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University of Tennessee at Chattanooga, ben.kegley@gmail.com

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The Effect of Co-Solvent & Ordered Lattice Structure on Catalysis of Biodiesel Production in Microreactors

By
Benjamin Jacob Dewey Kegley

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

Project Director: Dr. Frank Jones
Examination Date: April 22, 2014

Department Examiners:
Dr. Tricia Thomas
Dr. Bryan Ennis

Signatures:

Project Director

Department Examiner

Department Examiner

Liaison, Departmental Honors Committee

Chair, Departmental Honors Committee

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Acronyms and Abbreviations Used

<u>Acronym or Abbreviation</u>	<u>Description</u>
ASTM	American Society for Testing and Materials
CBG	Chemically Bound Glycerin
CO ₂	Carbon Dioxide
FAEE	Fatty Acid Ethyl Esters or Biodiesel (from ethanol not methanol)
FAME	Fatty Acid Methyl Ester or Biodiesel
FFA	Free Fatty Acids
FID	Flame Ionization Detector
GC	Gas Chromatograph (or Chromatography)
KOH	Potassium Hydroxide
MeOH	Methanol
MSTFA	N-Methyl-N-(trimethylsilyl) trifluoroacetamide
NaOH	Sodium Hydroxide
NiO	Nickel (II) Oxide
NMR	Nuclear Magnetic Resonance
RPM	Revolutions per Minute
SBO	Soybean Oil, a triglyceride feed

1.0 Abstract

In this study, stable single phase feedstocks for biodiesel production were successfully determined. The addition of free fatty acids, which are considered waste, to the soy bean oil and methanol processing feed as a co-solvent, produces a stable single phase. The single phase feedstock significantly increases initial global rates and supplements the oil with further biodiesel production. A stable single phase feedstock and increased reaction rates are desirable due to the use of continuous heterogeneous biodiesel production in microreactors currently being developed by this research group.

Further design improvements to the microreactor design have been determined. Such improvements include the introduction of ordered lattice structures. Once implemented on the next generation of microreactors, the new designs and the single phase feedstocks will result in a significantly improved continuous heterogeneous catalysis process for biodiesel production with processing times of seconds.

2.0 Introduction

With the fluctuating costs of fuel in today's society, alternative fuel sources are in demand more than ever. Even though the fuels of today, such as coal, natural gas, and other fossil fuels, are consistently dwindling, our dependence on them is growing. Furthermore, with the price on foreign fuels rapidly increasing, the US and the world are constantly looking for means of alternative fuel sources to lower the dependency on traditional fuels.

One typical alternative fuel is biodiesel. Commonly in industry, biodiesel is produced in batch reactors using homogeneous catalysis.¹ However, in these methods there are many disadvantages including unwanted byproducts, lengthy processing time, and bad use of catalyst. Dr. Frank Jones' microreactors research group, in response to the world's needs, is focused on the production of alternative fuel sources, specifically biodiesel.^{2,3} Biodiesel can be produced from various sources, including vegetable oil or animal fat; therefore, it can be used to help relieve the world's dependency on traditional fuels. The goals of the research group are to develop ways of producing biodiesel cheaper and purer by the use of microreaction technology. The small scale has the effect of significantly reducing processing time along with some other advantages when compared to traditional technology. Previous computational work by Jennifer Lewis (UTC DHON '10) simulated microreactors for biodiesel production.⁴ The optimal channel dimensions were found in this study. In addition, previous experimental work, by Trip Dacus (UTC DHON '10), determined promising heterogeneous catalysts to further speed up the reaction.⁵ Eric Snider,

(UTC DHON '12), studied the behavior of microreactors and determined that their processing time is as much as 3 orders of magnitude faster than stirred tanks while producing biodiesel.⁶ Dr. Jones' research group's microreaction technology is continually being developed and improved on.

The goal of this research project is to experimentally determine a stable single phase feedstock to overcome the phase boundaries of traditional processing. Using this single phase feedstock, increases in the initial reaction rates should become evident for both stirred and unstirred processes. Ultimately, the combination of the goals above and the implementation of design recommendations to next generation microreactors will result in a significantly improved continuous heterogeneous catalysis process for biodiesel production.

3.0 Background

3.1 Biodiesel Chemical Structure

Fatty acid methyl esters (FAME), better known as biodiesel, are an alternative fuel that can be produced from vegetable oil or animal fat. The chemical structure of a typical FAME molecule is shown below in Figure 1. This is an 18 carbon chain methyl ester.

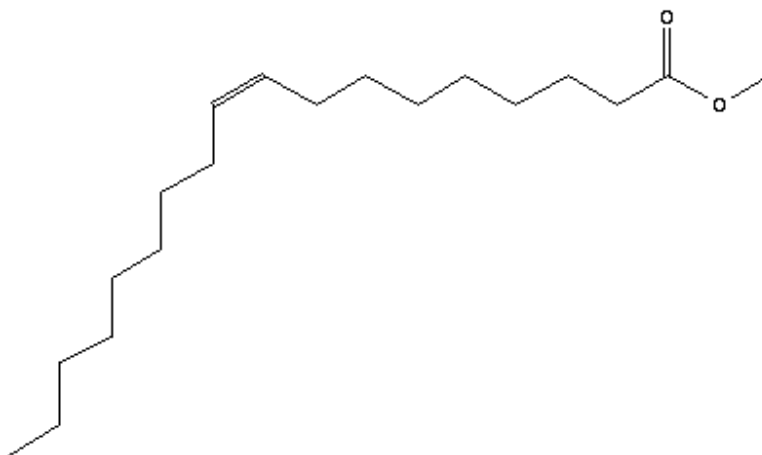


Figure 1: Chemical structure of a 9-Octadecenoic acid (Z) – methyl ester.⁷

Biodiesel is an oxygenated fuel and thus varies in chemical structure from an average diesel molecule. A generic diesel molecule, lacking the ester (O-R) and carbonyl oxygen (C=O) groups which make biodiesel oxygenated, is shown below in Figure 2.



Figure 2: Chemical structure of a general diesel molecule⁸

Due to these structural differences, there are many differences that can be seen when looking at the entire carbon life cycle for both fuels. Carbon dioxide (CO_2), a major product of combustion reactions, is produced by both fuels. However, biodiesel consumes almost as much carbon dioxide as it produces when combusted due to the oil needed to make FAME being mainly derived from plants, which consume the CO_2 while growing. Taking this into account, biodiesel, if it were to replace diesel, has the possibility of reducing net CO_2 emissions by 78%.⁹ Furthermore, the tailpipe emissions after combustion for biodiesel differ greatly from diesel as shown below, in Figure 3.

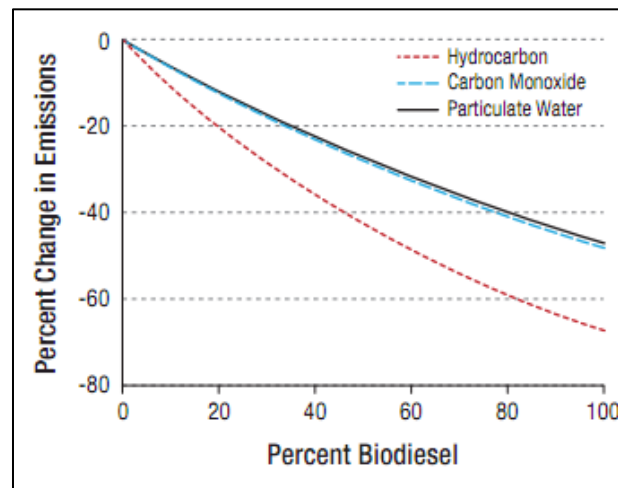


Figure 3: Changes in biodiesel tailpipe emissions. Different Biodiesel/Diesel blends are shown on the x-axis and change in emissions are plotted on the y-axis. Data taken from NREL.⁹

The unburned fuel, carbon monoxide, and particulate matter substantially decrease in biodiesel combustion. Due to the oxygenated chemical structure of biodiesel it burns more completely, which is the main reason for these lower emissions.

3.2 Biodiesel Production

The transesterification reaction, as shown in Figure 4, is one way FAME is produced. Vegetable oil or animal fat reacts with three methanol molecules to produce three methyl esters and glycerol.

