The Possibility of Producing Biodiesel Fuel from Wood Pulping by Products

Yan Pu

Western Michigan University

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THE POSSIBILITY OF PRODUCING BIODIESEL FUEL FROM WOOD PULPING BYPRODUCTS

by

Yan Pu

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Paper Engineering, Chemical Engineering and Imaging

Western Michigan University
Kalamazoo, Michigan
June 2008
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Yan Pu
Biodiesel fuel produced from biomass material is a renewable and promising substitute fuel for petroleum diesel fuel, and it is relatively environmentally friendly. The Pulping process involves a huge amount of lignocellulosic materials. There may be a great potential of combining this fact with the biodiesel production, as well as the present biodiesel technologies.

This thesis focuses on the esterification reaction behavior of three main components of tall oil fatty acids, which are byproducts of paper manufacture. They are stearic acid, palmitic acid and oleic acid. Three levels of both catalyst and methanol were employed in the esterification for each acid to find out the optimal reaction condition. It was found that with the medium catalyst and medium methanol amount, stearic acid showed the highest average reaction rate. Either the high catalyst level coupled with low methanol level or the medium catalyst level and high methanol level led to the highest average reaction rate for palmitic acid. Under low methanol level, both medium and high level of catalyst for oleic acid contributed to a high average reaction rate. A GC/MS analysis was also carried out to identify the final product of each reaction. Combined with the chromatograms and mass spectrums, we confirmed that the products we obtain were exactly targeted methyl esters.
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LIST OF ABBREVIATIONS

ARR average reaction rate (mol/mL • h)
A factor A, weight ratio of alcohol to free fatty acid
B factor B, amount of catalyst
C maximum obtainable conversion from the free fatty acid to ester
C concentration of the acid (mol/mL)
eij random error effect
F F distribution, which is most commonly used in variance analysis
H_{ab} test of zero interaction
RCB Randomized Complete Block
t reaction time (h)
n normal distribution
n number of observations in a model
N normalized, molar/L
N total amount of observation
u overall mean
p.p.m. parts-per-million
p.s.i. per square inch
v volume (mL)
\sigma^2 variance
\alpha_i effect due to level i of factor A only
List of Abbreviation—continued

\[ \beta_j \]  
Effect due to level j of factor B only

\[ (a \beta)_{ij} \]  
Interaction effect due to the combination of level i of factor A and level j of factor B
CHAPTER 1

INTRODUCTION

1.1 Biodiesel

Petroleum-base diesel (PD) is the most widely used fuel, especially in Europe (Lee et al., 2006). It plays an important role in the current fuel market. However, the fossil sources for producing PD are limited and un-renewable, and will eventually be exhausted. There are investigations showing that the petroleum supply of the world will be exhausted quite soon (Hirsh, 2006). Moreover, burning of petroleum-based diesel will contribute to global warming (Drake 2000; Tester et al. 2005) and acid rain, due to carbon dioxide and sulfuric compounds produced. Therefore, it is urgent to look for alternative sources of sustainable and environmentally friendly energy to solve the current social problems and concerns on fuels (Wyman, C. E., Goodman, B. J., 1993). Biodiesel fuel is one of the desirable candidates and offers particular promise because of its environmental benefits and the fact that it is made from sustainable and abundant resources.

Biodiesel is a renewable diesel fuel produced from biomass, vegetable oils, animal fats or waste cooking oil (Nye, M. J., 1983). Essentially, it is in the format of methyl esters of fatty acids. Biodiesel fuel can be used in any mixture ratio with petroleum diesel, as they have very similar characteristics. The existing engines can use 20% biodiesel blend without any modification or reduction in energy output. In addition, biodiesel has a high flash point (about 160°C), which follows it is safer to store and use, compared to petroleum fuels (flash point about 62°C) (Lee et al., 2006). Biodiesel also has higher cetane number, lower sulfur content and lower aromatics than conventional diesel fuel, thus allowing for cleaner
exhaust emissions (Vasudevan, 2005; Canakci et al., 2001).

In sum, biodiesel fuel owes better properties than that of petroleum diesel in that it is renewable, biodegradable, non-toxic and environmentally friendly (Canakci et al., 2001; Coltrain, D., 2002; Connemann et al., 1998).

Nowadays, biodiesel fuel is generally produced by chemical conversion of feedstock with alcohol in the presence of catalyst. The feedstock can be vegetable oil derived from oil seed crops (rapeseed, soybean, sunflower etc.), waste vegetable oil (Schuchardt et al, 1998; Zhang et al., 2003; Krawczyk, T., 1996) or animal fat (tallow). In seeds, oil energy content is around 45 GJ/t, similar to that of diesel of 42-50 GJ/t (Vasudevan, 2005). In the terms of alcohol used, methanol is considered to be of great advantage, as it allows the simultaneous separation of glycerin, while using other alcohols complicates the separation process (Demirbas, 2005).

There is a powerful potential to use lignocellulosic materials as an additional source for biodiesel fuel production, since lignocellulosic materials constitute by far the largest proportion of biomass (Berndes, 2003). The pulping industry consumes a huge volume of wood for paper making. Thus, there is much incentive to justify further work to maximize the utilization of its byproducts as another raw material for production of biodiesel fuel.

The pulping industry has already developed mature processes to yield cellulose in comparatively pure form for manufacturing all kinds of paper, at the same time incinerate the lignin portion of the wood to recover energy (Smook, 1992). Although it is a benefit to burn lignin to supply a large amount of energy needed to run the integrated pulping industry, we may find other ways to better utilize this byproduct of the paper industry, compared to the value of heat it can provide by just incinerating the pulping liquors. Biodiesel production from the byproduct of pulping industry is of such potential that it has already attracted
attention from biodiesel manufacturing people (Lee et al., 2006).

In spite of its desirable properties as a diesel fuel substitute, biodiesel from biomass also has some shortcomings:

The viscosity of biodiesel is somewhat higher than that of petroleum-base diesels, which may lead to gum formation in injectors (Vasudevan, 2005);

Biodiesel fuel tends to undergo crystallization of saturated fatty acid alkyl esters in very cold weather and may lead to a higher likelihood of more difficult starting of the motor by plugging the fuel filter and fuel lines (Lee et al., 2006). Biodiesel may crystallize at higher temperature than petrodiesel. One remedy of this involves blending the biodiesel with petrodiesel. It has been found that the cloud point and the pour point of biodiesel- petrodiesel blends decreases almost linearly with the content of petrodiesel (DOE, 2006b).

Biodiesel products have a relatively higher level of unsaturated hydrocarbon chains compared to petrodiesel, which may result in polymerization when the product is heated (Lee et al., 2006). This may also cause the formation of gums (Peterson et al., 1991). Moreover, the conjugated double bonds are susceptible to oxidation during storage, generating impurities that influence the performance of the diesel engines (Canakci, M., and Van Gerpen, J., 1999b). So it is recommended to minimize the level of highly unsaturated components (for example, linolenic acid) to ensure the highest quality of biodiesel.

Water in biodiesel has further problems. It can reduce the heat efficiency, as well as lead to emission and corrosion problems. Due to its high freezing point, ice created from water can plug lines. (Lee et al., 2006).

Further efforts should be focused on these issues to overcome these disadvantages of biodiesel, making it a more powerful and promising energy source.

