Catalyst studies with implications on the design and fabrication of microreactors

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Catalyst Studies with Implications on the Design and Fabrication of Microreactors

By
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Departmental Thesis
The University of Tennessee at Chattanooga
Department of Chemical Engineering

Project Director: Dr. Frank Jones
Examination Date: 3/21/2012

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<td>American Society for Testing and Materials</td>
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<tr>
<td>CBG</td>
<td>Chemically Bound Glycerin</td>
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<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>FAEE</td>
<td>Fatty Acid Ethyl Esters or Biodiesel (from ethanol not methanol)</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty Acid Methyl Ester or Biodiesel</td>
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<td>FFA</td>
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</tr>
<tr>
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<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph (or Chromatography)</td>
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<td>H₂SO₄</td>
<td>Sulfuric Acid</td>
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<tr>
<td>KOH</td>
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<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MSTFA</td>
<td>N-Methyl-N-(trimethylsilyl) trifluoroacetamide</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>NFPA</td>
<td>National Fire Protection Association</td>
</tr>
<tr>
<td>NiO</td>
<td>Nickel (II) Oxide</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>PtO₂</td>
<td>Platinum (IV) Oxide</td>
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<td>SBO</td>
<td>Soybean Oil, a triglyceride feed</td>
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1.0 Abstract:

Biodiesel, or fatty acid methyl ester (FAME), is a potential alternative, renewable fuel source to lessen foreign fuel dependency. Dr. Frank Jones' microreactor research group is investigating the use of microreactors to produce biodiesel. Microreactors can increase reaction rates, heat transfer, and lessen production costs due to their small size. The first generation of microreactors, coated with a nickel oxide (NiO) catalyst, has been developed and needs to be tested to determine their performance. Also, a catalyst study comparing NiO and platinum oxide (PtO₂) will be performed to find the better catalyst for FAME production.

Reactions with PtO₂ and NiO were performed at room temperature and methanol's reflux point (65°C) using free fatty acid (FFA) and soybean oil (SBO) feedstocks. It was found that PtO₂ could reach 40 percent conversion to FAME at room temperature with FFA but at higher temperature the catalyst was permanently altered and underwent side reactions. NiO did not react well with FFA at either temperature tested but performed well with SBO at 65°C proving it is the best catalyst for FAME production and for the microreactor system.

The first generation of microreactors was tested and conversions in stirred reactors that took hours were matched in minutes or seconds in the microreaction system. The microreactors perform at least 64 times quicker than conventional reaction methods proving the microreactors can be used for FAME production and reach higher conversion quicker than conventional reaction methods.
2.0 Introduction

In today’s world, alternative fuels are needed more than ever. Conventional fuels, such as coal, natural gas, and fossil fuel, are constantly being depleted; however, the world’s dependency on these fuels is still growing. Additionally, the price on foreign fuels is ever increasing. For these reasons, the United States and the world are pursuing alternative fuel sources to lessen the dependency on conventional fuels.

One such alternative fuel source currently being investigated is biodiesel. Biodiesel can be produced from vegetable oil or animal fat and thus can be used to alleviate the foreign fuel dependency. Before becoming a viable alternative fuel, however, the production cost must be less than foreign fuel costs. Research on a variety of feedstock oils, catalysts, and reactor types is under development to determine how to lessen processing costs.

Frank Jones’ microreactor research group is focused on the use of microfluidic technology for biodiesel production. Microreactors take a small volume of chemicals through micro-channels in order to speed up the processing time. By doing this, the research group hopes to develop a means of creating biodiesel purer and cheaper. The first objective of the research performed was to test the performance of the first generation of microreactors in producing biodiesel.

Current first generation microreactors have micro-channels coated with a nickel oxide (NiO) catalyst to increase reaction rates and lower activation energy. NiO is classified as a heterogeneous catalyst since it remains in a different phase,
solid, than the reactants, liquid, used in biodiesel production. There are many other
catalysts that could potentially be used to further increase reaction rates and lower
activation energy which will potentially further lessen biodiesel processing costs in
the microreactor system. One such catalyst currently being looked at is platinum (IV)
oxide (PtO$_2$). The second objective was to conduct a catalyst study of NiO and PtO$_2$
at different temperatures to determine which catalyst is most effective in biodiesel
production for future microreactors.

3.0 Background Information

3.1 Biodiesel Description

Fatty acid methyl ester (FAME), better known as biodiesel, is an alternative fuel that can be produced from non-fossil oil or animal fat; the chemical structure of a FAME molecule is shown in Figure 1.

![Chemical structure of a fatty acid methyl ester molecule](image)

Figure 1: Chemical structure of a fatty acid methyl ester molecule\(^1\)

A fatty acid chain on an oil molecule, such as oleic acid, reacts with an alcohol, such as methanol, to produce a FAME molecule. Similarly, ethanol can be used instead of methanol to produce biodiesel but fatty acid ethyl esters, FAEE, not FAME are produced. The fatty acid length varies based on feed oil used but normal chain lengths are 16 to 18 carbons.\(^2\) In comparison to traditional diesel molecules, biodiesel varies in chemical structure; an average diesel molecule’s chemical structure is shown below in Figure 2.
As shown in Figure 2, diesel is made of hydrocarbons and, thus, is lacking the ester and carbonyl oxygen groups found in biodiesel. Due to these structural differences, biodiesel and traditional diesel each have advantages and disadvantages for use as a fuel source. First, when looking at the entire carbon life cycle for both fuels vast differences can be seen. Carbon dioxide (CO₂) is a product from either fuels' combustion reactions which is a key greenhouse gas emission. However, biodiesel consumes almost as much carbon dioxide as it produces when burnt. Since the oil to make FAME is derived from plants, CO₂ is consumed by the plants while growing. Taking this into account, biodiesel, if it were to replace diesel, reduces CO₂ emissions by 78%. Also, the tailpipe emissions after combustion for biodiesel differ in many regards from diesel as shown in Figure 3.
The unburned fuel, carbon monoxide, and particulate matter substantially decrease in biodiesel combustion. Since biodiesel is an oxygenated fuel it burns more completely which is the main reason for these lower emissions. Lastly, due to the differences in chemical structure, biodiesel gels at higher temperatures than petroleum based diesel which is a significant disadvantage for biodiesel in the winter months or cold climates.4

3.2 Potential Feedstocks

Biodiesel is produced from non-fossil oils, primarily vegetable oils. Non-fossil oils (also known as triglycerides or lipids) are organic molecules found throughout any plant cell. The oil can be harvested or extracted from cells for use as a biodiesel feedstock. The most common triglyceride feedstock is soybean oil whose general structure is shown below in Figure 4.

\[
\begin{align*}
&\text{CH}_2 - \text{OOC} - \text{R} \\
&\text{CH} - \text{OOC} - \text{R'} \\
&\text{CH}_2 - \text{OOC} - \text{R''}
\end{align*}
\]

**Figure 4: Triglyceride chemical structure** 5

A triglyceride molecule is comprised of three fatty acid R-groups attached to a glycerol backbone. The fatty acid chains vary from R-group to R-group but average fatty acid compositions can be obtained for different non-fossil oil sources. For example, the composition of soybean oil R-groups is shown below in Table 1.
Table 1: Soybean Oil Fatty Acid Composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fatty Acid Name</th>
<th>Carbon Chain Length</th>
<th>Number of Double Bonds</th>
</tr>
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<tr>
<td>7%</td>
<td>Alpha-Linoleic Acid</td>
<td>18</td>
<td>3</td>
</tr>
<tr>
<td>54%</td>
<td>Linoleic Acid</td>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>24%</td>
<td>Oleic Acid</td>
<td>18</td>
<td>1</td>
</tr>
<tr>
<td>4%</td>
<td>Stearic Acid</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td>11%</td>
<td>Palmitic Acid</td>
<td>16</td>
<td>0</td>
</tr>
</tbody>
</table>

Linoleic acid and oleic acid make up the bulk of fatty acid groups in soybean oil molecules. Oleic acid, shown in Figure 5, is 18 carbons in length and has one double bond; linoleic acid is similar to this but with two double bonds.

![Oleic acid chemical structure](image)

Figure 5: Oleic acid chemical structure

When oils are heated up, such as during cooking, the fatty acid chains are susceptible to breaking off, leading to free fatty acids. One key advantage of biodiesel is the ability to use waste cooking oil as a potential feedstock. Not only can the triglycerides react but the free fatty acids that break off are able to react in certain conditions to produce biodiesel. This potential feedstock is cheaper than new oil feeds and can use waste that usually ends up in landfills.

Another potential feedstock is algae oil. Algae oil has been a main focus for many research efforts over the last couple of decades because it is not primarily used as food, can be grown quickly, and does not require much area to grow. Algae-based biodiesel is still early in development and there are still issues on efficiently lysing, or
extracting, the oil from the cells. While a means of efficiently extracting oil has not been developed, many believe that algae oil could be the answer to lessening the world’s dependency on fossil fuels. Other researchers in the research group are specifically working with algae to determine the best means for oil extraction.