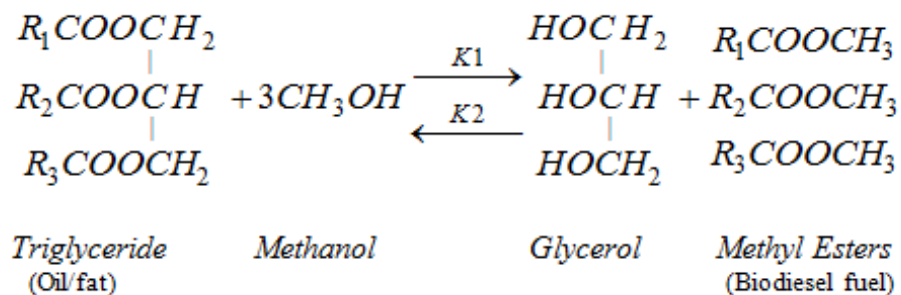


Figure 4. Overall Transesterification reaction of triglyceride with methanol ⁵

The reaction shown above is a net equation of three reactions that react in series to break down the triglyceride. Each of these three reactions requires a methanol and each produces a FAME molecule which yields the net equation shown in Figure 4. The series of reactions just described are illustrated below in Figure 5.

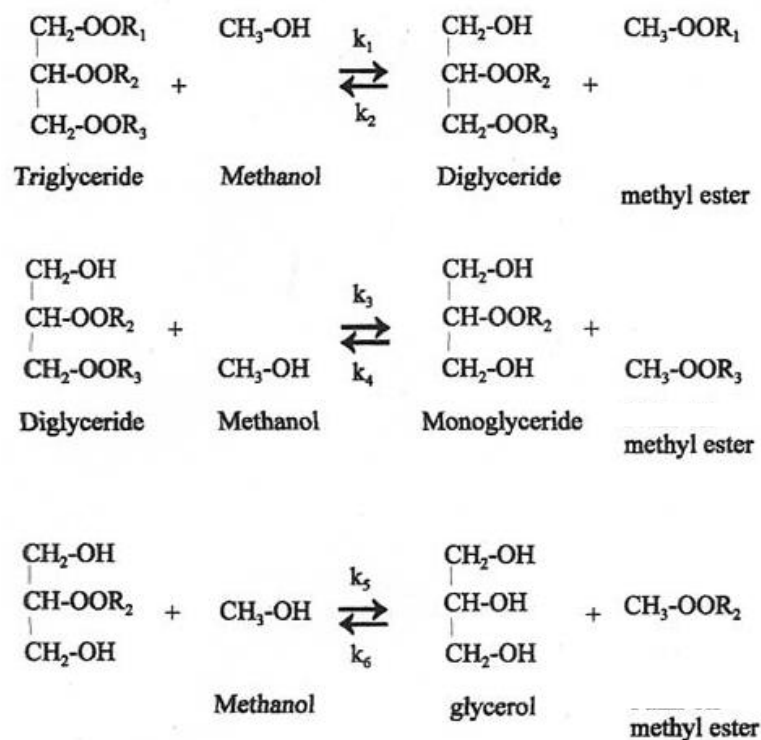


Figure 5: Detailed transesterification reactions of triglyceride and methanol.¹⁰

In the transesterification reaction, as the reaction proceeds, the breakdown of the triglyceride produces Free Fatty Acid (FFA) molecules. Biodiesel is also produced by the esterification reaction where FFA (considered waste material in traditional processing) and an alcohol react to produce a singular ester molecule and water. Esterification works through the removal of the hydroxide ion from the carbonyl carbon and replacing it with the methoxide ion forming the methyl ester and the water byproduct, as shown in Figure 6 on the following page.

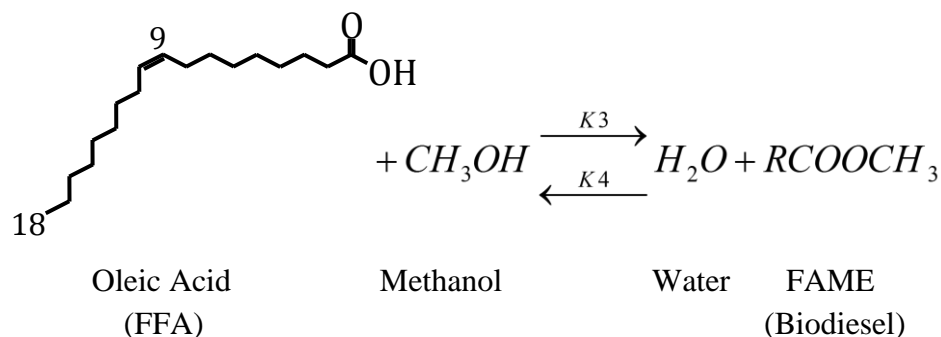


Figure 6. Esterification Reaction with Methanol ⁶

In these reactions, there are numerous possible combinations of feedstock chemicals that will all produce biodiesel. It is important to weigh the pros and cons of these feedstocks before processing can occur.

3.2.1 Potential Feedstocks

In general, a fatty acid chain on an oil molecule reacts with an alcohol to produce a fatty ester molecule, or biodiesel. The fatty acid length of the biodiesel molecule varies based on the feed oil used; however, typical chain lengths are 16 to 18 carbons.¹¹ When methanol, the smallest carbon chain alcohol, is used, FAME is produced. However, if ethanol is used instead of methanol to produce biodiesel fatty acid ethyl esters, FAEE, not FAME will be produced.

In this study, FAME is being produced using soybean oil (SBO), the FFA Oleic Acid, and methanol (MeOH). The fatty acid chains in SBO are summarized in Table 1, below.

Table 1: Soybean Oil Fatty Acid Composition. Data taken from Snider.^{6,12}

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

Typically, diesel fuels have 12 to 20 carbons in length. From Table 1, it should be seen that SBO is a good source for producing biodiesel due to the fatty acid chains starting off in the range of biodiesel carbon length, 16 to 18.¹¹ The use of Oleic Acid, as a source of FFA during testing, is also a good choice for the same reason. The chemical structure of Oleic Acid can be seen below in Figure 7.

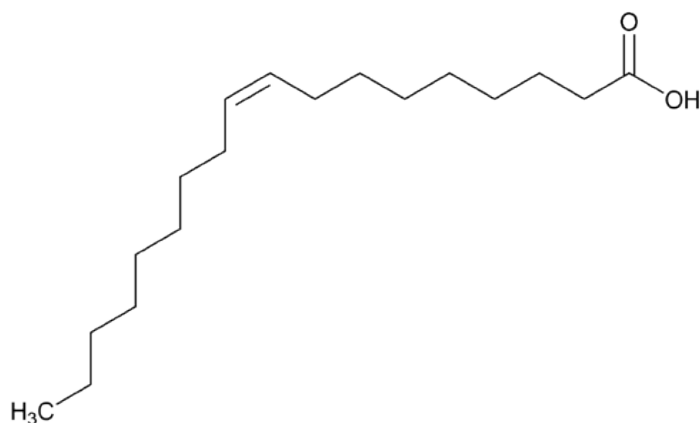


Figure 7. Free Fatty Acid structure of Oleic Acid.¹³

3.2.1.1 Co-Solvents

Traditional processing of biodiesel involves combining of the oil and alcohol, along with the homogeneous catalyst, into large stirred tanks. Even though this type of reacting produces large volumes of product, the downside is that it takes a significant amount of time for the reactions to overcome the two phase nature of the oil and alcohol. One of the highest contributing factors of reaction rates is phase boundaries. The mixing in stirred tanks helps overcome these boundaries; however, if mixing were not present, the rates would dramatically decrease. The possibility of starting the reaction with a single phase feedstock would eliminate the reactant phase boundaries.

There have been various studies on homogeneous biodiesel production to determine a co-solvent to produce a single phase feedstock. The co-solvent used in these studies is typically FAME. One such study using FAME as a co-solvent and potassium hydroxide (KOH) as a homogeneous catalyst was performed by Ji-Yeon Park et al.¹⁴ In this study, the use of FAME, the biodiesel product, in the reactant stream introduces benefits as well as disadvantages. Introducing FAME to the feedstock does produce a single phase, but when you add product to the reactant stream it can be costly and has the potential to slow the reaction or shift the equilibrium due to stressing the product side of the reaction. These disadvantages can be avoided by finding a co-solvent that does not increase costs or stress the backwards reaction.

