 60/40 SBO/PA mixture. From this point,
transesterification of SBO is the main reaction and the conversion of SBO is relatively lower than that of Palmitic acid; thus, the overall methyl ester yields for methanolysis of SBO/PA mixture containing 40-10% palmitic acid is relatively low, which is range from 84.3% to 91.0%. and the lowest yield is 84.3% from methanolysis of 60/40 SBO/PA mixture.

That the water content in the reaction system lowers the reaction rate, especially the methanolysis of SBO, is also supported by analysis of the distillation residues. The residue is a mixture of several compounds after the acid-catalyzed methanolysis products are distilled. As can be seen from table 5.5.2-3, the residues contain some methyl ester, although the major components are mostly triglycerides, diglycerides, and monoglycerides. The unreacted triglyceride for the methanolysis of 50/50 SBO/palmitic acid mixture after 10 hours reaction is 12%; whereas the content of unreacted triglyceride in methanolysis of neat SBO is only 1.4%. The monoglyceride and diglyceride contents for methanolysis of 50/50 SBO/PA mixture are 3.6% and 6.9% respectively; whereas, the corresponding contents for pure SBO are 0.5% and 1.1%. Thus, as the palmitic acid content increases the unreacted SBO, monoglyceride and triglyceride percentage increases.

The presence of significant amounts of mono-, di- and triglyceride in the residues (Table 5.5.2-3) indicates that acid-catalyzed process alone for the methanolysis of the SBO/palmitic acid mixtures is not adequate to obtain high conversion to methyl ester. This process still needs to be improved.

Gas chromatographic analysis of methyl ester product after 10 hour reaction shows that essentially no palmitic acid is left as expected. Subsequent to this work, it was shown in our laboratory that conversion to methyl ester from palmitic acid reached equilibrium after only 33 minutes (Dr. S.K.Konar private communication).
During the work, it was found that vigorous shaking of the separatory funnel caused emulsion during the separation of the organic product and aqueous layer. The addition of sodium chloride can help to break the emulsion, as does the use of hot water (45°C) in washing the methanolysis products.

MTBE-assisted one-phase acid-catalyzed methanolysis of the SBO/palmitic acid mixtures during the reaction contains mainly methyl ester, palmitic acid, soybean oil, methanol, MTBE, concentrated sulfuric acid, mono- di- and triglycerides. Reflux conditions are used to maximize the reaction temperature. For different reaction mixtures with different compositions, the minimum temperatures of the flask contents, which are required for good reflux will be different. Table 5.5.2-4 presents the relation between the minimum temperature required for good reflux and the content of PA. The boiling temperature rises as the content of palmitic acid increases. The boiling point of palmitic acid is 139°C at a pressure of 1mmHg. So its vapor pressure at 60°C is very small. The boiling points of MTBE and methanol are 53°C and 64°C respectively. The pressure of PA, therefore, lowers the vapor pressure of the mixture which in turn requires a higher temperature to return to the atmospheric vapor pressure.

Table 5.5.2-5 outlines the relation between the recoverable amount of MTBE and methanol mixture after 10 hour methanolysis and the content of palmitic acid. On the average 84% of methanol and MTBE mixture is recovered. This data is important for evaluation of the process because it shows that most of the excess methanol and cosolvent used in the reaction can be recycled. The recovery of methanol and MTBE was done by distillation. A reason for the loss of solvent may be due to the small percentage of residual methanol and MTBE left in the methyl esters. In industry, methanol and MTBE could be recovered by flash distillation
where the mixture would slowly be poured into a drum that was heated to a specific temperature. As the mixture contacts the sides of this flashing drum, the solvent, i.e. methanol and MTBE, would be vaporized, condensed and collected for reuse.

Methyl ester contents of distilled products from different substrates were determined by gas chromatography (see Table 5.5.2-2 and Figure 5.5.2-2). The results show over 99.0% pure methyl ester in each distilled product. The methyl palmitate (C16) is mainly from the methanolysis of palmitic acid and methyl ester (C18) is derived from SBO.

A 30:1 molar ratio of methanol to SBO is equivalent to 10:1 molar ratio of methanol to palmitic acid. In the methanolysis of substrate studied with different amounts of palmitic acid, the molar ratio described above is employed.