### 3.3 Biodiesel Production

Biodiesel or FAME is produced mainly from a reaction between a triglyceride feed and methanol; this reaction is called transesterification, and it is diagrammed in Figure 6.

\[
\begin{align*}
R_1 COOCH_2 & \quad HOC_2H_2 & \quad R_1 COOCH_3 \\
R_2 COOCH_2 + 3CH_3OH & \xrightarrow{K_1} HOC_2H & \xrightarrow{K_2} R_2 COOCH_3 \\
R_3 COOCH_2 & \xrightarrow{CH_2} HOC_2H & \xrightarrow{CH_2} R_3 COOCH_3
\end{align*}
\]

**Figure 6: Overall Transesterification reaction of triglyceride and methanol**

Three methanol molecules react with a triglyceride molecule to produce glycerol and three FAME molecules. The glycerol product can also be sold for profit since it is widely used in pharmaceutical and food industries. This reaction shown is actually a net equation of three reactions that breaks down the triglyceride first into a diglyceride(1) then a monoglyceride (2) and finally into glycerin (3). Each of these three reactions requires a methanol and each produces a FAME molecule which yields the net equation shown in Figure 6. The detailed reactions just described are diagrammed in Figure 7.
Figure 7: Detailed transesterification reactions of soybean oil and methanol

Free fatty acids which are found in waste cooking oil and low grade oil feedstocks are also capable of reacting with methanol to produce FAME. This reaction is called an esterification reaction and is diagrammed in Figure 8.

Figure 8: Esterification reaction of free fatty acid and methanol
Similar to a transesterification reaction, free fatty acid reacts with methanol to produce FAME and water instead of glycerol. Catalysts are required to enable both of these reactions to happen in a timely manner. Ideally, a catalyst able to equally convert free fatty acids and triglycerides to FAME needs to be established.

3.4 Catalyst Types

There are two main classes of catalysts used in most applications, homogeneous and heterogeneous, both of which can be broken into subcategories, acidic and basic. Homogeneous catalysts are in the same phase as the reactants, which for biodiesel reactions means they are liquid. Liquid catalysts for biodiesel production are the traditional approach that has been used for years, but they have their drawbacks. By being in the same phase, homogeneous catalysts allow for high catalyst to reactant contact which leads to quicker reaction rates. However, being in the same phase makes recycling of catalyst difficult and purification of products expensive. The most commonly used liquid catalysts are sodium hydroxide (NaOH) and potassium hydroxide (KOH) which are classified as basic catalysts based on how they interact with reactants in the transesterification mechanism. Base catalysts accept protons (H⁺) to initiate the reaction; for transesterification reactions, it is generally accepted that the base catalysts reacts with methanol (CH₃OH) accepting an H⁺ leaving a catalytically active CH₃O⁻ which reacts with triglycerides forming the FAME molecules (the entire mechanism is shown in Figure 9). ¹¹
The key problem with base homogeneous catalysis is when they are used with high free fatty acid feeds, such as waste cooking oil or low grade oil. Liquid base catalysts react with fatty acids in a secondary, non-catalytic way known as saponification; the reaction is diagrammed below in Figure 10. This reaction does not
form FAME but instead results in soap molecules which lead to pricey separation and purification, loss of free fatty acid feed, and bad use of catalyst.

\[
\text{H-O-C-R}_1 + \text{XOH} \rightarrow \text{X-O-C-R}_1 + \text{H}_2\text{O}
\]

**Free Fatty Acid**  **Base**  **Soap**  **Water**

*Figure 10: Saponification of fatty acids and bases*¹²

To alleviate the saponification problem, homogeneous acid catalysts, such as sulfuric acid (H₂SO₄), have been used. As an acid catalyst, the generally accepted mechanism involves donating protons (H⁺) to the carbonyl groups on the triglyceride molecules to allow the alcohol to react to form FAME; the entire mechanism is shown in Figure 11.¹¹ Unlike base catalysts, acid catalysts will not undergo saponification with free fatty acids which allows lower quality feeds to be used. However, liquid acid catalyzed reactions proceed over three times slower than base catalyzed reactions.¹¹
The other main category of catalysts used is heterogeneous or solid catalysts. These remain in a different phase from the reactants which change the dynamics of the reaction. Due to the phase boundaries, reactions involving heterogeneous catalysts take longer to react and require higher temperatures when compared to homogeneous
catalysts. However, no soap formation occurs when solid catalysts are used since no saponification is possible. Also, the catalyst can be recycled by being anchored inside of the reactor, therefore, eliminating even more separation costs. For these reasons, research is being conducted on heterogeneous catalysis to determine if they are an economically more feasible option when compared to their homogeneous equivalent.

For this research effort, two heterogeneous catalysts will be used: nickel (II) oxide (or NiO) and platinum (IV) oxide (PtO₂). NiO is a potential heterogeneous basic catalyst while PtO₂ is a potential heterogeneous acid catalyst. A catalyst study of these two potential solid catalysts makes up a primary objective of the work performed in this research effort. Final results from this study will be used in implementation into microfluidic reactors.

3.5 Microreactors

Microreactors are a novel approach to biodiesel production. Microreactors take a small volume of reactants through micro-channels in order to speed up the reaction rate or residence time. Processing time can be sped up primarily due to diffusion time advantages that microreactors have over conventional reaction methods. The equation for calculating diffusion time is shown below.

\[ t_D = \frac{l^2}{D} \]  

Where \( t_D \) = diffusion time (s), \( l \) = maximum diffusion length (m), and \( D \) = Diffusivity \((1 \times 10^{-9} \, \text{m}^2/\text{s})\).
Diffusion time is the time required for a molecule to traverse to a reactive surface which is usually a reactor wall. Previous work performed by the research group was performed in stainless steel high pressure vials which have a diameter of 6 mm. The maximum diffusion length in this case is the distance from the center to the reactor wall or 3 mm. This diffusion time in the conventional stainless steel reactor is approximately 2.5 hours. Microreactors used in the research project had dimensions of 50µm deep by 500 µm wide. This means that the maximum possible diffusion length is 50 µm (since the top glass on the microreactors is not sputtered with any catalyst). This results in a diffusion time of approximately 2.5 seconds. Quicker diffusion will speed up the processing time which in turn means cheaper operating costs. Microreactors are also an improvement over conventional methods due to heat transfer. The small size and liquid volume in a microfluidic device provides an ideal environment for optimum heat transfer.

Microreactors are manufactured by many processes, but the main approach is chemical etching. A pattern is etched on the surface of the substrate (usually silicon, glass, or ceramic). The designed pattern can be of any shape and size but most common channel designs are serpentine, as seen in Figure 12, or straight. Microreactors used in this research project are etched on a silicon surface. NiO is sputtered on the etched microchannels and a glass plate is adhered to the silicon wafer.
Before microreactors were fabricated, computational studies were performed to determine what design specifications were needed to convert feed oil to biodiesel. The software used to conduct these simulations was ESI-ACE+ Computational Fluid Dynamics (CFD). A microreactor channel grid was developed using ESI-ACE+ for a variety of cross section dimensions. This computational grid, as shown in Figure 13, simulates how an actual reaction will behave inside a manufactured microreactor, Figure 14.

From this study, the effect of flow rates, cross sectional area, and length on conversion, pressure drops, and residence time was determined. The ESI-ACE+ software was able to show how conversion to biodiesel from a feed oil and methanol changes as the fluid flows through the microreactor. An example simulation is shown below in Figure 15 which shows how biodiesel concentration increases through a micro-channel. Final results from this computational study are tabulated in Table 2.
Figure 13: A computational microreactor channel grid constructed using ESI-ACE+ Software. The channel cross section is 100 µm x 100 µm, about the size of a human hair. This computational grid simulates actual channels as shown in figure 2.\textsuperscript{14}

Figure 14: A Scanning Electron Micrograph (SEM) of a 500 µm x 125µm x 500mm biomicroreactor channel fabricated using a silicon plastic.\textsuperscript{14,15}
Figure 15: A biodiesel (FAME) molar concentration field at the entry of the channel for a 100 µm x 100 µm cross section channel with a total length of 1 cm. The fluid residence time is 6 seconds. Conversion to FAME at the end of the channel is 99.98%.14

Table 2: Comparison of Reactor Performances for different flow rates, lengths, and cross sectional areas.14