FFA is considered waste in most industrial processes and thus has the potential to reduce reactant costs. In the right ratios, FFA can be used as a co-solvent to bring the feedstock of SBO and MeOH to a single processing phase. Furthermore, due to esterification, FFA produces additional FAME and is thus a favorable co-solvent for biodiesel production.

3.2.2 Catalyst Types

Another important factor in biodiesel production is the selection of catalyst. In industrial processes, a homogeneous catalyst, typically sodium hydroxide (NaOH) or potassium hydroxide (KOH), is used in the large stirred tank batch reactors. Homogeneous catalysts are beneficial on this scale due to the simplicity of being able to pour the catalyst into the reactor and not having to clean it out after every batch. However, all oil types, including SBO, must be purified of FFA before processing can be carried out when using this catalyst. Purification must occur because if there is a significant amount of FFA present during the homogeneous reaction saponification occurs. This is an unwanted side reaction that is costly to avoid and produces costly product purification if it does occur. Furthermore, not only does any soap formed need to be removed, the homogeneous catalyst itself must be separated from the products. On the other hand, heterogeneous catalysis, the use of a catalyst in a separate physical phase, could be advantageous for biodiesel production by using a solid catalyst, which can easily be separated from product.

When considering heterogeneous catalysis, the phase boundaries and the presence of mixing in large scale reactors become more of an issue due to tendency for the catalyst to separate. The use of small scale reactors lined with catalyst could be used for continuous processing. These small scale reactors would bring the processing fluid closer to the catalyst surface, decreasing the dependency on stirring in batch processes. Using this single phase feedstock described previously, along with specifically designed reactors for heterogeneous catalysis, the continuous heterogeneous process begins to become more and more favorable.

3.3 Microreactors

Recently, the use of microreactors in the production of biodiesel is growing in popularity. This growth is due to the dramatic increase in reaction rates that are possible on the micro scale and the ability to process continuously versus traditional batch processes. The micro scale brings the reactive molecules much closer to reactive surfaces, resulting in extremely fast processing times. These improved processing times are a result of decreased diffusion time, the time it takes reactive molecules to reach the reactive surfaces. Diffusion time is defined by:

$$t_D = \frac{l^2}{D} \quad (1)$$

where t_D is diffusion time, l is length to the reactive surface, and D is the diffusivity ($1 \times 10^{-9} \text{ m}^2/\text{s}$). It should be noted that the micrometer scale, 10^{-6} m , produces a significant drop in diffusion time due to the squared length in the numerator. 6mm

stainless steel vials used by the research group have a calculated diffusion time of 2.5 hours, using Equation 1. A 100 μm channel has a calculated diffusion time of 2.5 seconds. This processing time advantage is the main reason for going to the micro scale.

Even though there are many studies being performed using microreactors, there are several interpretations of the micro scale. Several studies use homogeneous catalysis in microtube reactors, which are capillary tubes with inner diameters that range from 0.25 to 10 mm.¹⁵ The processing fluids are simply mixed and forced through the capillary tube resulting in the faster reactions as described previously. Other studies using homogeneous catalysis react in microstructured reactors similar to the one shown in Figure 8, on the following page. These reactors can have channel sizes ranging from 2 to 135 mm wide by 0.8 to 135 mm deep.¹⁵

When it comes to biodiesel production in microreactors, homogeneous catalysis is the only method used so far that has been found. Heterogeneous catalysis in microreactors to produce biodiesel is under development. Based on Tianming Xie's 2012 review article, *Biodiesel synthesis in microreactors*, there is only one commercialized heterogeneous catalysis process since 2006, which does not involve microreactors.¹⁵ This leads to a need for new developments in heterogeneous catalysis of biodiesel production, specifically in microreactors.

In this study, the microreactors used during experimentation apply heterogeneous catalysis. The reactors are also truly on the micro scale, having

dimensions of 500 μm wide by 50 μm deep. Lengths of either 15 cm (Figure 8) or 3 cm (Figure 9) are used by this lab.

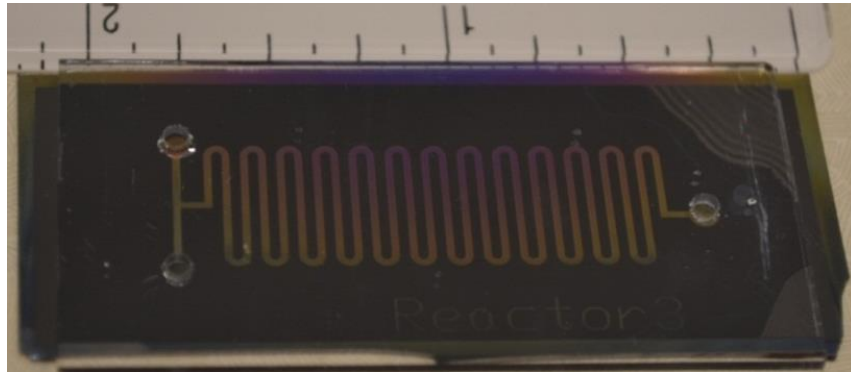


Figure 8: Wavy microreactor with 15 cm nominal length.



Figure 9: Straight microreactor with 3 cm nominal length.

A base metal catalyst is sputtered onto the channel surfaces by magnetron sputtering. This provides the reactive surfaces for the oil and MeOH to produce biodiesel. The scale, heterogeneous catalyst, and single phase processing fluid all together can decrease processing times by as much as 3600 times or more as detailed previously.

3.3.1 Ordered Lattice Structures

This study attempts to further reduce processing time by finding favorable catalyst lattice structures. The main catalyst being used by the research group is nickel (II) oxide nanopowder. It is highly successful in stirred tank batch reactors.⁶ This powder has three main lattice structures {(111), (200), and (220)} as shown in the spectra in Figure 10, provided by Sigma-Aldrich.

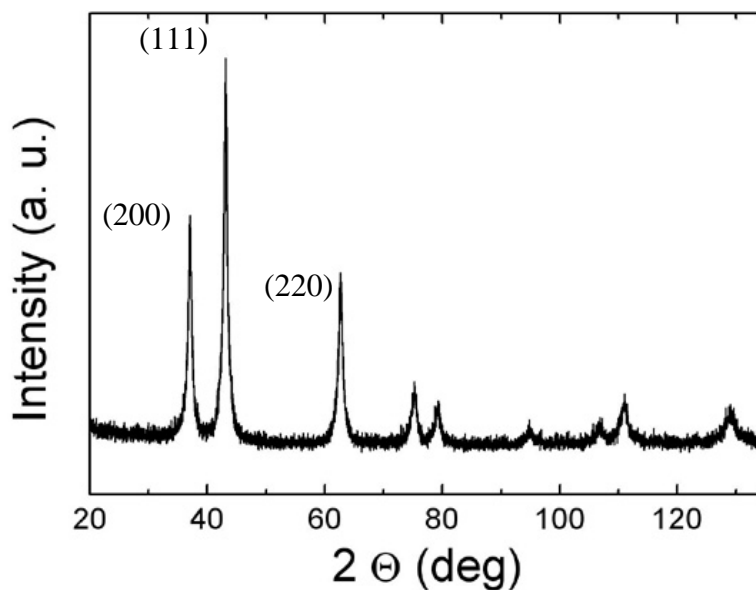


Figure 10. X-ray Diffraction Spectra of Nickel (II) Oxide catalyst nanopowder. Figure taken from Sigma-Aldrich.¹⁶

It has been found that various surface lattice structures of NiO can be produced on surfaces by varying the sputtering variables temperature, atmosphere, and power.^{17,18} Figure 11, below, shows the change in surface structure of NiO due to a change in temperature.