Biodiesel has been commercialized in many countries. The first industrial
plant for biodiesel production in the world was established in Australia in 1991, with the output ability of 10,000 tons per year (Agarwal et al., 2001). There is a report about two pilot projects on biodiesel used on commercial vehicles in Ireland (Agarwal et al., 2001). Biodiesel has been commercially used in U.S and Japan since 1990s (Mittelbach et al., 2001).

1.2 Tall Oil

Tall oil is a resinous, black, sticky liquid obtained from the kraft pulping process of paper making (Talor and King, 2001). During cooking, the resinous acids of the wood are converted to their sodium soaps which rise to the surface of the cooking liquor, along with the neutral components. These soaps can be removed by skimming and acidified to their respective free fatty acid and free rosin forms. The water-insoluble raw tall oil is separated by centrifuging, while the aqueous phase is sent back to the process to reuse the sulfur and sodium for further pulping of wood. Fatty acids (Table 1.1), rosin acids and neutral components generally make up this sticky material. (Taylor et al., 2001; Harvala et al., 1987; Koebner, 1983).

<table>
<thead>
<tr>
<th>Acids (less than 16 carbon atoms)</th>
<th>8.5%</th>
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<tr>
<td>Palmitic acid</td>
<td>35.9%</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>8.5%</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.0%</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>23.1%</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>17.8%</td>
</tr>
<tr>
<td>Unidentified unsat. Acids</td>
<td>2.9%</td>
</tr>
<tr>
<td>Eiccosanoic acid</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

Table 1.1 Fatty acid composition of a tall oil head fraction by GLC-analysis (Source: Koebner, 1983)
The structures of stearic acid, palmitic acid and oleic acid are illustrated below:

![Structures of stearic acid and palmitic acid](Website 1)

![Structure of oleic acid](Website 2)

*Figure 1.1 Structures of stearic acid and palmitic acid (Website 1)*

*Figure 1.2 Structure of oleic acid (Website 2)*

Actually, the chemical composition of tall oil depends on the age, species and geographical location of the trees used in the pulping process. (Gullichsen and Lindeberg, 1999). Table 1.2 gives composition of the extractives portion of tall oil producing by different wood species (Holmlund and Parviainen, 1999)

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<tr>
<td>Rosin acids (%)</td>
<td>42</td>
<td>30-35</td>
<td>20-30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fatty acids (%)</td>
<td>47</td>
<td>50-55</td>
<td>35-55</td>
<td>76</td>
<td>55-90</td>
</tr>
<tr>
<td>Neutrals (%)</td>
<td>11</td>
<td>5-10</td>
<td>18-25</td>
<td>24</td>
<td>5-35</td>
</tr>
</tbody>
</table>

*Table 1.2 Composition of tall oil extractives from different kraft black liquor (Lee et al., 2006)*
Another source shows how different regions affect the composition of tall oil (Table 1.3 from Foran, 1992):

<table>
<thead>
<tr>
<th></th>
<th>Southeastern U.S.</th>
<th>Northern U.S. &amp; Canada</th>
<th>Scandinavia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid no.</td>
<td>172</td>
<td>135</td>
<td>155</td>
</tr>
<tr>
<td>Resin acids (%)</td>
<td>40</td>
<td>30</td>
<td>42</td>
</tr>
<tr>
<td>Fatty acids (%)</td>
<td>50</td>
<td>40</td>
<td>39</td>
</tr>
</tbody>
</table>

*Table 1.3 Composition of crude tall oil by various regions (Source: Foran, 1992)*

The separation of raw soap of tall oil is a complicated process, since it is a complex compound consisting of water, lignin, inorganic acid etc. Lignin calcium and fibers are the main components to be separated from the raw soap. After several steps of separation and purification processes, the rosin content of raw soap can be reduced to 1-10% (Lee et al., 2006). The final product is comparatively pure tall oil fatty acid.

Tall oil fatty acids contains more oleic acid (one double bond acid) than linoleic (two-double bond acid) and linolenic acid (three-double bond acid), which means that the tall oil contains a lower level of unsaturated fatty acids compared to vegetable oil. This point can be viewed as an advantage of tall oil with respect to biodiesel production, since the high content of unsaturated fatty acids of vegetable oil can cause polymerization during combustion of biodiesel fuel, resulting in the formation of gums and associated plugging.

Besides fatty acid, there is an un-ignorable rosin acid fraction included in the tall oil. In order to convert such rosin into useful biodiesel, it is necessary to hydrogenate the double bonds within the ring structures of abietic and related products. The present thesis is focused on the tall oil fatty acids. Further study on
the possibility of biodiesel production from tall oil rosin acid is a topic of future research.

If we utilize the methods applying to the production of biodiesel fuel in the case of vegetable oil, as mentioned above, to the case of tall oil as a source material, we can expect the following shortcomings and benefits by using different production methods listed in Table 1.4.

<table>
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<th>Processing strategies</th>
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<tr>
<td>Alkaline catalysis</td>
<td>Saponification can cause problems</td>
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<tr>
<td>Acid catalysis</td>
<td>Promising; requires follow-up by alkaline transesterification</td>
</tr>
<tr>
<td>Enzymatic catalysis</td>
<td>Slow; water removal required; multiple stages required</td>
</tr>
<tr>
<td>Supercritical methanol</td>
<td>Fast; high pressure equipment; development required</td>
</tr>
</tbody>
</table>

*Table 1.4 Shortcomings and benefits of conversion strategies for biodiesel using tall oil from the Kraft pulping of wood REF (Lee et al., 2006)*

1.3 Objectives

The objectives of the present thesis were to investigate the basic reaction behavior of three main components of tall oil, namely stearic acid, palmitic acid and oleic acid, during esterification. Three different catalyst and methanol levels were selected for each acid to carry out the esterification reaction. The optimal catalyst and methanol should provide valuable reference data for the biodiesel and tall oil industry.

1.4 Thesis Outline

The first chapter gives a background of the present thesis with regard to biodiesel and tall oil. The second chapter provides a literature review of current biodiesel technologies. Chapter 3 talks about the experimental method, which
provides details of the experimental design and procedure. Chapter 4 discusses the results and a brief summary is offered by chapter 5, with conclusions and recommendations.
CHAPTER 2

LITERATURE REVIEW

2.1 Existing Biodiesel Technology

Before discussing the possibility of preparing biodiesel fuel from pulping industry byproducts, let us do some reviews of the most widely used technologies in biodiesel production. As mentioned above, these generally deal with vegetable oils. In the present thesis, when we talk about biodiesel fuel, unless specially stated, it means alkyl esters (usually methyl esters), which are converted from fatty acids or glycerol salts by esterification and transesterification processes respectively (Vasudevan, 2005).

