Comparative Tribological Property Evaluation of Trimethylolpropane-based Biolubricants derived from Methyl Oleate and Canola Biodiesel

A Thesis
Submitted to the College of Graduate Studies and Research
in Partial Fulfillment of the Requirements for the
Degree of Master of Science (M.Sc.)
in the Department of Chemical and Biological Engineering
University of Saskatchewan
Saskatoon, Saskatchewan
Canada

By
Phani Kiran Sripada

©Copyright Phani Kiran Sripada, December 2012. All Rights Reserved.
PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Postgraduate degree from the University of Saskatchewan, I agree that the Libraries of this University may make it freely available for inspection. I further agree that permission for copying of this thesis in any manner, in whole or in part, for scholarly purposes may be granted primarily by the professor or professors who supervised my thesis work or, in their absence, by the Head of the Department or the Dean of the College of Graduate Studies. Duplication or publication or any use of this thesis, in part or in whole for financial gain without prior written approval by the University of Saskatchewan is prohibited. It is also understood that due recognition shall be given to the author of this thesis and to the University of Saskatchewan in any use of the material therein.

Request for the permission to copy or make any other use of the material in this thesis, in whole or in part, should be addressed to:

Head
Department of Chemical and Biological Engineering
College of Engineering
University of Saskatchewan
57 Campus Drive
Saskatoon, SK S7N 5A9
Canada
ABSTRACT

Non-edible grade canola oil produced from green canola seeds has great potential for the production of oleo-chemicals which have extensive applications in various fields. It is proposed to develop a class of industrial-grade natural-synthetic lubricants from mixed canola fatty acid methyl esters (canola biodiesel) by transesterification with trimethylolpropane. First, methyl oleate was synthesized by esterification. The range of operating variables was: temperature (80-140°C), methanol-to-oleic acid molar-ratio (3.0-12.0) and catalyst loading (2-8 vol %). It was found that temperature and catalyst loading had significant effects on methyl oleate yield. The optimum synthesis conditions for obtaining a methyl oleate yield of 99.4 wt % were temperature of 120°C, methanol-to-oleic acid molar ratio of 9.0 and concentrated sulfuric acid loading of 4 vol %. Physicochemical characterization of methyl oleate yielded the following properties of the product: moisture content of 0.04 vol %, kinematic viscosity of 4.3 cSt at 40°C, cloud point of -3°C, pour point of -15°C and oxidative induction time of 1.14 h.

Model transesterification reactions were performed with methyl oleate using trimethylolpropane. The optimum synthesis conditions developed were obtained as temperature of 139°C, molar-ratio of methyl oleate-to-trimethylolpropane of 4.9 and catalyst loading of 1.4 wt %. Under these conditions, a 91.2 wt % triester yield was obtained after 5 h of reaction time. Response surface measurement studies were made by drawing 2D surface and 3D contour plots. A model equation was developed for predicting the final triester yield in terms of the actual reaction parameters. The fit of the model was confirmed by comparing the absolute error between modeled and actual values, which was within 5%. The observed difference between final triester yields from six replicate experiments at center point was within 2 wt %, while the standard deviation between them was less than 0.75%. Transesterification of canola biodiesel
with trimethylolpropane was performed under optimum reaction conditions developed earlier for transesterification of methyl oleate and resulted in 90.9 wt % yield of triester.

The physicochemical properties of methyl oleate-derived biolubricant and canola biodiesel-derived biolubricant were obtained in accordance with established ASTM, AOCS and EN standards in order to determine their suitability for lubricant applications. Methyl oleate-derived biolubricant was found to have the following tribological properties: viscosities of 48.9 and 9.3 cSt at 40 and 100°C, respectively; viscosity index of 191, cloud and pour points of -21 and -51°C, respectively; oxidative induction time of 2.08 h and wear scar diameter of 242 µm. Canola biodiesel-derived biolubricant had the following lubrication properties: viscosities of 40.5 and 7.8 cSt at 40 and 100°C, respectively; viscosity index of 204, cloud and pour points of -27 and -66°C, respectively; oxidative induction time of 0.74 h and wear scar diameter of 223 µm. Both biolubricants complied with ISO VG 46 standards and are ideally suitable for use in automobiles with minor modifications.
ACKNOWLEDGEMENTS

I wish to express my deepest appreciation and gratitude to my supervisor, Dr. Ajay K. Dalai and my advisory committee members, Dr. Jafar M. Soltan and Dr. Richard W. Evitts, whose guidance throughout my program facilitated me to the success of this research work. Special thanks must go to Dr. Ajay K. Dalai for giving the kind of impetus to my graduate program during the Catalysis course to improve my presentation skills and for giving his feedback on my reports, manuscript and thesis draft which helped better my writing.

I would like to thank R. Blondin, D. Cekic and H. Eunike of the Chemical Engineering Department for their technical assistance for various stages of this work. I extend my sincere thanks to H. Eunike and R. Blondin for help in repairing the gas chromatographs. I also would like to thank R. Prokopishyn for helping me provide the vacuum pump and taking time to run maintenance checks on it from time to time to ensure its smooth running.

I am also thankful to all the members of the Catalysis and Reaction Engineering Laboratory for their kind co-operation and support throughout my program. Special thanks must go to Dr. Rajesh V. Sharma for his constant support and mentoring in the lab. I must appreciate the financial support from ABIN, ADF, SCDC, NSERC and CRC funding for this research work.

Lastly, on a personal note, I am greatly indebted to my mom (Amma) for supporting me throughout my graduate program. Everything that I am today is because of her. I must commend her for the painstaking support and her relentless belief in my abilities. I would also thank my sister for always being with me in times of need and for her loving support. In the order of my acquaintance with them in Saskatoon, I must mention Vamsi, Sidhartha, Chirayu, Karthik, Naveen and Ashish for their constant mentoring, support, uplifting and morale boosting.
DEDICATION

I dedicate this work to

My Dad (nanna), whom I shall forever miss throughout my life....
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>COPYRIGHT</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>xiv</td>
</tr>
<tr>
<td>ABBREVIATIONS</td>
<td>xv</td>
</tr>
</tbody>
</table>

## 1. INTRODUCTION

1.1 Motivation to produce lubricants from renewable and biological sources

1.1.1 Economic considerations with production of mineral oil-derived lubricants

1.1.2 Environmental impact of applications of mineral oil-derived lubricants

1.1.3 Vegetable oil as renewable feedstocks for the production of biolubricants

1.1.4 Favorable properties of biolubricants

1.2 Knowledge gaps

1.3 Objectives
# 2. LITERATURE REVIEW

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Introduction</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Vegetable oils as lubricants</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>Problems associated with the use of vegetable oils as lubricants</td>
<td>8</td>
</tr>
<tr>
<td>2.4</td>
<td>Techniques to improve the properties of vegetable oils</td>
<td>9</td>
</tr>
<tr>
<td>2.5</td>
<td>Two-step transesterification route: Chemistry, catalysts and substrates</td>
<td>11</td>
</tr>
<tr>
<td>2.6</td>
<td>Preparation of vegetable oil-derived lubricant basestocks</td>
<td>12</td>
</tr>
<tr>
<td>2.7</td>
<td>Kinetic studies of transesterification reactions</td>
<td>16</td>
</tr>
<tr>
<td>2.8</td>
<td>Characterization and tribological evaluation of lubricants</td>
<td>17</td>
</tr>
<tr>
<td>2.9</td>
<td>Canola oil-based feedstocks for the production of biolubricants</td>
<td>19</td>
</tr>
</tbody>
</table>

# 3. EXPERIMENTAL

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Materials</td>
<td>21</td>
</tr>
<tr>
<td>3.2</td>
<td>System description</td>
<td>21</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Synthesis of methyl oleate by esterification of oleic acid with methanol</td>
<td>22</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Synthesis of biolubricants derived from methyl oleate and canola biodiesel</td>
<td>22</td>
</tr>
<tr>
<td>3.3</td>
<td>Experimental design and procedure</td>
<td>23</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Synthesis of methyl oleate by esterification of oleic acid with methanol</td>
<td>23</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Synthesis of biolubricants from methyl oleate and canola biodiesel</td>
<td>24</td>
</tr>
<tr>
<td>3.4</td>
<td>Analysis of products</td>
<td>26</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Analysis of methyl oleate</td>
<td>27</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Analysis of biolubricants</td>
<td>27</td>
</tr>
<tr>
<td>3.5</td>
<td>Characterization and evaluation of products</td>
<td>28</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Physicochemical characterization of methyl oleate</td>
<td>28</td>
</tr>
<tr>
<td>3.5.1.1</td>
<td>Moisture content</td>
<td>28</td>
</tr>
<tr>
<td>3.5.1.2</td>
<td>Kinematic viscosity at 40°C</td>
<td>28</td>
</tr>
<tr>
<td>3.5.1.3</td>
<td>Cloud point &amp; pour point</td>
<td>29</td>
</tr>
<tr>
<td>3.5.1.4</td>
<td>Oxidative stability</td>
<td>29</td>
</tr>
</tbody>
</table>
3.5.2 Comparative tribological property evaluation of biolubricants derived from methyl oleate and canola biodiesel

3.5.2.1 Kinematic viscosities at 40 and 100°C & viscosity index

3.5.2.2 Cloud point & pour point

3.5.2.3 Lubricity testing

3.5.2.4 Oxidative stability

4. RESULTS AND DISCUSSION

4.1 Synthesis of methyl oleate from oleic acid

4.1.1 Study of esterification reaction progression

4.1.2 Development of optimum synthesis conditions

4.1.2.1 Effect of temperature

4.1.2.2 Effect of molar-ratio

4.1.2.3 Effect of catalyst loading

4.1.3 Reproducibility studies

4.2 Physicochemical characterization of methyl oleate

4.2.1 Moisture (water and sediment) content

4.2.2 Kinematic viscosity at 40°C

4.2.3 Cloud point

4.2.4 Pour point

4.2.5 Oxidative stability

4.3 Synthesis of biolubricants from methyl oleate and canola biodiesel

4.3.1 Blank reaction of TMP with methyl oleate without catalyst

4.3.2 Design of experiments by central composite design approach

4.3.3 Study of progression of transesterification reaction of TMP with methyl oleate

4.3.4 Development and testing of CCD model for prediction of TE yield

4.3.5 Response surface measurement studies

4.3.6 Numerical optimization studies

4.3.7 Diagnostic study of TE model
4.3.8 Reproducibility studies of transesterification reaction of methyl oleate and trimethylolpropane 61

4.3.9 Transesterification reaction of trimethylolpropane with canola biodiesel 62

4.4 Comparative tribological property evaluation of biolubricants 62

4.4.1 Kinematic viscosities at 40 and 100°C and viscosity indices 62

4.4.2 Cloud point and pour point 64

4.4.3 Lubricity testing 66

4.4.4 Oxidative stability 68

5. CONCLUSIONS AND RECOMMENDATIONS 71

6. REFERENCES 77

APPENDIX A: Heterogeneous catalysts for transesterification reactions: A green chemistry approach 85

APPENDIX B: Structures of chemical compounds 92

APPENDIX C: Silylation 94

APPENDIX D: GC chromatograms 95
LIST OF TABLES

Table 2.1  Reported literature on transesterification of vegetable oils  
Table 2.2  Standard methods for tribological evaluation of lubricants  
Table 3.1  Experimental design for synthesis of methyl oleate from oleic acid  
Table 3.2  Design of experiments for transesterification of trimethylolpropane with methyl oleate  
Table 4.1  Reproducibility studies of concentrated sulfuric acid-catalyzed esterification reactions of oleic acid with methanol  
Table 4.2  Standards for the assessment of properties of methyl oleate  
Table 4.3  Physicochemical properties of methyl oleate obtained from concentrated sulfuric acid-catalyzed esterification of oleic acid with methanol at 120°C using methanol-to-oleic acid molar-ratio of 9.0 and 4.0 vol % concentrated sulfuric acid catalyst after 6 h of reaction  
Table 4.4  Results from transesterification reactions of trimethylolpropane with methyl oleate  
Table 4.5  Results from unpaired t-test for final tri-ester yields for 14 transesterification reactions of TMP with methyl oleate  
Table 4.6  Comparison of statistical parameters obtained from t-test for final tri-ester yields from transesterification reaction runs of TMP with methyl oleate  
Table 4.7  Diagnostic study of TE model to determine absolute error between experimental and modeled values for reactions between trimethylolpropane and methyl oleate  
Table 4.8  Comparison of tribological properties of TMP-based biolubricants obtained from methyl oleate and canola biodiesel  
Table A.1  Literature table of various hydrotalcite catalysts for transesterification reactions of vegetable oils
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Schematic of transesterification reaction of vegetable oil with methanol for biodiesel production</td>
<td>11</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Schematic diagram of experimental setup for transesterification reactions</td>
<td>23</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>Schematic of acid-catalyzed esterification reaction of oleic acid with methanol</td>
<td>33</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Progression of esterification reaction at temperature of 120°C, methanol-to-oleic acid molar-ratio of 9.0 and 4 vol % catalyst loading of concentrated sulfuric acid</td>
<td>33</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>Effect of temperature on methyl oleate yield at methanol-to-oleic acid molar-ratio of 9.0 and 4 vol % catalyst loading</td>
<td>35</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>Effect of methanol-to-oleic acid molar-ratio on methyl oleate yield at temperature of 120°C and 4 vol % catalyst loading</td>
<td>37</td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>Effect of catalyst loading on methyl oleate yield at temperature of 120°C and methanol-to-oleic acid molar-ratio of 9.0</td>
<td>39</td>
</tr>
<tr>
<td>Figure 4.6</td>
<td>Reaction scheme for transesterification of trimethylolpropane with methyl oleate</td>
<td>45</td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>Reaction scheme for transesterification of trimethylolpropane with canola biodiesel</td>
<td>45</td>
</tr>
<tr>
<td>Figure 4.8</td>
<td>Mechanism of transesterification reaction of trimethylolpropane with methyl oleate</td>
<td>46</td>
</tr>
<tr>
<td>Figure 4.9</td>
<td>Progression of transesterification reaction of TMP and methyl oleate at 110°C and methyl oleate-to-TMP molar-ratio of 4.0 without sodium methoxide</td>
<td>47</td>
</tr>
<tr>
<td>Figure 4.10</td>
<td>Progression of transesterification reaction of TMP and methyl oleate at temperature of 110°C, methyl oleate-to-TMP molar-ratio of 4.0 and 0.5 wt % sodium methoxide loading at 1 mbar pressure</td>
<td>50</td>
</tr>
<tr>
<td>Figure 4.11</td>
<td>Normal probability plot of residuals for transesterification reaction runs of TMP with methyl oleate</td>
<td>51</td>
</tr>
</tbody>
</table>
Figure 4.12 2D surface plot for effect of temperature and methyl oleate-to-TMP molar-ratio on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at 1.0 wt % sodium methoxide loading at 1 mbar pressure

Figure 4.13 2D surface plot for effect of temperature and sodium methoxide loading on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at methyl oleate-to-TMP molar-ratio of 4.0 and 1 mbar pressure

Figure 4.14 2D surface plot for effect of methyl oleate-to-TMP molar-ratio and sodium methoxide loading on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at 139ºC and 1 mbar pressure

Figure 4.15 Perturbation plot for different reaction parameters for transesterification of TMP with methyl oleate

Figure 4.16 3D contour plot for effect of temperature and methyl oleate-to-TMP molar-ratio on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at 1.0 wt % sodium methoxide loading and 1 mbar pressure

Figure 4.17 3D contour plot for effect of sodium methoxide loading and methyl oleate-to-TMP molar-ratio on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at 139ºC and 1 mbar pressure

Figure 4.18 2D surface plot for desirability against temperature and methyl oleate-to-TMP molar-ratio for transesterification of TMP with methyl oleate at 1.42 wt % sodium methoxide loading and 1 mbar pressure

Figure 4.19 3D contour plot for desirability against temperature and methyl oleate-to-TMP molar-ratio for transesterification of TMP with methyl oleate at 1.42 wt % sodium methoxide loading

Figure 4.20 Plot for model values (predicted) versus actual values (experimental) for TE yields from transesterification reactions of trimethylolpropane and methyl oleate
Figure 4.21  3D contour plot for standard error of design as a function of methyl oleate-to-TMP molar-ratio and temperature

Figure 4.22  Scatter plot for triester composition at different reaction times from six replicate reactions at temperature of 110°C, methyl oleate-to-TMP molar-ratio of 4.0 and 1.0 wt % sodium methoxide loading for transesterification reaction of trimethylolpropane and methyl oleate

Figure 4.23  Microscope images (20 x magnifications) of wear scar diameter on test samples obtained for: a) pure diesel standard, b) 10% (vol/vol) of methyl oleate-derived biolubricant in diesel, and c) 10% (vol/vol) of canola biodiesel-derived biolubricant in diesel

Figure 4.24  Conductivity plot for auto-oxidation of methyl oleate-derived biolubricant obtained from transesterification of TMP with methyl oleate at 139°C using methyl oleate-to-TMP molar-ratio of 4.9 and 1.4 wt % loading of sodium methoxide at 1 mbar pressure after 5 h

Figure 4.25  Conductivity plot for auto-oxidation of canola biodiesel-derived biolubricant obtained from transesterification of TMP with canola biodiesel at 139°C using canola biodiesel-to-TMP molar-ratio of 4.9, 1.4 wt % loading of sodium methoxide at 1 mbar pressure after 5 h

Figure B.1  Structure of 1,1,1-tris(hydroxymethyl)propane

Figure B.2  Structure of trimethylolpropane mono-oleate

Figure B.3  Structure of trimethylolpropane di-oleate

Figure B.4  Structure of trimethylolpropane tri-oleate

Figure D.1  GC chromatogram of underivatized products obtained after 5 h of reaction time. TMP: methyl oleate molar-ratio = 1:4, temperature = 110°C and NaOCH₃ loading = 0.5 wt %