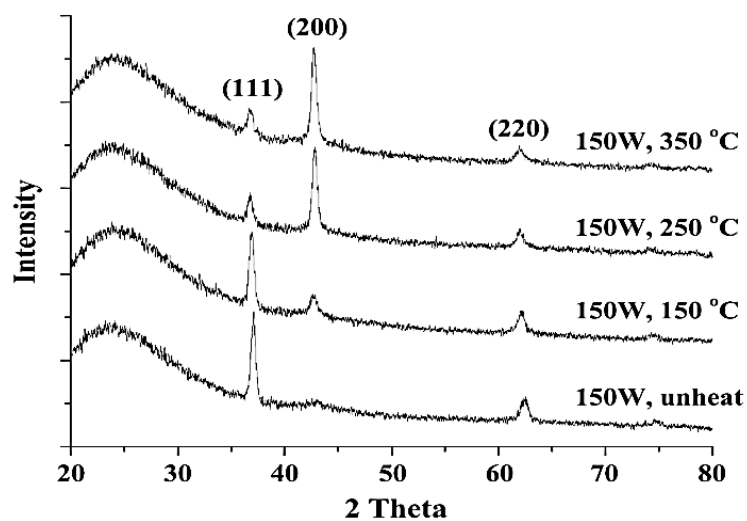


Figure 11. X-ray Diffraction Spectra of Nickel (II) Oxide sputtered film.
Figure taken from Chen et al.¹⁸

It has also been theorized that different lattice structures of the same catalyst perform at different efficiencies.¹⁹ The (111) structure is the closest packed crystalline solid, and thus has more catalyst per unit length. An example of the (111) surface structure can be seen on the following page in Figure 12. Notice that the bottom part of (b) is the bulk (111) structure of NiO. The surface of this structure is subsequently oxidized. Some Ni atoms from the bulk (111) structure then migrate into the oxidized layer, causing the vacancies seen in the figure below. The resulting structure is in a 2x2 Schottky defect formation.²⁰ These vacancies have unknown effects on catalysis.

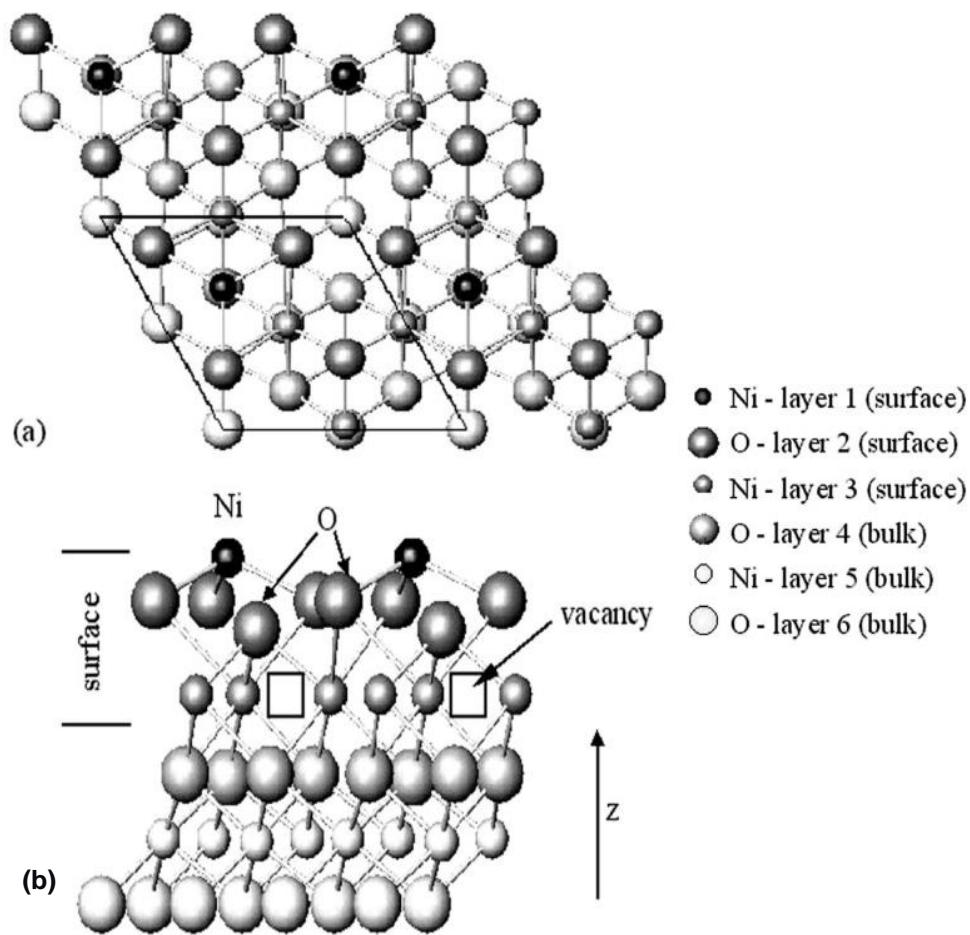


Figure 12. Top view (a) along with side view (b) of NiO (111) surface and bulk structures. Figure taken from Erdman et al.²⁰

4.0 Materials & Methods

4.1 Materials

As previously mentioned, biodiesel is being produced by means of the transesterification and esterification reactions. For these reactions, the materials used can be broken down into two categories: feedstock chemicals and catalyst. The following details the materials used for experimental studies.

4.1.1 Feedstock Chemicals

In this study three chemicals were used in the feedstock in various ratios. These chemicals are soybean oil (SBO), free fatty acid (FFA), and methanol (MeOH). The SBO used was food-grade vegetable oil (100% pure) purchased from Walmart. MeadWestvaco, a producer of paper products, supplied L-1 free fatty acid, or tall oil. This tall oil is comprised mainly of the oleic fatty acid, which is a monounsaturated 18-carbon chain fatty acid. The L-1 designation means the oil has 1% rosin acids. The rosin acid found in the free fatty acid feedstock is primarily abietic acid.²¹ The effects of the rosin acid on biodiesel production are unclear. Methanol was purchased from Fisher Scientific and is $\geq 99.9\%$ pure.²²

4.1.2 Catalyst

For reactions to take place in a reasonable time, a catalyst was used in all experimental studies. The catalyst used was Nickel (II) Oxide (NiO) nanopowder,

purchased from Sigma-Aldrich.¹⁶ The term nanopowder means the particle size is on the order of nanometers. NiO has a reported particle size of less than 50 nm. The NiO nanopowder is also reported to be comprised of three main crystal structures, (111), (200), and (220), as shown in Figure 10. The effects of crystal structure on reaction rate are currently unknown on the production of biodiesel.

4.2 Methods

The methods and procedures used in this study will now be discussed. All methods of experimental reactions include descriptions and suppliers of the equipment used. The method of purification before analysis and the procedures to perform the analytical chemistry are also detailed.

4.2.1 Miscibility Testing

SBO and MeOH are immiscible in any fractions. FFA is miscible in MeOH in any fraction. FFA is miscible in all fractions of SBO attempted in this study. FFA is therefore a co-solvent. An attempt was made to produce a single phase feedstock of SBO, MeOH, and FFA. The criteria for success is a feedstock that is indefinitely a single phase. The various fractions were tested by time (24 hours) and by centrifugation at 6000 RPM for 5 minutes. The Hermle Z206A centrifuge was used for this study, as seen in Figure 13.²³



Figure 13: Hermle Z206A centrifuge.

4.2.2 Reactors

To study the effects of the catalyst and co-solvent, three different methods of reacting were chosen. The first method being stirred tank batch reactors, which are the closest comparison to industrial processing of biodiesel. Second, stainless steel high temperature vials were used; these were needed in order to test the upper limits of the reactions. Lastly, microreactors were used to increase the rate of production.

4.2.2.1 Stirred Tank

The stirred tank reactors used were 25mL round bottom flasks purchased from Sigma-Aldrich.²⁴ These stirred tanks were maintained at methanol's reflux temperature, about 65 °C, with an EchoTherm Programmable Multiposition Stirring

Hot Plate.²⁵ At methanol's reflux temperature, methanol constantly vaporizes, and since the reactor is open to the atmosphere, water-jacketed reflux columns, also supplied by Sigma-Aldrich, were needed to condense the vapor back into the flask.²⁶ Each of the reflux columns were in series with the same water source instead of each with their own water source. It was experimentally determined that sufficient water flows are able to be achieved to cool all methanol vapors in each condenser. Flasks were placed in hot water baths at approximately 75°C to assure methanol stays at reflux throughout reaction. One centimeter Teflon coated stir bars were inserted into each flask with stirring at 800 RPM. The reflux reactor setup is shown below in Figure 14.