5.6.3 One-Phase Acid-Catalyzed Methanolysis of Palmitic Acid

MTBE-assisted one-phase acid-catalyzed methanolysis of palmitic acid resulted in purity of 99.8% methyl palmitate. Two-phase cosolvent-free acid catalyzed methanolysis of palmitic acid under the same reaction condition reached a purity of 99.4% methyl palmitate. Therefore, the one-phase methanolysis of pure palmitic acid is slightly superior to “two-phase” methanolysis of pure palmitic acid.

Since methyl palmitate is sparingly soluble in methanol, once formed it immediately separates from the reaction mixture. Theoretically, for this equilibrium reaction, separation of methyl palmitate is advantageous to the completing of the reaction. In fact, the results indicate that methyl palmitate separation has no significant effect on the rate and completeness of the reaction.
5.6.4 Investigation of Cosolvent (MTBE) Degradation

When MTBE mixes with concentrated sulfuric acid at high temperature (100-150°C), the following acid-catalyzed reaction could occur:

\[
\begin{align*}
\text{H}_2\text{SO}_4 & \quad \text{CH}_3\text{-C( CH}_3\text{)_2-}\text{OCH}_3 \\
\text{Heating} & \quad \text{CH}_3\text{-C( CH}_3\text{)=CH}_2 & + & \quad \text{CH}_3\text{OH}
\end{align*}
\]

The volatile alkene would be vaporized, hereby leading to the loss of MTBE.

A simple test was carried out to determine the possibility of producing isobutylene. After 5 hour of reflux, the total weight of mixture was virtually unchanged. Therefore, neither the reaction temperature nor acid concentration was high enough to cause this reaction.

Part IV One-Phase Two-Step Transesterification Process

5.7 Results

In the first-step, the palmitic acid content of the reaction mixture after 3 hours of MTBE-assisted one-phase acid-catalyzed methanolysis of 50/50 SBO/palmitic acid mixture with 2wt.% H\textsubscript{2}SO\textsubscript{4} as catalyst was determined by GC. The results show that palmitic acid content is 1.4 % after 3 hour one-phase acid-catalyzed methanolysis of the mixture of SBO/palmitic acid (50/50 by weight)
The one-phase two-step methanolysis process speeds up the reaction time from 10 hours to 3.5 hours. Table 5.7-1 presents comparison of methyl ester yield from: (a) acid-catalyzed MTBE-assisted one-phase methanolysis of the mixture of 50 % PA and 50 % SBO after 10 hours; (b) two-step methanolysis of mixture of 50% PA and 50% SBO after 3.5 hours (30:1 methanol/oil; 10:1 methanol/palmitic acid molar ratio, reacted in 3 hours, at 57°C, and 2 wt.% concentrated H₂SO₄ in first-step; 10 min., room temperature and 1 wt.% NaOH catalyst in second-step). Table 5.7-2 lists the comparison of GC analysis results of residues remaining after methanolysis product was distilled from two-step process with that from acid-catalyzed methanolysis alone.

The gas chromatograms of residue remaining after distillation of methanolysis product are presented in Appendix D-3.

<table>
<thead>
<tr>
<th>Type of reaction</th>
<th>Subs. Mass (g)</th>
<th>Distilled Product (g)</th>
<th>ME in distilled product (%)</th>
<th>Residue (g)</th>
<th>ME in residue (%)</th>
<th>Purity (%)</th>
<th>Yield of ME (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>two-step acid/base catalyzed methanolysis</td>
<td>20.0</td>
<td>19.5</td>
<td>99.9</td>
<td>0.8</td>
<td>70.7</td>
<td>98.7</td>
<td>97.8</td>
</tr>
<tr>
<td>acid-catalyzed methanolysis</td>
<td>20.0</td>
<td>17.4</td>
<td>99.0</td>
<td>3.1</td>
<td>27.3</td>
<td>88.2</td>
<td>88.2</td>
</tr>
</tbody>
</table>

Theoretical amount of methyl ester: 20.5g
Table 5.7-2 The composition of residues from two-step methanolysis and from acid-catalyzed methanolysis