Sometimes, vegetable oil itself is used as a biofuel used in modified vehicle engines. However, untreated vegetable oil can cause problems in unmodified diesel engines (Demirbas, 2005; Canakci et al., 2001). Its high viscosity and low volatility can result in incomplete burning, forming deposits in the fuel injector and piston ring sticking (Pestes and Stanislao, 1984; Canakci, M., and Van Gerpen, J., 1999a). There are many ways to reduce or eliminate these effects. Recent literature suggests the most promising means may be transesterification of vegetable oil, since the physical characteristics of the corresponding fatty acid esters are very similar to those of petroleum diesel and the process is comparatively simple (Demirbas, 2005; Kusdiana and Saka, 2001a, 2001b, 2004a, 2004b; Minami and Saka, 2006). There are other approaches to prepare biodiesel from vegetable oil, all of which are promotions of the transesterificate-method, which will be reviewed below in this thesis.
Alkali-catalyzed Process

Alkali catalysis is a common conventional way to transesterify vegetable oil in the presence of an alkaline catalyst, such as sodium hydroxide (Kusniana and Saka, 2001a; Peterson et al., 1995; Zhang, Y. et al., 2003), sodium methoxide, potassium hydroxide, sodium amide, sodium hydride etc. (Vasudevan, 2005), when the source material is a relatively pure mixture of triglycerides. Figure 2.1 shows the schematic reaction of alkali-catalyzed process.

\[
\begin{align*}
R_1\text{-COO-CH}_2 & + 3 \text{CH}_3\text{OH} \\
R_2\text{-COO-CH}_2 & \quad \text{Methanol, Alkaline solution, Catalyst, heat} \\
R_3\text{-COO-CH}_2 & \\
\text{Triglycerides} & \\
R_1\text{-COO-CH}_3 & \quad \text{HO-CH}_2 \\
R_2\text{-COO-CH}_3 & \quad \text{HO-CH} \\
R_3\text{-COO-CH}_3 & \quad \text{HO-CH}_2 \\
\text{Fatty acid methyl esters} & \\
\text{Glycerol} & 
\end{align*}
\]

Figure 2.1 Transesterification reaction suitable for relative pure vegetable oils using alkali catalyst (Schuchardt, U., and Sercheli, R., 1998)

To allow the reaction to be carried out, the temperature employed is usually set up at 55-70 °C (Boiling point of Methanol is 64.7 °C) (Lee et al., 2006). Excess of the alcohol is added to minimize the competing reactions (Demirbas, 2005). The usual reaction time can be one to eight hours, depending on the temperature and concentrations used (Lee et al., 2006). Glycerin is the byproduct after the separating and refining process.

In the alkali-catalyzed process, free fatty acids of the vegetable oil react with alkaline catalyst to form saponified products, converting most free fatty acids to their corresponding soap form, which is believed to make separation of the byproduct a challenge. Saponification of fatty acids is illustrated in Figure 2.2.
Therefore, this method is efficiently carried out only in the case of sufficiently low levels of both water and free fatty acids in the raw material.

\[
\text{R-COOH} \quad \text{Fatty acid} \quad \downarrow \quad \text{NaOH or KOH} \\
\text{R-COO·M⁺} + \text{H₂O} \quad \text{Fatty acid soap} \quad \text{Water} \\
(M⁺ = \text{Na⁺ or K⁺})
\]

*Figure 2.2 Saponification reaction of fatty acids with alkali catalyst (Schuchardt, U., and Sercheli, R., 1998)*

**Acid-catalyzed Process**

The transesterification process for acid-catalysis uses an acid (H₂SO₄, H₃PO₄, HCl, etc.), preferably sulfuric acid. Though this method is claimed more tolerant with free fatty acid, it has been indicated that the acid-catalyzed process is too slow to be practical for converting triglycerides to biodiesel (Canakci et al., 2001; Freedman, B., Pryde, E. H., and Mounts, T. L., 1984; Freedman, B., Pryde, E. H., 1982). Acid catalysis is just effective for converting free fatty acids to esters (esterification), but it is not an appropriate method for vegetable oils, which involves triglycerides (Zheng, 2006).

In order to use acid catalyst in the case of vegetable oils, which include triglycerides, Canakci et al. created a two-stage process in 2001 (Canakci et al., 2001). The free fatty acids are converted to the corresponding esters (esterification) in the first stage of this process by the catalysis of acid. Alkaline catalyst is applied in the mixture in the second stage for transesterification of the triglycerides, as was shown in Figure 2.1 (Lee et al., 2006).
The acid-catalyzed process can avoid saponification of free fatty acids by converting them to esters, however, compared to alkaline-catalyzed process it has a much lower efficiency. The time spent in order to get complete reaction may be the crucial obstacle for the acid-catalyzed process applying to biodiesel production industriously.

**Enzyme-catalyzed Process**

Enzyme-catalyzed transesterification processes are not yet commercially developed, but there already have been some results reported (Abigor et al., 2000). It provides a prospective means to produce biodiesel when the raw materials contain high levels of free fatty acid. This method uses lipase as the catalyst, the first stage is transesterification of triglycerides and the second stage is esterification of fatty acid (Figure 2.1), the conversion degree obtained can be as high as 98.5%. The second stage is shown in Figure 2.3 (Lee et al., 2006).

![Reaction equation](image)

**Figure 2.3 Esterification catalyzed by an enzyme (Lee et al., 2006)**

However, the reaction yield (98.5% is good for high free fatty acids) as well as the reaction time are undesirable compared to the acid/alkali-catalyzed
processes. It also involves six stages of transferring the enzyme to fresh substrate mixture (Demirbas, 2005; Lee et al., 2006).

Moreover, water produced during the esterification process can cause problems (Figure 2.3). Water has the ability to hinder the enzyme activity (Lee et al., 2006). In order to put the enzyme-catalyzed process into industrial application, there still needs to be more studies on optimizing the reaction conditions, such as temperature, pH, type of enzyme, etc. to establish suitable characteristics of this method.

**New Heterogeneous Catalyst Process**

This process uses solid catalysts, so it is a heterogeneous catalyzed process (Bournay et al., 2005; Suppes, G. J. et al., 2003). Solid metal oxides such as zinc, aluminum and magnesium are examples of the catalysts. The reaction is performed at higher temperature and pressure compared with the homogeneous catalysis processes such as alkali-catalyzed and acid-catalyzed processes, which require either catalyst recovery or complicated purification steps, and it proceeds without catalysts lost. Two successive stages of reaction and glycerin separation are needed in this method. Excess alcohol is removed by evaporation and recycled to process. Just a general description of this process was found, further study of this process is needed. This process requires vary clean oil though.

**Non-catalytic Supercritical Methanol Process**

The term “supercritical” means that the temperature and pressure of the solvent are sufficiently high, above or near its vapor-liquid critical point, so that the properties of the solvent are neither completely liquid-like nor completely gas-like, thus imparting the solvent some unusual properties, which lead to innovative technologies (Arai, 2002; Brunner, 2004). Supercritical fluid has a density greater
than that of gases but rather comparable to that of liquids. The viscosity and diffusivity are intermediate between liquid and gas, so it has a solvent power like liquids with mass transfer characteristics like gases (Harvala et al., 1987). The critical temperature and critical pressure of methanol are, respectively, 239°C and 8.09 MPa (Saka and Kusdiana, 2000; Demirbas, 2005).

A non-catalyzed biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield, because of simultaneous transesterification of triglycerides and methyl esterification of free fatty acids (Demirbas, 2005). One such method involves a one-step transesterification and esterification with supercritical methanol (Saka and Kusdiana, 2000; Kusdiana and Saka 2001). In this experiment, the batch-type reaction vessel is preheated at 350°C, at a pressure of 20MPa, with a molar ratio of 1:42 of the rapeseed oil to methanol, and a 4-min treatment period. This method has been proven to produce a high yield, and is comparatively simpler than the common method in which the catalyst and saponified products have to be removed and purified.

Kusdiana and Saka (2004) then developed a two-step method consisting of hydrolysis of triglycerides in subcritical water and subsequent methyl esterification of the fatty acids by supercritical methanol treatment, which aimed at finding an alternative method for biodiesel fuel production that has a lower reaction condition than the one-step supercritical methanol method.