Figure D.2  GC chromatogram of derivatized products obtained after 5 h of reaction time. TMP: methyl oleate molar-ratio = 1:4, temperature = 110°C, NaOCH₃ loading = 0.5 wt %
NOMENCLATURE

α-carbon  alpha-carbon: first carbon that attaches to a functional group
α-hydrogen alpha-hydrogen: hydrogen attached to an alpha-carbon
β-carbon  beta-carbon: second carbon from the functional group
β-hydrogen beta-hydrogen: hydrogen atom on a beta-carbon
C_{16:0} carbon chain with sixteen carbon atoms and no double bonds
(Palmitic acid)
cSt  centi Stoke (CGS unit of kinematic viscosity)
E_a  energy of activation
HT2  Mg-Al hydrotalcite with Mg: Al atomic ratio = 2:1
k    rate constant
k_1  rate-constant of irreversible reaction of formation of ME from FAME
k_2  rate-constant of irreversible reaction of formation of DE from ME
k_3  rate-constant of irreversible reaction of formation of TE from DE
R    Chevron Richmond Lubricants Oil Plant
R1   alkyl group 1 (triglyceride skeleton)
R2   alkyl group 2 (triglyceride skeleton)
R3   alkyl group 3 (triglyceride skeleton)
t_{1/2} halflife period
T_o  onset temperature
T_s  start temperature
Z    Arrhenius frequency factor
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAS</td>
<td>atomic absorption spectroscopy</td>
</tr>
<tr>
<td>ACO</td>
<td>acid cottonseed oil</td>
</tr>
<tr>
<td>AFF</td>
<td>animal fat feedstock</td>
</tr>
<tr>
<td>ANOVA</td>
<td>analysis of variance</td>
</tr>
<tr>
<td>AOCS</td>
<td>American Oil Chemists’ Society</td>
</tr>
<tr>
<td>AOM</td>
<td>active oxygen method</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing Materials</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CCD</td>
<td>central composite design</td>
</tr>
<tr>
<td>CEC</td>
<td>Co-ordinating European Council</td>
</tr>
<tr>
<td>CETOP</td>
<td>Comité Européen des Transmissions Oileohydraulics et Pneumatiques (European Oil Hydraulic and Pneumatic Committee)</td>
</tr>
<tr>
<td>CHT</td>
<td>calcined hydrotalcite</td>
</tr>
<tr>
<td>CMAH</td>
<td>calcined magnesium aluminium hydrotalcite</td>
</tr>
<tr>
<td>DE</td>
<td>diester</td>
</tr>
<tr>
<td>DIN</td>
<td>Deutsche Industrial Norms (German Standards Agency)</td>
</tr>
<tr>
<td>EN</td>
<td>European Norm</td>
</tr>
<tr>
<td>ESO</td>
<td>epoxidized soybean oil</td>
</tr>
<tr>
<td>FA</td>
<td>fatty acid</td>
</tr>
<tr>
<td>FAME</td>
<td>fatty acid methyl ester</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transformed infrared spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>Gly-Tbut</td>
<td>glyceryl tributyrate</td>
</tr>
<tr>
<td>HACO</td>
<td>high acidity and water content cottonseed oil</td>
</tr>
<tr>
<td>HFRR</td>
<td>high frequency reciprocating rig</td>
</tr>
<tr>
<td>HT</td>
<td>hydrotalcite</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>JCO</td>
<td>Jatropha Curcas Oil</td>
</tr>
<tr>
<td>LDH</td>
<td>layered double hydroxide</td>
</tr>
</tbody>
</table>
MAH magnesium-aluminium (Mg-Al) hydrotalcite
MATLAB Matrix Laboratory (Mathworks Inc.)
ME monoester
MeOH methanol
min minute
NMR nuclear magnetic resonance
NPG neopentyl glycol
OECD Organization for Economic Co-operation and Development
OIT oxidative induction time
OSI oil stability index
PAO poly-alpha olefins
PDSC pressure differential scanning calorimetry
PE pentaerythritol
PKOME palm kernel oil methyl ester
PSMO Penn State Micro-Oxidation thin-film test
POME palm oil methyl ester
PP pour point
PPD pour point depressant
PV Peroxide Value
RBOT Rotating Bomb Oxidation Test
RCO refined cottonseed oil
RLV Chevron Richmond Lubricants Oil Plant (Vacuum Distilled product of Lower Boiling Fraction)
RP Provisional Recommendations
SD standard deviation
SEM scanning electron microscopy
TCP tricaprylin
TE triester
TGA/DTA thermogravimetric/differential thermal analysis
TLC thin layer chromatography
TMB trimethylolbutane
TME  trimethylolethane
TMP  trimethylolpropane
TPD  temperature-programmed desorption
UCBO  UnConventional Base Oil
VG 46  Viscosity Grade 46 (standard specification for light gear industrial oil)
VHVI  Very High Viscosity Index
VI  viscosity index
VTT  Valtion Teknillinen Tutkimuskeskus (Finnish: Technical Research Centre of Finland)
XPS  X-ray photoelectron spectroscopy
XRD  X-ray diffraction
Chapter 1

INTRODUCTION

1.1 Motivation to produce lubricants from renewable and biological sources

Lubricants serve great applications in industries, automobiles, aviation machinery and helicopter transmissions by performing critical functions such as reducing friction, removal of wear particles, increasing efficiency, minimizing energy losses and uniformly distributing heat. The most common types of lubricants in current use are automotive transmission fluids, hydraulic fluids, metal working fluids, cold rolling oils, fire resistant hydraulic fluids, industrial gear oils, neat cutting oils and automotive gear lubricants [Nagendramma et al., 2012]. Since 1991, the world demand for lubricants has been around 35 million tons/year. In 2004, the worldwide consumption of lubricants was estimated at 37.4 million tonnes. 53% automotive lubricants, 32% industrial lubricants, 5% marine oils and 10% process oils made up the total consumption sectors [Mang et al., 2007]. The world lubricant demand is anticipated to increase by 1.6% per year, with 40.5 million metric tonnes of lubricants expected to be consumed in 2012 alone. A vast majority of these lubricants are mineral oil-based and are obtained primarily from petroleum derivatives.

A vast majority of these lubricants are used for a class of applications, called total-loss applications. It has been estimated that about 5-10 million tons of petroleum products enter the environment each year, with more than half ending up polluting the environment through total-loss applications, accidental spillage, nonrecoverable usage, volatility, industrial and municipal waste, urban runoff and refinery process [Carnes et al., 2004]. Estimates for the loss of hydraulic fluids are as high as 70-80% [Erhan et al., 2008]. These lubricants are highly toxic to the
environment and have poor biodegradability [Horner et al., 2002)]. The most serious problems of these losses are soil, water and air contamination, which pose a considerable threat to plant, animal and human life [Sallimon et al., 2010]. Strong environmental concerns and growing regulations over contamination and pollution in the environment have increased the need for renewable and biodegradable lubricants [Fox et al., 2007]. There has been a lot of active research and development in this area due to increasing pressure from public demand, industrial concern and government agencies. Petroleum sources are limited, and due to the soaring prices of crude oil, there is a need to search for alternative sources for producing lubricants. Considering the long-term polluting effects of these mineral oil-based lubricants on the environment, there is a need for cheap and renewable feedstocks for the production of biodegradable feedstocks.

1.1.1 Economic considerations with production of mineral oil-derived lubricants

A typical mineral oil-based lubricant used for industrial purposes is composed of base oil, diluent, coloring agent and additives such as pour point depressants, viscosity enhancers and antioxidants. All these components dictate the overall manufacturing cost of the lubricant, and thereby determining its selling price. The intensive reaction conditions employed in the manufacture of these lubricants leads to high production costs. Depleting reserves and increased dependence on the Middle East for oil imports is leading to an increase in the cost of crude oil. A significant proportion of the investment incurred in the production of lubricants is owed to the price of petroleum feedstocks.

1.1.2 Environmental impact of applications of mineral oil-derived lubricants

As discussed earlier, a vast majority of these lubricants end up polluting the environment. By their very nature, these lubricants are chemically obtained and cannot be degraded by the
bacteria in the soil once assimilated by the soil. Potato and other tubers would easily be contaminated if the soil is embedded with lubricants. It is an alarming scenario, considering the amount of lubricants that enter water sources through direct deposition by human means or by erosion of the surface soil-containing lubricants by virtue of rain. Aquatic ecosystem is adversely affected in the presence of large concentrations of lubricants. Fishes die off owing to the high toxicity of lubricants. Such a breed of fish is not fit for human consumption, and can lead to several diseases. Additives such as poly-alpha olefins (PAOs) have excellent cold-flow properties, by virtue of which, they reduce the cloud point and pour point of lubricants. However, they are highly volatile and easily escape in to ambient air under atmospheric pressure. Once in the air stream, these lubricants can then freely move around and cause significant hazards. This route leads to various diseases such as asthma and bronchitis.

1.1.3 Vegetable oils as renewable feedstocks for production of biolubricants

Traditionally, vegetable oils such as cottonseed oil, sunflower oil, mustard oil, olive oil, rapeseed oil, canola oil, palm oil and palm kernel oil served as vital ingredients for cooking purposes. Vegetable oils are excellent substitutes for mineral oils in the production of lubricants. These are characterized by high viscosity indices (almost twice of mineral oils), low volatilities and correspondingly high flash points and excellent biodegradability [Honary et al., 2004]. Thus, they act as environmentally friendly, renewable sources for commercial utilization to produce biologically-derived lubricants [Howell et al., 2007]. However, their viability for industrial-scale application for production of lubricants is seriously limited on account of their high costs and the perennial food versus fuel debate. In developed economies such as Canada, especially in Saskatchewan, canola oil is available in plenty as surplus. The excess canola oil offers a viable alternative to mineral oil for producing lubricants.
1.1.4 Favorable properties of biolubricants

Mineral oil-based lubricants offer good lubrication properties and applications in various environments; however, they have serious shortcomings, such as poor biodegradability and high toxicity. In contrast, biolubricants have been shown to have excellent properties such as non-toxicity, excellent environmental biodegradability, favorable viscosities, high viscosity indices and excellent lubricity [Aluyor et al., 2009a]. Also, the costs incurred in the production of biolubricants are far lesser than that for mineral oil-based lubricants.

1.2 Knowledge gaps

Literature review has been performed on utilization of vegetable oils and their derivatives for the production of biodegradable lubricants. So far, there is no reported scientific investigation on the application of canola biodiesel for transesterification with TMP to produce polyol-based natural-synthetic canola-based biolubricants. Also, reported model compound studies in this area of research are very few and those with methyl oleate are absent.

1.3 Objectives

The overall objective of this research work is to synthesize a class of natural-synthetic TMP-based lubricants by utilizing the transesterification reaction with canola biodiesel. The study was performed in three different phases as follows:

**Phase I:** In this phase, oleic acid was utilized to synthesize methyl oleate by esterification catalyzed by concentrated sulfuric acid. The effects of temperature (80-140°C), methanol-to-oleic acid molar-ratio (3.0-12.0) and catalyst loading (2-8 vol %) were studied on methyl oleate yield and these conditions were optimized to obtain the highest methyl oleate yield. The
produced methyl oleate was characterized for its various physicochemical properties such as moisture content, kinematic viscosity at 40°C, cloud point, pour point and oxidative stability.

**Phase II:** In this phase, model transesterification reactions of methyl oleate with TMP were investigated. The effects of temperature (80-140°C), methyl oleate-to-TMP molar-ratio (3.0-5.0) and catalyst loading (0.5-1.5 wt %) were studied on the yield of TMP trioleate (TE), the main component of methyl oleate-derived biolubricant. The operating conditions were optimized and the interaction effects between them studied to maximize the yield of TE. The developed optimum synthesis conditions were applied to the transesterification of canola biodiesel with TMP to synthesize canola biodiesel-derived biolubricant.

**Phase III:** In this phase, methyl oleate-derived and canola biodiesel-derived biolubricants were characterized for their physicochemical properties and evaluated for their potential for tribological applications. A comparison of their tribological properties was made.
Chapter 2
LITERATURE REVIEW

2.1 Introduction

A lubricant is generally a liquid substance which is introduced between two moving surfaces to reduce friction, improve efficiency and reduce. Lubricants dissolve or transport foreign particles and distribute heat. In addition to serving these primary purposes, lubricating oils are also required to carry out a range of other functions, including the removal of heat, corrosion prevention and transfer of power. Lubricants must also provide a liquid seal at moving contacts and remove wear particles. The most important properties of lubricants which determine their applicability and efficiency are viscosity, viscosity index, oxidative stability, thermal stability, flash point, low-temperature fluidity, corrosivity, wear-resistance, biodegradability and non-toxicity. The most fundamental requirement of lubricants is that the oil should remain in liquid state over a wide temperature-range, which could be as much as 300ºC for aviation lubricants. In commercial uses, the usable liquid range is limited by the pour point at low temperatures and flash point at higher temperatures. The pour point of a fluid is defined as the lowest temperature below which it would cease to flow. Similarly, another property is cloud point, which is the temperature at which the dissolved solids in the fluid are no longer completely soluble and precipitate as a second phase, giving the fluid a cloudy appearance. The cloud point is generally higher than the pour point in most cases. The flash point is termed as the lowest temperature at which a liquid can vaporize to form an ignitable mixture in air. This point marks the temperature beyond which there is a risk of lubricant loss to the surrounding environment. Thus, greater the difference between the pour point and flash point, broader is the range of temperature over which the lubricant could be used safely. Viscosity of the lubricating
liquid is a critical factor which determines the temperature range over which the lubricant offers the best performance. If the lubricating fluid is very thick, it would lead to loss of energy due to viscous forces and heating up of the liquid. Similarly, if the fluid is very thin, it would not lubricate the machinery efficiently by allowing the metal surfaces to come in contact with each other, which would lead to excessive wearing. In the case of liquid lubricants, viscosity generally decreases as the temperature increases. Viscosity index (VI) is a measure of the amount of change in the viscosity of a fluid with a change in temperature. Fluids with high viscosity indices show a very small change in viscosity with temperature. Oxidative stability is the property by which the lubricant is able to resist oxidation, and is necessary for satisfactory performance in a variety of environmental conditions. Thermal stability becomes important when the lubricant is intended to be used at high temperatures, during which degradation of its lubricating properties may occur by polymerization or by formation of undesirable compounds.

Croda Lubricants, Chevron Corporation, Exxon Mobil and Shell are some of the leading lubricants’ manufacturing companies. Croda Lubricants are the leading global suppliers of lubricant base fluids and additives. Chevron Corporation is one of the world’s six ‘super major’ oil companies. Shell, another member of the elite club of super major oils companies, is a world-leader in producing aviation lubricants which have applications in aero planes and flight equipment and demand the most stringent requirements.

2.2 Vegetable oils as lubricants

Vegetable oils have biodegradability of over 95% [Kodali et al., 2001]. Being renewable in nature, these sources could be produced in vast amounts. A chromatographic analysis of vegetable oils [Aluyor et al., 2009b] elucidates their applicability as lubricants with a wide range of advantages such as high biodegradability [Emmanuel et al., 2009], low pollution of the
environment, and compatibility with additives, low production cost, wide production possibilities, low toxicity, high flash points, low volatility and high viscosity indices. The majority of vegetable oils consist primarily of triglycerides [Fox et al., 2007]. The fatty acid chains in vegetable oil triglycerides are all of similar length, between 12 and 22 carbons, with varying levels of unsaturation. The triglyceride structure of vegetable oils provides qualities desirable in a lubricant. Long, polar fatty acid chains provide high strength lubricant films that interact strongly with metallic surfaces, thus reducing both friction and wear. The strong intermolecular interactions are also resilient to changes in temperature providing a more stable viscosity, or high viscosity index. The ester linkages deliver inherent lubricity and enable the oils to adhere to metal surfaces. Furthermore, vegetable oils have higher solubilizing capacity for contaminants and additives than mineral base fluids. In all of these technical properties, the vegetable oils are comparable or better than mineral oils.

Several vegetable oils such as rapeseed oil, soybean oil, palm oil, palm kernel oil, olive oil and jatropha curcas-derived oil have been used as lubricants. Vegetable oils have displayed excellent lubrication properties in laboratory investigations. Apart from excellent ecological advantages, vegetable oils have ideal chemical properties, such as low volatility because of the high molecular weight of the triglyceride molecule and narrow range of viscosity change with temperature.

2.3 Problems associated with the use of vegetable oils as lubricants

Despite the ecological and economic advantages offered by vegetable oils, their use is only limited and the present market share of these lubricants is relatively small (< 2%) due to their inherent disadvantages, viz., insufficient thermal and oxidative stability, poor low temperature fluidity and hydrolytic instability. The poor oxidative stability is mainly attributed to
the presence of double bonds in the fatty acid chains of triglyceride molecule. The presence of α-hydrogens (bis-allylic protons) in the triglyceride molecule makes the vegetable oils highly susceptible to radical attack and subsequent oxidative degradation, which results in polar oxy compounds [Erhan et al., 2008]. This oxypolymerization process ultimately results in insoluble deposit formation and an increase in oil acidity and viscosity. Vegetable oils also cause corrosion to metals. The presence of ester functionalities renders these oils susceptible to hydrolytic breakdown. Low-temperature studies have also shown that most vegetable oils undergo cloudiness, precipitation and solidification at cold temperatures, thus giving rise to poor low-temperature properties.

A review by Fox et al. [2007] addresses oxidation as a limitation of vegetable oil-based lubricants. Oxidative stability of triglyceride-based vegetable oils is primarily limited by the degree of unsaturated double bonds. Unsaturated carbon–carbon bonds function as active sites for many reactions, primarily oxidation. A majority of triglyceride-based vegetable oils contain unsaturated fatty acids and are susceptible to oxidation. The greater the level of unsaturation, i.e., more the number of double bonds, more susceptible the oil becomes to oxidation.