<table>
<thead>
<tr>
<th>Type of reaction</th>
<th>Residue amount (g)</th>
<th>Time (hr)</th>
<th>Methyl ester (%)</th>
<th>Monoglyceride (%)</th>
<th>Diglyceride (%)</th>
<th>Triglyceride (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50 SBO/PA mixture (two-step)</td>
<td>0.8</td>
<td>3.5</td>
<td>70.7</td>
<td>7.0</td>
<td>10.2</td>
<td>12.1</td>
</tr>
<tr>
<td>50/50 SBO/PA mixture (acid-catalysis alone)</td>
<td>3.1</td>
<td>10</td>
<td>27.3</td>
<td>11.6</td>
<td>22.1</td>
<td>39.0</td>
</tr>
</tbody>
</table>

5.8 Discussion

Table 5.5.2-2 in Section 5.5.2 shows that the compositional yields (purity) of methyl ester (range from 89.3% to 87.7%) for one-phase MTBE-assisted, acid-catalyzed methanolysis of the SBO/palmitic acid mixtures which contain 60% to 20% palmitic acid, are unsatisfactory. On the other hand, the analysis results of residues remaining after methanolysis products were distilled show that almost no PA was left. It indicates that one-phase MTBE-assisted, acid-catalyzed methanolysis of palmitic acid in the mixture of SBO/PA is almost complete in a very short time. This conclusion is supported by the results of the content of PA after the 3 hour methanolysis of the mixture of 50/50 palmitic acid/SBO, which is only 1.4%.

Table 5.5.2-3 in Section 5.5.2 shows that there are considerable amounts of mono-, di-, and triglycerides in the SBO/PA methanolysis products. For acid-catalyzed methanolysis of the 50/50 SBO/PA mixture, the mono-, di-, and triglyceride contents after 10 hour reaction are 3.6%, 6.9%, 12% (based on SBO weight in the mixture) respectively. This indicates that the
rate of acid-catalyzed methanolysis of SBO in the substrates containing free fatty acid (FFA) is very slow.

Base-catalyzed MTBE-assisted one-phase methanolysis of SBO which contains low FFA is much faster than the acid-catalyzed reaction. As can be seen from Figure 5.3-1, one-phase MTBE-assisted base-catalyzed methanolysis of neat SBO employing 1 wt.% sodium hydroxide reached 99.6% methyl ester content in 8 minutes. In contrast, the results from Table 5.5.1-1 show that one-phase MTBE-assisted acid-catalyzed methanolysis of neat SBO employing 2 wt.% concentrated sulfuric acid achieved 96.6% methyl ester in 10 hours. It is obvious from this comparison that methanolysis of SBO is best handled by a base-catalyzed system after most of palmitic acid has been converted. Therefore, for the methanolysis of the mixture of 50/50 SBO/palmitic acid, it is reasonable that acid-catalyzed methanolysis of PA is in first stage, and then the unreacted SBO can be switched to base-catalyzed reaction in the second stage. The result is two-step methanolysis process.

It was anticipated that a two-step one-phase process which first employs acid-catalysis for methanolysis of palmitic acid and then base-catalysis for methanolysis of SBO should improve the methyl ester yields. In order to allow for the FFA content remaining after the first step, a calculated excess of NaOH was used. Table 5.7-1 shows that the purities of products from the two-step process and the one-step process are 98.7% and 88.2% respectively. The results from Table 5.7-2 show that the triglyceride, diglyceride and monoglyceride contents are 0.48%, 0.41%, and 0.28% respectively in two-step process whereas, in acid-catalyzed reaction they are 6.0%, 3.5% and 1.8%. It is apparent that two-step process is superior to the single step methanolysis. It is worth noting that in order to avoid undesired soap formation, anhydrous sodium sulfate was added to the reaction mixture after 3 hours of acid-catalysis, to
absorb the water produced during the first step reaction. The concentration of hydroxide is critical. If the concentration is too high, soap will form. Thus, maintaining the 1 wt.% of NaOH is necessary. As at any higher concentrations, such as 1.5 wt.%, soap will be visible.