It was found that, compared to one-step supercritical methanol method, the two-step method has a higher yield at the same reaction time period and treated with the same temperature. It requires mild reaction conditions for hydrolysis and methyl esterification in terms of a lower energy requirement.
Superiority of Supercritical Methanol Method

The supercritical methanol method has many advantages over other methods mentioned above (Saka and Kusdiana, 2000; Demirbas, 2005). Compared to the supercritical methanol process, the use of catalyst, either alkaline or acid catalyst, in the common methods results in a much more complicated process. The time needed to complete the reaction is long, which contributes to the low efficiency. The afterward purification procedure is also time and energy consuming.

The supercritical methanol process doesn’t involve these problems, since the solubility of vegetable oil in methanol is increased by the decrease in the dielectric constant of methanol that occurs in the supercritical state of methanol (Saka and Kusdiana, 2000). This enhances the reaction rate by forming a homogeneous system.

The yield of the supercritically-prepared methyl ester is higher than that prepared from the common methods. The increased yield would be due to the conversion of free fatty acids to corresponding methyl esters, while in the common processes free fatty acids are converted to saponified products by the alkaline catalyst.

In summary, the advantage of the supercritical methanol process is that this method requires much less time, but gives a higher yield. Because there is no catalyst involved in this method, the procedure is briefer and environmentally friendly.

Prospects for Tall Oil as a Source Material for Biodiesel Production

The conventional alkaline pulping process produces a byproduct called tall oil, which is a mixture of triglyceride oils, fatty acids, resin acids, and other related materials (Johansson, 1982). Though it is a common action to incinerate these
materials to recover their energy, there are some potential incentives to convert these materials to higher value products.

Some people may point out that this is just a change of the location at which the material is being incinerated, in the diesel engine instead of in the recovery boiler. In addition, biodiesel fuel demands a much higher standard, such as higher purity and other properties (acid number, sulfur content, water content etc.) (Van Gerpen, 2004). The most motivational factor to promote this issue may be in the price difference. The price of tall oil varies from $90-$160 per ton (Lee et al., 2006), which means less than $1 price per gallon. However, the price of diesel fuel has nearly doubled from $1.57 in 2004 to $2.90 in 2006 and over $4.00 today per gallon (Lee et al., 2006).

2.2 Basic Principle of Chemical Kinetics

In chemical kinetics, a rate constant is defined to describe how fast the chemical reaction is (Website 3). For example, E and F are the reactants to produce G. The chemical reaction can be illustrated in a simple version:

\[ E + F \rightarrow G \] (1)

The reaction rate for this chemical reaction is in form of:

\[ r = k \left[ E \right]^x \left[ F \right]^y \] (2)

where \( r \) is the chemical reaction rate, \( [E] \) and \( [F] \) represent the concentrations of E and F (moles per unit volume). \( x \) and \( y \) are the orders of E and F respectively, and they depend on the chemical mechanism. When the chemical reaction is a single-step one, the orders are equal to the stoichiometric coefficients, otherwise, the case can be very complicated.

\( k \) is the so called reaction rate constant, which can be affected by all the factors beside concentration, such as temperature, agitator speed and so on (Website 4). When the concentration of one of the reactants (F) is fixed, say, its
amount is much more than any other reactant, a pseudo constant can be obtained. At this point, the concentration of the excess reactant gets involved in the rate constant, and the reaction form can be simplified to
\[ r = k \cdot [E]^x. \]  
(3)

Common types of reactions are first-order reaction and second order reaction. First-order reaction can be express in the way of,
\[ r = k \cdot [E], \]  
(4)

The integrated first-order rate law is
\[ \ln[E] = -kt + \ln[E]_0 \]  
(5)

where \( t \) is the reaction time, \([E]_0\) is the initial concentration of \( E \).

While a second-order reaction is in the form of,
\[ r = k[E]^2, \]  
(6)

The corresponding integrated second-order rate is
\[ 1/[E] = kt + 1/[E]_0. \]  
(7)

Thus, when the plot of \( \ln[E] \) vs. time is linear, it’s a first-order reaction, and if the plot of \( 1/[E] \) vs. time is linear, it indicates that this is a second-order reaction.
CHAPTER 3

EXPERIMENTAL METHODS

3.1 Experimental Design

3.1.1 Esterification Reaction

Three fatty acids were investigated in the present thesis. They are stearic acid, palmitic acid and oleic acid. Since they are all free fatty acids, the acid-catalyzed method was chosen because of the reasons stated in the literature review section. The reaction taking place turned out to be esterification, because there is no ester involved in the reactants, as in the vegetable case. Esterification reaction variables that influence the yield of esters produced from the targeted acids were selected as weight ratio of alcohol to free fatty acid (Factor A) and amount of catalyst applied (Factor B). Both of these two variables included three different levels. For the weight ratio of alcohol (methanol) to free fatty acid, 150%, 250% and 500% were selected, with corresponding molar ratio to fatty acid of 13, 22 and 44, respectively. 0.05%, 0.15% and 0.25% were selected for the catalyst amount, based on the weight of free fatty acids used. The maximum obtainable conversion from the free fatty acid to ester (C), overall reaction rate (k) and overall reaction time (t) needed to obtain maximum were chosen as response variables.

Each of the three levels of Factor A was observed with each level of Factor B, then, Factor A and Factor B were completely crossed, by which means gave out totally 9 treatments for each of the free fatty acids.

Because of time-related (each treatment would take up to 10 hours to finish) and cost considerations, it was decided to take \( n = 1 \) observation from each
treatment. The 9 treatments were totally crossed and randomly distributed by the Minitab. The Table 3.1 is the design of experiments provided by Minitab.

<table>
<thead>
<tr>
<th>Catalyst(%)</th>
<th>Methanol(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
</tr>
<tr>
<td>7</td>
<td>0.05</td>
</tr>
<tr>
<td>8</td>
<td>0.25</td>
</tr>
<tr>
<td>9</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 3.1 The DOE layout from Minitab

After carefully reviewing this design of experiments, it was found that the Randomized Complete Block (RCB) Design is satisfied in this case, which is the fixed model when both Factor A and Factor B are fixed (Stoline, M. R., 2008). In our case, methanol is one of the reactants, while catalyst plays the role of an assistant, by using various amounts of which there may be considerable differences in the final product conversion rate. In the light of these consideration, with these designs, primary importance was attached to inferences about Factor A treatment differences; Factor B block differences are of secondary interest.

The RCB model used is illustrated below:

\[ y_{ij} = u + \alpha_i + \beta_j + e_{ij}; \quad i = 1, 2, 3; j = 1, 2, 3 \]  \quad (8)

where,

i ) \( \sum \alpha_i = 0 \) (Factor A fixed);

ii ) \( \sum \beta_j = 0 \) (Factor B fixed);
iii) The eij’s are N=3^2=9 independently and identically distributed n(0, \sigma^2) (normally distributed random variable with exception of 0 and variance of \sigma^2).

Interaction was assumed to be zero in this additive model, because with just one observation, interaction and error are confounded and can not be separated, thus, the test for H_{ab}: (\alpha \beta)_{ij}=0 is not possible for any model (Stoline, M. R., 2008).

A SAS program associated with RCB design was employed at the final experimental analysis stage.

After the esterification reaction of the three fatty acids is completed, one final sample randomly collected from each acid group will be analyzed by GC/MS to identify the component in the product.