<table>
<thead>
<tr>
<th>Cross Section</th>
<th>Residence Time</th>
<th>Reynolds #</th>
<th>Flow Rate (m³/s)</th>
<th>Length (mm)</th>
<th>ΔP (kPa)</th>
<th>Conv (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50µm x 50µm</td>
<td>60</td>
<td>0.000006</td>
<td>4.17 x 10⁻¹³</td>
<td>0.075</td>
<td>185</td>
<td>97.3</td>
</tr>
<tr>
<td>100µm x 100µm</td>
<td>60</td>
<td>0.00001</td>
<td>1.67 x 10⁻¹²</td>
<td>0.2</td>
<td>46.5</td>
<td>96.3</td>
</tr>
<tr>
<td>50µm x 500µm</td>
<td>300</td>
<td>0.000006</td>
<td>4.17 x 10⁻¹³</td>
<td>0.2</td>
<td>83</td>
<td>94.8</td>
</tr>
<tr>
<td>50µm x 50µm</td>
<td>6</td>
<td>0.00006</td>
<td>4.17 x 10⁻¹²</td>
<td>0.45</td>
<td>1850</td>
<td>95.7</td>
</tr>
<tr>
<td>100µm x 100µm</td>
<td>6</td>
<td>0.0001</td>
<td>1.67 x 10⁻¹¹</td>
<td>1.2</td>
<td>464.9</td>
<td>96.3</td>
</tr>
<tr>
<td>10µm x 500µm</td>
<td>6</td>
<td>0.00015</td>
<td>8.34 x 10⁻¹²</td>
<td>0.25</td>
<td>253</td>
<td>99.7</td>
</tr>
<tr>
<td>50µm x 500µm</td>
<td>6</td>
<td>0.00006</td>
<td>4.17 x 10⁻¹²</td>
<td>1.8</td>
<td>165</td>
<td>95.5</td>
</tr>
</tbody>
</table>
The first generation of microreactors was fabricated using a cross sectional area of 50 µm x 500 µm. From Table 2, it is evident that in as short as 0.2 mm in length, conversions were simulated at nearly 95%. For ease of fabrication, straight channel reactors with a length of 3 cm were chosen. Serpentine reactors were fabricated on similar silicon wafers but the wavy-flow on the wafer resulted in a nominal length of 15 cm. Each reactor has two entrance ports (one for methanol and one for an oil feed) as well as a single exit port, NiO catalyst sputtered on the etched microchannel on the silicon wafer, and a glass plate adhered to the top. Example microreactors used in this project are shown in Figure 16 and 17.

Figure 16: Serpentine microreactor used in this research project

Figure 17: Straight flow microreactor used in this research project
The research group’s overall goal for microreactors is an entire microreaction system that can be used commercially to produce large quantities of biodiesel. This can be done by placing hundreds of thousands of microreactors inside a computer sized tower, which would be able to produce hundreds of liters per day. This setup would be ideal for a small business such as a gas station to own since they could produce their own biodiesel for consumers on site, lessening their foreign fuel dependency. Farms and restaurants with potential feedstock oils (vegetable oils and waste cooking oils, respectively) being produced would also be ideal applications for these microreactor systems as well.
4.0 Methodology

4.1 Measuring Viscosity

Viscosities of soybean oil (SBO), free fatty acids (tall oil), methanol (MeOH), and various mixtures of these three components were experimentally determined using the Gilmont Falling Ball Viscometer. The viscometer, shown in Figure 18, is used to measure the descent time of a small sphere (made of stainless steel, tantalum, or glass) in the fluid whose viscosity needs to be determined. Knowing this descent time, the viscosity is calculated with the following 16:

\[ \mu = K(\rho_f - \rho)t \]  

Where, \( \mu \) is the viscosity (centipoise), \( \rho_f \) is the density of the ball (g/mL), \( \rho \) is the density of the fluid (g/mL), \( K \) is the viscometer constant, and \( t \) is the time of descent (minutes). The Viscometer constant depends on the device being used; for all experiments, tube size number 2 was used which corresponds to a constant of 3.3.

![Figure 18: Gilmont Falling Ball Viscometer with Glass Sphere](image)

**Procedure:**

1) Prepare the fluid to be measured in a small beaker or graduated cylinder; approximately 5 ml of liquid is required for the Gilmont tube.

2) Add the mixture to the Gilmont tube until ¼ inches is without fluid. This space will be taken up by the cap and the sphere.
3) Select the appropriate ball and drop it in the viscometer. There are three different ball types, each only valid for a range of viscosities as shown below in Table 3.

<table>
<thead>
<tr>
<th>Table 3: Viscosity Range for Each Sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
</tr>
<tr>
<td>Viscosity Range (Centipoise)</td>
</tr>
</tbody>
</table>

4) Remove the top cap of the lid assembly to allow the air to evacuate the Gilmont tube while closing the lid. Tighten the lid on the tube and place the top cap back on to ensure no liquid escapes.

5) Readings are taken by turning the tube upside down and recording the time required for the ball to fall between the red markings on the Gilmont tube as shown in Figure 18.

6) A Polystat Immersion Circulator was used for heating the Gilmont tube to the temperature the measurement is to be taken. Once the temperature bath is up to the desired temperature, place the Gilmont tube in the bath. The entire setup is diagrammed below in Figure 19.
7) Since the Gilmont apparatus needs to remain closed, the temperature in the tube cannot be taken to see if it is up to temperature. It was experimentally determined that two minutes is needed for the tube and the liquid (soybean oil was tested) inside to rise in temperature from 20°C to 40°C. Since methanol has a slightly higher specific heat and at higher temperatures heat losses will be greater it is assumed that five minutes is sufficient time to heat the mixtures.

8) After five minutes, remove the tube from the bath and quickly measure the descent time.
4.2 Miscibility Testing

For miscibility testing, samples were prepared at different molar ratios of reactants and potential products to determine if certain mixtures would remain in one phase or whether they separated out. Separation of phases can be a slow process, so, in order to speed up the separation time, a centrifuge was used; a Hermle Z206A centrifuge was used for all miscibility testing shown below in Figure 20. For all miscibility testing, the following procedure was used.

![Figure 20: Hermle Z206A Centrifuge](image)

1) Desired molar ratios need to be converted to volumetric ratios. For this research effort, reactant mixtures (methanol, free fatty acids, and soybean oil)
and reactant/product mixtures (methanol, soybean oil, glycerol, and FAME) were solely investigated.

2) Samples should be prepped following volumetric ratios into 15mL centrifuge tubes, shown in Figure 21. The volume in each tube is irrelevant as long as an equal volume is added to each tube. To better see phase separations, volumes greater than 10 mL were used.

3) Once the samples are prepped in the tubes, they can be added to the rotor in the centrifuge, shown in Figure 22. To keep the centrifuge balanced, tubes of equal volume must be added evenly to equally distribute the weight.

4) Centrifuge trials were run at speeds of up to 4500 revolutions per minute and for 2 minutes.

5) After, the centrifuge has stopped spinning, the samples can be removed (slowly and upright so as to avoid any unwanted mixing). The tubes should then be observed to see if any phase separation has occurred.
Different reaction products and reactant ratios were examined to determine if certain ratios remain in one phase. Due to the creeping flow (Reynolds numbers much less than one) behavior in microfluidic channels, any phase separation could potentially greatly inhibit or even stop a reaction from taking place. If mixtures can be determined where only one phase remains, boundaries can be overcome to potentially help make microreactors a more viable option for biodiesel production.
4.3 Stirred Tank Reactor Setup

A catalyst comparison was performed between nickel oxide and platinum oxide at room temperature and methanol's boiling point, approximately 65°C. All experiments were performed using stirred tank reactors. An EchoTherm Programmable Multiposition Stirring Hot Plates was used to perform five reactions at the same time for both room temperature and reflux work. For room temperature work, 25 mL volumetric flasks were used for all reactions. Since methanol is present at very low vapor pressures, the volumetric flasks are capped throughout all trials. One centimeter in length Teflon coated stir bars are inserted into each flask and the stirring hot plate is set at 800 RPM. The room temperature reactor setup is shown below in Figure 23. Different oil to methanol ratios, catalyst weight percent, and residence times were investigated using this setup.

Figure 23: Room Temperature Stirred Tank Setup
Similarly, comparisons were attempted at methanol's boiling point. The same stirring hot plate was used, but 25 mL round bottom flasks with reflux columns were used instead of simply volumetric flasks. At methanol's reflux point, methanol is constantly vaporizing, so, as a result, a water-jacketed reflux column condenses methanol vapor back into the flask. Due to lab limitations, each of five water jackets is in chain with the same water source instead of each with their own water source. It was experimentally determined that quick enough water flows are able to be achieved to sufficiently cool all methanol vapor in each condenser. Flasks are placed in hot water baths at approximately 75°C to make sure methanol stays at reflux throughout. One centimeter in length Teflon coated stir bars are inserted into each flask and the stirring hot plate is set at 800 RPM. The reflux reactor setup is shown below in Figure 24.

![Reflex reactor setup used in catalyst comparison](image)

Figure 24: Reflux reactor setup used in catalyst comparison
4.4 Microreactor Experimental Setup

The first generation of microreactors was tested at a variety of flow rates and temperatures to determine their effectiveness at biodiesel production. Microreactors can only handle ultralow flow rates, so, in order to provide these flow rates, a syringe pump is used. A Cole-Parmer® Touch-Screen Syringe Pump, which is able to deliver flows as low as five picoliters per minute to the microcontroller, is used in all microreactor work. For this project, flows between 250 nanoliters/minute and 2 microliters/minute were mainly tested.