### 2.4 Techniques to improve the properties of vegetable oils

Some of these inherent shortcomings of vegetable oils could be overcome by reducing polyunsaturation in triglyceride structures of vegetable oils. Several techniques have been employed to modify the vegetable oils. Genetic modification [Sharma et al., 2006] is a reported technique in the literature but is quite complex to carry out and is often not preferred due to the high expenditure involved. Enzymatic modification [Asadauskas et al., 1999; Yunus et al., 2003] using biocatalysts like candida rugosa lipase and immobilized Rhizomucor miehei lipase Lipozyme IM 20 has shown that high conversions are attainable in short reaction times, but with
the serious disadvantage of enzyme inactivation at high temperatures and high cost of the enzymes. Chemical modification [Uosukainen et al., 1998; Adhvaryu et al., 2002; Hwang et al., 2003; Yunus et al., 2003; Gryglewicz et al., 2006; Sharma et al., 2006; Sejidov et al., 2007; Sern et al., 2008; Ghazi et al., 2009] can overcome the inherent shortcomings in vegetable oils by reducing or eliminating unsaturation and is by far the best known technique because of its application to a wide variety of feed stocks and the range of operating parameters over which the reactions can be studied. Other improvements can be made by using modified vegetable oils in combination with additives such as antioxidants, pour point depressants and diluents or functional fluids [Asadauskas et al., 1999; Pop et al., 2008; Alias et al., 2009]. However, these additives are quite expensive and are derived from mineral oil feed stocks, hence, their biodegradability is questionable.

High oleic varieties of vegetable oils are considered to be potential candidates to replace conventional mineral oil-based lubricating oils and synthetic esters because of their greater oxidative stability. Because of a higher percentage of oleic acid, these oils require less processing and provide higher oxidative stability and excellent pour points with relatively low trans- and saturated fatty acid contents. The double bonds in triglyceride chain are potential sites for chemical modification and can be epoxidized with hydrogen peroxide, either in acetic or formic acid to give epoxidized soybean oil (ESO) [Adhvaryu et al., 2002; Hwang et al., 2003]. ESO is a promising intermediate for chemical modification, because the epoxy groups are susceptible to ring-opening reactions. These epoxy sites (sites of unsaturation) of ESO could be converted to the diester derivatives in either a one- or two-step reaction.

Esterification and transesterification are promising chemical modification techniques to overcome the shortcomings in vegetable oils. In esterification [Sern et al., 2008; Adhvaryu et al.,
long chain fatty acids obtained from vegetable oils are esterified with polyols such as neopentyl glycol, pentaerythritol, trimethylolbutane, trimethylolmethane and trimethylolpropane. Extraction of these fatty acids via the hydrolysis of triglycerides in vegetable oils is not feasible and involves soap formation as a serious problem. The most efficient route is the transesterification of methyl esters of vegetable oils (biodiesel) with above polyols [Uosukainen et al., 1998; Gryglewicz et al., 2003; Yunus et al., 2002, 2003, 2004a, 2004b, 2005; Ghazi et al., 2009] to produce the polyol esters of vegetable oils which have excellent lubricating properties.

2.5 Two-step transesterification route: Chemistry, catalysts and substrates

Transesterification as defined by Leung et al. [2010] is the reaction in which a triglyceride molecule reacts with three moles of methanol to result in glycerol and mixtures of fatty acid methyl esters, according to the reaction scheme, as shown in Figure 2.1.

Figure 2.1: Schematic of transesterification reaction of vegetable oil with methanol for biodiesel production.
The reaction is generally catalyzed by bases such as NaOH, KOH, NaOCH$_3$ and NaOC$_2$H$_5$. The reaction proceeds in three steps with the production of one mole of fatty acid methyl ester in each step until all three moles of methanol are consumed to produce a mixture of three moles of fatty acid methyl esters, which are termed biodiesel, with one mole of glycerol obtained as a by-product. Alternatively, acids and enzymes can be used to catalyze the reaction.

The transesterification of vegetable oil-derived methyl esters with polyols is essentially the reverse of the transesterification reaction shown above, in which glycerol is replaced by a commercial polyol. The most significant advantage of using a polyol instead of glycerol is that the absence of β-hydrogens enhances the thermal stability of the lubricant at high temperatures by preventing self-polymerization to form free fatty acids. There has been a lot of studies on transesterification of fatty acid methyl esters (FAME) derived from a variety of vegetable oils including rapeseed oil [Linko et al., 1997; Uosukainen et al., 1998; Gryglewicz et al., 2003], palm oil and palm kernel oil [Yunus et al., 2002-2005], Jatropha Curcas [Ghazi et al., 2009] and olive oil [Gryglewicz et al., 2003]. Several polyols have been used for this purpose, such as neopentyl glycol, pentaerythritol, trimethylolbutane, trimethylolethane and trimethylolpropane.

2.6 Preparation of vegetable oil-derived lubricant basestocks

There has been a lot of work reported on the transesterification reaction of vegetable oil methyl esters with trimethylolpropane (TMP) as the polyol. Gryglewicz et al. [2003] reported the use of natural fats such as rapeseed oil, olive oil and lard for the preparation of neopentyl glycol (NPG) and TMP esters using calcium methoxide as catalyst. The synthesized esters had viscosities in the range of 13.5-37.6 cSt at 40°C, pour points between -10.5 to -17.5°C and very high viscosity indices (> 200). The esters of NPG were characterized by higher stability in thermo-oxidative conditions, while the olive oil based esters showed the highest thermo-
oxidative resistance due to the low content of polyunsaturated acids. Table 2.1 contains the available literature on the subject of transesterification reactions of vegetable oils for the synthesis of biolubricants.

Table 2.1: Reported literature on transesterification of vegetable oils.

<table>
<thead>
<tr>
<th>Researcher(s)</th>
<th>Source of feedstock</th>
<th>Polyol</th>
<th>Catalyst(s)</th>
<th>Tribological properties of biolubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linko et al. [1997]</td>
<td>Rapeseed oil fatty acid methyl esters</td>
<td>TMP</td>
<td>Immobilized <em>Rhizomucor miehei</em> lipase Lipozyme IM 20</td>
<td>Product was not characterized</td>
</tr>
<tr>
<td>Uosukainen et al. [1998]</td>
<td>Rapeseed oil fatty acids</td>
<td>TMP</td>
<td>Enzymatic pathway: Candida rugosa lipase Chemical pathway: Sodium methoxide, Sodium ethoxide (alkaline catalysts)</td>
<td>Kinematic viscosity at 40°C: 32.9 cSt, Cold viscosity at -10°C:1030 cSt, pour point: -41°C, viscosity index: 220</td>
</tr>
<tr>
<td>Gryglewicz et al. [2003]</td>
<td>Rapeseed Oil Olive oil, Lard</td>
<td>NPG, TMP</td>
<td>Calcium methoxide</td>
<td>Viscosity range: 13.5-37.6 cSt, pour point: -10.5 to -17.5°C, viscosity index: &gt;200</td>
</tr>
<tr>
<td>Yunus et al. [2002, 2003, 2004a, 2004b, 2005]</td>
<td>Palm oil, palm kernel oil, high-oleic palm oil</td>
<td>TMP</td>
<td>Sodium methoxide</td>
<td>Palm oil and palm kernel oil: Viscosity at 40°C: 39.7-49.7 cSt, pour point: -1 to 1°C, viscosity index: 167-187</td>
</tr>
<tr>
<td>Ghazi et al. [2009]</td>
<td>Jatropha Curcas Oil (JCO)-derived biodiesel</td>
<td>TMP</td>
<td>Sodium methoxide</td>
<td>Kinematic viscosity at 40°C: 43.9 cSt, kinematic viscosity at 100°C: 8.71 cSt, pour point: -6°C, viscosity index: 180</td>
</tr>
</tbody>
</table>

*Uosukainen et al. [1998] studied the synthesis of TMP esters of rapeseed oil fatty acids by enzymatic and chemical means and obtained near complete conversions in both cases. *Candida rugosa* lipase was used as a biocatalyst and sodium methoxide and ethoxide were used as alkaline catalysts. A maximum conversion of about 70% to TE was obtained at a temperature of 47°C, which increased when the temperature was held at 85 to 110°C for 2.5 h and
subsequently increased up to 120°C for 8 h. They found that the TMP esters of rapeseed oil had good cold stability, friction and wear characteristics, and resistance to oxidation at elevated temperatures. Yunus et al. [2003] developed an optimum method for synthesizing TMP esters of palm oil and studied the effects of temperature, pressure, molar ratio of palm methyl esters to TMP and catalyst amount. They concluded that temperatures in the range of 80 to 140°C and pressures in the range of 0.1 to 500 mbar had a significant impact on the conversion of the reaction. In comparison, molar ratio of reactants and catalyst loading mainly affected the overall yield of the reaction. They reported the optimal reaction conditions to be as follows: - duration: 1 h; temperature: 130°C; pressure: 20 mbar; catalyst: sodium methoxide at 0.8% w/w; and molar ratio of POME: TMP at 3.9:1. TMP ester of palm oil containing 98% w/w TE was successfully synthesized in less than one hour. In another work, Yunus et al. [2003] made use of palm kernel oil to synthesize TMP esters using sodium methoxide as catalyst and obtained approximately 98% w/w conversion to palm kernel TMP triesters. Once again, they found that temperature and vacuum pressure were the key parameters which had strong effects on the rate and reversibility of the reaction. They determined that a reduced pressure of at least 20 mbar was crucial for high product yield at the optimal operating temperature of 130°C. The non-additived palm and palm kernel TMP esters had the following lubrication properties: viscosity at 40°C in the range of 39.7 to 49.7 cSt, pour point between -1 to 1°C and high viscosity indices in the range of 167-187. As an extension to their earlier work, Yunus et al. [2005] synthesized TMP esters of palm oil with high oleic acid content which had pour points between -10 to -32°C. They fractionated the POME at 150-180°C and 0.1 mbar prior to the synthesis to reduce the saturated fatty acid content and transesterified the fractionated palm methyl esters with TMP. They studied the effects of composition on pour points, viscosity and viscosity index of the product. They concluded that the
concentration of $C_{16:0}$ (Palmitic) methyl ester in the starting material should be below 10% w/w for the pour points of the TMP esters of palm oil to be below -30°C. In addition, they proved that the reaction conversion to the triester should also be maintained above 90% w/w to produce TMP esters with excellent pour points. It was shown that operating temperature had a negligible effect on the reaction yield as long as the temperature was kept above 120°C.

Ghazi et al. [2009] studied the production of Jatropha oil-based lubricant via a two-step process, first, the transesterification of Jatropha Curcas-derived Jatropha oil to Jatropha methyl esters (JME), and second, the transesterification of JME with TMP in the presence of sodium methoxide catalyst. Transesterification of Jatropha oil was carried out at 65°C for 1 hour using 1-2% wt/wt NaOH as catalyst, while, transesterification of JME was carried out at 150°C with pressure kept at 10 mbar. They found the conversion of JME to Jatropha biolubricant to be more than 80%, however, the ratio of JME-to-TMP was maintained at 4:1 to maintain the forward reaction. It was found that the basic properties of Jatropha biolubricant were comparable with other plant-based lubricants. Linko et al. [1997] studied the transesterification of TMP and a mixture of rapeseed oil fatty acid methyl esters by immobilized lipase without using additional organic solvent. The conversion to the polyol TE with immobilized *Rhizomucor miehei* lipase Lipozyme IM 20 was found to be about 75% after 24 h at 58°C, 5.3 kPa, with no added water and the highest conversion of about 90°C was obtained in 66 h.
2.7 Kinetic studies of transesterification reactions

The kinetics of the transesterification reaction between POME and TMP to polyol esters was investigated by Yunus et al. [2004]. They obtained a kinetic model of the reaction by assuming a series of irreversible elementary reactions at various temperatures. However, the rate constants were determined under limited conditions. The optimal ratios of $k_2/k_1$ and $k_3/k_1$ were found to be 0.70-0.80 and 0.21-0.25 respectively. Sodium methoxide was used as the catalyst for the reaction between POME and PKOME with TMP. The POME-to-TMP molar ratio and catalyst weight percentage were held constant at 10:1 and 0.4% respectively. They found that temperatures (70-110°C) and molar ratio of POME-to-TMP had significant impact on reaction kinetics. It was noticed that when a large excess of POME was used and methanol produced was continually withdrawn via vacuum, the reaction reached completion in less than 20 min at 80°C. The final product after removal of the unreacted POME was found to contain approximately 98 wt % TE.

Kamil et al. [2010] developed a mathematical model utilizing nonlinear regression method and described the chemical kinetics of transesterification of POME with TMP. The model was developed based on the reverse mechanism of transesterification reaction and described concentration changes of TMP, ME and DE. They validated the developed model against data in the literature. They determined the reaction rate constants using MATLAB version 7.2 and found that the ratios of rate constants obtained were well in agreement with those reported in the literature and observed a good correlation between model simulations and experimental data.
2.8 Characterization and tribological evaluation of lubricants

The properties of lubricants which are important for their commercial applications are high viscosity indices (VI), low pour points and good oxidative and thermal stability. In a study, Yunus et al. [2004] assessed the lubrication properties of TMP esters of palm oil and palm kernel oil in terms of their viscosity, viscosity index and pour point in accordance with the standards followed by the American Society for Testing Materials (ASTM). They evaluated the wear and friction properties using a four-ball test machine and studied the oxidative stability with the Penn State Micro-oxidation thin-film test. High VI ranging from 170 to 200 were recorded for these base stocks. The pour points which were between 4 to -1°C were improved to at least -33°C in high-oleic palm oil TMP esters. They also studied the effects of chemical structure and impurities on wear properties and oxidative stability. It was found that the presence of methyl esters improved wear, but the hydroxyl groups in mono- and di-esters had negative effects at high concentrations. They showed that the differences in chemical structures of the TMP esters of palm oil and palm kernel oil affected the friction and wear properties.

Oxidative stability is an important factor which determines the efficiency of a lubricant when performing in adverse environmental conditions, thus, determining the oxidative stability is a crucial task. Adhvaryu et al. [2000] evaluated the oxidative stability of a series of vegetable oils and oils derived from genetically modified vegetables using pressure differential scanning calorimetry (PDSC). They computed the kinetic and thermodynamic parameters and explained the variation in results in terms of structural data derived from quantitative $^1$H and $^{13}$C NMR spectroscopy. They calculated the activation energy ($E_a$) for oxidation reaction and various other kinetic parameters, viz., rate constant ($k$), Arrhenius frequency factor ($Z$) and half-life period ($t_{1/2}$). They showed that the presence of C-C unsaturation in the fatty acid chain, their nature and
relative abundance affected the thermal and oxidative stability of the oil, and subsequently their kinetic and thermodynamic parameters. They correlated the structural parameters obtained from the quantitative analysis of the NMR spectra with start ($T_s$) and onset ($T_o$) temperature of vegetable oil oxidation, and certain important kinetic parameters ($E_a$ and $k$). Using a novel approach, they developed statistical methods as predictive tools for quick assessment of oxidative and thermodynamic data. These correlations revealed that in addition to nature and abundance of C=C, relative abundance of other structural parameters (e.g. bis-allylic methylene group, allylic-CH$_2$ and $\alpha$-CH$_2$ to C=O) influenced oxidation and kinetic data.

Läubli et al. [1986] compared the oxidative stability of fats and oils by Active Oxygen Method (AOM; AOCS Method Cd 12-57) with that of Rancimat method. The AOM is known to be very costly and labor intensive because of the repeated peroxide value determinations involved. The alternative Rancimat method is based on the conductometric determination of volatile degradation products and features automatic plotting of conductivity against time. They performed the evaluation graphically after the completion of the experiment and showed that the labor required for this method was considerably less as it was not necessary to perform titrations at regular intervals. They showed that the induction times determined with both methods using six different fats and oils showed a good correlation. It was proved that the Rancimat method yielded results equivalent to the AOCS method Cd 12-57, but offered a real alternative for the determination of oxidative stabilities owing to the appreciable saving in labor.

In another work reported by Jayadas et al. [2008], the oxidative behavior of vegetable oils was studied using Fourier-transformed infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) spectroscopic methods and thermogravimetric/differential thermal analysis (TGA/DTA) techniques. The properties of vegetable oils were determined by their fatty acid
(FA) composition. A high content of polyunsaturated FAs, like linoleic and linolenic acids decreases the thermal-oxidative stability. FTIR spectroscopy was used as a quick method to measure the degree of unsaturation in vegetable oils. NMR spectroscopy was used to quantitatively evaluate the degree of unsaturation in vegetable oils. TGA/DTA techniques were used to evaluate the oxidative properties of vegetable oils. In this study, TGA/DTA analyses were performed on different vegetable oils under isothermal conditions at 150°C for 3 h. TGA/DTA thermograms showed weight changes and thermal activities in terms of exothermic or endothermic heat flows during the oxidative reactions. The oxidative degradation was evaluated in terms of the weight gain by the respective vegetable oils under the test conditions, due to the formation of oxidative polymerization products and the value of exothermic peaks were obtained from the DTA. The comparative study of the oxidative performance of different vegetable oils showed that higher the degrees of unsaturation, higher are the weight gains and the exothermic peaks. The evaluation of the effect of a chosen antioxidant showed marked improvement on the oxidative stability of vegetable oils.

Uosukainen et al. [1998] evaluated the lubrication properties of TMP esters of rapeseed oil by several techniques. These are displayed in Table 2.2.

2.9 Canola oil-based feedstocks for the production of biolubricants

Canola oil stands for Canadian oil, low acid and is obtained from the seeds of Brassica napus and Brassica rapa. These cultivars, low in erucic acid and glucosinolates, are very different from high erucic-rapeseed oil in their chemical and physical properties, and nutritional profiles. Canola oil has excellent properties including high triglyceride content and a homogeneous fatty acid composition. Canola biodiesel is produced from green seeds of canola by transesterification with methanol. The presence of unsaturation in canola oil renders the
produced biodiesel with excellent low temperature properties and moderate oxidative and thermal stability and the biodiesel produced is best suited for Canadian winters.

Table 2.2: Standard methods for tribological evaluation of lubricants.