A supercritical CO2 method was performed to compare the performance of esterification reaction under high temperature and high pressure with the regular heating means. Again, 150%, 250% and 500% methanol excess amounts were applied. Instead of sulfuric acid, CO2 was employed as the catalyst.

3.2 Experimental Procedures

3.2.1 Methyl Esters Preparation from Fatty Acids

Apparatus

\textit{a. Reaction:} A 500 ml three-neck round-bottom flask equipped with a trap moisture burette, a condenser as well as a thermometer was applied (Figure 3.1). The condenser used cold city water to cool down the methanol vapor, which is then trapped in the moisture collector, allowing a constant circulation of methanol in the system. A heating mantle was used to provide the energy needed.
b. Titration: The reaction was monitored off-line by the means of titration (AOCS., 1998). A pipette (1 mL) coupled with a fast release pipette pump was used to withdraw the samples from the reactor. A 50 mL burette was employed to dispense a known concentration of sodium hydroxide solution. Flasks were available to hold the samples and to receive the titrant from the burette (Figure 3.2).
Analysis: An HP6890/HP5973MSD GC/MS system coupled with Chemstation software was employed to identify the composition of the esterification product.

Materials

We started our investigation with three fatty acids, which are the main components presented in the tall oil fatty acid. The acids we used were stearic acid (95+%, Alfa Aesar, a Johnson Matthey Co.), palmitic acid (95+%, Tokyo Chemical Industry Co., LTD) and oleic acid (95+%, EMD Chemical Inc.), of which the first two represent no double bond acids and the third one represents one double bond fatty acid.
b. Alcohol: Liquid methanol (reagent grade, Rollie Williams-Paint Spot Co.), the core alcohol needed as one of reactants in this experiment to perform esterification reaction with the fatty acids mentioned above.

c. Catalysts: Sulfuric acid (95~98%, Reagent A.C.S, Fisher Scientific Co.). In our case, we used methanol to react with free fatty acids, which means that an acid-catalyzed process was necessary. Sulfuric acid of high concentration has the function of dehydration, which promotes the reaction to the forward direction.

d. Titration: Sodium hydroxide (99%), deionized water, isopropanol (anhydrous 99%, Rollie Williams-Paint Spot Co.) and phenolphthalein solution (prepared by our lab) were used in the titration procedure. To track the reaction process and analyze the acid value we made normalized sodium hydroxide solutions of various concentrations (0.01N, 0.025N and 0.1N) by dissolving 0.4g, 1g and 4g anhydrous sodium hydroxide, respectively, into 1L deionized water (AOCS., 1991). These normalized solutions were kept in 1L long-neck volumetric flasks. Isopropanol was used as a solvent to dissolve samples withdrawn from the reactor, while phenolphthalein solution was added as the indicator. To test the acid value, the sign of the end point for titration is a transparent solution turning to pink.

**Procedures**

We applied the acid-catalyzed process to carry out the esterification reaction, in which case sulfuric acid was added as the catalyst. To set up the reaction system, the water-cooled condenser was mounted on the top of the reactor, coupled with a moisture trap burette as a connector between the round-
bottom reactor and condenser. A thermometer was also equipped on the reactor, with the top liquid bulb totally immersed in the liquid during the reaction to monitor the reaction temperature.

A solution of sulfuric acid in methanol was prepared at room temperature. The amount of sulfuric acid used was based on the weight percentage of the fatty acid to be reacted. As mentioned in the experimental design section, the designed sulfuric percentages were 0.05%, 0.15% and 0.25% of the weight of fatty acids. 50g fatty acid was chosen to be reacted in each treatment, according to the capability of the reactor and the amount of corresponding methanol will be consumed. Based on the quantity of the fatty acid to be reacted (50g), 6.185g sulfuric acid was accurately measured and dissolved into methanol to make up 250 mL solution after cooled to room temperature before use. Thus, every 1 mL of this solution represents 0.05% catalyst needed, 3 mL represents 0.15% and 5 mL represents 0.25%.

The solution was charged into the reactor with the measured amount of fatty acid inside. Cooled water and heat were then turned on. The mixture was heated up to 65°C. From the very beginning of the reflux observed, 1 mL sample was withdrawn from the mixture every 15 minutes by using the pipette. Meanwhile, titrations of these samples were also done at the same rate to track the acid value trend all the way until the reaction approached to its equilibrium stage, that is, the acid value hardly changed anymore in terms of the sodium hydroxide solution consumed stopped to decrease, or even began to rise.

The next step was to drive off the remaining un-reacted methanol as well as water produced during the reaction out of the system by turning up the heat and let out the methanol collected in the trap moisture burette regularly until no more methanol was observed to be accumulated in the barrette branch. The temperature
kept rising at a very high rate during this period and could get up to as high as 140 °C.

After that, a 1 mL sample from the final product was taken and titrated for its acid value. The above procedures were started over again by compensating the same amount of methanol (no more catalyst needed), until the tested acid value of the final residue dropped below 8 mL of 0.025N sodium hydroxide solution per mL residue.

In order to diminish the interference of sulfuric acid on the acid value to minimum, a separate titration was carried out by distributing 1mL, 3mL and 5mL the same sulfuric-methanol solution into the same volume of deionized water as the operated situation, to simulate the actual treatment. The volume of deionized water is calculated by adding the acid and methanol volume for each run together. 1mL of these solution were taken to titrate for their acid value, the real acid value of the fatty acid should be obtained by subtracting the acid value tested from sulfuric acid. The result turned out to be that almost no sulfuric acid could be detected by even using the 0.01N sodium hydroxide solution. In the light of this, the sulfuric acid interference could be seemed as ignorable during the reaction period.

The final products from each treatment were kept in an oven at a constant temperature of 50°C.

3.2.2 Supercritical CO₂ method

The esterification reaction was also carried out by a SFT-150 SFE system, which was set up at the temperature of 150°C, pressure of 4000 p.s.i. Oleic acid was selected to perform the esterification reaction, since it is oil-like rather than a solid, and therefore can readily be collected and operated in the supercritical system. The reaction took place in a sealed 100mL steel vessel, which can stand
high pressure and temperature. 150%, 250% and 500% methanol was used, the same amount as in the acid catalyzed method.

The supercritical system was first preheated to 150°C, this would take as long as 1 hour. The pump was then turned on to pump the CO₂ into the reactor, thus, pressurizing the vessel to 4000 p.s.i.

Acid values were measured after 2 and 4 hours of reaction period for each treatment. An identical measurement procedure was carried out as described in section 3.2.1.

To terminate the supercritical condition, the switch on the side of the machine was released carefully, allowing the gas inside to escape slowly. The cover of the vessel was able to be opened only after the pressure shown on the display screen was 0.

3.2.3 GC/MS Analysis

An HP6890/HP5973MSD GC/MS system coupled with Chemstation software was applied to analyze the component of the final product.

One sample from the final product of each fatty acid group was randomly selected to verify that the products we obtained from the acid-catalyst esterification reactions were exactly the corresponding methyl esters.

Each sample was diluted in pure isopropanol to make up a 100 p.p.m solution for GC/MS test. For each test run, 1 µL solution was injected, by using a 10 µL syringe, into the GC/MS system, which employed a standard 16 min test loop. The Chemstation software was available to on-line monitor the process of the analysis and provide the mass spectrum and chromatogram by the end of each run.

Stearic acid, palmitic acid and oleic acid diluted in isopropanol, as well as pure isopropanol itself were also analyzed by GC/MS, respectively, to obtain
comparative background to regular analysis.