Different temperatures were also tested in the microreactors. Heat was provided to the microreactor via a Minco resistance heater, shown in Figure 25. Power is provided to the resistance heater at different voltages which results in different temperature outputs from the resistance heater. This method was used to result in temperatures up to methanol’s boiling point in the microreactor system. The entire microreactor system is diagrammed in Figure 25.
Figure 25: The top photo, read from left to right, shows the experimental setup. A syringe pump injects the reactants into the microreactor; the products exit and are stored. The middle photo is a close-up of the microreactor. Channel dimensions are 50 microns deep x 500 microns wide x nominal length of 15 centimeters. The reactants enter as two streams on the left and the biodiesel and glycerin products exit as one stream on the right. The bottom image is the on-platform heating system underneath the microreactor.
4.5 Purification Process

Before samples can be analyzed, catalyst and methanol must be removed from the unreacted oil and products. First step to purifying any sample is the removal of the catalyst. For microreactor samples, this is not required since catalyst remains in the reactor throughout. Catalyst needs to be removed as quickly as possible for room temperature work since any catalyst-reactant exposure adds to the potential reaction time. When using free fatty acid as a feed, simple gravity filtration through filter paper is sufficient. However, when soybean oil feeds are used, gravity filtration cannot be used. This is due to the larger molecular size of soybean oil making it more difficult to filter. As a result, syringe filters were used so as to allow forced filtration rather than just gravity. A picture of a syringe filter used is shown below in Figure 25.

![Figure 26: Syringe filter used for soybean oil purification](image)

After catalyst is removed, methanol also needs to be separated out of the sample. Due to the great boiling point difference between methanol and the oil feed and products formed, methanol can be flashed out of samples at temperature above
65°C. When methanol is fully removed, samples will stop boiling and are then ready for analysis. It is important to remove samples shortly after boiling ceases since samples are capable of burning if left heated too long which may be a factor in analytic results.
4.6 Acid Number Analysis

When using free fatty acid (FFA) as the feedstock while making biodiesel, acid number can be used to determine the conversion to product. This acid number analysis takes advantage of the FFA’s acidic nature by using simple acid-base neutralization. In accordance with American Society for Testing and Materials (ASTM) D974, potassium hydroxide, KOH, with a normality of 0.1000N was used for neutralizing FFA samples.\(^1\) Neutralization of the FFA was noted with a p-Naphtholbenzein indicator. A known amount of analyte, products and unreacted FFA, are added to the titration solvent (100:1:99 toluene: water: isopropyl alcohol volume per volume solution) before the KOH is used for neutralization. From neutralizing the FFA, the acid number can be determined which is defined as:

\[
\text{Acid Number} = \frac{\text{mg KOH}}{\text{g Analyte}}
\]  

[3]

This acid number in previous research efforts has been related to reaction conversion by use of a calibration curve which was constructed using mixtures of FFA and biodiesel in ratios equivalent to different conversions. Conversion is defined as follows:

\[
\text{Percent Conversion} = \frac{\text{mol}_{\text{FFA initial}} - \text{mol}_{\text{FFA final}}}{\text{mol}_{\text{FFA initial}}} \times 100\%
\]  

[4]

A previous researcher for the group constructed the calibration curve as shown in Figure 27.\(^10\) This calibration was fit to a linear trendline and the linear equation can be used to compare acid number to conversion.
Acid Number Calibration for Free Fatty Acid

\[ y = -0.0047x + 0.9957 \]
\[ R^2 = 0.9987 \]

Figure 27: Acid Number vs. Conversion Calibration

The calibration curve, however, did not match NMR, nuclear magnetic resonance, spectroscopy results which were performed on some of the FFA samples. It is not entirely clear as to why there is a deviation between the two analytical techniques but the difference was significant. As a result, a different approach was used for acid number analysis used in this research project.

A direct comparison between an original feed solution was compared to each sample. In other words a non-reacted 24:1 (methanol: FFA molar ratio) was analyzed using acid number. After reaction is complete a 24:1 sample’s acid number is also determined. This leads to the following equation for determining acid number.

\[
\% \text{ Conversion} = \frac{(\text{Non-Reacted Acid #} - \text{Sample Acid #})}{\text{Non Reacted Acid #}} \times 100\% \quad [5]
\]
This equation was used for determining conversion in all free fatty acid samples. The procedure for running acid number analysis is as follows:

1. Measure and record a known amount of sample into a 250 mL Erlenmeyer flask. (usually between .10 grams and .50 grams)
2. To the flask add 50mL of titration solvent
   (100:99:1 volume ratio of toluene: isopropyl alcohol: water)
3. To the flask add 0.5 mL of titration indicator (a solution of 10g p-Naphtholbenzein/1 Liter of titration solvent). Sample should be orange color after adding pH indicator; color is shown below in Figure 28.
4. To the flask, add potassium hydroxide (KOH .1000N) slowly until blue-green color change is evident. Color change is shown below in Figure 29. Record the mL of KOH required to reach this color change.
5. Determine mass of KOH added using the following equation:
   \[
   \text{Mass KOH (mg)} = (\text{mL KOH added}) \times 0.1000N \times \text{Molecular Weight KOH} \quad [6]
   \]
6. Determine the Acid Number using the following equation:
   \[
   \text{Acid Number} = \frac{\text{Mass KOH (mg)}}{\text{grams of sample added}} \quad [7]
   \]
4.7 Gas Chromatography

Acid number analysis is only a valid analysis technique for free fatty acid feeds. This is because titrations measure the acidity of the fatty acids but triglyceride or oil feeds are not acidic; thus, a different analytical analysis is required. One method for analyzing conversion can be done via gas chromatography. Gas chromatography involves separating the components in a reaction mixture based on their volatility. The oven on the gas chromatographer (GC) is heated as the sample is injected. Over time, the samples travel through the capillary column, carried by an inert gas (usually helium). The smaller, more volatile components leave the column quicker than larger, less volatile components. This allows nearly pure component to leave the oven which are quantified via flame ionization detector (FID).

Details for properly setting up a GC for triglyceride analysis can be found in ASTM D6584. For this research effort, a SRI 8610C GC was used, equipped with a MXT-Biodiesel TG column (15m in length and .32mm in inner diameter). The GC setup is shown below in Figure 30. Procedure for running samples through the GC is as follows:
1. Measure out approximately .10 grams of sample to be analyzed after purification (no catalyst or methanol) in an 8 mL vial.

2. To this vial, add 100 µL of N-Methyl-N-(trimethylsilyl) trifluoroacetamide (more commonly known as MSTFA). MSTFA is a silylation derivitization reagent. Certain organic groups, such as carboxylic acid, amine, thiol, and hydroxyl groups, are known to cause problems when the GC is separating components. MSTFA causes these groups to be replaced by an alkylsilyl group, such as -SiMe3. This makes compounds with these organic groups more stable and less volatile, helping improve GC analysis.24

3. After 15 to 20 minutes, add approximately 8 ml of n-Heptane to the vial.
4. Measure 1µL of an internal standard solution (50µL Butanetriol and 50µL of Tricaprin derivitized and diluted with n-Heptane) and 1 µL of the prepared solution and inject into the GC.

5. The GC analysis can be performed now after turning on the helium, hydrogen, and compressed air gasses which are needed for inert or carrier gas and FID.

6. Using the Peak Simple software on adjacent computer, analysis can be started. Parameters for performing the analysis are found in ASTM D6584.

A sample analysis is shown in Figure 30 should be seen. The glycerol, FAME, monoglycerides, diglycerides, and triglycerides peaks show up at different retention times as seen in Figure 31.

![Figure 31: Example GC result screen with average retention times for each component](image)
Conversion of biodiesel is not measured directly but instead by the loss of chemically bound glycerin (CBG). Total CBG is determined as follows:\textsuperscript{22}

\[ CBG = \text{Area of Triglycerides + Diglycerides + Monoglycerides} / (\text{Tricaprin})[8] \]

Using stoichiometric ratios, solutions equivalent to 0%, 20%, 40%, 60%, 80%, and 100% conversion from SBO to FAME were prepared, a CBG calibration curve was developed that allows conversion to FAME to be measured from GC analysis; Figure 32 represents the constructed calibration curve.

\[ y = -0.0079x + 1.0402 \]
\[ R^2 = 0.9935 \]

Figure 32: GC calibration curve used for determining FAME conversion from disappearance of CBG
4.8 Chemicals Used

4.8.1 Feedstock Chemicals

Three different chemicals comprised all feed options used in this research effort: free fatty acid, soybean oil, and methanol. The free fatty acid, or tall oil, used was received from MeadWestvaco, a producer of various paper products. For all experiments, L-1 free fatty acid was used and it is composed primarily of the fatty acid oleic acid. Oleic acid, diagrammed in Figure 4, is a monounsaturated, 18-carbon chain fatty acid. The L-1 name refers to the rosin acid impurity. L-1 designates that less than one percent rosin acids are found in the free fatty acid. The rosin acid found in the free fatty acid feedstock is primarily abietic acid as show in Figure 33.

![Abietic acid molecular structure](image)

**Figure 33: Abietic acid molecular structure**

Rosin acids are wood preservatives naturally produced by wood and are extracted during the paper production process. The effects of the rosin acid on biodiesel production are unclear.

For a soybean oil feed, 100% vegetable oil was purchased at local grocery stores. Readily available vegetable oil is comprised of pure soybean oil and was used
for all SBO experiments. Methanol was purchased from Fisher Scientific and has .004% water content.