<table>
<thead>
<tr>
<th>Lubrication property</th>
<th>Standard (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>ASTM D445</td>
</tr>
<tr>
<td>Filterability</td>
<td>CETOP RP 124-H-standard</td>
</tr>
<tr>
<td>Particle purity</td>
<td>ISO 4406 Standard</td>
</tr>
<tr>
<td>Cold Stability</td>
<td>VTT Standard</td>
</tr>
<tr>
<td>Cold Viscosity and Viscosity Behavior</td>
<td>ASTM D445</td>
</tr>
<tr>
<td>Foaming</td>
<td>ASTM D892</td>
</tr>
<tr>
<td>Color</td>
<td>ASTM D1500</td>
</tr>
<tr>
<td>Pour Point</td>
<td>ASTM D97</td>
</tr>
<tr>
<td>Friction and Wear</td>
<td>Fourball test (ASTM D2783)</td>
</tr>
<tr>
<td>Oxidation Stability</td>
<td>ASTM D525, DIN 51586, DIN 51554</td>
</tr>
<tr>
<td>Corrosion Stability</td>
<td>Cincinnati-Milacron Test</td>
</tr>
<tr>
<td>Biodegradability</td>
<td>CEC-L-33-A-93 (OR) OECD-301</td>
</tr>
</tbody>
</table>
Chapter 3

EXPERIMENTAL

This section provides details about the experiments conducted in this research. It includes a system description of the experimental approach, schematic diagrams, experimental procedures, product analysis and the research plan.

3.1 Materials

Oleic acid, technical grade [90% purity] was procured from Alfa Aesar, Edmonton, Canada [Johnson Matthey Company]. TMP, ACS Grade, 99.8% purity, was procured from Alfa Aesar, Edmonton, Canada [Johnson Matthey Company]. Methanol, anhydrous, ACS Grade, 99.8%; Ethyl acetate, anhydrous, 99.8% and hexane, mixture of isomers, anhydrous, >99%, were all purchased from Sigma-Aldrich, Ontario, Canada. Sulfuric acid, Certified ACS Plus, 99.8%, 35.2 N/17.6 M and alumina, basic, 60-325 mesh was purchased from Fisher Chemical [Fisher Scientific, Edmonton, Canada]. Canola biodiesel is procured from Milligan Biofuels, Saskatchewan, Canada. N,O-bis [trimethylsilyl] trifluoroacetamide [BSTFA], derivatization grade was purchased from Supelco [Sigma-Aldrich, Ontario, Canada]. Anhydrous sodium sulfate, Certified ACS Grade, >99% was purchased from Fluka, Edmonton, Canada.

3.2 System description

This section is further divided into two parts for three phases of this research. The first part deals with the system description of Phase I, which deals with the synthesis and physicochemical characterization of methyl oleate by esterification of oleic acid and methanol using concentrated sulfuric acid as catalyst. The second part deals with the system description of Phase II, which deals with the synthesis of biolubricants from methyl oleate and canola biodiesel.
Phase III deals with the comparative tribological property evaluation of biolubricants derived from methyl oleate and canola biodiesel. The system description for this phase is included in the experimental procedure itself.

### 3.2.1 Synthesis of methyl oleate by esterification of oleic acid with methanol

Batch runs of esterification experiments were performed at atmospheric pressure in a setup proposed by Sepúlveda et al. [2011]. The experimental setup comprised of a two-neck round-bottom glass reactor on an oil-bath, heated over a hot plate and stirred by a magnetic needle. One neck of the reactor was equipped with a reflux condenser enabled with a continuous flow of cool water to allow for the continuous reflux of methanol vapors. The other neck served two purposes, one to read the temperature during different times of reaction and the other to act as a sampling port for withdrawing samples at different times of reaction.

### 3.2.2 Synthesis of biolubricants derived from methyl oleate and canola biodiesel

Experiments were performed under high vacuum in a 500-mL 3-neck round-bottom glass reactor equipped with a magnetic stirring system, on an oil-bath heated over a hot plate. The schematic diagram is shown in Figure 3.1. The three necks of the reactor were each fitted with a sampling port for collecting samples, a thermometer adaptor for the continuous measurement of temperature and a reflux condenser equipped with a continuous flow of cool water. This cool water flow was used to maintain reflux of hot vapors emanating from the reactor. The vacuum fitting system consisted of a high vacuum pipe connecting the top of the reflux condenser to a T-junction, and then to a high vacuum gauge to read the vacuum pressure and then to a vacuum pump to maintain a steady vacuum.
Figure 3.1: Schematic diagram of experimental setup for transesterification reactions.

3.3 Experimental design and procedure

3.3.1 Synthesis of methyl oleate by esterification of oleic acid with methanol

Esterification of oleic with methanol in Phase I was carried out by studying the effect of one parameter at a time, while holding all other parameters constant. The range of the parameters is shown in Table 3.1. Optimum experiments were repeated once to check for reproducibility of data. The percentage difference in reproducibility of the experimental data is calculated for repeated trials and reported.

Table 3.1: Experimental design for synthesis of methyl oleate from oleic acid.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Temperature (°C)</th>
<th>Molar-ratio</th>
<th>Catalyst loading (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>80-140</td>
<td>-</td>
<td>9.0</td>
<td>2-8</td>
</tr>
<tr>
<td>Molar-ratio</td>
<td>3.0-12.0</td>
<td>80-140</td>
<td>3.0-12.0</td>
<td>4</td>
</tr>
<tr>
<td>Catalyst loading (vol %)</td>
<td>2-8</td>
<td>80-140</td>
<td>3.0-12.0</td>
<td>2-8</td>
</tr>
</tbody>
</table>
The batch weight of oleic acid was 150 g for all esterification experiments. The oleic acid was first weighed and transferred to a glass reactor which is dipped completely inside the heating oil in a glass vessel placed over a hot plate. The oleic acid solution was heated to the required temperature under constant stirring at 600 rpm by a magnetic needle. Meanwhile, until the required temperature was achieved, a mixture of concentrated sulfuric acid and methanol was carefully prepared. This was done as direct addition of concentrated sulfuric acid would char the oleic acid. This mixture was added to the reactor slowly along the walls to prevent splashing/spillover. The time t=0 was noted and the reflux condenser was connected with a supply of cool water turned on. Temperature measurement was made from the other neck whilst withdrawing samples periodically. The duration of esterification reaction was 5 h in all experiments. At the end of the reaction, the reactor was cooled in a fume-hood and then the product was transferred to a separating funnel. The product layer was separated, washed with distilled water to remove traces of methanol and concentrated sulfuric acid until the pH of the solution reached 7. The product was then extracted in ethyl acetate. This extracted layer was dried in anhydrous sodium sulfate and then was passed through basic alumina to remove unreacted oleic acid. The product layer is passed through a rotary evaporator (Rotavapor® R-210/ R-215, B’U’CHI, Switzerland) to separate ethyl acetate. This solvent-free product was weighed, stored in amber bottles and preserved in a refrigerator at 4°C.

3.3.2 Synthesis of biolubricants from methyl oleate and canola biodiesel

Transesterification of methyl oleate with TMP in the first part of Phase II was carried out by design of experiments using Central Composite Design (CCD) approach of Design Expert Software Version 8.0.7.1. A set of 20 experiments (15 unique) were designed, with the center point experiment replicated 5 times, for a total of 6. The net maximum difference between TE
yield percent among the six replicates is computed along with the standard deviation between the 6 trials. The remaining 14 experiments were each repeated to check for reproducibility under exact conditions. The absolute error between the set of 14 experiments was calculated and reported. Hence, a total of 34 experiments were performed. Table 3.2 shows the design of experiments. The software determines the optimum conditions of temperature, molar-ratio of reactants and catalyst loading to obtain for maximum yield of TE. At these optimum conditions, two experiments are performed for the transesterification of canola biodiesel with trimethylolpropane. The final TE yield values after 5 h of reaction time are compared to determine if the developed optimum synthesis conditions are applicable to the transesterification of canola biodiesel.

**Table 3.2: Design of experiments for transesterification of trimethylolpropane with methyl oleate.**

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Temperature (°C)</th>
<th>Molar-ratio of methyl oleate-to-TMP</th>
<th>Catalyst loading (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>4</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>4</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
<td>5</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>140</td>
<td>4</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>110</td>
<td>4</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>9</td>
<td>80</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>80</td>
<td>5</td>
<td>1.5</td>
</tr>
<tr>
<td>12</td>
<td>140</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>13</td>
<td>140</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>14</td>
<td>140</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>15</td>
<td>140</td>
<td>5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

This phase deals with the synthesis of biolubricants derived from methyl oleate and canola biodiesel after reaction with trimethylolpropane. The experimental procedure for transesterification of methyl oleate and canola biodiesel is the same and the reactions are
performed in the same setup. The batch weight of methyl oleate/canola biodiesel was 150 g in all transesterification experiments. Methyl oleate/canola biodiesel was weighed and added to the 3-neck glass reactor and heated to the desired temperature. Once this temperature was reached, the calculated weights of TMP and catalyst were added one after the other and the reactor was connected with reflux condenser with the cool water supply turned on. Vacuum was applied gradually to avoid spillover of reaction materials and time t=0 was noted. Samples were withdrawn at periodic intervals of time. Temperature measurement was made continuously at all times of the reaction. The duration of reaction was 5 h in all experiments. At the end of the reaction, the reactor was cooled in a fume-hood and then the reaction mixture was transferred into a separating funnel. Acidic water containing 10 vol % of o-phosphoric acid (35 wt %) solution in distilled water was used to arrest the rate of reaction by extracting sodium methoxide. This layer was disposed, while the product layer containing the mixture of esters was re-transferred into the same separating funnel. Further water washing was done to remove residual sodium methoxide and ethyl acetate was added to extract the product layer. Water washing was continued until the pH of the solution reached 7. The ethyl acetate-extracted product layer was passed through a bed of anhydrous sodium methoxide for drying to take place. The final product was weighed and stored in amber bottles and preserved in refrigerator at 4°C.

3.4 Analysis of products

Methyl oleate synthesized from Phase I and biolubricants derived from methyl oleate and canola biodiesel synthesized from Phase II were analyzed for their composition by GC. The experimental procedure for performing analysis of products is described in subsequent sections.
3.4.1 Analysis of methyl oleate

The quantification of the yield of methyl oleate was performed by an Agilent 7890A GC instrument on an SGE HT5 column, 15 m x 0.25 mm i.d., and 0.15 µm thickness. The temperature program for product analysis was incorporated from an earlier work (Sepúlveda et al., 2011). The program involved holding at 80°C for 2 min, then heating to 240°C at 5°C/min, and then finally holding at 240°C for 10 min. The injector was held at 200°C, while the detector was at 260°C. A split-ratio of 1:10 was employed. All the samples were derivatized using N,O-BSTFA to convert the fatty acid functionalities to the more volatile silyl groups, to ease their elution in the GC and prevent deposition in the column. The run-time for each analysis was 44 min. This ensured smooth peaks and proper elution of the two components, viz., oleic acid and methyl oleate. The solutions for GC injections were prepared using ethyl acetate as solvent. 1.0 µL of injection volume was used in each run.

3.4.2 Analysis of biolubricants

The quantification of TE yield was performed by an Agilent 7890A GC instrument on an SGE HT5 column, 15 m x 0.25 mm i.d., and 0.15 µm thickness. The temperature program for product analysis was incorporated from an earlier work [Yunus et al., 2003]. The program involved holding at 80°C for 2 min, then heating to 340°C at 5°C/min, and then finally holding at 340°C for 5 min. The injector was held at 300°C, while the detector was at 360°C. A split-ratio of 1:10 was employed. All the samples were derivatized using N,O-BSTFA to convert the polar –OH groups to more volatile silyl groups, to ease their elution in the GC and prevent deposition in the column. The run-time for each analysis was 59 min. This ensured smooth peaks and proper elution of the ester products, viz., ME, DE and TE. The solutions for GC injections were prepared using ethyl acetate as solvent. 1.0 µL of injection volume was used in each run.
3.5 **Characterization and evaluation of products**

The methyl oleate obtained from esterification of oleic acid with methanol was characterized for its properties such as moisture content, kinematic viscosity at 40ºC, cloud point, pour point and oxidative stability. TMP-based biolubricants derived from methyl oleate and canola biodiesel were evaluated for tribological applications by determining their kinematic viscosities at 40 and 100ºC, kinematic viscosity index, cloud point, pour point, lubricity and oxidative stability.

3.5.1 **Physicochemical characterization of methyl oleate**

The synthesized methyl oleate is characterized for its various physicochemical properties. The procedure for determination of each of the properties is described below. The measurements were obtained in duplicate and the average of two values is reported, unless otherwise stated.

3.5.1.1 **Moisture content**

The moisture content of methyl oleate is determined in accordance with ASTM standard method E1064 - 08 using a C30 Compact Karl Fischer Coulometer (Mettler-Toledo Inc., USA). A standard aqueous solution, containing exactly 1 wt % by water is used for pre-titration and the instrument is calibrated for accuracy in measuring the moisture content.

3.5.1.2 **Kinematic viscosity at 40ºC**

The viscosity of methyl oleate is measured at a temperature of 40ºC. Measurements are made using a DV-II+ Pro Viscometer (Brookfield, USA) equipped with a constant-temperature bath. Viscosity is calculated in accordance with ASTM standard method D445 - 11.
3.5.1.3 *Cloud point & pour point*

Cloud point is denoted as the highest temperature at which haziness is observed, while pour point is the lowest temperature at which movement of the oil is observed. Cloud point and pour point are determined in accordance with ASTM standard methods D2500 - 11 and D97 - 11, respectively, using a K46100 Cloud Point & Pour Point Apparatus (Koehler Instrument Company, Inc., USA). These values are reported in integral multiples of ±3°C.

3.5.1.4 *Oxidative stability*

Oxidative stability of methyl oleate is determined in accordance with AOCS Cd 12b - 92 standard method, using Metrohm 743 Rancimat® (Metrohm, Canada) equipment at a standard temperature of 110°C under a continuous flow of air at 15 L/h. 3 g of methyl oleate is pre-weighed and placed in a test chamber. In a conductivity cell, 60 mL of Millipore water is added. The oxidation induction time (OIT) is computed for the specimen. The time at which a steady increase in the conductivity value of the conductivity cell is recorded, is denoted as the OIT.

3.5.2 *Tribological evaluation of biolubricants derived from methyl oleate and canola biodiesel*

This phase deals with evaluation of lubrication properties of biolubricants derived from methyl oleate and canola biodiesel. Properties such as viscosities at 40 and 100°C, viscosity index, oxidative stability, cloud point and pour point and wear scar diameter were evaluated. The different equipment used for the evaluation and the procedure is explained in the subsequent sections.
3.5.2.1 *Kinematic viscosities at 40 and 100°C & viscosity indices*

The viscosities of biolubricants derived from methyl oleate and canola biodiesel synthesized in Phase II were measured at 40 and 100°C. Viscosity index is another parameter of importance while evaluating lubrication performance of lubricants. Viscosity measurements were made using a DV-II+ Pro Viscometer (Brookfield, USA), equipped with a constant-temperature bath. Viscosities were measured in accordance with ASTM standard D445 – 12.

3.5.2.2 *Cloud point & pour point*

Cloud point and pour point were determined in accordance with ASTM standard methods, D2500 - 11 and D97 – 11, respectively, using a K46100 Cloud Point & Pour Point Apparatus (Koehler Instrument Company, Inc., USA). These values were reported in integral multiples of ±3°C. Cloud point and pour point measurements were done in an automatic cooling chamber, factory preset at -36°C. A test-jar was filled with the test sample and introduced into the cooling chamber. A high-pour thermometer was used to monitor the temperature of the specimen during continuous cooling. Observations were made once the temperature read 9°C; by removing the test jar out of the chamber. From then on, for a drop of every 3°C, the jar was keenly observed. The temperature at which cloudy appearance was first seen and the entire liquid turned hazy was reported as the cloud point. The test jar was put back in to the cooling chamber. Below the cloud point temperature, observations were made by tilting the jar at an angle of 45° and observing movement for 3 s. The temperature at which there was no observed movement is reported as the pour point of the specimen.
3.5.2.3 Lubricity testing

Lubricity testing was made in specific equipment known as High Frequency Reciprocating Rig (HFRR) apparatus according to ASTM D6079 – 04. This equipment determines the wear scar diameter. 6 mL of test lubricant is added to a bath vessel. The test sample was placed in a sample container onto a metal surface. The ball was in contact with the metal surface at 50 Hz for 75 minutes, and the wear scar diameter on the ball surface was then measured using a microscope.

3.5.2.4 Oxidative stability

Oxidative stability was determined in accordance with AOCS Cd 12b - 92 standard method using Metrohm 743 Rancimat® (Metrohm, Canada) equipment at a standard temperature of 110°C under a continuous flow of air at 15 L/h. 3 g of test sample was pre-weighed and placed in a test chamber. In a conductivity cell, 60 mL of Millipore water was added. The oxidation induction time (OIT) was computed for each specimen. The time after which there was a steady increase in conductivity of the conductivity cell is determined as the OIT.
Chapter 4

RESULTS AND DISCUSSIONS

This chapter presents the experimental results and discussions from phases I to IV of this research work. Section 4.1 deals with the development of optimum conditions for the synthesis and physicochemical characterization of methyl oleate, synthesized from oleic acid and methanol. The results and discussions of the effects of different parameters of temperature, molar-ratio and catalyst loading during the transesterification of methyl oleate with TMP are presented in section 4.2. Section 4.3 presents the results and discussions from the application of optimum synthesis conditions developed from section 4.2 to the transesterification of canola biodiesel with TMP. Section 4.4 deals with the comparative tribological property evaluation of biolubricants derived from methyl oleate and canola biodiesel.

Optimal experiments were repeated for each parameter to check for reproducibility of the data. Absolute error in replicate runs was reported in each figure.