Helium was used as the carrier gas at a flow rate of 3ml/min measured at 80°C, and with the gas inlet pressure of 200 kPa. The detector temperature was set at 250°C.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Acid Value vs. Time

Three typical plots describe how acid values of the three fatty acids changed during the period of reactions are given in Figure 4.1, Figure 4.2 and Figure 4.3. In these graphs, each line composed of different shape of dots represents different composition of catalyst and methanol feed into the reaction systems. The acid value of each fatty acid sample was measured by 0.1 normalized sodium hydroxide solution as prepared in the description in the methods section.

![Acid Value vs. Time of Stearic Acid](image)

*Figure 4.1 Normalized acid value of stearic acid as a function of time under various compositions of catalyst and methanol*
Figure 4. 2 Normalized acid value of palmitic acid as a function of time under various compositions of catalyst and methanol

Figure 4. 3 Normalized acid value of oleic acid as a function of time under various compositions of catalyst and methanol

To better illustrate how different amounts of catalyst or methanol affect the reaction process in terms of reduction of the acid value, the figures below are
arranged in the way of keeping one of the variables (catalyst amount or methanol amount) constant, while ranging through another variable. All the figures show the tracking of acid value for the first run of each reaction.

4.1.1 Stearic Acid

We can see from the figures below that, for stearic acid, with 0.15% (Figure 4.6) and 0.25% (Figure 4.8) catalyst added into the system, the more methanol excess, the faster the reaction reached equilibrium. There is reflected in the time needed to let the reaction become steady in a shorter reaction period, in turn leading to a higher average reaction rate, which will be discussed later. However, under 0.05% catalyst usage (Figure 4.4), the least methanol amount (150%) seems to result in the shortest reaction period while the medium amount (250%) of methanol spent more time than the other two did.

![Acid Value vs. Time Under 0.05% Catalyst for Stearic Acid](image)

*Figure 4.4 Acid value of stearic acid as a function of time under 0.05% catalyst*
Figure 4.5 Normalized acid value of stearic acid as a function of time under 0.05% catalyst

From the normalized figure (Figure 4.5), under 0.05% catalyst level the higher the methanol level employed, the lower the efficiency of the reaction was.

Figure 4.6 Acid value of stearic acid as a function of time under 0.15% catalyst
Figure 4. 7 Normalized acid value of stearic acid as a function of time under 0.15% catalyst

Under 0.15% catalyst (Figure 4.7), the efficiency of the low methanol level (square dots) is lower than the other two levels of methanol used.

Figure 4. 8 Acid value of stearic acid as a function of time under 0.25% catalyst
The highest catalyst applied (0.25%, Figure 4.9) leads to the medium and high level of methanol lines nearly overlapping each other, while the efficiency of the low methanol level applied is the highest.

**Figure 4.9** Normalized acid value of stearic acid as a function of time under 0.25% catalyst

**Figure 4.10** Normalized acid value of stearic acid as a function of time under 150% methanol

33
Figure 4.11 Normalized acid value of stearic acid as a function of time under 250% methanol

Figure 4.12 Normalized acid value of stearic acid as a function of time under 500% methanol
Basically, the more catalyst added, the shorter the time the reaction took to reach a steady state. Again, there are two overlapping lines in the medium methanol amount (250%) graph (Figure 4.11). The lines, representing 0.15% and 0.25% catalyst can not be distinguished from one another. Nevertheless, with more methanol added into the system (500%) as in Figure 4.12 shows, these two lines move apart from each other again, which may imply that a larger methanol amount holds the potential for more catalyst to enhance the reaction.

In light of the discussion above, we may infer that under medium level of methanol, increasing the amount of catalyst from the medium to high level does not make much improvement in the reaction process.

4.1.2 Palmitic Acid

With the lowest catalyst amount (0.05%) in the system (Figure 4.14), the three lines representing different levels of methanol used show little differences, both in time and the final acid values. At the beginning, the acid values of the three cases were close to each other, but after reaching a certain point (about 100 min), the acid values began to move apart, the low methanol level leaded to higher efficiency, while the medium methanol level has the lowest efficiency.
Figure 4.13 Acid value of palmitic acid as a function of time under 0.05% catalyst

Figure 4.14 Normalized acid value of palmitic acid as a function of time under 0.05% catalyst
Figure 4. 15 Acid value of palmitic acid as a function of time under 0.15% catalyst

Figure 4. 16 Normalized acid value of palmitic acid as a function of time under 0.15% catalyst

Figure 4.16 and Figure 4.18 are similar, in that, the lines almost overlap one another regardless of the level of methanol employed, which suggests that under medium and high level of catalyst usage, more methanol does not improve the efficiency of the reaction significantly.
Figure 4.17 Acid value of palmitic acid as a function of time under 0.25% catalyst

Figure 4.18 Normalized acid value of palmitic acid as a function of time under 0.25% catalyst
Figure 4.19 Normalized acid value of palmitic acid as a function of time under 150% methanol

The effect of catalyst level on the reaction process under the same methanol usage is apparent in Figure 4.19. Each line is clearly apart from the others in this case and the rate difference is also apparent. The higher catalyst level apparently contributes to a more complete and faster reaction.

Figure 4.20 Normalized acid value of palmitic acid as a function of time under 250% methanol
Figure 4.21 Normalized acid value of palmitic acid as a function of time under 500% methanol

Under 250% and 500% methanol usage, as shown in Figure 4.20 and Figure 4.21, the high level and medium levels of catalyst used did not make significant differences, judging from the closeness of oblique squares and triangle dots lines. This may suggest that under medium to high methanol amount, there is no need to increase the catalyst amount.

4.1.3 Oleic Acid

From Figure 4.5 as well as Figure 4.13 and Figure 4.22, we can easily determine that under one specific catalyst and methanol composition for all these fatty acids, the time needed to complete the whole reaction is much longer than any other combinations, that is, with 0.05% (low level) catalyst and 250% (medium level) methanol. Under this combination, the time spent can be as much as almost 600 minutes. This may advise us that we should avoid using this recipe.
Figure 4.22 Acid value of oleic acid as a function of time under 0.05% catalyst

Figure 4.23 Normalized acid value of oleic acid as a function of time under 0.05% catalyst

The three lines in Figure 4.25 and Figure 4.27 are not far apart from one another, except for early times, which implies that for oleic acid, under medium
(0.15%) or high (0.25%) catalyst level, using higher levels of methanol will not make significant differences, since they achieve the same results as lower level methanol used and time is also wasted. It is of interest to note from these two graphs that, the least methanol used (150%) took the least time to get steady. Generally, the lower methanol level leads to a higher efficiency, especially at the beginning of the reaction.

![Acid Value vs. Time Under 0.15% Catalyst for Oleic Acid](image1)

**Figure 4. 24 Acid value of oleic acid as a function of time under 0.15% catalyst**

![Acid Value vs. Time Under 0.15% Catalyst for Oleic Acid (normalized)](image2)

**Figure 4. 25 Normalized acid value of oleic acid as a function of time under 0.15% catalyst**
Figure 4.26 Acid value of oleic acid as a function of time under 0.25% catalyst

Figure 4.27 Normalized acid value of oleic acid as a function of time under 0.25% catalyst

Figure 4.28 to Figure 4.30 are all in the same pattern, that is, under all levels of methanol, medium (0.15%) and high (0.25%) level of catalyst show no significant differences in the track of acid value (overlapped), even the times
needed are almost the same. This indicates that there is no need to add a high level of catalyst into the system to push the reaction forward. The medium catalyst amount is already more than enough.