4.8.2 Catalysts

Nickel oxide and platinum oxide were the only two catalysts used in this research effort. For both catalysts, nanopowder was used meaning the particle size for each solid catalyst is on the order of magnitude of nanometers. Both catalysts were purchased from Sigma Aldrich. According to the manufacturer, the nickel (II) oxide powder has a particle size of less than 50 nm. The powder is comprised of three main crystal structures, (111), (200), and (220), as shown below in the following X-ray diffraction scan. It is unclear what effect crystal structures have on conversion to biodiesel.

![X-ray Diffraction scan of Nickel Oxide Catalyst Used](image)

Figure 34: X-ray Diffraction scan of Nickel Oxide Catalyst Used
The platinum (IV) oxide nanopowder did not specify crystal structures or powder size, but instead surface area. The PtO₂ catalyst has a surface area of 60m² per gram of powder. It is unclear what the particle size is for this catalyst, but, from experimental observations, the particle size seems to be smaller than the nickel oxide powder. This is based on the differences in powder fluidity.
5.0 Results

5.1 Viscosity Testing

In order to determine the viscosity of solutions entering into the microreactors, different mixtures of FFA, SBO, and MeOH were tested to see how the viscosity changes. Mixtures were tested at 20°C, 40°C, 60°C, and 80°C using a falling ball viscometer. If methanol was present in the mixture, 60°C was the testing limit because MeOH has a normal boiling point of 65°C. Results from this study are shown in Figure 35.

![Viscosities of FFA, MeOH, SBO, and Mixtures versus Temperature](image)

**Figure 35:** Viscosities at various temperatures for free fatty acid, soybean oil, methanol, and mixtures. All mixture ratios are reported as volume ratios.
Viscosities of methanol are from the literature and viscosities of SBO were measured by previously by the research group. Each data point represents an average of four viscosity readings and error bars for 95% confidence intervals are shown; these error bars are often smaller than the symbol for the data point and can’t be seen. From Figure 35, it is shown that the introduction of any methanol into the mixture decreases the viscosity significantly. Figure 36 shows the same information presented in Figure 35 except the pure FFA and SBO data has been removed so as to better show the viscosities of the mixtures on a more appropriate scale.

Figure 36: A close-up look at the viscosities in Figure 2 excluding 100% FFA and SBO in order to see the mixtures and methanol on an appropriate scale
All mixtures in Figures 35 and 36 are highly miscible (tested for 24 hours). Mixing significantly reduces the viscosities of pure liquids. The 1:1 and 1:2 MeOH to FFA volume ratios were investigated since they represent mixtures that probably will be used with the microreactor system. The 1:1 volume ratio would be the simplest to prepare and, as shown in the Figure 3, has a viscosity range of just under 3 centipoise (at 20°C) down to about 1.5 centipoise (at 60°C). Process fluid with these low viscosities should be relatively easy to pump through the microreactors. This 1:1 volume ratio corresponds to approximately an 8:1 MeOH to FFA molar ratio. Thus, the methanol is in great stoichiometric excess since only 1 MeOH is needed for every FFA as shown previously in Figure 7 (esterification reaction).

For the ½:1 volume ratio, the molar ratio is reduced to 4:1 which is still in sufficient stoichiometric excess for processing. The components remained perfectly miscible after 24 hours, but the viscosity was over two times greater than the 1:1 mixture. The higher viscosity will cause higher pressure drops and perhaps difficulties in pumping this mixture through the microreactor. In tabulated form, the volume ratio and the corresponding molar ratio for each mixture tested are shown in Table 4.

<table>
<thead>
<tr>
<th>Table 4: Comparison of Volume and Molar Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume Ratio (MeOH:FFA:SBO)</td>
</tr>
<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td>1:2</td>
</tr>
<tr>
<td>1:1</td>
</tr>
<tr>
<td>1:1:1</td>
</tr>
</tbody>
</table>

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Conversions from volume ratios to molar ratios were performed using molecular weight and densities for each fluid as shown in Table 5. The density of the soybean oil and free fatty were found experimentally. The methanol density and molecular weights were found from the literature. 30, 31

<table>
<thead>
<tr>
<th></th>
<th>Density (g/ml)</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Fatty Acid</td>
<td>0.86</td>
<td>280</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.79</td>
<td>32.04</td>
</tr>
<tr>
<td>Soybean Oil</td>
<td>0.92</td>
<td>840</td>
</tr>
</tbody>
</table>

Lastly, three component mixtures were investigated. Soybean oil is immiscible in methanol. This leads to difficulties in the two components reacting, even with stirring. However, FFA can be used as a co-solvent since it is miscible in both SBO and MeOH. Adding these three in equal volume quantities (1:1:1) resulted in a one phase solution. The viscosities for this mixture were similar to the ½:1 MeOH to FFA mixture. The 1:1:1 mixture has a molar ratio of 8:1:1/3 MeOH:FFA:SBO. This ratio is a good candidate for three-component process feed fluid since it is easy to prepare, has low viscosities, and has a sufficient MeOH excess.
5.2 Miscibility Testing

To fully test how miscible these mixtures are, each mixture (1:1, 1:2, 1:1:1 MeOH:FFA:SBO volume ratios) was centrifuged at high speeds to see if under great stress phase separation occurs. Along with these three mixtures, a fourth mixture was tested that simulates yellow grease (waste cooking oil) composition (approximately 15% FFA in SBO by volume). The fourth mixture was composed of 1:1 yellow grease to methanol (v/v). Before centrifugation, each mixture seemed perfectly miscible. Results from this study are tabulated below:

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Does Phase Separation Occur?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200 RPM</td>
</tr>
<tr>
<td>1:1 MeOH:FFA</td>
<td>No</td>
</tr>
<tr>
<td>1:2 MeOH:FFA</td>
<td>No</td>
</tr>
<tr>
<td>1:1:1 MeOH:FFA:SBO</td>
<td>No</td>
</tr>
<tr>
<td>1:1 MeOH:Yellow Grease</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The yellow grease simulated mixture is the only tested mixture that has any phase separation occur after centrifugation of up to 3000 RPM. All of the first three mixtures are viable microreactor feedstocks since no phase separation is likely to occur.

As previously discussed, methanol and soybean oil are not miscible without a co-solvent such as fatty acids. Another potential co-solvent maybe the products of the transesterification reaction: FAME and glycerol. Different conversions of soybean oil and methanol were simulated using B100 (100% biodiesel) and pharmaceutical grade
glycerin as products. Stoichiometric ratios from the transesterification reaction were used to determine volumes of products present at different conversions. Each “reacted” mixture was prepared and mixed together; time to phase separation was measured at two temperatures: room temperature and 60°C. Results from this study are shown in Table 7.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Time to Separation (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72:1 MeOH:SBO (0% Conversion)</td>
<td>23  15</td>
</tr>
<tr>
<td>72:1 MeOH:SBO (25% Conversion)</td>
<td>24  22</td>
</tr>
<tr>
<td>72:1 MeOH:SBO (50% Conversion)</td>
<td>38  25</td>
</tr>
<tr>
<td>23:1 MeOH:SBO (50% Conversion)</td>
<td>46  33</td>
</tr>
</tbody>
</table>

No simulated conversion mixture was found to remain in one phase for even one minute. Higher temperatures caused the phase separation to occur even quicker than at room temperature. While conversion is able to help with phase separation, the products are not present in large enough amounts to make it an acceptable co-solvent in reactions. Without fatty acids present, any reaction using SBO and MeOH alone has significant phase boundaries to overcome that are seemingly a challenge for microreactors. Unless methanol is boiling, microreactors have no mixing (due to creeping flow) so SBO and MeOH alone would potentially stay in separate phases through the length of the reactor with little or no conversion. As a result, any SBO tests in the microreactors should require a FFA co-solvent to eliminate phase boundaries.
5.3 The Effect of Catalyst Mass Fraction

Before running experiments for the catalyst comparison of NiO and PtO₂ the amount of catalyst required for trials needs to be determined. The catalysts used are expensive to purchase, especially PtO₂, so the minimum amount of catalyst needed for effective conversion levels must be determined. All previous work by the research group has been done using 4 weight percent catalyst of the total reactants (SBO or FFA + MeOH).⁸,¹⁰ Experiments with platinum oxide at room temperature were performed using 4 wt%, 2 wt%, and 1 wt% to see if a noticeable conversion difference is seen. Results of these trials are shown in Figure 37.

![Weight Percent of Catalyst's Effect on Biodiesel Conversion](image)

**Figure 37**: Comparison of Catalyst Weight Percent on Biodiesel Conversion. Trials were performed using PtO₂ catalyst at room temperature in stirred tank reactors with a 5 hour reaction or residence time.
It is evident that at higher weight percentages of catalyst, the conversion to biodiesel is significantly greater. This is due to the higher catalyst surface area brought on by a higher catalyst concentration. As a result, for all trials performed in the stirred tank reactors, a 4 wt% of catalyst will be used.