It is evident from the results that this one-phase two-step process was successful for the methanolysis of substrates containing high contents of FFA. It is relatively fast, and convenient for industrial application. Higher ester conversion could eliminate the necessity for distillation of the product. As mention earlier, the results of a co-worker in Boocock’s group have shown that palmitic acid conversion is complete in about 33 minutes (Dr. S.K. Konar private communication). It is anticipated that shortening the reaction time in the first-step acid-catalysis methanolysis should achieve a high methyl ester conversion, improve the energy saving (reaction temperature at 57°C) and decrease the cost. Both MTBE and methanol can be easily co-distilled and recycled. Theoretically, MTBE is not consumed, but a small make-up amount would be required in an industrial process.
Chapter 6

Conclusions

1. Soybean oil/palmitic acid mixtures can be converted in high yield to methyl esters in a two-step one-phase reaction. Methyl tert-butyl ether (MTBE) can be used to form one phase. Treatment of the one-phase mixtures at the boiling point of the methanol/MTBE with 2 wt.% sulfuric acid for 0.5 - 3 hours causes almost complete conversion of the palmitic acid to methyl ester. A fast base-catalyzed reaction then converts the remaining soybean oil to methyl ester.

2. The palmitic acid content in the reaction mixture (50/50 SBO/PA) after 3 hour MTBE assisted one-phase acid-catalyzed methanolysis is 1.4%.
3. A 98.7% methyl ester content of the product resulted in about 3.5 hours. Whereas, MTBE-assisted one-phase methanolysis of same substrate in acid-catalysis only resulted in 88.2% methyl ester content in 10 hours.

4. Methyl tert-butyl ether (MTBE) is an excellent cosolvent for forming single phases in pure SBO and SBO/palmitic acid mixtures with methanol. For a 27:1 methanol to pure SBO (20g) molar ratio, the minimum MTBE amount required to produce one-phase reaction system at room temperature is 27.7 mL. For a 30:1 methanol to pure SBO (20g) molar ratio, the minimum MTBE amount required to produce one-phase reaction system at 57°C is 25 mL. For a 10:1 methanol to pure palmitic acid (20g) molar ratio, the minimum MTBE amount required to produce one-phase reaction system at 64°C is 4.5 mL. For the SBO/palmitic acid mixtures (20g) of different palmitic acid composition, the minimum MTBE amount required to produce one-phase reaction system is in the range of 4.5 mL to 25 mL.

5. The reaction temperature required for good reflux in MTBE-assisted one-phase acid-catalyzed methanolysis of SBO and the SBO/palmitic acid mixtures increases as the content of palmitic acid in reaction mixture increases.

6. MTBE-assisted one-phase base-catalyzed methanolysis of pure SBO, employing a 27:1 molar ratio of methanol/SBO and 1 wt.% sodium hydroxide as catalyst, results in 99.8% ester content in 8 minutes. No soap is observed in this reaction.

7. At 2 wt.% concentrated sulfuric acid level, a 96.6% ester content of the product resulted from a 10 hour MTBE-assisted one-phase acid-catalyzed methanolysis of pure SBO, employing a 30:1 molar ratio of methanol/SBO, at 57°C and atmospheric pressure.

8. MTBE-assisted one-phase acid-catalyzed methanolysis of pure palmitic acid, employing a
10:1 molar ratio of methanol/palmitic acid and 2 wt.% concentrated sulfuric acid as catalyst, resulted in 99.8 % ester content in 10 hours.

9. The methyl ester yields of MTBE-assisted one-phase acid-catalyzed methanolysis of the SBO/palmitic acid mixtures, employing a 10:1 molar ratio of methanol/PA, 30:1 molar ratio of methanol/SBO, 2 wt.% concentrated sulfuric acid as catalyst increased as the palmitic acid content increased from 40 wt.% to 90 wt.%; but the yields decreased as the PA content increased from 10 wt.% to 40 wt.%. The lowest methyl ester yield is 84.3% for the methanolysis of substrate which contains 40 wt.% PA and 60 wt.% SBO.

10. No MTBE was lost during MTBE-assisted one-phase acid-catalyzed methanolysis.
Chapter 7

Recommendations

1. It is recommended that one-phase acid-catalyzed methylation of fatty acid for shorter reaction time be investigated with a view to shortening further the combined two-step reaction time.

2. Following 1 above, a two-step transesterification process in shorter reaction time should be developed.

3. One-phase cosolvent-assisted methanolysis of other waste feedstocks such as waste fats containing fatty acid should be investigated.