Figure 14: Reflux reactor experimental setup.

4.2.2.2 High Temperature Unstirred

The stainless steel high temperature reactors used were 5mL precision milled Retsch Mixing Jars purchased from the Gilson Company.²⁷ These vials were maintained at 180 °C in a 20GC Gravity Convection Oven from Quincy Lab, Inc.²⁸ At 180 °C, methanol's vapor pressure is approximately 26 atmospheres. Due to this high pressure, the vials are screwed closed and sealed while the reaction takes place with no stirring. These reactors can be seen below in Figure 15.



Figure 15: High Temperature/Pressure Stainless Steel reactors.

4.2.2.3 Microreactors

The microreactors used in this study were manufactured by Johns Hopkins University using designs from the UTC Microreactor Research group.⁴ The channels are coated by magnetron sputtering with a metal base catalyst, Nickel (II) Oxide.

Microfluidic channel size is 50 μm by 500 μm with length of 3 or 15 cm, which leads to extremely low flow rates. In order to provide these flow rates accurately, a Cole-Parmer[®] Touch-Screen Syringe Pump is used.²⁹ This syringe pump is able to deliver flows as low as five picoliters per minute to the microreactor. In this study, flows between 250 nanoliters/minute and 2 microliters/minute were mainly tested. The experimental setup can be seen in Figure 16 below.

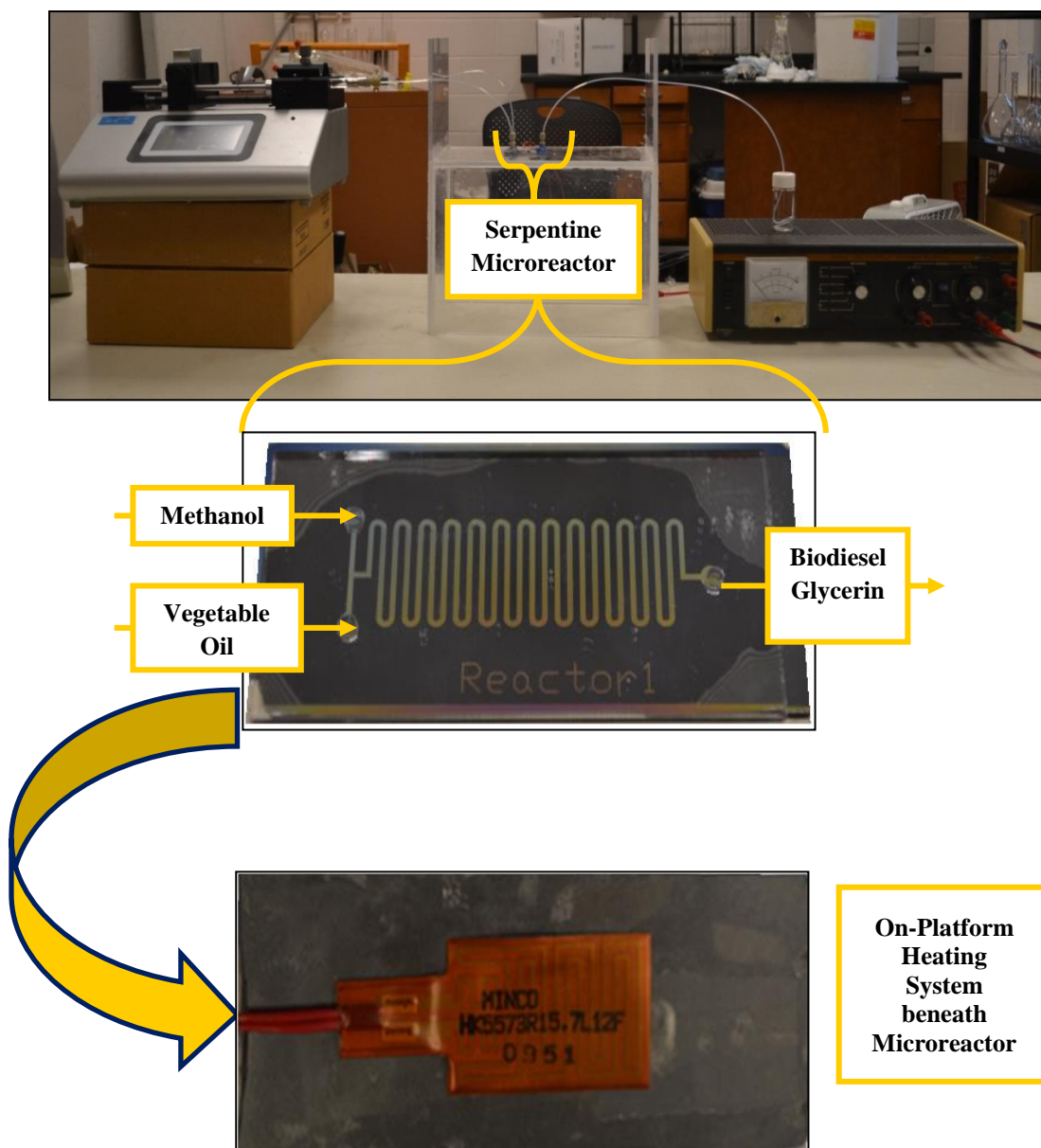


Figure 16: The top photo, read from left to right, shows the experimental setup. A syringe pump injects the reactants into the microreactor; the products exit and are stored. The middle photo is a close-up of the microreactor. Channel dimensions are 50 microns deep x 500 microns wide x nominal length 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.

Figure taken from Snider.⁶

4.2.3 Analytical Chemistry

To determine conversions of feedstock to product, two different analytical chemistry (AC) methods were used. For SBO conversion, gas chromatography was used for conversion to FAME. However, due to the similarity in chemical structure of FFA and FAME, gas chromatography is not a suitable choice of AC for measuring FFA conversion. Acid number analysis was used as an alternative to determine conversions of FFA in the feedstock. Before samples could be analyzed, they had to be prepared for analysis.

4.2.3.1 Preparation

The catalyst and methanol must be removed from the unreacted oil and products. The first step to purifying any sample is the removal of the catalyst. For microreactor samples, this is not required since the catalyst remains in the reactor throughout. For all other samples, the Hermle Z206A centrifuge, as previously mentioned, was operated at its maximum speed of 6000 rpm, to separate the catalyst.²³ This correlates to a relative centrifugal force of 4180 times gravity, which plays a key role in greatly decreasing the time required for separation. The time required for separation can be determined using Stoke's Law for spheres, which is as follows:

$$\mu = \frac{[2 * R^2 * (\rho_s - \rho) * g]}{[9 * \nu_t]} \quad (2)$$

where μ is the viscosity of the fluid, R is the radius of the falling particle, ρ_s is the density of the particle, ρ is the density of the fluid, g is gravity, and v_t is the terminal velocity. After solving for the terminal velocity, the time it will take for the particle to fall a known distance can be calculated. This equation is only valid, however, if the Reynolds' number is less than 1, which implies creeping flow.³⁰ The NiO nanopowder used has particle size of less than 50nm; therefore, when in oil, creeping flow is an accurate assumption.

Once the catalyst is removed, methanol also needs to be separated out of the sample. Due to the difference between boiling points of methanol and the oil feed and products formed, methanol can be vaporized out of samples at temperatures above 65°C. When methanol is fully removed, samples are then ready for analysis.

4.2.3.2 Gas Chromatography

The method for analyzing conversion of SBO was gas chromatography. The following chemicals used for gas chromatography analysis were supplied by Sigma-Aldrich, n-Heptane ($\geq 99.5\%$), Tricaprin (GC $\geq 99\%$), and Pyridine (anhydrous, 99.8%).³¹⁻³³ This study used a SRI 8610C GC equipped with a MXT-Biodiesel TG column (15m in length and .32mm in inner diameter).^{34,35} ASTM D6584 was reviewed for proper set up and calibration of the GC.³⁶

Gas chromatography differentiates the components in a solution based on their respective boiling points. When injected into the gas chromatographer (GC), the components in a sample of product attach to the capillary column inside of the GC

oven. The GC separates these components by increasing the temperature slowly over a known amount of time. As temperature rises, volatility causes components to vaporize. The smaller, more volatile components leave the column more quickly than larger, less volatile components. When components vaporize, a carrier gas, typically helium, transports the vaporized portions of the sample through the capillary column to the detector. The detector used in this study is a flame ionization detector (FID). FID's burn the components in a hydrogen flame to ionize the molecules. The GC then records the charge of the ionized molecules from the FID and plots this data versus time. The millivolt (mV) reading can then be integrated and correlated to concentration. The integration is performed by the computer interface software Peak Simple.