5.4 The Effect of Molar Ratio

Preliminary work was performed to determine how much methanol is needed for stirred tank reactor experiments. Three different molar ratios of MeOH to FFA were tried: 4:1, 8:1, 24:1. Each is in significant methanol excess since the esterification reaction proceeds in a 1:1 MeOH: FFA stoichiometric ratio. Excess methanol, a reactant, helps push the reaction equilibrium toward products. Also, each of these molar ratios represents relatively simple volumetric ratios which will allow for easy and precise measurements (1:2, 1:1, and 3:1 MeOH: FFA volume ratios, respectively). To test these ratios, 4 wt% platinum oxide catalyst was used in each ratio in the stirred tanks at room temperature with a 5 hour residence time. Results from these preliminary tests are shown below in Figure 37.
**Figure 38: How molar ratios of MeOH and FFA influence conversion to biodiesel. 95% confidence intervals are expressed on data columns.**

From Figure 38, it is evident that higher concentrations of methanol lead to higher levels of FAME conversion. It is possible that even higher MeOH concentration will allow for greater conversion but any higher ratio will result in too little FFA and, thus, too little FAME for analysis. More work can be done on ratios to optimize the MeOH: FFA, MeOH: SBO, or even MeOH: FFA: SBO molecular ratios for biodiesel production but that is not the goal of this research effort. All that is required here is to find a ratio that produces significant conversion to biodiesel. For all stirred tank experiments with FFA feed were performed with a 24:1 MeOH: FFA molar ratio. All SBO experiments were run using the same volume ratio, 3:1; this corresponds to approximately a 72:1 MeOH:SBO.
5.5 Reactions at Room Temperature

After determining the best molar ratio and catalyst weight percent, experiments were tried first at room temperature. One of the main disadvantages of heterogeneous catalysis is that high temperatures are needed before conversions to FAME can be found. If a catalyst can be found that produces significant conversion at lower temperatures, especially room temperature, operating costs can be significantly cut.

5.5.1 Using Free Fatty Acid as a Feed

Free fatty acid (FFA) represents a major impurity in low grade oils or waste cooking oil. Being able to reach high conversions with FFA as a feed means lower grade feed can be used which would cut chemical costs. Trials were run in stirred tank reactors with NiO and PtO$_2$ at room temperature. Samples were taken at various residence times, and catalyst was immediately removed to stop any further reactions. Results from these trials are shown in Figure 39 for NiO. From Figure 39, it is shown that minimal conversions are obtained from NiO catalyzed reactions at room temperature. Only trace amounts of FAME are obtained after two hours and about 10% conversion after 4 hours.

A similar reaction scheme was run with platinum oxide. As seen in Figure 40, platinum oxide reaches significantly higher conversions at room temperature than the nickel oxide catalyst was able to reach. This is even more clearly seen when the results for both catalysts are plotted together, as shown in Figure 41.
Figure 39: Conversions to Biodiesel at Room Temperature using NiO catalyst

Figure 40: Conversions to Biodiesel at Room Temperature using PtO₂ catalyst
Figure 41: Comparison of NiO and PtO₂ Conversion to Biodiesel at Room Temperature

There is a very evident difference between the catalytic activity of NiO and PtO₂ when working at room temperature. Within 15 minutes platinum oxide is able to convert 40% of a free fatty acid feed to biodiesel while the NiO alternative produces a trace of FAME after two hours. PtO₂ appears to level off to equilibrium after 15 minutes.

There is a possibility that after significant time nickel oxide will reach conversions similar to platinum oxide results. Processing times longer than 4 hours are unrealistic for a biodiesel industrial scale-up. To determine how longer residence times affect conversion, trials were run for 8 hours, 24 hours, and 96 hours (for NiO). Results for the longer residence times for NiO and PtO₂ are shown in Figure 42.
Room temperature results at longer residence times for NiO and PtO₂

![Graph showing conversion percentage over time for NiO and PtO₂](image)

**Figure 42: Room Temperature Results for Longer Residence Times**

Even after 96 hours, conversions with NiO seem to be at approximately the same level as after 4 hours. It would appear as if NiO has reached equilibrium after 4 hours at approximately 10% conversion to FAME. The PtO₂ results seem to show the same result. 24 hours results do not show higher conversion, but, instead a slight drop-off, down to 34% conversion. This drop-off pattern is also found by others researching heterogeneous catalysts for biodiesel.²² While neither of these catalysts is able to reach complete conversion to FAME at room temperature, platinum oxide shows significant potential.

This platinum oxide catalyst shows great promise for the microreactor systems. Microreactors have the potential of processing what would normally take hours in a conventional (stirred tank) reactor in a matter of seconds. If fifteen minutes
is required to reach 40% conversion in stirred tanks, a microreactor could reach the same conversion levels almost instantaneously. As a result, platinum oxide is a good catalyst candidate for future microreactor designs.

5.5.2 Using Soybean Oil as a Feed

To go along with the FFA work performed at room temperature, trials were also run using soybean oil as a feed. The reactions involved with producing FAME from FFA are entirely different than SBO reactions so success with one does not insure success with the other. FFA feeds undergo esterification, diagrammed previously in Figure 8. FFA and Methanol react to produce FAME and water. SBO feeds, on the other hand, undergo transesterification, diagrammed previously in Figure 6. SBO and MeOH produce FAME and glycerol instead of water. Activation energies are not necessarily the same in both reactions. Only a single test trial point was first run to see if there is any noticeable conversion taking place with each catalyst. Samples were drawn at 30 minutes, 4 hours, and 24 hours to get an overview of what level of conversions are possible and how quickly they are forming.

Using GC analysis, no conversion was able to be seen with either catalyst, even after 24 hour reaction times. The activation energy to begin transesterification seems to be higher than the esterification reaction undergone with the FFA feed. Neither catalyst is able to lower the activation energy to make room temperature conversion to biodiesel possible.
5.6 Reflux Catalyst Comparison

At higher temperatures, reaction rates normally increase as activation energy barriers are overcome. For comparison to room temperature work, trials were performed at methanol’s reflux point or 65°C. At reflux, methanol is constantly vaporizing so condensers are used to recycle escaping methanol vapor. Water baths were set at 75°C so as to make sure MeOH remained at its boiling point, 65°C. At these higher energy conditions, platinum oxide and nickel oxide catalysts were tested with free fatty acid and soybean oil as feedstocks.

5.6.1 Using Free Fatty Acid as a Feed

Using FFA as a feed, samples were drawn at different times for both NiO and PtO₂ trials. Conversions to FAME using NiO as a catalyst are shown below in Figure 43. From this figure it can be seen that NiO is able to quickly reach approximately 15% conversion to FAME (in 15 minutes), but conversion seems to equilibrate at that point. Even after 4 hours, only 15% conversion is reached. To better see the effect of temperature, conversion results from room temperature and methanol reflux temperature are compiled in Figure 44 for the NiO catalyst.
At 4 hours, room temperature experiments reach, statistically (due to overlapping error bars), the same conversion as reflux trials were able to reach in 15
minutes. While reflux is able to reach higher conversions quicker, work at both temperatures reach nearly identical results. However, both temperatures only manage to achieve minimal conversion to biodiesel making the NiO catalyst a bad choice for FFA feeds at low temperatures. From previous work, NiO was shown to be able to produce high levels of conversion at very high temperatures. Extensive work was performed at 180°C in batch reactors. Figure 45 shows compiled results for all different temperature work performed with NiO and FFA.

![FFA Results with NiO Catalyst](image)

**Figure 45: All FFA and NiO work performed by the research group**

At high temperatures, significant conversion is possible but at the expense of significant energy/operating costs. The cost to work at these high temperatures on an industrial scale is also high due to capital costs since high pressure reactors and parts are significantly more expensive.
Similarly to nickel oxide, work was done with platinum oxide at reflux using a FFA feed. From Figure 46 below, the conversion, based on acid number analysis, rises, but, after 30 minutes, it begins to drop. After an hour, conversion to FAME was reading -8% which, obviously, is not true. Acid number indirectly measures FAME conversion by measuring the disappearance of FFA or simply acidity.\textsuperscript{21,22} Negative results simply means the acidity in the sample had increased from the original feed. It would seem as if an alternative side reaction is taking place besides the esterification reaction to FAME.

![FAME Conversion with PtO2 at Reflux](image)

**Figure 46: Conversion to FAME using Platinum Oxide Catalyst at Reflux**

The higher conversion levels at room temperature with the platinum oxide when compared to nickel oxide results seem to be saying PtO\textsubscript{2} is a better, more potent catalyst. When higher temperatures and, thus, higher energy levels are present, PtO\textsubscript{2} may cause an unwanted side reaction. First, there is a color change that takes place
during the reaction. The platinum oxide powder begins a light brown color and in the first half-hour, changes to black.

Along with the color change, the reactivity of the platinum oxide catalyst changes. All FFA trials underwent catalyst removal by gravity filtration through filter paper. As the black powder was being filtered in reflux experiments, it began to spark and eventually ignite, burning the filter paper in the process (filter paper is shown in Figure 47 after being extinguished with water). This behavior never once occurred in room temperature work. Perhaps, an unknown chemical reaction involving the platinum oxide occurs at higher temperature or energy.