4. MTBE-assisted one-phase methanolysis employing other acid catalyst, such as H$_3$PO$_4$, HCl, should be studied.
References


17. Eckey, E.W., JAOCS, 33, p575-597 (1956)


29. Gutierrez, R.J., 'Use of Vegetable Oils in International Combustion Engines', 1st


Regan, D.L. and Gartside, G., ‘Liquid Fuels from Micro-algae in Australia’, CSIRO Division of Chemical Technology, Bayview Ave., Private Bag 10, Clayton, Victoria, Australia, 3168; (03)542-2244.


Stern, R., Hillion, G., Gateau, P., and Guibet, J.C., ‘Preparation of Methyl Esters from Crude Vegetable Oils and Soapstock’, Proceedings from World Conference on
Emerging Technologies in the Fats and Oils Industry (Cannes), p420-422 (1986)


71. ‘Vegetable Oil Fuel’, Proceeding of the International Conference of Plant and Vegetable Oils as Fuels, Fargo, The American Society of Agricultural Engineers (ASAE) publication 4-82, ASAE, St. Joseph, MI 49085, (August 1982)


Appendix A  Calculation

1. Theoretical Amount of Methyl Ester Calculation

\[ \text{SBO} + 3 \text{ Methanol} \rightarrow 3 \text{ Methyl ester} + \text{ Glycerol} \]

Molecular weights:
- SBO = 872.4
- Methanol = 32
- Glycerol = 92
- Mixture of methyl ester = 876.4

If 20g SBO converts to methyl ester completely, the theoretical amount of methyl ester would be \( \frac{876.4 \times 20}{872.4} = 20.1 \text{g} \).

2. The Theoretical Amount of Methyl Palmitate Amount Calculation

\[ \text{Palmitic acid} + \text{ Methanol} \rightarrow \text{ Methyl palmitate} + \text{ Water} \]

Molecular weights:
- Palmitic acid = 256.43
- Methanol = 32
- Methyl palmitate = 270.43
- Water = 18

If 20g Palmitic acid (99%) converts to methyl ester completely, the theoretical amount of methyl palmitate would be \( 270.43 \times 19.8 / 256.43 = 20.9 \text{g} \).

3. The Amount of Na\(_2\)CO\(_3\) Required to Neutralize the Sulfuric Acid:

\[ \text{Sodium carbonate} + \text{ Sulfuric acid} \rightarrow \text{ Sodium sulfate} + \text{ Water} + \text{ Carbon dioxide} \]

Molecular weights:
- Sodium carbonate = 105.99
- Sulfuric acid = 98.08

To neutralize 2 wt% H\(_2\)SO\(_4\) (98%), the amount of Na\(_2\)CO\(_3\) required = \( 0.4 \times 98\% \times \frac{105.99}{98.08} = 0.42 \text{g} \).
Appendix B  Kinetic Data from the Literature

1. Butanolysis of SBO at 77°C, 1 wt.% H₂SO₄ and 30:1 molar ratio of methanol to SBO (data adapted from reference Freedman et al., 1986 Figure 2)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester Yields (%)</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td>62</td>
<td>75</td>
</tr>
</tbody>
</table>

2. One-phase THF-assisted methanolysis of SBO at 70°C, 2 wt.% H₂SO₄ catalyst and 30:1 molar ratio of methanol to SBO (data adapted from Boocock et al., 1998 Table 1)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester Yields (%)</td>
<td>47.4</td>
<td>85.6</td>
<td>91.9</td>
<td>95.9</td>
<td>97.9</td>
</tr>
</tbody>
</table>

3. One-phase THF-assisted methanolysis of SBO at 70°C, using both 1 wt.% and 2 wt.% H₂SO₄ and 30:1 molar ratio of methanol to SBO (data adapted from Boocock et al., 1998 Figure 6)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester Yields (%) for 2 wt.% H₂SO₄</td>
<td>47.4</td>
<td>85.6</td>
<td>91.9</td>
<td>95.9</td>
<td>97.9</td>
</tr>
<tr>
<td>Ester Yields (%) for 1 wt.% H₂SO₄</td>
<td>18.9</td>
<td>79.6</td>
<td>85.3</td>
<td>89.8</td>
<td>94.9</td>
</tr>
</tbody>
</table>

4. One-phase THF-assisted methanolysis of SBO at room temperature, 1 wt.% NaOH as catalyst and 8:1 molar ratio of methanol to SBO (data adapted from Mao, 1995 Figure-5.10)