4.1 Synthesis of methyl oleate from oleic acid

Synthesis of methyl oleate was performed by the esterification of oleic acid with methanol, catalyzed by concentrated sulfuric acid. Esterification reaction was studied over a range of experimental parameters, viz., temperature: 80-140°C, molar-ratio: 3.0-12.0 and catalyst loading: 2-8 vol %. All these parameters were varied over four levels, hence, a total of 64 experiments were performed to study the dependence of yield of methyl oleate on temperature, molar-ratio and catalyst loading.
4.1.1 Study of progression of esterification reaction of oleic acid and methanol

The schematic of esterification reaction of oleic acid with methanol for the synthesis of methyl oleate is shown in Figure 4.1. According to the stoichiometry of esterification reaction, for every 1 mol of oleic acid, 1 mol of methanol is required, which results in the formation of 1 mol of the product, methyl oleate and 1 mol of by-product, water.

![Schematic of esterification reaction](image)

**Figure 4.1:** Schematic of acid-catalyzed esterification of oleic acid with methanol.

The dependence of methyl oleate yield on reaction parameters such as temperature, molar-ratio and catalyst loading was studied by monitoring the reaction progression. A model reaction was carried out at a temperature of 120°C, methanol-to-oleic acid molar-ratio of 9.0 and catalyst loading of 4 vol % to investigate the behavior of yield of methyl oleate as a function of time. Figure 4.2 shows a plot of methyl oleate yield versus time.

![Plot of methyl oleate yield versus time](image)

**Figure 4.2:** Progression of esterification reaction at temperature of 120°C, methanol-to-oleic acid molar-ratio of 9.0 and 4 vol % catalyst loading of concentrated sulfuric acid.
It was observed that methyl oleate had a boiling point of 170°C, while oleic acid after derivatization had a boiling point of 185°C. Methyl oleate yields were found to be low at shorter durations, with yields of only 6.2 wt % after 20 min. The yield of methyl oleate increased slowly until 30 min, when 13.2 wt % was obtained. However, beyond 30 min, the yield rapidly increased and within 2 h, 99.4 wt % methyl oleate yield was obtained. After 2 h, the methyl oleate yield was more or less constant and in the range of 99.2-99.4 wt %.

4.1.2 Development of optimum synthesis conditions for esterification of oleic acid

4.1.2.1 Effect of temperature

In this work, the dependence of methyl oleate yield on temperature was investigated at 80, 100, 120 and 140°C, while holding molar-ratio at 9.0 and catalyst loading at 4 vol %. Figure 4.3 shows the effect of temperature on the methyl oleate yield. As expected, the reaction rates were lower at lower temperatures. Higher temperatures led to greater reaction rates. The obtained methyl oleate yields at 80°C were low when compared with those at 100°C, which were again lower when compared with those at 120°C. However, there was a reversal at 140 °C, which exhibited the lowest methyl oleate yield among all temperatures. The yields of methyl oleate at all temperatures increased slowly until 30 min, with reported yields of only 7.9, 11.3 and 18.1 wt % at temperatures of 80, 100 and 120°C, respectively. Beyond 30 min, an increase in reaction rate was observed for all temperatures. The poor methyl oleate yields obtained at 140°C were due to the charring effect of concentrated sulfuric acid, which is only more significant at high temperatures. A reaction carried out at a temperature of 140°C, molar-ratio of methanol-to-oleic acid of 3.0 and catalyst loading of 6 vol % was stopped within the first ten minutes. The methyl oleate yield in this case was found to be only 12.3 wt %, as confirmed by GC.
Figure 4.3: Effect of temperature on methyl oleate yield at methanol-to-oleic acid molar-ratio of 9.0 and 4 vol % catalyst loading.
Among the other three temperatures of 80, 100 and 120°C, the best methyl oleate yield was obtained at 120°C. At a temperature of 120°C, methyl oleate yield reached 86.3 wt % within the first 1 h, and 99.2 wt % in just 1.5 h. Beyond 2 h, the methyl oleate yield became more or less constant and ranged between 99.2–99.4 wt %. This was obvious as higher temperatures lead to greater reaction rates, and subsequently greater yields of methyl oleate. The methyl oleate yields obtained at 100°C were also impressive, with calculated values of 64.7, 88.7 and 93.9 wt % after 1, 2 and 3 h, respectively. The rate of increase in methyl oleate yield was slow for 100°C and peaked at 93.9 wt % after 3 h, whereas, at 120°C, the methyl oleate yield reached 99.3 wt % in only 2 h. The obtained yields at 80°C were lowest among 80, 100 and 120°C. It was observed that at 80°C, even after 3 h, the methyl oleate yield was only 62.0 wt % after 2 h, at which time almost complete conversion to methyl oleate was observed at 120°C. Even after 3 h, the obtained methyl oleate yield was only 70.2 wt %, which remained constant beyond this time and varied between 70.1–70.3 wt %.

4.1.2.2 Effect of molar-ratio

In this work, methanol-to-oleic acid molar-ratio was varied in the range of 3.0 to 12.0. Figure 4.4 shows the effect of methanol-to-oleic acid molar-ratio on methyl oleate yield, while holding the temperature at 120°C and catalyst loading at 4 vol %. Liu et al. [2006a] reported that at lower molar-ratios, there was pronounced inhibition effect of water on acid catalysis. For a molar-ratio of 3.0, methyl oleate yield increased slowly with time, reaching only a value of 29.9 wt % after 1 h. The maximum obtained yield was 64.2 wt % after 4 h of reaction time; beyond which, the yield started to decrease. The decreased presence of methanol at lower molar-ratios was attributed to be the reason the shift in equilibrium to the forward direction was not maintained.
Figure 4.4: Effect of methanol-to-oleic acid molar-ratio on methyl oleate yield at temperature of 120°C and 4 vol % catalyst loading.
For higher molar-ratios, viz., 9.0 and 12.0; the reverse reaction was not observed to occur, even after 4 h of reaction time. In both cases, methyl oleate yield was found to be above 90 wt % in less than 2 h. The difference in methyl oleate yields in these cases was less than 1.0 wt %; hence, a molar-ratio of 9.0 was concluded to be optimum, which closely concurred with the previously reported value of 8.8 by Chongkhong et al. [2009].

4.1.2.3 Effect of catalyst loading

The catalytic effect of concentrated sulfuric acid on methyl oleate yield was studied at loadings of 2, 4, 6 and 8 vol %, while holding the temperature at 120°C and methanol-to-oleic acid molar-ratio at 9.0. Figure 4.5 shows the effect of catalyst loading on methyl oleate yield. For 2 vol % catalyst loading, the rate of increase of methyl oleate yield with time was the lowest among all loadings. The reason for this was that there was not enough active sulfuric acid for the complete conversion to methyl oleate, a finding previously observed by Aranda et al. [2008]. As higher loadings of sulfuric acid were employed, viz., 4, 6 and 8 vol %, a clear increase in reaction rates was observed. However, the yield of methyl oleate was found to be highest at a catalyst loading of 4 vol % and lowest at 8 vol %. This could be explained by the charring effect of concentrated sulfuric acid. Because the final yield of methyl oleate using 4, 6 and 8 vol % loading of concentrated sulfuric acid after 6 h of reaction time was in the order of 99.1, 90.9 and 83.3 wt %, respectively, the optimum catalyst loading was chosen to be 4 vol %. The developed optimum conditions for esterification were less mild compared to other investigations [Lucena et al., 2011; Dastjerdi et al., 2012], but, however, the low reactivity and high hydrophobicity of the oleic acid necessitated the use of higher reaction temperatures and catalyst loadings, as reported earlier by Liu et al. [2006b].
Figure 4.5: Effect of catalyst loading on methyl oleate yield at a temperature of 120°C and methanol-to-oleic acid molar-ratio of 9.0.
4.1.3 Reproducibility studies

Out of the total combinations of experimental runs which were performed, some experiments were repeated to check for reproducibility of results. The results from 9 such experiments are shown in Table 4.1. The reaction duration in all cases was 6 h. Experiments were repeated under exact conditions, keeping in mind, the importance of reproducibility.

The replicates (trial 2) showed a good match to their originals (trial 1), while the absolute error between the original and replicate values was found to be less than 4%.

Table 4.1: Reproducibility studies of concentrated sulfuric acid-catalyzed esterification reactions of oleic acid with methanol.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Molar-ratio of methanol-to-oleic acid</th>
<th>Catalyst loading (vol %)</th>
<th>Methyl oleate yield - trial 1 (wt %)</th>
<th>Methyl oleate yield - trial 2 (wt %)</th>
<th>Absolute error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>9.0</td>
<td>4</td>
<td>81.1</td>
<td>84.0</td>
<td>4</td>
</tr>
<tr>
<td>100</td>
<td>3.0</td>
<td>4</td>
<td>41</td>
<td>42.3</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>6.0</td>
<td>4</td>
<td>63</td>
<td>60.9</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>9.0</td>
<td>4</td>
<td>94.5</td>
<td>95.1</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>12.0</td>
<td>4</td>
<td>99.5</td>
<td>99.0</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>9.0</td>
<td>2</td>
<td>79.2</td>
<td>78.4</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>9.0</td>
<td>4</td>
<td>99.4</td>
<td>99.1</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>9.0</td>
<td>6</td>
<td>90.4</td>
<td>88.3</td>
<td>2</td>
</tr>
<tr>
<td>120</td>
<td>9.0</td>
<td>8</td>
<td>82.9</td>
<td>83.7</td>
<td>1</td>
</tr>
</tbody>
</table>

4.2 Physicochemical characterization of methyl oleate

The produced methyl oleate was characterized for its various physicochemical properties such as moisture content, viscosity at 40°C, cloud point, pour point and oxidative stability in accordance with ASTM and AOCS standards. Table 4.2 lists the standard methods used to characterize the produced methyl oleate. The physicochemical properties of the produced methyl oleate are listed in Table 4.3.
Table 4.2: Standards for assessment of properties of methyl oleate.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Property (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM E1064 - 08</td>
<td>Water &amp; sediment content</td>
</tr>
<tr>
<td>ASTM D445 - 12</td>
<td>Viscosity at 40°C</td>
</tr>
<tr>
<td>EN 14112 (AOCS Cd 12b-92)</td>
<td>Oxidative stability (Metrohm 743 Rancimat®)</td>
</tr>
<tr>
<td>ASTM D2500 - 11</td>
<td>Cloud point</td>
</tr>
<tr>
<td>ASTM D97 - 11</td>
<td>Pour point</td>
</tr>
</tbody>
</table>

Table 4.3: Physicochemical properties of methyl oleate obtained from concentrated sulfuric acid-catalyzed esterification of oleic acid with methanol at 120°C using methanol-to-oleic acid molar-ratio of 9.0 and 4.0 vol % concentrated sulfuric acid catalyst after 6 h of reaction.

<table>
<thead>
<tr>
<th>Physicochemical property</th>
<th>Obtained value</th>
<th>Specification value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (vol %)</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Viscosity at 40°C (cSt)</td>
<td>4.3</td>
<td>1.9-6.0</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>-3</td>
<td>-2</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>-15</td>
<td>-15</td>
</tr>
<tr>
<td>Oxidative induction time (h)</td>
<td>1.14</td>
<td>3</td>
</tr>
</tbody>
</table>

4.2.1 Moisture (water and sediment) content

The presence of moisture in fuel has detrimental effects on its properties which result in lower heating value, difficulties in ignition to sustain combustion, inefficient combustion and energy losses during ignition of the fuel. The fuel burning can become erratic and is harmful to the engine components. In this work, the produced methyl oleate was found to have a moisture content of 0.04 vol %, which is in accordance with ASTM standard D2709, with sets a permissible maximum value of 0.05 vol %.
4.2.2 Kinematic viscosity at 40ºC

The viscosity of a fluid is defined as the resistance offered by the fluid to shear or tensile stress. Rather, in simple terms, viscosity describes a fluid’s internal resistance to flow. Higher the viscosity of a fluid, thicker the fluid, and greater is the opposition it offers to flow. On the other hand, fluids with lower viscosities tend to flow easily and offer relatively less resistance when a shear is applied on their surface. Viscosities of fluids, viz., liquids and gases tend to decrease with increase in temperature. Hence, when the temperature of a fluid is increased, it flows more easily. Viscosity of biodiesel is one of its most important properties, as it determines the temperature range over which the fluid meets some flow specifications. ASTM standard D445-11 requires that the viscosity of a fluid be measured at a standard temperature of 40ºC. In this regard, the experimentally obtained viscosity value equal to 4.3 mm²/sec is within the range of 1.9-6.0 mm²/sec.

4.2.3 Cloud point

Low-temperature fluidity is one of the most important considerations when judging the performance of biodiesel in automobiles, especially during Canadian winters. Cloud point is defined as the lowest point in temperature at which the dissolved solids in a liquid no longer remain homogeneous but separate out in to crystals, giving the liquid a cloudy appearance. Cloud point measurements were made in an automatic cooling chamber, factory preset at -36ºC, using solvents such as acetone, methanol, ethanol, petroleum ether and dry ice as the cooling media. A test-jar was filled with methyl oleate and introduced into the cooling chamber. A low-temperature thermometer was used to monitor the temperature during continuous cooling. Observations were made by removing the test-jar out of the chamber. Cloudy appearance was first seen at 0ºC. At -3ºC, the cloud was seen to rise up through the liquid towards the surface.
and the entire liquid turned hazy. This was reported as the cloud point. This value of cloud point is very much in agreement with the reported value of -2°C as the cloud point of canola biodiesel.

4.2.4 Pour point

Pour point is defined as the temperature below which the fluid no longer flows and freezes out. In other words, it is the lowest temperature at which the liquid pours, hence, the term, pour point. Pour point measurements were made in the same setup used for cloud point determination. Below the cloud point temperature, observations were made by removing the test jar from the cooling bath and tilting the jar at an angle of 45° for 3 s to observe movement, if any. At -15°C, the fluid solidified completely and did not show any movement. This was confirmed to be the pour point. The reported value of pour point for canola biodiesel is -15°C; hence, there is an excellent agreement with reported value.

4.2.5 Oxidative stability

Biodiesel oxidation can proceed through two mechanisms, namely oxidation and auto-oxidation [Lapuerta et al., 2012]. This mechanism is free-radical chain reaction which initiates when the oxygen in the atmosphere reacts with unsaturated methyl esters, especially those with two or more double-bonds in its molecule. The primary products are hydro-peroxides and free radicals, these being subsequently used to self-sustain the process. Later, other reactions are triggered to form acids and polymers which adversely affect some fuel properties (acid and peroxide value, ester content, viscosity) and even the injection process in the engine (polymers may block injector nozzles). For determining the oxidation stability of biodiesel fuel, an accelerated method run at 110°C is specified by the standard methods, EN 14112 or AOCS Cd 12b-92. The equipment determines the oxidative induction time (OIT). The oxidative stability is a measure of the extent of resistance offered by the fuel to oxidation under increased
temperatures. Oxidative stability is an important fuel property, because it provides relevant information about storage, whose importance increases in warm climates [Freire et al., 2012]. The speed of oxidation depends on the number and position of double bonds, since allylic hydrogens are more susceptible to oxidation.

The sharp point in time from which the conductivity increases rapidly is 1.14 h. This is the determined OIT value of methyl oleate, which is significantly lower when compared to the recommended value of 3 h. The main cause for this is the high degree of unsaturation due to oleic and polyunsaturated functionalities. The point at which there was a sudden increase in the conductivity of the solution denoted the starting time at which oxidative degradation of methyl oleate ensued.

4.3 Synthesis of biolubricants from methyl oleate and canola biodiesel

The first section involves the synthesis of methyl oleate-derived biolubricant by performing transesterification of methyl oleate and TMP to better understand reaction progression and mechanism of transesterification. Optimum reaction conditions of temperature, molar-ratio of reactants and catalyst loading for the synthesis of methyl oleate-derived biolubricant were developed.

In the second part, these developed optimized conditions were used for the transesterification of canola biodiesel with TMP to synthesize canola biodiesel-derived biolubricant. Finally, in the third part, a comparative tribological property evaluation of methyl oleate-derived and canola biodiesel-derived biolubricants was made.

The transesterification reaction of trimethylolpropane with methyl oleate follows a simple stoichiometry as shown in Figure 4.6. For every 1 mol of TMP, stoichiometry indicates that 3
mol of methyl oleate are required. This results in 1 mol of the final TMP trioleate (as the main product) and 3 mol of methanol, obtained as by-product. Similarly, a generic reaction scheme for the transesterification of TMP with canola biodiesel is shown in Figure 4.7. Equilibrium governs this reaction, hence, a net forward reaction has to be maintained using a combination of excess biodiesel and continuous removal of methanol vapors generated in the reaction system.

![Reaction Scheme](image)

**Figure 4.6:** Reaction scheme for transesterification of trimethylolpropane with methyl oleate.

![Reaction Scheme](image)

**Figure 4.7:** Reaction scheme for transesterification of trimethylolpropane with canola biodiesel.

The mechanism of transesterification reaction of trimethylolpropane with methyl esters of vegetable oil was shown to follow a series of step-wise reactions by several researchers, including Yunus et al. [2003], Gryglewicz et al. [2003] and Ghazi et al. [2009]. Figure 4.8 shows the different steps involved in the transesterification reaction of TMP with methyl oleate.
Figure 4.8: Mechanism of transesterification reaction of trimethylolpropane with methyl oleate.
4.3.1 Blank reaction of TMP with methyl oleate without catalyst

A blank reaction was carried out at 110ºC with methyl oleate-to-TMP molar-ratio of 4.0 without sodium methoxide to observe reaction progress, if any. Figure 4.9 shows the trend in the behavior of ester yields at various times. It is clear that the reaction hardly proceeded without catalyst. This confirmed that sodium methoxide was essential for the conversion of TMP to esters, thus during the absence of catalyst, the reaction did not occur.

Figure 4.9: Progression of transesterification reaction of TMP and methyl oleate at 110ºC and methyl oleate-to-TMP molar-ratio of 4.0 without sodium methoxide.