Platinum oxide, according to the distributor, is also used in the oxidation of primary alcohols. Methanol, a primary alcohol, would be a perfect candidate for this application. When alcohols are oxidized, the following general reaction scheme takes place.

\[
\begin{align*}
R-\text{CH}_2\text{OH} & \overset{[\text{O}]}{\longrightarrow} R-\text{C} \overset{+\text{H}_2\text{O}}{\longrightarrow} R-\text{C} \overset{-\text{H}_2\text{O}}{\longrightarrow} R-\text{C} \overset{[\text{O}]}{\longrightarrow} R-\text{C} \\
\text{primary alcohol} & \quad \text{aldehyde} & \quad \text{aldehyde hydrate} & \quad \text{carboxylic acid}
\end{align*}
\]

**Figure 48: Oxidation of a Primary Alcohol**
According to Figure 48, a primary alcohol, such as methanol, is oxidized to an aldehyde which is oxidized to carboxylic acid.\textsuperscript{34} Platinum Oxide could potentially be able to oxidize the methanol to formaldehyde when at reflux; this is further supported since alcohol oxidation usually is performed at the alcohol's reflux point.\textsuperscript{34} At room temperature, the activation energy barrier was not broken, but, at reflux, this barrier was broken. Since it permanently alters the PtO\textsubscript{2}, the esterification reaction stops being catalyzed. However, a formaldehyde product does not explain the results from Figure 46 (since the acidity would not increase by formaldehyde production). Esterification started taking place in the early stages which produced water (and positive conversions). Water allows methanol to be fully oxidized to formic acid. This possible outcome explains why the reaction started with positive results since no formic acid was forming but FAME was. FAME production also meant water production, and, thus the full oxidation of MeOH to formic acid. This would then explain the negative, more acidic results.

Furthermore, platinum oxide in this process would be twice reduced which would result in elemental platinum. This reduction process is done in other applications to produce platinum black, a very potent catalyst commonly used in hydrogen fuel cells.\textsuperscript{32} Platinum black is an elemental platinum nanopowder which is black in color. This explains the color change and methanol oxidation.

Platinum oxide nanopowder has a flammability rating set by the National Fire Protection Association (NFPA) of 0 which means the "material will not burn."\textsuperscript{33} Platinum black, on the other hand, has been awarded an NFPA flammability rating of
3 or "solids that can be ignited under almost all ambient temperature conditions."\textsuperscript{33}

The high flammability and color change can be explained by platinum black formation which would be a product of methanol oxidation. Without actual identification of formic acid, formaldehyde, or platinum black this hypothesized explanation cannot be confirmed.

Regardless of what is happening at reflux with the platinum oxide catalyst, no conversion to biodiesel appears to be taking place, the catalyst is permanently altered, and it is difficult to reuse (due to spontaneous combustion at ambient temperatures). For these reasons, platinum oxide is not an ideal choice for catalysis of esterification at reflux. However, it works well at room temperature, far better than nickel oxide.
5.6.2 Using Soybean Oil as a Feed

Stirred tank experiments at methanol’s reflux point have also been performed with both catalysts using soybean oil. Soybean oil trials at reflux with NiO catalyst were previously performed by the research group and are shown below in Figure 49.

![SBO Conversions to FAME with NiO as Catalyst at Reflux Conditions](image)

**Figure 49: Conversion of SBO to FAME using NiO catalyst at Methanol’s reflux point in Stirred tank reactors**

Conversions shown in Figure 49 were determined by NMR analysis instead of GC analysis which was used for other SBO trials. In 220 minutes or nearly 4 hours, 99% conversion to FAME is reached. This is a much higher conversion level than was ever reached using an FFA feed at reflux. To better show the difference in conversions between FFA and SBO feeds at reflux, the graph below combines both of these results.
Figure 50: Comparison of FFA and SBO results with NiO catalyst at reflux conditions

From this comparison, FFA conversions reach their max much quicker than the SBO conversions. However, FFA reaches equilibrium after 15 minutes and remains there, while SBO conversions rise to near 100%. Transesterification of a triglyceride molecule is a much different reaction than esterification of a FFA. Under transesterification, three reactions occur: triglycerides react to diglycerides, diglycerides to monoglycerides, and monoglycerides to glycerin. Since the products from each reaction are the reactants for the next, reaching equilibrium is less likely to happen. NiO is a viable catalyst for conversions of SBO to FAME.

Previous work from the research group also focused on higher temperature reactions. Using high pressure stainless steel reactors, tests were performed at 180 C and about 27 bars with SBO and NiO catalyst. The results from this study are compared to the reflux (65 C) results as shown below in Figure 51.
Figure 51: 180C and 65C results for NiO Catalyst using a SBO Feed

In the stainless steel vials, no stirring takes place which is a major factor for heterogeneous catalyzed reactions. The solid catalyst falls out of solution relatively quick and the only “stirring” happening is due to boiling methanol. Also SBO and MeOH are immiscible so mixing is vital for these reactions. In the stirred tanks, at 65 C, there is ample stirring. Ultimately, the time required to reach nearly 100% conversions is nearly equivalent in both scenarios. This is a good example of the impact of stirring on time to conversion. With SBO as a feed, NiO is a good catalyst option for temperatures as low as reflux.

Experiments were also performed using platinum oxide catalyst with SBO feed at methanol reflux. Due to the high price of PtO2 nanopowder, one reaction setup was performed first to determine whether high enough levels of conversion are found to run full sweeps of reactions at this temperature. Samples were taken at different
time intervals so as to determine how conversion to FAME changes with time. Conversion results for this trial are shown below in Figure 52.

![SBO Results at Reflux using PtO2 Catalyst](image)

**Figure 52: SBO to FAME Conversion with PtO2 Catalyst at Methanol Reflux**

Platinum oxide at reflux temperatures using a FFA feed had significant issues. The catalyst was permanently altered in the process and little or no FAME was produced. Using soybean oil feed however, 60% conversion to FAME is produced with the platinum oxide catalyst after 4 hours. It was thought that formic acid was being produced by oxidizing methanol when FFA feed was being used. No side reactions are apparent using SBO and PtO2.

In Figure 53 below, a comparison of the SBO to FAME conversion results for NiO and PtO2 catalysts at methanol reflux (65°C) are shown. Each catalyst produces significant conversion to FAME, but NiO catalyzed reactions are somewhat quicker. Platinum oxide performed better with FFA at room temperature than NiO but at
reflux with SBO the result appears to be the opposite. In 4 hours, NiO causes 99% conversion while PtO₂ yields 60% conversion.

![Comparison of NiO and PtO₂ SBO to FAME conversions at MeOH Reflux](image)

**Figure 53: Comparison of NiO and PtO₂ conversion results with SBO at reflux**

The reason for the difference in conversions between the two however is more likely a physical barrier rather than due to catalytic activity. Using a NiO catalyst, the nanopowder was present in both phase layers: oil and methanol. However, platinum oxide with SBO feed becomes stuck in the oil layer as seen in Figure 54.
Figure 54: Platinum Oxide (dark brown/black color) trapped in bottom phase even with stirring

The point of the stirred tank reactors is to increase mixing since magnetic stir bars can be used. This is vital for SBO and MeOH trials since they are immiscible. Due to the phase boundaries in PtO₂ experiments, conversion to FAME was lower than NiO, which did not suffer from these boundaries. The reason for the different behavior by the two catalysts is unknown, but the smaller platinum oxide particle size or the higher particle density (NiO = 6.7 g/ml vs. PtO₂ = 10.2 g/ml) might be responsible for the difference.
5.7 Microreactors

It has been theoretically determined that reaction times can be cut from hours to seconds using microreactors.\textsuperscript{14} This is due to the diffusion time being significantly less in the microreactor system compared to a standard reactor used in most practices as described in Equation 1. For the first generation of microreactors, the cross sectional area of the microchannels is 50µm deep x 500µm wide. Straight channel reactors with a length of 3 cm were chosen. Serpentine reactors were fabricated on similar silicon wafers but the wavy-flow on the wafer resulted in a nominal length of 15 cm. Each reactor is equipped with two entrance ports (one for methanol and one for an oil feed) as well as a single exit port, NiO catalyst sputtered on the etched microchannel on the silicon wafer, and a glass plate adhered to the top. Example microreactors used in this project were shown in Figure 16 and 17. Conversions in the microreactors are compared to conventional stirred tank reactors conversions using SBO and FFA feeds.

5.7.1 Using Free Fatty Acid Feed

In the microreactor's current state, it was thought that only one phase feeds have a possibility of reacting. In the first generation of microreactors, only the floor and triangle surfaces (silicon wafer) were sputtered with NiO catalyst somewhat limiting its abilities. Also the flow rates were in the creeping flow region (Reynolds number at approximately 0.000006 which is \(< < 1\) and little to no mixing will take place. One phase feeds where mixing is less essential should have a much greater probability of working.
This was the primary objective behind miscibility testing, as seen in section 5.2, to determine what ratios can stay in one phase. All FFA and MeOH mixtures remained as one phase, and the 1:1:1 MeOH:FFA:SBO volume ratios stayed as one phase. All microreactor FFA trials were run using a 1:1 MeOH:FFA volume ratio (8:1 FFA: MeOH molar ratio) due to low viscosity, ease of preparation, and quicker results (since 50% of volume leaving can be analyzed).