To determine conversion of SBO molecules to biodiesel, the loss of chemically bound glycerin (CBG) is compared to the initial amount of CBG.²² CBG is determined as follows:

$$CBG = \frac{(Triglycerides+Diglycerides+Monoglycerides)}{Tricaprin} * 100 \quad (3)$$

where it is the sum of the individual areas of the triglycerides, diglycerides, and monoglycerides peaks divided by the area of the tricaprins peak. Using the following equation, CBG conversion can be calculated:

$$CBG \text{ conversion } (\%) = \frac{(CBG_i - CBG_t)}{CBG_i} * 100 \quad (4)$$

where CBG_i is the initial concentration of chemically bound glycerin and CBG_t is the concentration after time t of reaction.³⁷

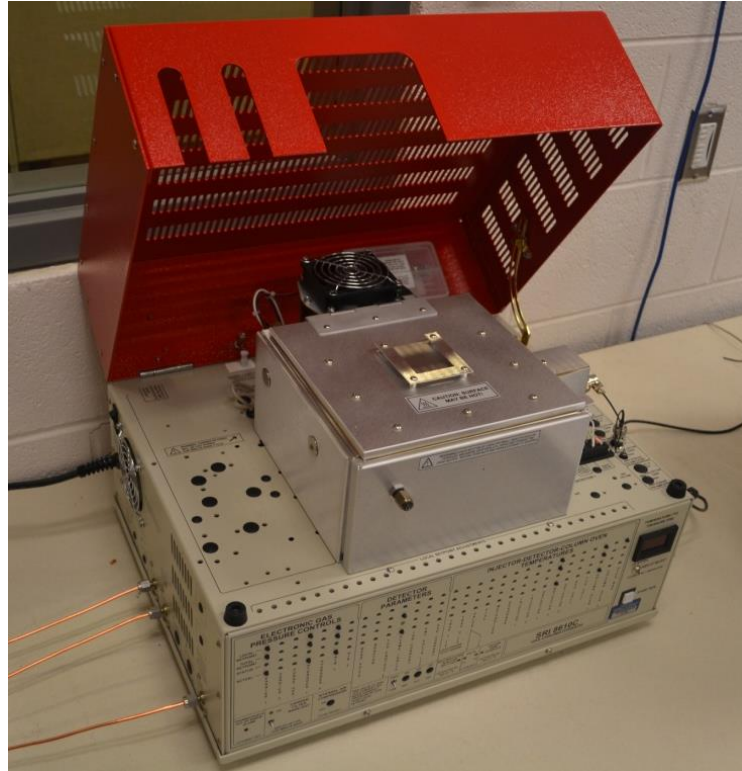


Figure 17: SRI 8610C GC for FAME analysis from triglycerides

1. Prepare the GC for analysis by turning on Peak Simple, turning on the helium, hydrogen, and compressed air gasses, and then allow the GC to reach operational temperatures.
2. Measure out approximately 0.100 grams of sample to be analyzed after purification (no catalyst or methanol) in an 8 mL vial.
3. To this vial, add 100 μ L 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.³⁸

4. Also to the vial, add 100µL of the internal standard Tricaprin.
5. Let the mixture react for 20 minutes, then add 8 ml of n-Heptane to the vial.
6. When this process is complete and the GC is ready for use, measure 1µL of the solution in the 8 mL vial and inject into the GC.
7. Start the Peak Simple software to analyze the sample.
8. After Peak Simple has produced the chromatograph, export the reported area data to Excel to calculate conversion on the sample.

4.2.3.3 Acid Number Analysis

In order to determine the conversion levels of FFA, acid number (AN) analysis was performed following ASTM D974.^{39,40} AN is determined by titration neutralization of FFA. The following chemicals used for AN analysis were supplied by Sigma-Aldrich: 2-propanol (anhydrous, 99.5%), 0.1N Potassium Hydroxide in isopropanol, α -Naphtholbenzein indicator, and toluene (anhydrous, 99.8%).⁴¹⁻⁴⁴

Acid number and conversion are defined as followed:

$$AN = \frac{mg\ KOH}{g\ Analyte} \quad (5)$$

$$Percent\ Conversion = \frac{AN_{initial} - AN_{final}}{AN_{initial}} \times 100\% \quad (6)$$

The method for AN analysis used 0.01N Potassium Hydroxide, KOH, to neutralize the FFA. Neutralization of the FFA was noted with α -Naphtholbenzein indicator. A known amount of analyte was added to 10mL of the titration solvent (100:99:1 toluene: isopropyl alcohol: water volume per volume solution) before the KOH is used for titration.

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 10mL 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 in color after adding pH indicator.

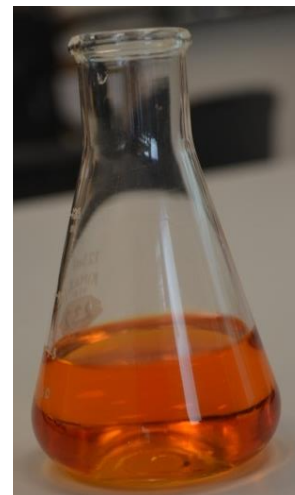


Figure 18: Initial Acid Number Color

4. To the flask, add the potassium hydroxide (KOH .01N) slowly until blue-green color change is evident. Record the mL of KOH required to achieve this color change.
5. Determine mass of KOH added using the following equation:

Mass KOH (mg) =

(mL KOH added)* .01N*Molecular Weight KOH

6. Determine the Acid Number using the following equation:
Acid Number = Mass KOH (mg)/grams of sample added

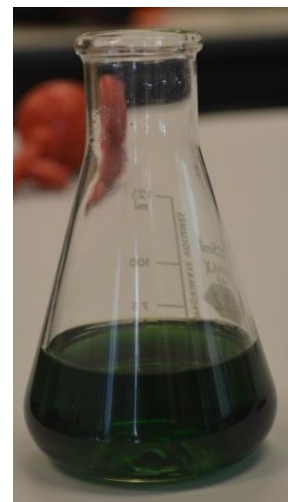


Figure 19: Acid Number Endpoint Color

5.0 Results

The goal of this research project is to experimentally determine a stable single phase feedstock to overcome the phase boundaries of traditional processing. Using a single phase feedstock should increase the initial reaction rates for both stirred and unstirred processes.

Microreactor design issues are considered, especially catalyst coating techniques. Ultimately, the application of the goals above with the implementation of design recommendations to next generation microreactors will result in a significantly improved continuous heterogeneous catalysis process for biodiesel production.

5.1 Miscibility Testing

SBO and MeOH are immiscible. When reacting SBO and MeOH for biodiesel production, phase boundaries becomes an important issue to examine. However, FFA, on the other hand, is miscible in both SBO and MeOH. In the right ratio, FFA will act as a co-solvent, resulting in a single phase processing fluid. However, kinetically, the higher the molar ratio of MeOH, the easier the reaction will take place. In the group's previous work, the molar ratio of MeOH to SBO was 72:1.⁶ This excess of MeOH drives the reaction forward; therefore, the molar excess of MeOH is a favorable ratio to consider when finding a single phase feedstock.

Various ratios of reactants were prepared in order to determine a mixture that would produce a stable single phase feedstock. A criterion for a stable single phase

mixture is a 24 hour plus resting time without separation. Also phase stability was tested by centrifugation at 6000 RPM for 5 minutes. Various volumetric ratios were examined and the results can be seen in the Table 2.

Table 2: Phase studied feedstock volume ratios with corresponding mass and molar ratios with phase separation indication.