4.3.2 Design of experiments by central composite design approach

The transesterification of TMP with methyl oleate was investigated in the following range of reaction parameters, temperature: 80-140ºC, molar-ratio: 3-5 and catalyst loading: 0.5-1.5 wt %. The pressure was maintained at 1 mbar. A Central Composite Design (CCD) approach was implemented using Stat-Ease Design-Expert® software, version 8.0.7.1. Each of the factors was varied over three-levels. As a result, a total of 20 experiments were suggested by the CCD model. Table 4.4 shows the results of triester yields from the 20 experiments.
Table 4.4: Results from transesterification reactions of trimethylolpropane with methyl oleate.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Molar-ratio of methyl oleate-to-trimethylolpropane (mole: mole)</th>
<th>Catalyst loading (wt %)</th>
<th>Product composition (wt %)</th>
<th>Tri-ester yield from replicate experiment (wt %)</th>
<th>Absolute error for tri-ester yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mono-ester</td>
<td>Di-ester</td>
<td>Tri-ester</td>
</tr>
<tr>
<td>80</td>
<td>3</td>
<td>0.5</td>
<td>23.1</td>
<td>29.6</td>
<td>47.3</td>
</tr>
<tr>
<td>80</td>
<td>3</td>
<td>1.5</td>
<td>22.9</td>
<td>26.3</td>
<td>50.8</td>
</tr>
<tr>
<td>80</td>
<td>4</td>
<td>1.0</td>
<td>22.2</td>
<td>25.5</td>
<td>52.3</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
<td>0.5</td>
<td>22.4</td>
<td>26.4</td>
<td>51.2</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
<td>1.5</td>
<td>22.0</td>
<td>21.3</td>
<td>56.7</td>
</tr>
<tr>
<td>110</td>
<td>3</td>
<td>1.0</td>
<td>6.2</td>
<td>32.0</td>
<td>61.8</td>
</tr>
<tr>
<td>110</td>
<td>4</td>
<td>0.5</td>
<td>5.9</td>
<td>30.8</td>
<td>63.3</td>
</tr>
<tr>
<td>110</td>
<td>4</td>
<td>1.5</td>
<td>5.8</td>
<td>20.2</td>
<td>74.0</td>
</tr>
<tr>
<td>110</td>
<td>5</td>
<td>1.0</td>
<td>5.5</td>
<td>21.6</td>
<td>72.9</td>
</tr>
<tr>
<td>140</td>
<td>3</td>
<td>0.5</td>
<td>0.1</td>
<td>22.6</td>
<td>77.3</td>
</tr>
<tr>
<td>140</td>
<td>3</td>
<td>1.5</td>
<td>0.2</td>
<td>19.7</td>
<td>80.1</td>
</tr>
<tr>
<td>140</td>
<td>4</td>
<td>1.0</td>
<td>0.0</td>
<td>9.9</td>
<td>90.1</td>
</tr>
<tr>
<td>140</td>
<td>5</td>
<td>0.5</td>
<td>0.1</td>
<td>18.7</td>
<td>81.2</td>
</tr>
<tr>
<td>140</td>
<td>5</td>
<td>1.5</td>
<td>0.0</td>
<td>8.8</td>
<td>91.2</td>
</tr>
</tbody>
</table>
From Table 4.4, it is clear that the highest triester yield of 91.2 wt % is obtained at 140°C, reactant molar-ratio of 5.0 and 1.5 wt % sodium methoxide loading after 5 h. This was expected as higher reaction rates would be observed at higher temperatures. 14 experiments are each repeated once to check for reproducibility. The obtained tri-ester yields from the original (TE₁) and replicate (TE₂) runs are statistically analyzed to determine if they are significantly different. An unpaired t-test is performed for the two sets of tri-ester yields. The intermediate values used in the calculations were t (test statistic) = 0.041, df (degrees of freedom) = 26 and standard error of difference = 5.754. The results of t-test are shown in Tables 4.5 and 4.6.

**Table 4.5:** Results from unpaired t-test for final tri-ester yields for 14 transesterification reactions of TMP with methyl oleate.

<table>
<thead>
<tr>
<th>Parameter to be determined</th>
<th>Parameter value obtained</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>P value and statistical significance</td>
<td>Two-tailed P value = 0.97</td>
<td>By conventional criteria, this difference is considered to be not statistically significant.</td>
</tr>
<tr>
<td>Confidence interval</td>
<td>Difference of means (TE₁ – TE₂) = 0.236</td>
<td>95% confidence interval of this difference: From -11.592 to 12.064</td>
</tr>
</tbody>
</table>

**Table 4.6:** Comparison of statistical parameters obtained from t-test for final tri-ester yields from transesterification reaction runs of TMP with methyl oleate.

<table>
<thead>
<tr>
<th>Parameter evaluated</th>
<th>TE₁</th>
<th>TE₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>67.871</td>
<td>67.636</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>15.025</td>
<td>15.421</td>
</tr>
<tr>
<td>Standard error of the mean</td>
<td>4.016</td>
<td>4.121</td>
</tr>
<tr>
<td>Number of data points</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

The null hypothesis in this case assumes that the two sets of TE values are not too different from each other. From the results, a P value of 0.97 (much greater than 0.05) implies that the null hypothesis can be accepted. Hence, there is no significant difference between the two sets of final tri-ester yields.
4.3.3 Study of progression of transesterification reaction of trimethylolpropane with methyl oleate

A reaction was performed at 110°C with reactant molar-ratio of 4.0 and 0.5 wt % catalyst loading. The reaction was performed at 1 mbar pressure. Figure 4.10 explains the plot of ester yield at different reaction times. It can be explained that transesterification proceeds stepwise, wherein, first monoester formation reaches a maximum value after about 15 minutes. The boiling point range for mono-esters is found to be 170-190°C. Then, after this time, a steady formation of diester is seen. The di-ester components were found to have a boiling point range of 210-220°C. When the diester formation also passes through a maximum value, triester starts increasing at a rapid rate. The boiling point range of tri-esters was 275-290°C. This reaction mechanism is found to be in agreement with that reported earlier [Yunus et al., 2003].

![Graph showing progression of transesterification reaction](image)

**Figure 4.10:** Progression of transesterification reaction of TMP and methyl oleate at temperature of 110°C, methyl oleate-to-TMP molar-ratio of 4.0 and 0.5 wt % sodium methoxide loading at 1 mbar pressure.
4.3.4 Development and testing of CCD model for prediction of TE yield

From the CCD module, a quadratic model was suggested with a high R-Squared value of 0.984. Analysis of variance (ANOVA) was performed, which confirmed the adequacy of the quadratic model. Eq. 4.1 shows the model developed for the yield of triester.

\[
\text{YIELD of TE} \, (\%) = 0.287 \times \text{TEMPERATURE} + 25.343 \times \text{MOLAR-ratio} + 9.853 \times \text{CATALYST loading} + 2.3 \times \text{MOLAR-ratio} \times \text{CATALYST loading} - 3.305 \times \text{MOLAR-ratio}^2 - 8.019 \times \text{CATALYST loading}^2 - 39.932
\]

The diagnosis of the model was performed by analyzing normal probability plot of residuals. Figure 4.11 shows the plot. From the figure, the data points appear almost linear.

![Normal probability plot of residuals for transesterification reaction runs of TMP with methyl oleate.](image)

**Figure 4.11:** Normal probability plot of residuals for transesterification reaction runs of TMP with methyl oleate.
4.3.5 Response surface measurement studies

2-factor-at-a-time response surface plots were drawn for the three reaction parameters of temperature, molar-ratio of reactants and catalyst loading. The TE yield was found to vary between 47.3 and 91.2 wt %. Figure 4.12 shows a plot for the effect of temperature and molar-ratio on TE yield. The catalyst loading was fixed at 1.0 wt %. Figure 4.13 shows a plot for the effect of temperature and catalyst loading on TE yield. The molar-ratio was fixed at 4.0. Figure 4.14 shows a plot for the effect of molar-ratio and catalyst loading on TE yield. The temperature was fixed at 110ºC.

![2D surface plot for effect of temperature and methyl oleate-to-TMP molar-ratio on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at 1.0 wt % sodium methoxide loading at 1 mbar pressure.](image)

*Figure 4.12:* 2D surface plot for effect of temperature and methyl oleate-to-TMP molar-ratio on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at 1.0 wt % sodium methoxide loading at 1 mbar pressure.
**Figure 4.13:** 2D surface plot for effect of temperature and sodium methoxide loading on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at methyl oleate-to-TMP molar-ratio of 4.0 and 1 mbar pressure.

**Figure 4.14:** 2D surface plot for effect of methyl oleate-to-TMP molar-ratio and sodium methoxide loading on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at 139°C and 1 mbar pressure.
Figure 4.15 shows a perturbation plot, wherein all the three factors could be seen in one response plot. This plot provides silhouette views of the response surface. The main benefit of this plot is when selecting axes and constants in contour and 3D plots.

![Perturbation plot for different reaction parameters for transesterification of TMP with methyl oleate.](image)

**Figure 4.15:** Perturbation plot for different reaction parameters for transesterification of TMP with methyl oleate.

Finally, 3D surface plots were drawn to see how TE yield varied as a function of the two factors chosen for display. Two such plots are shown in Figures 4.16 and 4.17 for determining the effect of temperature and methyl oleate-to-TMP molar-ratio on TE yield and the effect of methyl oleate-to-TMP molar-ratio and sodium methoxide loading, respectively.
Figure 4.16 3D contour plot for effect of temperature and methyl oleate-to-TMP molar-ratio on tri-ester yield obtained from transesterification reaction of TMP with methyl oleate at 1.0 wt % sodium methoxide loading and 1 mbar pressure.
Finally, predicted responses were generated using Point Prediction node (under Optimization node in the CCD module). Temperature, molar-ratio of reactants and catalyst loading were all fixed in the range of 80-140ºC, 3-5 and 0.5-1.5 wt %, respectively and TE yield was maximized within the experimental range of 47.3 to 91.2 wt %. Using these criteria, the software came up with the following best solution, temperature of 138.8ºC (~139ºC), molar-ratio of 4.89 (~4.9) and catalyst loading of 1.42 wt % (~1.4 wt %) for obtaining TE yield equal to 91.2 wt %, at a desirability value of 1.00. Figures 4.18 and 4.19 show surface and contour plots for desirability, wherein desirability is plotted against temperature and molar-ratio respectively.
while fixing the sodium methoxide loading at 1.42 wt %. Yunus et al. [2003a] determined the optimum synthesis conditions for maximum conversion to TMP triester derived from palm oil methyl esters to be: temperature: 130°C, vacuum pressure: 20 mbar, catalyst: sodium methoxide at 0.8% w/w; molar-ratio of palm oil methyl esters-to-TMP at 3.9:1. Ghazi et al. [2009] utilized a temperature of 150°C, with pressure of 10 mbar, molar-ratio of jatropha methyl esters-to-TMP of 4:1.

**Figure 4.18:** 2D surface plot for desirability against temperature and methyl oleate-to-TMP molar-ratio for transesterification of TMP with methyl oleate at 1.42 wt % sodium methoxide loading and 1 mbar pressure.
Figure 4.19: 3D contour plot for desirability against temperature and methyl oleate-to-TMP molar-ratio for transesterification of TMP with methyl oleate at 1.42 wt % sodium methoxide loading.

4.3.7 Diagnostic study of TE model

At these developed optimum synthesis conditions, the theoretical maximum TE yield as suggested by the model was 91.2 wt %. A confirmatory experiment was conducted to verify the accuracy and applicability of the developed optimum conditions, when, a TE yield of 90.6 wt % was obtained. Hence, the optimum synthesis conditions developed were found to be valid for the experimental data. Thus, the optimum reaction conditions for the transesterification of methyl oleate and TMP are temperature of 139°C, reactant molar-ratio of 4.9 and catalyst loading of 1.4 wt. %, at which TE yield is 91.2 wt %. Figure 4.20 shows a comparison plot of predicted versus actual values. The fit between modeled and experimental values is found to be excellent. Table
4.7 shows the calculated error between the experimental and modeled values. It is clearly seen that the absolute error between them is less than 5% for all experimental runs. Hence, it can be concluded that the fit of the model to the experimental data is very good. Figure 4.21 shows a plot for standard error of design as a function of methyl oleate-to-TMP molar-ratio and temperature.

![Graph](image)

**Figure 4.20:** Plot for model values (predicted) versus actual values (experimental) for TE yields from transesterification reactions of trimethylolpropane and methyl oleate.
Table 4.7: Diagnostic study of TE model to determine absolute error between experimental and modeled values for reactions between trimethylolpropane and methyl oleate.

<table>
<thead>
<tr>
<th>Standard order</th>
<th>Actual value (wt %)</th>
<th>Predicted value (wt %)</th>
<th>Absolute error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47.30</td>
<td>46.03</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>77.30</td>
<td>76.10</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>51.20</td>
<td>49.61</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>81.20</td>
<td>82.28</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>50.80</td>
<td>49.28</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>80.10</td>
<td>81.25</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>56.70</td>
<td>57.46</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard order</th>
<th>Actual value (wt %)</th>
<th>Predicted value (wt %)</th>
<th>Absolute error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>91.20</td>
<td>92.03</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>90.10</td>
<td>88.23</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>61.80</td>
<td>64.63</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>72.90</td>
<td>71.81</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>63.30</td>
<td>66.27</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>74.00</td>
<td>72.77</td>
<td>2</td>
</tr>
<tr>
<td>14</td>
<td>72.10</td>
<td>71.52</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 4.21: 3D contour plot for standard error of design as a function of methyl oleate-to-TMP molar-ratio and temperature.
4.3.8 Reproducibility studies of transesterification reactions of trimethylolpropane with methyl oleate

Studies were performed to check for reproducibility of data obtained from transesterification reactions of TMP with methyl oleate. The center point experiment was performed 6 times as indicated by the CCD model. The final TE yields varied between 90.1-92.3 wt %. Figure 4.22 shows a plot of the six experiments at the center point. It was observed that the replicates showed excellent similarities in product development. It was seen that these yields differed by less than 2.0 wt %, while the standard deviation between these values was found to be less than 0.75%. Thus, it is confirmed that the transesterification experiments were repeatable.

All the remaining 14 experiments were each performed twice to check if they were repeatable. The percentage error for each run was found to be less than 3%. Thus, it is confirmed that the transesterification experiments were reproducible.

Figure 4.22: Scatter plot for triester composition at different reaction times from six replicate reactions at temperature of 110°C, methyl oleate-to-trimethylolpropane molar ratio of 4.0 and 1.0 wt % sodium methoxide loading for transesterification reaction of trimethylolpropane and methyl oleate.
4.3.9 Transesterification reaction of trimethylolpropane with canola biodiesel

The optimum synthesis conditions developed for the transesterification of methyl oleate with trimethylolpropane were applied to the transesterification of TMP with canola biodiesel for the synthesis of canola biodiesel-derived biolubricant. It was observed that the triester composition in canola biodiesel-derived biolubricant after 5 h of reaction time was 90.9 wt %.

4.4 Comparative tribological evaluation of biolubricants

The best biolubricant product obtained from methyl oleate under the developed optimum synthesis conditions was evaluated for its lubrication properties. These properties were then compared with those of canola biodiesel-derived biolubricant. Table 4.8 shows a comparison of lubrication properties of both biolubricants with reference to ISO VG 46 specifications.

<table>
<thead>
<tr>
<th>Tribological property</th>
<th>Methyl oleate-derived biolubricant</th>
<th>Canola biodiesel-derived biolubricant</th>
<th>ISO VG 46 specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 40°C (cSt)</td>
<td>48.9</td>
<td>40.5</td>
<td>&gt;41.4</td>
</tr>
<tr>
<td>Viscosity at 100°C (cSt)</td>
<td>9.3</td>
<td>7.8</td>
<td>&gt;4.1</td>
</tr>
<tr>
<td>Viscosity index</td>
<td>191</td>
<td>204</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>-21</td>
<td>-27</td>
<td></td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>-51</td>
<td>-66</td>
<td>-10</td>
</tr>
<tr>
<td>Oxidative induction time (h)</td>
<td>2.08</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Wear scar diameter (µm)</td>
<td>242</td>
<td>223</td>
<td></td>
</tr>
</tbody>
</table>

4.4.1 Kinematic viscosities at 40 and 100°C and kinematic viscosity indices

Viscosity determination is important from the point of view of the ability of the lubricant to efficiently lubricate contact surfaces. In particular, kinematic viscosities were determined at 40 and 100°C. Methyl oleate-derived biolubricant had kinematic viscosities of 48.9 and 9.3 cSt at 40
and 100°C, respectively. Canola biodiesel-derived biolubricant on the other hand was found to have kinematic viscosities of 40.5 and 7.8 cSt at 40 and 100°C, respectively. Other researchers reported kinematic viscosities at 40°C of 39.7–54.1 cSt for TMP esters of palm and palm kernel oil [Yunus et al., 2003b], 43.9 cSt for TMP esters of jatropha curcas oil [Ghazi et al., 2009] and 11.2–36.1 cSt for TMP esters of 10-Undecenoic acid [Padmaja et al., 2012]. Similarly, they reported kinematic viscosities at 100°C of 7.7–9.8 cSt [Yunus et al., 2003b], 8.7 cSt [Ghazi et al., 2009] and 3.2–7.3 cSt [Padmaja et al., 2012]. In comparison, TMP-based biolubricants derived from methyl oleate and canola biodiesel exhibited very favorable viscosities. ISO VG 46 is a standard specification for light gear oil lubricant [Naegley, 1992]. This specification was used for comparison purpose as pointed out earlier by Ghazi et al. [2009]. All the tribological properties of biolubricants were found to meet these specifications, except for the viscosity of canola biodiesel-derived biolubricant, viz., 40.5 cSt at 40°C, which was only just smaller than the recommended value of 41.4 cSt. This was due to the high monounsaturation and polyunsaturation in canola biodiesel, which effectively resulted in lower viscosity.