Figure 4. 28 Normalized acid value of oleic acid as a function of time under 150% methanol

Figure 4. 29 Normalized acid value of oleic acid as a function of time under 250% methanol
4.2 Reaction Order

The Figures below are drawn in the format of lnC versus time for each acid.

From the basic linear shape of every line, we can infer that these esterification reactions are first order reactions, at least initially.
Figure 4. 31 lnC as a function of time of stearic acid

Figure 4. 32 lnC as a function of time of palmitic acid
Section 4.1 just focused on the first run of each reaction and looked into the reaction separately by sorting different catalyst and methanol usage amounts. This may not well illustrate the whole reaction behavior of each fatty acid in terms of taking both catalyst and methanol factors into consideration and drawing sound conclusions. This section mainly concentrates on the concept of average reaction rate, which may be of the most interest. Since the highest average reaction rate means you can achieve the highest conversion degree within the shortest time, which is a situation pursued by every chemical industry. Thus, to determine the optimal combination of catalyst and methanol is the objective of this section.

Because some of the reactions were carried out in 2 or more runs, the total reaction times needed to calculate the average reaction rate were obtained by adding the time spent in each run separately. Assume that $C_{t=0}$ represents the
original concentration of the fatty acid, $C_{in}$ is the final acid concentration after the esterification reaction, $t$ is the total time needed to end up one batch of reaction, $t_i$ is the sum of the time for each run, $v$ is the volume of the sodium hydroxide consumed (mL), $N$ is the normalized concentration of sodium hydroxide solution (mol/L). Concentrations of the fatty acid were calculated according to the titration results of the original acid and the final product (after driving off methanol).

The average reaction rates were calculated by the following formulation:

$$ARR \text{ (average reaction rate)} = \frac{(C_{acid(t=0)} - C_{acid(t=t)})t}{t_i} \quad (9)$$

$$C_{acid} = v_{NaOH} \cdot N_{NaOH} / 1000 \quad (10)$$

Table 4.1 shows the acid value of each raw fatty acid:

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Acid Value (mol/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic Acid</td>
<td>0.003130</td>
</tr>
<tr>
<td>Palmitic Acid</td>
<td>0.003245</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>0.003797</td>
</tr>
</tbody>
</table>

*Table 4.1 Acid value of the original fatty acids*

4.3.1 Main Effects Plot

Figure 4.34 to Figure 4.36 are main effects plots for average reaction rate of each fatty acid. For stearic acid (Figure 4.34), the medium and high catalyst level give a higher average reaction rate results (especially medium level), while low catalyst level yields a much lower average reaction rate. Medium and high levels of methanol usage play the same role in terms of obtaining the same average reaction rate.
Figure 4.34 Main effects plot (data means) for the average reaction rate of stearic acid

Palmitic acid (Figure 4.35) and oleic acid (Figure 4.36) are comparable to each other in that, medium and high catalyst levels give desirable ARR, again the low catalyst level contributes to much lower ARR values. Different from stearic acid, medium methanol usage tends to give the lowest ARR in both palmitic and oleic acid cases. Especially, the low methanol level turned out to be leading to a high ARR outcome in the oleic acid case.

Figure 4.35 Main effects plot (data means) for the average reaction rate of palmitic acid
Figure 4.36 Main effects plot (data means) for the average reaction rate of oleic acid

Figure 4.37, Figure 4.38 and Figure 4.39 are main effects plots for the first order rate constants of each fatty acid.

Figure 4.37 Main effects plot for the first order rate constant of stearic acid
From the main effects plots above we can see that there is an increasing trend in the first order rate constant of stearic acid and palmitic acid while the amount of catalyst is increasing. However, for oleic acid, medium amount of catalyst performed the best in terms of the first order rate constant. Basically, the first order rate constants of each fatty acid decrease as the amount of methanol increases.
4.3.2 Interaction Plots

From Figure 4.40 to Figure 4.42 we can see that there exists an interaction between the catalyst and methanol levels, since the lines in these plots are not parallel to one another. The highest dot in each graph implies the optimum combination of catalyst and methanol amount because it gave the best average reaction rate outcome.

From Figure 4.40 we can see that with the medium catalyst and medium methanol amount introduced into the system, the highest ARR was achieved, while the medium catalyst and high methanol level was second only to it. The low catalyst level generally contributed to low ARR at all methanol levels. Under high catalyst level (0.25%), the dots were closely gathered at a middle level of ARR, regardless how much methanol was used.

![Interaction Plot for ARR of SA](image)

*Figure 4. 40 Interaction plot for average reaction rate of stearic acid*
Figure 4.41 Interaction plot for average reaction rate of palmitic acid

Figure 4.41 shows that the optimal combination for palmitic acid was either the highest catalyst and lowest methanol amount or the medium catalyst level and high methanol level. The low ARR obtained from the low catalyst level was expected.

Figure 4.42 Interaction plot for average reaction rate of oleic acid

Figure 4.42 tells us that, under a low methanol level (solid circle dots), both medium and high levels of catalyst gave the same and the largest ARR. The
difference of ARR between all levels of catalyst under the high methanol usage (oblique squares) is not significant, all kept at the medium level. There seems to be a linear relation between ARR and catalyst levels under the medium methanol amount.

Figure 4.43 Interaction plot for the first order rate constant of stearic acid

Figure 4.44 Interaction plot for the first order rate constant of palmitic acid
We can get similar results from looking at the interaction plots (Figure 4.43, Figure 4.44 and Figure 4.45) for the first order rate constants of each acid as from the main effect plots.

4.3.3 Surface and Contour Plots

By combining surface and contour plots of average reaction rate versus catalyst and methanol, we can more readily and directly draw conclusions as were described in the previous sections.

We can see from Figure 4.46 and Figure 4.47 that a high overall reaction rate was obtained under medium catalyst and medium methanol level for the stearic acid case.
Figure 4.46 Surface plot of average reaction rate of stearic acid versus catalyst and methanol

Figure 4.47 Contour plot of average reaction rate of stearic acid versus catalyst and methanol
Figure 4. 48 Surface plot of average reaction rate of palmitic acid versus catalyst and methanol

Figure 4. 49 Contour plot of average reaction rate of palmitic acid versus catalyst and methanol
Figure 4. 50 Surface plot of average reaction rate of oleic acid versus catalyst and methanol

Figure 4. 51 Contour plot of average reaction rate of oleic acid versus catalyst and methanol

The Surface plot and contour plot of average reaction rate for palmitic acid (Figure 4.48 and Figure 4.49) tell us that either a high level methanol and medium
level catalyst or low level methanol and high level catalyst can give a high average reaction rate.

From Figure 4.50 and Figure 4.51 we can generally determine that, under low methanol usage and high catalyst level, high overall reaction rate can be obtained for oleic acid.

**Figure 4.52 Surface plot of first order rate constant of stearic acid versus catalyst and methanol**

**Figure 4.53 Contour plot of first order rate constant of stearic acid versus catalyst and methanol**
Figure 4. 54 Surface plot of first order rate constant of palmitic acid versus catalyst and methanol

Figure 4. 55 Contour plot of first order rate constant of palmitic acid versus catalyst and methanol
From the surface and contour plots (Figure 4.52 to Figure 4.57) of first order rate constants of every fatty acid, we can readily see that generally, with high
level of catalyst and low level of methanol for stearic acid and palmitic acid, the highest first order rate constant can be obtained. For oleic acid, the optimum combination turned out to be the medium level of catalyst and low level of methanol, to obtain the highest first order rate constant.