Volume Ratio			Mass Ratio			Mole Ratio			Single Phase
SBO	FFA	MeOH	SBO	FFA	MeOH	SBO	FFA	MeOH	
1	0.5	0.75	1	0.47	0.64	1	1.4	16.9	No
1	0.5	1	1	0.47	0.86	1	1.4	22.5	No
1	0.5	2	1	0.47	1.72	1	1.4	45.0	No
1	0.75	0.5	1	0.70	0.43	1	2.1	11.3	Yes
1	0.75	0.75	1	0.70	0.64	1	2.1	16.9	Yes
1	0.75	1	1	0.70	0.86	1	2.1	22.5	No
1	1	1	1	0.93	0.86	1	2.8	22.5	Yes
1	1	2	1	0.93	1.72	1	2.8	45.0	No
1.5	1	1	1	0.62	0.57	1	1.9	15.0	Yes
2	1	1	1	0.47	0.43	1	1.4	11.3	No

Several ratios produce a steady, single phase, feedstock. For ease of experimental purposes, the 1:1:1 volume ratio was chosen for two predominant reasons. This ratio is volumetrically easy to measure, and also has the highest molar amount of MeOH while remaining in a single phase. The molar ratio of MeOH to SBO used previously in stirred tank reactors was 72:1, and the ratio for unstirred reactors was 24:1. Both of these feed were 2 liquid phases. The chosen molar ratio of MeOH:FFA:SBO for this study is approximately 23:3:1, which is a clear processing disadvantage. However, the one (liquid) phase nature of this feed should overcome equilibrium disadvantage.

5.2 Reactors

The effects of the co-solvent FFA on biodiesel production will now be discussed. The results of the three different reactors, described in section 4.2.2, will be detailed individually. Conversions using a single phase feedstock, having a ratio of SBO:FFA:MeOH of 1:1:1 will be compared to conversions of 2 phase reactions of SBO and MeOH.

5.2.1 Stirred Tank Reactors

Experiments were performed at methanol's reflux point, about 65°C, in stirred tank reactors. At reflux, methanol is constantly vaporizing; therefore, condensers were used to recycle escaping methanol vapor due to the reactors being open to the atmosphere. Water baths were set at 75°C so as to make sure MeOH remained at its reflux temperature. Stir bars are set at 800 RPM.

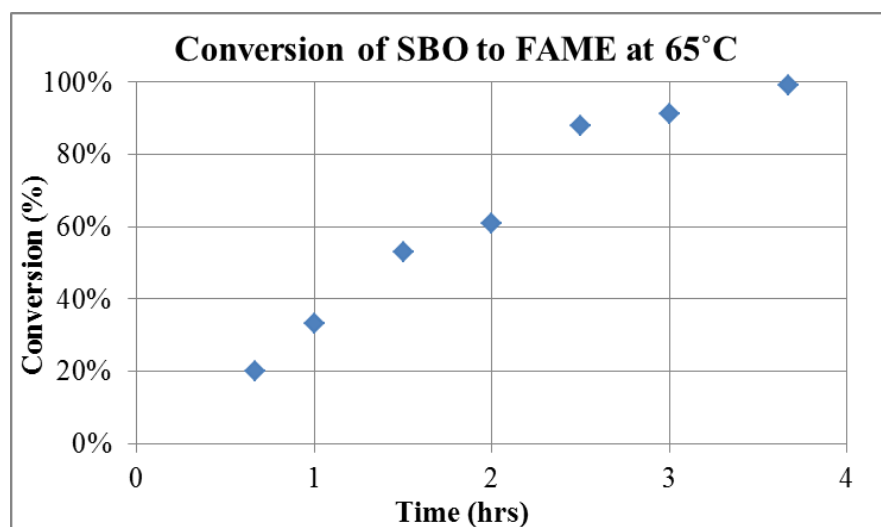


Figure 20: Conversion of SBO to FAME in Stirred Tank reactors at 65°C with 2 phase feedstock. Data taken from Snider.⁶

The conversion of SBO to FAME in stirred tank reactors was previously studied in our research group, and conversion is shown in Figure 20.⁶ The conversion, for these results only, was measured using an NMR. The conversion was determined by comparing the loss of triglycerides only in reacted samples. This method has the potential to yield an overestimate of conversion, since not all the triglycerides convert directly to FAME. Some triglycerides convert to di and mono glyceride intermediates. The time required to reach full conversion (between 3 and 4 hours) is comparable to industrial processes.

5.2.1.1 Effect of Co-Solvent in Stirred Tank Reactors

In order to reduce the initial rates, the co-solvent FFA was introduced and the effects on the beginning of the reaction were analyzed. A comparison of initial rates of conversion to FAME for SBO:MeOH 2-phase feedstock versus SBO:FFA:MeOH single phase feedstock (where FFA acts as a co-solvent) are illustrated in Figure 21. Initial rates for single phase feedstocks are significantly higher due to the removal of the multi-phase reaction rate resistances.

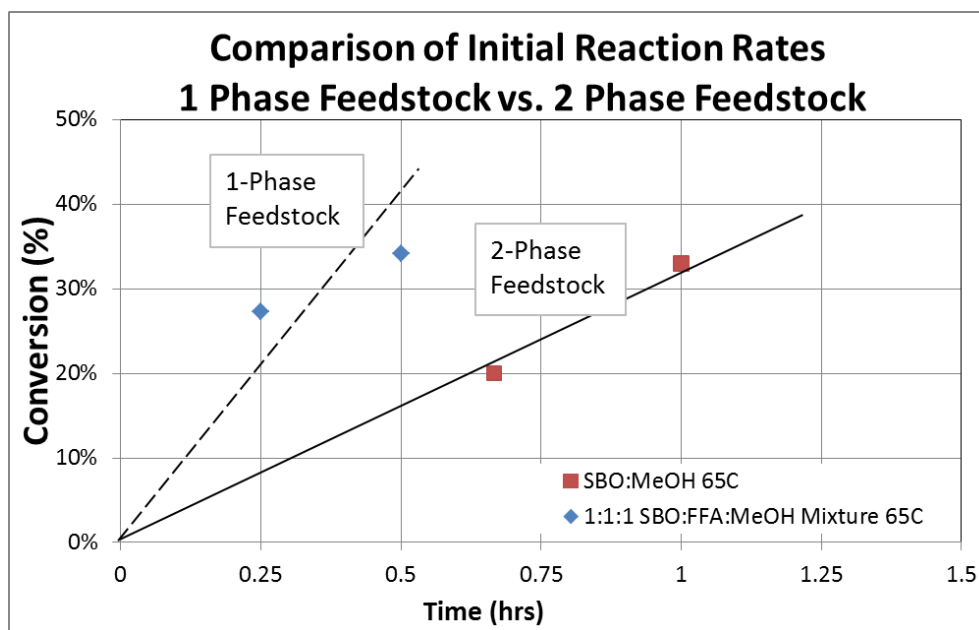


Figure 21: Effect of FFA as a co-solvent on conversion to FAME in Stirred Tank reactors at 65°C.

Figure 22, illustrates the benefits of co-solvents on reaction rates in stirred tanks during biodiesel production. There is an S-curve nature to the conversions over time due to reactants initially having to overcome the phase boundaries. As co-solvent levels are increased, the initial rates increase and the S-curves shifts to the

left. This illustration is based on the findings of Park et al., as mentioned in section 3.2.1.1.¹⁴ Park's study used FAME as the co-solvent and the homogeneous catalyst KOH. This study, on the other hand, uses FFA as co-solvent along with a heterogeneous catalyst.