The viscosity of fluids tends to decrease as temperature is increased. To quantify the extent of change in the viscosity with change in temperature, a factor known as viscosity index (VI) is used. Higher the value of this index, lesser is the change in viscosity of the lubricant with a change in temperature. Using the kinematic viscosity values at 40 and 100°C, viscosity indices for both lubricants were calculated. Methyl oleate-derived biolubricant was found to have a very high VI value of 191, whereas canola biodiesel-derived biolubricant had an even better VI value of 204. The viscosity indices for both biolubricants are extremely good (>190), but canola biodiesel-derived biolubricant exhibited a higher viscosity index, probably because of the high polyunsaturation in canola biodiesel fatty acid chain. Gryglewicz et al. [2003] reported the
synthesis of neopentyl glycol and trimethylolpropane esters of olive oil, rapeseed oil and lard fatty acids which had very high VI values of 209-235. Yunus et al. [2003b] found that TMP esters of palm and palm kernel oil exhibited very high VI values of 167-187. Ghazi et al. [2009] reported VI value of 180 for jatropha curcas-derived TMP esters, while, Padmaja et al. [2012] obtained VI values of 162-172 for polyol esters of 10-undecenoic acid. Åkerman et al. [2011] reported that TMP esters of C5-C18 fatty acids had VI values of 80-208. In comparison, methyl oleate-derived and canola biodiesel-derived TMP-based biolubricants had much higher VI values than most other lubricants.

4.4.2 Cloud point and pour point

Low-temperature fluidity is the most important property for a lubricant to perform in extremely cold environments, typical during the harsh winters of Canada, especially in Saskatchewan. A measure of the cloud point and pour point values determine the cold flow properties of a lubricant. Cloud point is denoted as the highest temperature at which haziness is observed, while pour point is the lowest temperature at which movement is observed. The cloud point values for both biolubricants were found to be very low. Methyl oleate-derived biolubricant was found to have a cloud point of -21°C, while canola biodiesel-derived biolubricant had a cloud point value of -27°C. Methyl oleate-derived biolubricant was found to have a pour point of -51°C. However, this value dwarfs in comparison to canola biodiesel-derived biolubricant, which had an even lower pour point value of -66°C, one of the lowest pour points obtained for vegetable oil-derived lubricants. This could be attributed to the high percentage of polyunsaturation (~30%) in canola biodiesel, while methyl oleate is almost exclusively monounsaturated. Hence, both biolubricants are applicable for use in automobiles during the extremely cold Canadian winters, with minor modifications.
Gryglewicz et al. [2003] prepared NPG and TMP esters from natural fats such as rapeseed oil, olive oil and lard. The synthesized esters had pour points between -10.5 to -17.5°C. The NPG esters had lower pour points than the corresponding TMP esters. However, natural lard-based esters had a very high pour point of +33°C, owing to their high saturated acids content. A lot of work has been reported by Yunus et al. [2002-2005] on the development of TMP-based triesters from palm and palm kernel oil methyl esters. They synthesized TMP-based lubricants from palm kernel oil methyl esters, which had high pour points between +1 and -1°C. These properties were found to be inferior due to a high level of saturation (>80%) in the fatty acid chain composition of palm kernel oil [Yunus et al., 2003b]. Using palm oil methyl esters in another reported work, they obtained palm oil-based TMP esters with pour point value of -1°C, which were improved to at least -33°C for high oleic content palm oil TMP esters [Yunus et al., 2005]. This was achieved by fractionating palm oil to remove saturated moieties. This greatly improved the pour points of palm-based TMP triesters [Yunus et al., 2004]. Ghazi et al. [2009] synthesized TMP-based triesters of jatropha curcas oil with high pour point of -6°C. This is far too high for Canadian winters, however it was pointed out that the pour point values could be lowered by blending the jatropha biolubricant with petro-based additives. In another work, Padmaja et al. [2011] reported the synthesis of 10-Undecenoic acid-based polyol esters with low pour points in the range of +3 to -36°C, with pentaerythritol tetra-undecenoate having a high pour point of +3°C, while TMP-tri-undecenoate had a reported pour point value of -36°C.

Other techniques have been followed to reduce the pour points of lubricants for efficient use in low-temperature environments. One of them involves blending the vegetable oils with additives like pour point depressant (PPD) and diluents like 2-ethylhexyl oleate, isobutyl oleate, trimethylolpropane trioleate, pentaerythritol tetraoleate and diisodecyl adipate. Another approach
deals with epoxidation of vegetable oils prior to the actual reaction in order to reduce the unsaturation levels. In a major reported work, Asadauskas et al. [1999] used PPD, polyalpha olefin 2 (PAO 2) and diluents like 2-ethylhexyl oleate, isobutyl oleate, trimethylolpropane trioleate, pentaerythritol tetraoleate and diisodecyl adipate and studied the effect of their dilution on pour points of vegetable oils. Soybean oil, high-oleic sunflower oil and canola oil were all blended with just 2% (w/w) of PPD, which reduced their pour points from -9, -12 and -18°C to -18, -24 and -33°C, respectively. Hwang et al. [2001] modified ESO with various alcohols to produce soybean oil-based lubricants with good oxidative stability and low pour points. Using 1% (vol/vol) of PPD, the pour points of lubricant products were significantly reduced from the range of -9 to -45°C. In another work, Hwang et al. [2003] developed lubricant basestocks from soybean oil by first performing its epoxidation to result in epoxidized soybean oil (ESO). The sulfuric acid-catalyzed reaction of ESO and 2-ethylhexanol involved ring-opening at epoxy group followed by transesterification at ester group. Using 0.5 and 1% PPD, they were successful in obtaining products with pour points of -21 and -30°C.

4.4.3 Lubricity testing

The frictional wear resulted by the addition of the biolubricants to a reference diesel sample was studied on a High Frequency Reciprocating Rig (HFRR) apparatus. A pure diesel sample, Castrol Magna oil was used for reference purpose. Figures 4.23 a), b) and c) show images of wear scar on the surface of test samples when 100% pure diesel, 10% (vol/vol) solution of methyl oleate-derived biolubricant in diesel and 10% (vol/vol) solution of canola biodiesel-derived biolubricant in diesel. As is evident, the highest wear scar diameter of 380 µm resulted when only pure diesel was employed. However, when diluted with 10% (vol/vol) solution of biolubricant, there was a significant reduction in wear scar. The application of 10%
(vol/vol) solution of canola biodiesel-derived biolubricant in diesel reduced the wear scar diameter to 223 µm, while 10% (vol/vol) solution of methyl oleate-derived biolubricant in diesel resulted in a slightly greater wear scar diameter of 242 µm. Both biolubricants reduced wear scar by 35-40%. It was thus concluded that canola biodiesel-derived biolubricant performed slightly better when compared with methyl oleate-derived biolubricant. Yunus et al. [20] reported that TMP esters of palm and palm kernel oil had resulted in wear scar diameters of 200–350 and 200–400 µm, respectively. Comparatively, the TMP esters of methyl oleate and canola biodiesel exhibited superior lubricity performance.

![Microscope images](image)

**Figure 4.23:** Microscope images (20 x magnifications) of wear scar diameter on test samples obtained for: a) pure diesel standard, b) 10% (vol/vol) of methyl oleate-derived biolubricant in diesel, and c) 10% (vol/vol) of canola biodiesel-derived biolubricant in diesel.
4.4.4 Oxidative stability

Oxidative stability of oils and fats can be determined using several techniques like the Penn State Micro-Oxidation (PSMO) thin-film test [Yunus et al., 2004], the Rotating Bomb Oxidation Test (RBOT) [Padmaja et al., 2012], determination of peroxide value (PV) [Swern, 1970], pressurized differential scanning calorimetry (PDSC) [Adhvaryu et al., 2002], the Active Oxygen Method (AOM) and the Rancimat method [Läubli et al., 1986]. In the current work, the oxidative stability of the two biolubricants was determined using the Rancimat method which determines a parameter known as oxidative induction time (OIT). It is defined as the elapsed time between the start of the test and the moment at which a sudden increase in the conductivity is detected. It signifies the earliest point in time when oxidative degradation ensues. The lower the OIT value, the lower is the oxidative stability. Figures 4.24 and 4.25 show the conductivity plots obtained for auto-oxidation of methyl oleate-derived biolubricant and canola biodiesel-derived biolubricant in the Rancimat® 743 equipment. Owing to the high monounsaturation and polyunsaturation, the obtained OIT values were found to be quite low, with methyl oleate-derived biolubricant and canola biodiesel-derived biolubricant having values of 2.08 and 0.74 h, respectively. Hence, methyl oleate-derived biolubricant is close to three times more stable when compared with canola biodiesel-derived biolubricant under oxidative conditions. This is attributed to the high monounsaturation and polyunsaturation in canola biodiesel-derived biolubricant.
Figure 4.24: Conductivity plot for auto-oxidation of methyl oleate-derived biolubricant obtained from transesterification of TMP with methyl oleate at 139°C using methyl oleate-to-TMP molar-ratio of 4.9 and 1.4 wt. % loading of sodium methoxide loading at 1 mbar pressure after 5 h.

Figure 4.25: Conductivity plot for auto-oxidation of canola biodiesel-derived biolubricant obtained from transesterification of TMP with canola biodiesel at 139°C using canola biodiesel-to-TMP molar-ratio of 4.9, 1.4 wt. % loading of sodium methoxide loading at 1 mbar pressure after 5 h.

Lapuerta et al. [2012] studied the effect of the test temperature and anti-oxidant addition on the oxidation stability of commercial biodiesel fuels derived from used cooking oil, soybean oil and animal fats. They studied oxidation of the test samples at five different temperatures
between 110 and 130°C in a Rancimat apparatus. A commercial anti-oxidant in the form of butyl hydroxyl toluene was used. They concluded that there was a drastic decrease in the OIT when the test temperature increased from 110 to 130°C. The OIT for used cooking oil, soybean oil and animal fats were 0.77, 3.61 and 15.88 h, respectively when oxidized at 110°C, without the use of any anti-oxidant. In another study, Freire et al. [2012] evaluated the oxidative stability of quaternary mixtures of vegetable oils, viz., soybean, cotton, jatropha curcas and babassu used for the production of biodiesel. The obtained OIT using the Rancimat method for pure vegetable oils were 11.46, 3.49, 6.93 and 45.00 h, respectively for soybean, cotton, jatropha curcas and babassu oils. They prepared five different quaternary mixtures of the four vegetable oils, which had OIT between 5.62 and 13.69 h, all measured by Rancimat method.
Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

It is concluded that high-purity industrial grade lubricants can be effectively synthesized by the transesterification reaction route in a short reaction time.

The following conclusions were made regarding esterification of oleic acid to produce methyl oleate and its subsequent physicochemical characterization:

1. The progression of esterification reaction was monitored by performing the reaction at temperature of 120°C, methanol-to-oleic acid molar-ratio of 9.0 and catalyst loading of 4.0 vol %. It was concluded that during the first 30 min of reaction, methyl oleate yield increased slowly and only reached a little over 10 wt %. Beyond 30 min, however, the yield increased rapidly with near complete conversion in just 1.5 h. The yield, however, did not seem to increase any further.

2. Temperature had the most significant influence on the rate of esterification reaction, with methyl oleate yield reaching 99.4 wt % at 120°C in 2 h. However, temperatures above 120°C were not found to be favorable for the synthesis of methyl oleate, probably due to the charring effect of concentrated sulfuric acid.

3. Methanol-to-oleic acid molar-ratio was the second-most important factor that affected methyl oleate yield. At lower molar-ratios, there was pronounced inhibition effect of water on acid catalysis and reversibility of esterification reaction. For molar-ratios of 3.0 and 6.0, it was found that the final methyl oleate yield after 6 h was only 61.3 and 77.2 wt
%, respectively. Higher molar-ratios such as 9.0 and 12.0 resulted in methyl oleate yields of 94.4 and 95.3 wt %, respectively.

4. Catalyst loading was found to have the least impact on product yield. It was concluded that at 2 vol % catalyst loading, there was not enough active sulfuric acid for the complete conversion of oleic acid to methyl oleate. Methyl oleate yield peaked at 75.7 wt % after 3 h and did not increase much further. At higher loadings of 4, 6 and 8 vol %, methyl oleate yields of 99.1, 91.3 and 82.6 wt %, respectively were observed. This was attributed to the charring effect of concentrated sulfuric acid. Catalyst loading of 4 vol % was determined to maximize methyl oleate yield.

5. Optimum number of esterification experiments was repeated to check for accuracy of experiments and reproducibility of results. A set of 10 experimental runs were repeated once when it was observed that the absolute error between successive trials was found to be less than 3%. Thus, it could be concluded that esterification reactions of oleic acid with methanol were repeatable under given conditions.

6. Physicochemical characterization of methyl oleate was performed using ASTM and AOCS standards. The produced methyl oleate confirmed to ASTM D6791 – 11b grade biodiesel for all properties except for its oxidative stability. The reason for the low OIT value of 1.14 h was attributed to oxidative degradation due to atmospheric exposure.

The following conclusions were made with respect to the transesterification of methyl oleate with trimethylolpropane to synthesize methyl oleate-derived biolubricant:

1. A study of the progression of transesterification reaction showed that it proceeded step-wise in a series of three reactions and each reaction led to formation of ME, DE and TE successively. During the first half hour, ME yield went through a maximum and then
became almost zero with almost no formation of TE. Beyond the first half hour, and until 1 h, DE also went through a maximum and then TE formation started to occur. After about 2 h, TE yield peaked at 81.3 wt %.

2. Among the three reaction parameters, temperature and methyl oleate-to-TMP molar-ratio played the most part in determining the final TE yield. Higher temperatures led to higher reaction rates and greater TE yields. Molar-ratio of 3.0 was found to be inadequate to result in TE yields greater than 70 wt %. 0.5 wt % catalyst loading was found to be ineffective, while loadings of 1.0 and 1.5 wt % resulted in higher TE yields.

3. It was concluded that the optimum synthesis conditions developed by the CCD model for prediction of TE yield were temperature of 139°C, molar-ratio of reactants of 4.9 and catalyst loading of 1.4 wt %. The predicted TE yield at these conditions was 91.2 wt %.

4. Experiments performed to verify the suitability of the developed optimum conditions proved that the TE yield was very close of the predicted value, as yields of 90.9 wt % and 91.1 wt % were obtained. This proved that the developed optimum conditions worked well for transesterification of methyl oleate with TMP.

5. Transesterification reactions of methyl oleate with trimethylolpropane were repeated to check for reproducibility of results. The center point experiments were repeated six times and it was observed that the replicates showed excellent similarities in product development. The absolute difference in final TE yields was observed to be less than 2 wt %, while the standard deviation between the replicate runs was less than 0.75%. The remaining 14 experiments were each repeated once. It was found that the absolute error between the replicate runs is less than 5%. Thus, it was established that the transesterification reactions of methyl oleate with trimethylolpropane were reproducible.
6. An equation was developed by CCD for predicting final TE yield. The model was found to show a strong dependency on temperature and molar-ratio and interaction between molar-ratio and catalyst loading. When a comparison was made between the experimental and predicted values, it was found that the two values did not differ by more than 5%. Thus, the model was determined to be sufficient to accurately predict final TE yield.

The following conclusions were made regarding the synthesis of canola biodiesel-derived biolubricant from canola biodiesel via transesterification with trimethylolpropane:

1. The optimum synthesis conditions developed for the transesterification of TMP with methyl oleate were utilized to the transesterification of TMP with canola biodiesel. A final TE yield of 90.9 wt % was obtained after 5 h of reaction.

2. A reproducibility check was made to see if the transesterification of TMP with canola biodiesel was repeatable. The second experiment resulted in a final TE yield of 90.7 wt %. Thus, it was confirmed that the transesterification reaction of TMP with canola biodiesel under the developed optimum conditions was found to be reproducible, to within an absolute error of 2%.

The following conclusions were derived from the comparison of tribological properties of biolubricants derived from methyl oleate and canola biodiesel:

1. The viscosities of both biolubricants met ISO VG 46 specifications for industrial grade light gear oil standard except for the viscosity of canola biodiesel-derived biolubricant at 40°C, which was only marginally smaller than the recommended value.

2. Methyl oleate-derived biolubricant and canola biodiesel-derived biolubricant were found to exhibit high viscosity indices (>190), thus, both the lubricants would show very little change in viscosity with temperature changes.
3. The low-temperature properties of the lubricants were outstanding, as was expected because of the high unsaturation in the fatty acid chain sequence. The observed cloud points were -21 and -27°C for methyl oleate-derived biolubricant and canola biodiesel-derived biolubricant, respectively. Similarly, the lubricants showed very low pour points of -51 and -66°C for methyl oleate-derived biolubricant and canola biodiesel-derived biolubricant, respectively.

4. Due to the high unsaturation and polyunsaturation in methyl oleate-derived biolubricant and canola biodiesel-derived biolubricant, respectively, the oxidative stability suffered, as is evident by the very low OIT values of 2.08 h and 0.74 h, respectively for methyl oleate-derived and canola biodiesel-derived biolubricant. Thus, the two lubricants would have restricted applications in oxidizing atmospheres as there would be significant oxidative degradation.

5. Both the lubricants performed well in the lubricity test conducted on an HFRR setup, however, canola biodiesel-derived biolubricant exhibited a better overall performance as it resulted in a wear scar having a diameter of only 223 µm; while, methyl oleate-derived biolubricant, in comparison, had a slightly greater wear scar diameter of 242 µm.

5.2 Recommendations

The following recommendations were made for further studies.

1. The esterification reactions in Phase I were carried out without statistical design of experiments. It is recommended to pursue experimental design of reaction parameters such as temperature, molar-ratio and catalyst loading to optimize operating conditions in both semi-batch and continuous systems.
2. The esterification reactions of oleic acid were investigated using concentrated sulfuric acid as homogeneous catalyst. It is advised to use commercial heterogeneous acid catalysts.

3. In the present work, the application of sodium methoxide as a homogeneous base catalyst was made as part of product development studies. It is recommended to employ heterogeneous catalysts such as hydrotalcites for performing the transesterification reactions. See Appendix A for literature on heterogeneous catalysts.