A straight channel microreactor was operated at 68°C and 50°C. In the microreactors, reflux seems to occur at about 68°C. This is somewhat higher than in the open, stirred tank reactor due to slightly higher pressures. In later trials, vapor phase methanol resulted in many leaks at the microreactor entrance and exit ports. To resolve this issue, temperature was dialed down to approximately 50°C which extended the microreactor's lifespan.

Flow rates through the microreactor were also varied. Higher flow rates result in less time in the microreactor times which means less time to react. To determine how residence time, time in the microreactor, affects conversion, different flow rates are tested. Results from different flow rates and temperatures in the microreactors are shown in Figure 55.
At higher temperatures, the conversion to FAME is consistently greater than lower temperatures when comparing similar residence times. At a residence time of 22.5 seconds (2μL/min), the conversions are 12% at 50°C and 14% at 68°C. At a 45 second residence (1 μL/min) the conversion at 68°C is 18%. Higher residence times or reaction times allow higher conversions to FAME. Higher temperatures have the same effect when compared to lower temperatures in microreactors.

The goal of the microreactor system is to do what traditionally would take hours in standard size reactors in a matter of seconds. In order to test this, microreactor conversions are compared to similar results with NiO catalyst and FFA feed at reflux in stirred tanks in Figure 56.
Conversions in the microreactor seem to peak at about 45 seconds at 18%. This is slightly higher than conversions in stirred tank reactors at reflux using NiO catalyst. However, microreactors are able to match FAME conversion from FFA at methanol’s reflux temperature in 22.5 seconds which took 15 minutes in stirred tank reactors. This means the microreactors in this scenario are performing 40 times faster than traditional reactors.

Microreactors were also run at room temperature in a serpentine reactor, shown in Figure 16. This reactor is 5 times as long allowing for longer residence times. Also, in principle, the stirred tank reactor should produce a similar conversion to the microreactor eventually. Therefore, very long stirred tank reactor residence times were tried and the results are shown in Figure 57.
It was originally thought that at room temperature using NiO the reactions seem to reach equilibrium at 4 hours, but the microreactor results at room temperature seem to be able to reach higher levels of conversion. Conversions for the stirred tank reactor seem to have leveled off at about 10% after 4 hours. However, the microreactor seems to maintain a higher level of conversion (about 17%) versus the conventional batch-type stirred tank reactor (about 10%). The overall comparison is significantly in favor of the microreactor. In microreactors, conversions in 3.75 are at least equal to conversions in a stirred tank that took 4 hours. This is equivalent to 64 times quicker than the conventional means of producing biodiesel. However, the microreactor could potentially be about 128 times faster (comparing to 8 hours), 380 times (24 hour comparison), 1500 times faster (comparing to 96 hours), or even quicker. More work needs to be performed to determine exactly how much faster the
microreactor system is than traditional methods, especially work, where equilibrium
is not reached so quickly.

5.7.2 Using Soybean Oil Feed

Equilibrium is not reached quickly when using SBO and NiO in the stirred
tank reactors, and, in 4 hours, near 100% conversions are reached. In stirred tanks a
72:1 MeOH:SBO molar ratio is used since some of the methanol will be in trapped in
the vapor recovery system at any time. For the microreactor comparison, SBO and
MeOH are tested at MeOH reflux (68°C due to higher pressure) in a 1:1 volume ratio
(24:1 MeOH:SBO molar ratio). The difference in feed molar ratio is significant. A
higher ratio may produce a higher conversion. However, it is a constraint of the
experimental system that feed streams must be fed at equal volumes, which in this
case leads to the 24:1 ratio.

SBO and MeOH are immiscible and, without mixing, phase boundaries will
limit microreactor performance. Trials are performed in the microreactor with SBO
and MeOH and 74% conversion to FAME is found in 3.75 minutes in the
microreactor. This result is compared to SBO reflux conversions to FAME in Figure
58.
Figure 58: Comparison of microreactor results to SBO stirred tank results at methanol's reflux point (65°C)

Even with phase boundaries conversion close of 75% +/- 20% are found on average. The microreactor most nearly matches the stirred tank conversion that took 120 to 150 minutes to reach. In other words, microreactors are capable of matching conversions found with stirred tanks 32 to 40 times quicker. One phase mixtures in microreactors are performing around 64 times quicker than conventional methods, but those results are of a different reaction (esterification vs. transesterification) and are less inhibited by no mixing. With no mixing, it was originally thought that conversion to FAME in microreactor systems would be minimal when phase boundaries are present but conversion results in Figure 58 prove otherwise.

The present microreaction system successfully turns hours of processing time into minutes. Additionally, it operates continuously, therefore, continually re-using catalyst without any re-conditioning.
5.7.3 Additional comments about microreactor residence time

The microreactor is a continuous device where two fluids enter the reaction channel separately, mix, heat up from room temperature to intended reaction temperature, and then react. Clearly, the entire time any element of process fluid lives in the microreactor is not spent reacting at the intended conditions. Pre-heating and pre-mixing the reactants may significantly reduce the required residence time and/or increase conversion.

The pressures are not constant throughout the length of the micro channel. At entry, the pressure is somewhat higher than atmospheric. Depending on the flow rate, it can easily be as high as 2 atmospheres. This means that methanol boiling temperature is higher (in the case above about 68°C, the temperature of the microreactor platform) than at atmospheric pressure (about 65°C). Therefore, reflux temperature changes (reduces) at every point along the channel. It has been noticed that near the exit of the channel, methanol boiling takes place and methanol vapor slugs are formed. Therefore, it is unlikely that any reaction takes place toward the end of a channel, further reducing the active residence time.

5.7.4 Suggestions for Future Microreactor Design

While results from the microreactor system showed much potential, different problems arose that need to be taken into consideration in the second generation of microreactors. The first and most troublesome issue is leaking. Ports for entering and exiting the reactor are attached by adhesive rings only. This method is not strong enough to withstand the pressures developed inside the reactors or the methanol vapor
at or near boiling temperatures. Chemical adhesives had to constantly be reapplied to keep the ports from losing adhesion to the glass surface.

If the adhesion rings are to be kept, the durability of the reactors needs to be considered. Silicon wafers are easily cracked which is an issue when microreactors must be clamped and heated in order to get the adhesive rings to stick. Of the two reactors used in this project, one of them was severely cracked during this adhesion step. It is possible to sputter onto glass microchannels instead of the standard silicon wafer which would increase rigidity and thus microreactor lifespan.

The microreactor performance can also be improved by introducing 2 catalyst coating changes: sputtering on the roof of the channel, and nano-structuring the coating. The channel roof has no coating in the present microreactors. This was done so one could see into the channel through the clear glass roof. In principle, sputtering on the roof will decrease diffusion time to surfaces by a factor of 4. (Recall $t_D = \frac{l^2}{D}$). For example, this may reduce the processing time in the case shown in Figure 57 from 3.75 minutes to less than one.

The catalyst coating on the surfaces of the present microreactors has an unknown lattice structure. At the time of fabrication, no one considered the effects of lattice structure on catalytic activity. Subsequently, various researchers have discovered methods to produce known lattice structures using magnetron sputtering of NiO on glass. Three distinct crystalline structures { (111), (200), and (220) } are in the NiO nanopowder as shown in Figure 34. These structures can be produced by the recently discovered methods. Essentially, temperature, power and atmosphere in the
sputtering chamber are manipulated during the sputtering process to produce the desired structure. It is possible that one structure or some combination of structures will perform best. It has been suggested by other research efforts that lattice structure may have significant impact on conversion. The research group recently received an NSF grant to investigate this possibility.

6.0 Conclusions

One goal of this research effort was to conduct a catalyst comparison between nickel oxide and platinum oxide at room temperature and methanol reflux (65°C). The comparison was performed at room temperature and methanol’s reflux point using free fatty acid and soybean oil feedstocks to determine which catalyst performs better in biodiesel production. Platinum oxide successfully produced moderate levels of conversion to biodiesel with free fatty acid as a feedstock at room temperature which nickel oxide was unable to do. However, at higher temperatures, platinum oxide is permanently when using FFA due to unwanted side reactions. In contrast, nickel oxide catalyzed reaction reach low conversion at reflux with FFA feed. High conversion with a soybean oil feed was possible for both platinum oxide and nickel oxide, but nickel oxide reaches higher level quicker. Due to this reason, it can be concluded that for biodiesel production in microreactor systems nickel oxide is the better catalyst option. Platinum oxide can be permanently altered by side reactions which make it an economically unfeasible option.
The primary objective of this research effort was to test the performance of
the first generation of microreactors in producing biodiesel. The microreactor
successfully converted both FFA and SBO to FAME. In fact, its performance was far
superior to stirred tank reactors in processing time. Generally, the microreactor
produced equivalent or superior conversions in nearly 2 orders of magnitude faster
than stirred tanks. Microreactors can potentially dramatically change biodiesel
production costs. If this can be done, the world’s dependency on foreign fuels can be
lessened and replaced by alternative, renewable biodiesel fuel.
7.0 References


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<http://chemlabs.uoregon.edu/Safety/NFPA_Red.html>.