From the results summarized above, we can determine that for the esterification reactions carried out by each fatty acid, the catalyst plays the main role in assisting the process of the reaction, while methanol plays a negative effect upon increasing its usage. This may be because increasing the usage of methanol can also dilute the effectiveness of the catalyst.

There were significant differences between the results of first order rate constant and average reaction rate with regard to setting the optimal catalyst and methanol combinations to obtain the highest value for both of them. This is probably because for the average reaction rate, what we focused on was the overall outcome, regardless of how much time and energy consumed. However, the first order rate constant can give us clue of the optimum reaction time to obtain a desirable result.

### 4.4 Supercritical CO₂ Results

The tables below summarize the conversion degrees and average reaction rates obtained by using the supercritical CO₂ method to perform the esterification reaction.

<table>
<thead>
<tr>
<th>Conversion Degree</th>
<th>2 hours</th>
<th>4 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>150%</td>
<td>0.661</td>
<td>0.772</td>
</tr>
<tr>
<td>250%</td>
<td>0.631</td>
<td>0.776</td>
</tr>
<tr>
<td>500%</td>
<td>0.454</td>
<td>0.567</td>
</tr>
</tbody>
</table>

*Table 4. 2 Conversion degrees of esterification reaction under supercritical condition after 2 and 4 hours with different levels of methanol*
<table>
<thead>
<tr>
<th>ARR (mol/mL·h)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>150%</td>
<td>$7.41 \times 10^{-1}$</td>
</tr>
<tr>
<td>250%</td>
<td>$7.94 \times 10^{-1}$</td>
</tr>
<tr>
<td>500%</td>
<td>$5.87 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

**Table 4.3 Average reaction rate of esterification reaction under supercritical condition after 4 hours with different levels of methanol**

From Table 4.2 and Table 4.3 we can determine that under the highest methanol usage, the lowest final conversion degree and average reaction rate were obtained. This probably can be explained by a diluting effect, that is, more methanol being involved in the reaction system can limit the amount of CO$_2$, which performs as the catalyst, to get into the reactor. The medium level of methanol contributed to the highest conversion degree and average reaction rate.

Furthermore, the results of conversion degree and average reaction rate obtained by the supercritical CO$_2$ method were lower than the results obtained by the regular method. This is probably because though the temperature was as high as 150°C, it is still below the critical temperature of methanol (239°C). In other words, the reaction conditions were not truly supercritical.

**4.5 GC/MS Analysis Results**

Figure 4.58 shows the chromatogram of anhydrous isopropanol, which was used as the solvent for samples and fatty acids to carry out the GC/MS analysis. Other chromatograms will all be compared with this single isopropanol one to isolate the peaks of either fatty acids or methyl esters.
Comparing the chromatogram of stearic acid in isopropanol (Figure 4.59) with Figure 4.58 we can see that the peak for stearic acid was not so obvious; just
some weak peaks were found between 10 and 12 minutes. The same situation was found when looking at Figure 4.60 and Figure 4.61, which are chromatograms of palmitic acid and oleic acid in isopropanol.
This behavior was expected, because fatty acids are reactive substances, many of them are too polar to chromatograph desirably (Blau K. and Darbre A., 1993). This is a particularly true in gas chromatography, since free fatty acids tend to tail because of non-specific interaction with the inert support. Associated with this effect, they are also not as volatile as GC requires analysis in the vapor phase. On the other hand, their derivatives such as esters of corresponding fatty acids are less polar, more volatile and can lead to better GC performance. Thus, the most common way to test fatty acids by using GC/MS is to perform esterification preliminarily to make up necessary derivatives of acids, which facilitate the analysis (Liu, K.S., 1994).
Figure 4.62 Chromatogram of methyl stearate in isopropanol

Figure 4.62 is the chromatogram of methyl stearate in isopropanol solvent. We can see that, there is a strong peak between 12 and 13 minutes. By checking its mass spectrum (Figure 4.63), we can confidently claim that it is the peak of methyl stearate (Website 5), which is our aimed product in the esterification of stearic acid.
Figure 4. 63 Mass spectrum of methyl stearate

Figure 4. 64 Chromatogram of methyl palmitate in isopropanol
Figure 4.65 Mass spectrum of methyl palmitate

Figure 4.64 shows the chromatogram of methyl palmitate in isopropanol. At about 12 minutes, there is a peak dominating the whole chromatogram. The mass spectrum of the corresponding peak is shown in Figure 4.65, which is identical with the mass spectrum of methyl palmitate (Website 6).
For methyl oleate, we can recognize a couple of non-ignorable peaks appearing between 11 and 13 minutes (Figure 4.66), among which three of them can be confirmed to be related methyl esters by the software (Website 7). The highest peak represents 13-octadecenoic acid methyl ester (Figure 4.67). The other two smaller peaks are 9-hexadecenoic acid methyl ester and hexadecenoic acid methyl ester, respectively. 13-octadecenoic acid methyl ester and 9-hexadecenoic acid methyl ester both have a double bond in them, which marks that they are fractions of oleic acid itself. The mass spectrums of each methyl ester from oleic acid are shown in Figure 4.67, Figure 4.68 and Figure 4.69.
Figure 4. 67 Mass spectrum of 13-octadecenoic acid, methyl ester

Figure 4. 68 Mass spectrum of 9-hexadecenoic acid, methyl ester
Figure 4. Mass spectrum of hexadecanoic acid, methyl ester
CHAPTER 5

GENERAL CONCLUSIONS

5.1 Summary

In this thesis, esterifications of three fatty acids with methanol were carried out by the acid-catalyzed method. Three different catalyst and methanol levels were selected to undertake these esterification reactions. The progress of these reactions was tracked by off-line acid value testing in terms of the titration method. The conversion degree (yield) and overall reaction rate were calculated in the light of titration results.

All the esterification reactions were performed until they reached a balance. This is the premise of the investigation of the average reaction rate. The statistical analysis of the average reaction rates obtained by every combination of catalyst and methanol, for each fatty acid, shows that there is no significant difference between them. This is probably due to the large premise, since every reaction was carried out to the extent that it does not proceed any more, there was no specific time being set up. Generally, the combined effect of catalyst and methanol on the average reaction was complex. There is no constant result between these fatty acids.

The optimum catalyst and methanol combination for each fatty acid were obtained:

For stearic acid, with the medium catalyst and medium methanol amount introduced into the system, the highest ARR was achieved.

The optimal combination for palmitic acid was either the highest catalyst and lowest methanol amount or the medium catalyst level and high methanol
Under the low methanol level, both medium and high level of catalyst gave the largest ARR for oleic acid.

5.2 Recommendations

To magnify the effect of different catalyst and methanol combinations on the yield or average reaction rate, a specified time should be set up before each reaction, say, to keep every reaction going for the same period.

Effort should be made to better control the consistency of the temperature for each reaction trial, since it is also a key factor that influence the kinetics of reaction.

Replication of each reaction is recommended if time is not an issue, to better perform the statistical analysis of the results by a sound analysis model.

A scaled up esterification reaction study is necessary to give better reference to industry manufacturing. A continuous process system is also suggested to study the suitability and practical capability for industrial purposes.
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