4. In these studies, material balance for transesterification reactions was not possible to account for extent of conversion of TMP. It is recommended to consider a methodology that would enable performing an overall material balance.

5. In this research, model compound studies were restricted to methyl oleate, as a major component of canola biodiesel. It is recommended to investigate the transesterification reactions using possible model compounds such as methyl stearate, methyl elaidate, methyl linoleate and methyl linolenate.

6. In the present study, the source of commercial polyol for transesterification was trimethylolpropane. It is recommended to investigate transesterification reactions using other polyols such as neopentyl glycol, pentaerythritol, trimethylolbutane and trimethylolethane.
Chapter 6

REFERENCES


APPENDIX A: Heterogeneous catalysts for transesterification reactions: A green chemistry approach

The previous reported literature was on the application of homogeneous catalysts for transesterification of vegetable oils. This approach offers excellent reaction rates and near-complete product yields, with good conversion and selectivity. However, there are problems associated with their use such as difficulty in separating catalyst from reaction mixture, material loss, extensive product separation processes and environmental pollution. All these factors lead to high production costs which make the processes on industrial-level unprofitable. Heterogeneous catalysts open a new avenue in this direction as they offer unique advantages such as ease of separation from reaction mixture, minimal loss and tunable basicity. All these factors make heterogeneously-catalyzed transesterification reactions environmentally-friendly processes. Heterogeneous catalysts have intrinsic properties associated with their catalytic performance such as surface area, pore size distribution and pore volume. They differ in their mechanism of transesterification when compared with homogeneous catalysts, in effect that, Lewis basicity becomes of importance, as electron transfer controls reaction-rates.

An excellent review by Sharma et al. [2011] highlights the significant developments which have taken place in the last few years on the application of heterogeneous catalysts for an efficient and eco-friendly synthesis of biodiesel. Transesterification of vegetable oils has been carried out by heterogeneous base catalysts, such as those of pure oxides of Ca [Liu et al., 2008], Mg [Di Serio et al., 2006; Dossin et al., 2006], mixed oxides of Mg and Al [Cantrell et al., 2005; Xie et al., 2006; Barakos et al., 2008; Shumaker et al., 2008; Zeng et al., 2008; Chantrasa et al., 2011], mixed oxides of Mg, Co and Al [Li et al., 2009], mixed oxides of Zn and Al [Bournay et
al., 2005], Ca and Zn [Ngamcharussrivichai et al., 2008], mixed oxides of Ca, Mg and Al [Gao et al., 2010], Ca and Zr [Kawashima et al., 2008] and solid superbase catalysts comprising of rare earth metal oxides, such as KF/Eu$_2$O$_3$ [Sun et al., 2008].

A promising class of heterogeneous base catalysts for transesterification is calcined hydrotalcites derived from layered double hydroxides (LDHs) of Mg/Al, Mg/Fe, Li/Al, etc. The excellent catalytic activity of these species is attributed to high Lewis basicity of O$^{2-}$ as the main active site, along with catalytic sites of medium and low basicity, such as hydroxyl (OH$^-$) ions and metal-oxygen bonds respectively. Among these heterogeneous catalysts, hydrotalcites are especially very appealing, because of their excellent textural properties like high surface area, mesoporosity, high activity, reusability, minimal leaching, etc. The following table presents a compilation of these catalysts. Table A.1 lists a variety of these hydrotalcite catalysts, used for transesterification reactions.
Table A.1: Literature table of various hydrotalcite catalysts for transesterification reactions of vegetable oils.

<table>
<thead>
<tr>
<th>Research group</th>
<th>Catalyst synthesis and characterization</th>
<th>Feedstocks</th>
<th>Reaction conditions</th>
<th>Yield/conversion/selectivity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xie et al. [2006]</td>
<td>Calcined Mg-Al hydrotalcites (HTs) Mg/Al ratio: 2, 2.5, 3.0, 3.5, 4.0 Co-precipitation method Calcination temperatures: 573-1073 K Precursors: Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O Basicity-imparting compounds: NaOH, Na$_2$CO$_3$ Characterization: SEM, XRD, FT-IR, TG-DTA, Hammett indicator-benzene carboxylic acid titration</td>
<td>Soybean oil, methanol</td>
<td>Methanol reflux Range of conditions: molar ratio of methanol: soybean oil = 2:1-20:1, reaction time = 2-20 h, catalyst loading = 1.0-9.0%, stirring speed: 100, 600 rpm</td>
<td>Soybean oil conversion = 67% at optimum reaction conditions of molar-ratio of soybean oil: methanol = 15:1, catalyst loading = 7.5%, stirring speed of 600 rpm for 9 h</td>
<td>1. Optimum Mg/Al ratio obtained is 3.0 2. Highest basicity (3.6 mmol/g) obtained at Mg/Al=3.0, calcined at 773 K 3. Strong Bronsted basic sites (hydroxyl groups) in double layers and coordinatively unsaturated O$^-$ ions (Lewis basic sites) in calcined HTs are responsible for their catalytic activity</td>
</tr>
<tr>
<td>Zeng et al. [2008]</td>
<td>Calcined Mg-Al hydrotalcites (MAHs) Mg/Al ratio: 1.0, 3.0, 4.0, 6.0 Calcination temperatures: 673-1073 K for 7 h Co-precipitation method at high supersaturation Precursors: Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O Basicity-imparting compounds: NaOH, Na$_2$CO$_3$ Characterization: Powder XRD, FTIR, TGA-DTA, SEM</td>
<td>Rape oil, methanol</td>
<td>Methanol: oil molar ratio = 3:1 to 9:1, Catalyst loading: 0.5-2.5%, temperature: 55-75°C, atmospheric pressure, stirring speed: 100-500 rpm, reflux condenser and teflon stirrer</td>
<td>Maximum ester conversion of 90.5% at optimized conditions of: methanol/oil molar-ratio = 6:1, catalyst loading = 1.5% (w/w of oil), stirring speed = 300 rpm, temperature = 65°C for 4 h</td>
<td>1. HT catalyst containing Mg/Al ratio = 3.0, calcined at 773 K and aged for 12 h exhibits best catalytic activity 2. Highest basicity (3.6 mmol/g) obtained at Mg/Al = 3.0 and at calcination temperature of 773 K</td>
</tr>
<tr>
<td>Research group</td>
<td>Catalyst synthesis and characterization</td>
<td>Feedstocks</td>
<td>Reaction conditions</td>
<td>Yield/conversion/selectivity</td>
<td>Comments</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------------------------</td>
<td>------------</td>
<td>---------------------</td>
<td>----------------------------</td>
<td>----------</td>
</tr>
</tbody>
</table>
| Li et al. [2009] | Mixed oxide catalysts derived from Mg-Co-Al-La layered double hydroxides (LDHs) | Canola oil, ethanol | 1. Mg₅CoAl as catalyst: Effects of reaction temperature, ethanol-to-oil molar ratio, particle size, and catalyst stability studied  
2. Reaction conditions: Ethanol: oil molar-ratio = 7:1, 8:1, 11:1, 14:1, and 16:1  
3. Reaction temperature: 413, 433, 443, 453, 473 K  
4. Particle size: <100 µm, >1 mm | 1. Maximum yield of 96-97% obtained at 473 K, ethanol-to-oil molar-ratio of 16:1, particle size of <100 µm and catalyst loading of 2 wt % | 1. Mg₅CoAl catalyst is found to be catalytically very active and stable; reusable, maintained its activity after 7 cycles  
2. Kinetic study of transesterification of canola oil is modeled as a first-order reaction, with activation energy being 60.5 kJ/mol  
3. Mg₅Al is found to be active initially, but it disintegrated into a gel-like material after 5 h and was unrecoverable for reuse  
4. No correlation found between activity and basicity/surface Mg concentration  
5. Addition of La or increase Mg concentration has very little influence on catalytic activity |
<table>
<thead>
<tr>
<th>Research group</th>
<th>Catalyst synthesis and characterization</th>
<th>Feedstocks</th>
<th>Reaction conditions</th>
<th>Yield/conversion/selectivity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cantrell et al. [2005]</strong></td>
<td>Calcined Mg-Al hydrotalcites (HTs): $[\text{Mg}_{1-x} \text{Al}_x\text{(OH)}_2]^{x+}(\text{CO}_3)^{2-} (x = 0.25-0.55)$</td>
<td>Glyceryl tributyrate (Gly-Tbut), methanol (MeOH)</td>
<td>Stirred batch reactor Product analysis by GC Temperature: 333 K, 0.05 g calcined catalyst, Gly-Tbut: hexyl ether (internal standard:methanol molar-ratio = 4:1:120 (0.0025 mol of hexyl ether), Reaction time: 3 h</td>
<td>1. Catalyst selectivity: &gt;98% 2. Rate of tributyrate conversion and formation of methyl butanoate and diglyceride are first-order in triglyceride concentration</td>
<td>1. All catalysts exhibit a hydrotalcite phase with a steady lattice expansion observed with increasing Mg content 2. There is a decrease in both the Al and Mg photoelectron binding energies with Mg incorporation. This correlates with the increased intra-layer electron density. 3. Reaction rate increases steadily with Mg content. 4. The rate of reaction also correlates with intralayer electron density, which is associated with increased basicity.</td>
</tr>
<tr>
<td><strong>Gao et al. [2010]</strong></td>
<td>Calcined KF/Ca-Mg-Al hydrotalcites (HTs) as solid base catalysts KF mass ratio: 100%, different mole ratios of Ca, Mg and Al</td>
<td>Palm oil, methanol</td>
<td>Transesterification reactions carried out in a 100 mL four-necked flask, with thermostat and mechanical stirring system at reflux temperature Reaction conditions: temperature: 338 K, methanol:oil molar-ratio and 5% (wt/wt oil) catalyst loading.</td>
<td>1. Biodiesel yield: &gt;90% within 10 min of reaction at 338 K, 12:1 methanol/oil molar-ratio and 5% (wt/wt oil) catalyst loading. 2. Optimum cation ratio of Ca:Mg:Al = 2:2:0:8:1 with KF mass ratio = 100% resulted in a 99.6% yield of biodiesel in 10 min.</td>
<td>1. Catalyst with excess Mg$^{2+}$ has more hydrotalcite peaks in XRD 2. Excess Ca$^{2+}$ though may affect the formation of the lay structure of HT and too much Ca$^{2+}$ would destroy the regular layer structure. This lead to much stronger peaks of CaAlF$_5$, KCaF$_3$, and KCaCO$_3$.F. These sites play a more important role in building the catalyst activity than KMgF$_3$, as is clear by the slightly higher FAME yield obtained for the excess Ca$^{2+}$ catalyst than the Mg$^{2+}$-excess one. 3. Samples with excess Ca$^{2+}$ showed distinct peaks belonging to CaCO$_3$, implying that the Ca$^{2+}$ actually aggregated and formed a non-active center.</td>
</tr>
<tr>
<td>Research group</td>
<td>Catalyst synthesis and characterization</td>
<td>Feedstocks</td>
<td>Reaction conditions</td>
<td>Yield/conversion/selectivity</td>
<td>Comments</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------------------------</td>
<td>-------------</td>
<td>--------------------</td>
<td>-----------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Shumaker et al. 2008</td>
<td>Calcined Li-Al, Mg-Al and Mg-Fe layered double hydroxides (LDHs)</td>
<td>1. Glyceryl tributyrate (Gly-Tbut), methanol</td>
<td>1. Glyceryl tributyrate reaction: Stirred batch reactor at reflux temperature (65°C)</td>
<td>Maximum activity was observed for Li-Al HT catalysts calcined at a temperature of 450-500°C:</td>
<td>1. CO₂-TPD results show the presence of sites of weak, medium and strong basicity on Mg-Al and Li-Al catalysts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Soybean oil, methanol</td>
<td>2. Soybean oil transesterification:</td>
<td>Yield (%) after 3 h: Mg-Al: 32, 20, Mg-Fe: 24, MgO: 37, Li-Al: &gt;98</td>
<td>2. Li-Al is found to contain higher concentrations of medium and strong base sites (main sites active in transesterification)</td>
</tr>
<tr>
<td></td>
<td>Mg(NO₃)₃.6H₂O + Al(NO₃)₃.9H₂O (or) Fe(NO₃)₃.9H₂O (total metals = 0.4 mol) + Aqueous solution of Na₂CO₃ and NaOH</td>
<td>100 ml two-neck flask</td>
<td>Methanol:oil molar-ratio = 15:1</td>
<td>Yield (%): Li-Al (1 wt %, 2 h): 80, MgO (1 wt %, 2 h): &lt;2, Mg-Al (3 wt %, 6 h): 14</td>
<td>3. Calcined Li-Al LDH is found be catalytically more active than calcined Mg-Al and Mg-Fe LDHs as base catalyst for transesterification reaction</td>
</tr>
<tr>
<td></td>
<td>1. Mg-Al and Mg-Fe catalysts’ synthesis: (Co-precipitation method)</td>
<td>Catalyst loading: 1-3 wt % w.r.t. vegetable oil</td>
<td>Reaction time: 6 h</td>
<td></td>
<td>4. XPS and XRD data indicate that an amorphous Li-Al mixed oxide is the catalytically active phase</td>
</tr>
<tr>
<td></td>
<td>2. Synthesis of calcined Li-Al catalysts: (Co-precipitation method)</td>
<td></td>
<td></td>
<td></td>
<td>5. Lithium leaching from Li-Al LDH catalyst is minimal during short duration reactions, but more pronounced in fixed bed reactors when operated over longer times</td>
</tr>
<tr>
<td></td>
<td>Calcination at temperatures of 450-500°C for 2 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Research group</td>
<td>Catalyst synthesis and characterization</td>
<td>Feedstocks</td>
<td>Reaction conditions</td>
<td>Yield/conversion/selectivity</td>
<td>Comments</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------------------------</td>
<td>------------</td>
<td>---------------------</td>
<td>-----------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Chantrasa et al. [2011]</td>
<td>Calcined Mg/Al hydrotalcite (CHT): Mg₆Al₂(CO₃)(OH)₁₆·₄H₂O as solid base catalyst</td>
<td>Tricaprylin (TCP), methanol (MeOH)</td>
<td>Temperature range: 60-120°C, pressure: 110 psi, molar-ratio of MeOH:TCP = 15:1, catalyst loading = 1 g, stirring speed = 2140 rpm</td>
<td>Yield 1. Apparent reaction orders w.r.t. TCP and MeOH were 0.70 and 1.92 respectively at 60°C, with rate-constant 1.08 x 10⁻⁶ mol⁻¹L¹.⁶⁴min⁻¹. 2. At 120°C, these reaction orders were 0.54 and 1.10 respectively with 3.43 x 10⁻⁵ mol⁻¹L⁰.⁶⁴min⁻¹ as rate constant.</td>
<td>1. Apparent activation energy was found to be 38.4 kJ/mol without mass transport limitations. Effect of solvent was not observed. 2. Eley-Rideal mechanism was used to fit the data obtained at 120°C, with surface reaction of adsorbed methanol and tricaprylin from liquid phase being the rate determining step.</td>
</tr>
<tr>
<td>Barakos et al. [2008]</td>
<td>Basic solid Mg-Al-CO₃ hydrotalcite catalyst (HT2 - Mg:Al atomic ratio = 2:1) in powder form</td>
<td>Refined cottonseed oil (RCO), acid cottonseed oil (ACO), high acidity and water content cottonseed oil (HACO) and animal fat feedstock (AFF), methanol</td>
<td>Reactions carried out in a Series 4560 Bench Top Mini Batch Reactor (Parr)</td>
<td>Yield 1. 100% conversion observed for RCO within 3 h, while only 1.5 h for ACO heated at 210°C 2. Triglyceride conversion to biodiesel was about 99% for HACO and AFF within 3 h</td>
<td>1. Non-calcined and calcined form of the catalyst were tested in this study, when it was realized that the activity of the non-calcined catalyst was lower than the initial activity of the non-calcined catalytic system, but it appeared the same with the reused non-calcined system. 2. The diglyceride and monoglyceride concentrations in the product were considerably reduced with the removal of the glycerin phase, and further reaction of the oil phase with the fresh reactants</td>
</tr>
</tbody>
</table>
APPENDIX B: Structures of relevant chemical compounds

Many chemical compounds were discussed in the present thesis. This appendix attempts to present the molecular formula and chemical structure of some of these compounds.

**Figure B.1:** Structure of 1,1,1-tris(hydroxymethyl)propane.

**Figure B.2:** Structure of trimethylolpropane mono-oleate (ME).
Figure B.3: Structure of trimethylolpropane di-oleate (DE).

Figure B.4: Structure of trimethylolpropane tri-oleate (TE).
APPENDIX C: Silylation

In the present study, the partial esters, ME and DE, were found to have high polarity, due to the presence –OH groups. In order to decrease their polarity and making their elution easy in the GC column, derivatization was performed. Silylation is the conversion of the polar –OH groups in a molecule to volatile trimethylsilyl groups. This can be achieved by using a variety of reagents, such as Trimethylsilane (TMS), Trimethylsilyl chloride (TMSC), Hexamethyldisilazane (HMDS), Bis(trimethylsilyl)acetamide (BSA) and N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA). In this study, BSTFA was used for silylation purposes as it has high reactivity and achieves near complete conversion.
APPENDIX D: GC chromatograms

D.1 Effect of derivatization with N,O-BSTFA

Derivatization with N,O-BSTFA greatly helped ease the elution of polar components, i.e., ME and DE from the GC column. Figures D.1 and D.2 show chromatograms obtained for underivatized and derivatized products, respectively analyzed on Agilent 7890A GC.
Figure D.1: GC chromatogram of underivatized products obtained after 5 h of reaction time. TMP: methyl oleate molar-ratio = 1:4, temperature = 110°C, NaOCH₃ loading = 0.5 wt %.
Figure D.2: GC chromatogram of derivatized products obtained after 5 h of reaction time. TMP: methyl oleate molar-ratio = 1:4, temperature = 110°C, NaOCH$_3$ loading = 0.5 wt %.