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester composition (%)</td>
<td>64</td>
<td>74.9</td>
<td>81</td>
<td>84.3</td>
<td>85.9</td>
<td>87.7</td>
<td>88</td>
<td>88.9</td>
<td>89.8</td>
</tr>
</tbody>
</table>
Appendix C  Data for the One-Phase Methanolysis of SBO

1. Data for base-catalyzed MTBE-assisted one-phase methanolysis of SBO (Figure 5.3.1)

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Methyl ester %</th>
<th>monoglyceride %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>68.6</td>
<td>7.8</td>
</tr>
<tr>
<td>2</td>
<td>93.3</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>96.9</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>97</td>
<td>2.3</td>
</tr>
<tr>
<td>5</td>
<td>98.9</td>
<td>1.1</td>
</tr>
<tr>
<td>6</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>99.4</td>
<td>0.6</td>
</tr>
<tr>
<td>8</td>
<td>99.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

2. Data for acid-catalyzed MTBE-assisted one-phase methanolysis of SBO/PA mixtures (Figure 5.5.2-1)

<table>
<thead>
<tr>
<th>Type of Substrates</th>
<th>Theoretical Methyl Ester Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>98.8</td>
</tr>
<tr>
<td>90%PA 10%SBO</td>
<td>97.6</td>
</tr>
<tr>
<td>80%PA 20%SBO</td>
<td>94.4</td>
</tr>
<tr>
<td>70%PA 30%SBO</td>
<td>93.7</td>
</tr>
<tr>
<td>60%PA 40%SBO</td>
<td>89.1</td>
</tr>
<tr>
<td>50%PA 50%SBO</td>
<td>88.2</td>
</tr>
<tr>
<td>40%PA 60%SBO</td>
<td>84.4</td>
</tr>
<tr>
<td>30%PA 70%SBO</td>
<td>86.4</td>
</tr>
<tr>
<td>20%PA 80%SBO</td>
<td>87.6</td>
</tr>
<tr>
<td>10%PA 90%SBO</td>
<td>91.2</td>
</tr>
<tr>
<td>SBO</td>
<td>93.2</td>
</tr>
</tbody>
</table>
Appendix D - 1

Gas Chromatograms of Residues Remaining after Products from Acid-Catalyzed MTBE - Assisted One-Phase Methanolysis of SBO Were Distilled
Figure D-1.1 Gas Chromatogram of Residue Remaining After 1 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from SBO Was Distilled.
Figure D-1.2 Gas Chromatogram of Residue Remaining After 3 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from SBO Was Distilled.
Figure D-1.3 Gas Chromatogram of Residue Remaining After 5 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from SBO Was Distilled.
Figure D-1.4 Gas Chromatogram of Residue Remaining After 7 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from SBO Was Distilled.
Figure D-1.5 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from SBO Was Distilled.
Appendix D - 2

Gas Chromatograms of Residues Remaining after Products from Acid-Catalyzed MTBE - Assisted One-Phase Methanolysis of SBO/PA Mixtures Were Distilled
Figure D-2.1 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 10/90 SBO/PA mixture Was Distilled.
Figure D-2.2 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 20/80 SBO/PA mixture Was Distilled.
Figure D-2.3 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 30/70 SBO/PA mixture Was Distilled.
Figure D-2.4 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 40/60 SBO/PA mixture Was Distilled.
Figure D-2.5 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 50/50 SBO/PA mixture Was Distilled.
Figure D-2.6 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 60/40 SBO/PA mixture Was Distilled.
Figure D-2.7 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 70/30 SBO/PA mixture Was Distilled.
Figure D-2.8 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 80/20 SBO/PAt mixture Was Distilled.
Figure D-2.9 Gas Chromatogram of Residue Remaining After 10 hour Acid-Catalyzed MTBE-Assisted One-Phase Methanolysis Product from 90/10 SBO/PA mixture Was Distilled.
Appendix D - 3

Gas Chromatograms of Residues Remaining after products from MTBE - Assisted One-Phase Two-Step Methanolysis of SBO/PA Mixtures were distilled
Figure D-3.1 Gas Chromatogram of Residue Remaining After MTBE-Assisted One-Phase Two-Step Methanolysis Product from 50/50 SBO/PA mixture Was Distilled.