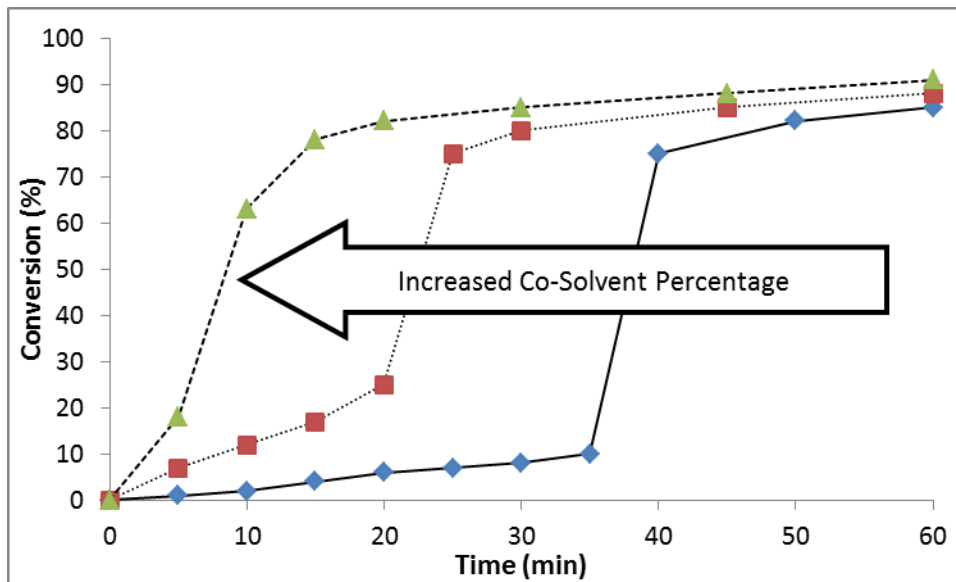


Figure 22: Anticipated Effect of FFA as a co-solvent on initial rates of conversion to FAME. Data taken from Park et al.¹⁴

The results shown in Figure 21 show a similar behavior to Figure 22. The initial reaction rates (shown as slopes) are significantly different. It should be seen that the 1 phase initial reaction rate is approximately 150% higher than that of the 2 phase rate. This is in spite of the equilibrium disadvantage of the single phase fluid due to a much lower MeOH molar ratio.

Another advantage of our feedstock over the findings of Park and others is that we can use oil “contaminated” with FFA as feedstock. This makes the feedstock cheaper. Also, other solid base catalysts cannot be used to convert FFA to FAME.^{37,45}

5.2.2 High Temperature Unstirred Reactors

Experiments were performed at 180°C and approximately 26 atmospheres in sealed, stainless steel, vials. Having sealed vials does not allow stirring for these reactors. At elevated temperatures and pressures, the physical and chemical behavior of the reaction in the unstirred reactor is unclear. When the catalyst and feed are loaded, the catalyst powder is a solid phase at the bottom, and the oil phase is above it and a MeOH phase is on top. This is a difficult geometry for MeOH and oil molecules to meet at the catalyst surfaces to react.

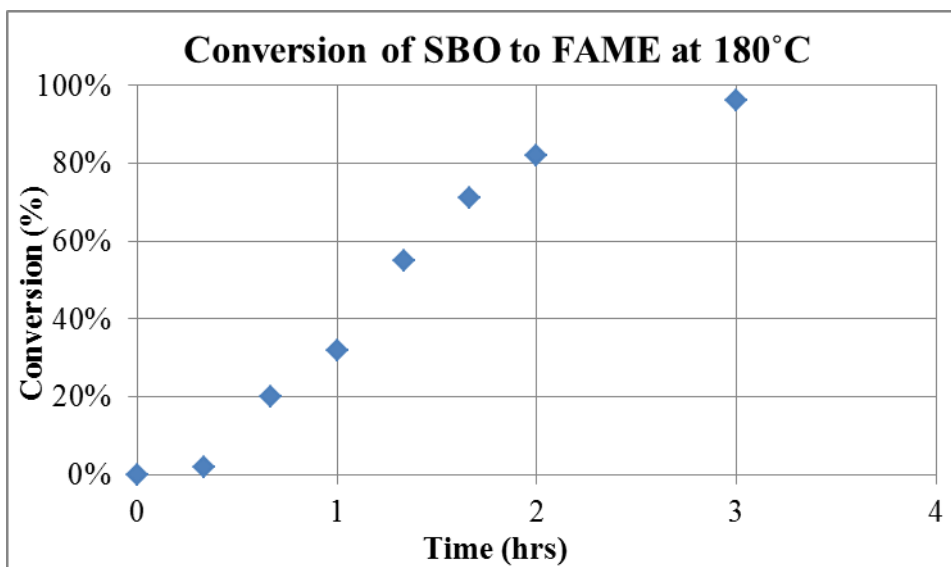


Figure 23: Conversion of SBO to FAME in High Temperature reactors at 180°C with 2 phase feedstock.

The conversions determined in Figure 23 were found using Gas Chromatography following ASTM D6584 standard. Notice the S-curve nature of the conversions over time. This behavior is similar to the results of Park shown in Figure 22. Due to the complicated initial 3 phase layered nature of the feed and the lack of stirring, a significant lag in initial rates is expected. The total reaction time is reduced from stirred tanks reactors, as seen in Figure 20, from almost 4 hours to about 3 hours.

5.2.2.1 Effect of Co-Solvent in High Temperature Unstirred Reactors

An FFA co-solvent was added to increase initial reaction rates. A comparison of initial reaction rates for 1 phase and 2-phase feedstocks in stainless steel vials is shown in Figure 24. A time lag for 2 phase feedstock again produces an S-curve conversion pattern. The 1 phase system seems to successfully eliminate any reaction rate time lag. This improvement is in spite of the MeOH to SBO molar ratio being reduced from 24:1 for the 2 phase feed to 22.5:2.8:1 (MeOH:FFA:SBO) for the 1 phase feed.

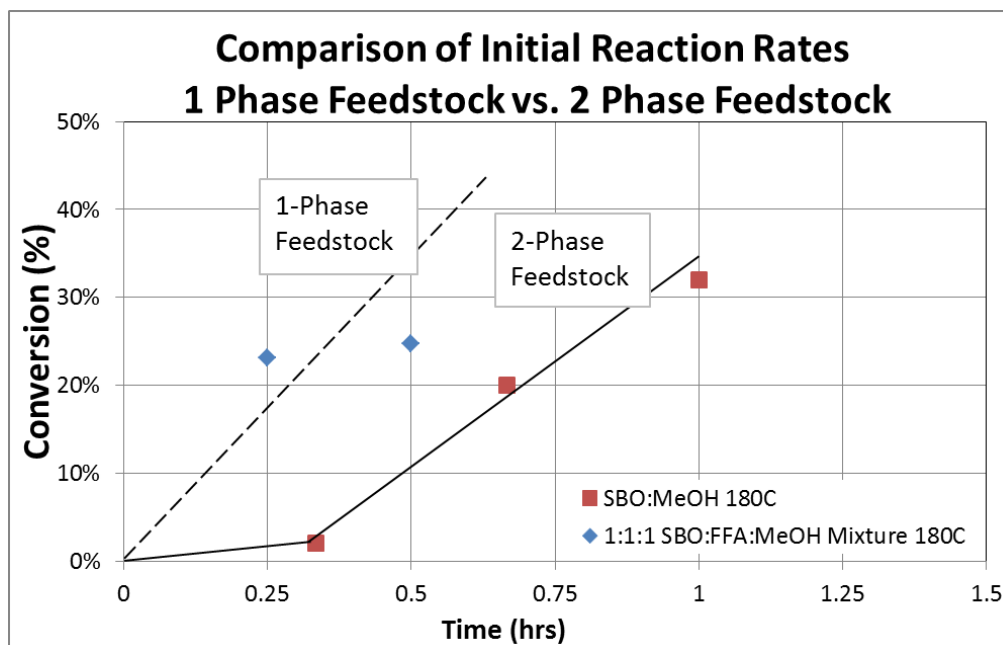


Figure 24: Effect of FFA as a co-solvent on conversion to FAME in High Temperature reactors at 180°C.

Both of these differences add individual benefits to the production of biodiesel. The most significant benefit is the use of a co-solvent that significantly increases reaction rates and is considered industrial waste, and is thus cost effective. The heterogeneous catalyst adds the benefit of now being able to process continuously. These benefits make the possibility of continuous processing feasible by using lower amounts of energy to produce a source of energy.

5.2.3 Microreactors

Microreactors have been used in this study, following the methods in 4.2.2.3, to produce levels of conversion equivalent to that of industrial processes in significantly less amounts of time. Figure 25, below, compares the conversion of

SBO to FAME in a microreactor versus the conversion in stirred tank reactors. In roughly 4 minutes, microreactors produce conversions equivalent to 2.5 hours of traditional processing. This is a tremendous improvement over the industrial method.

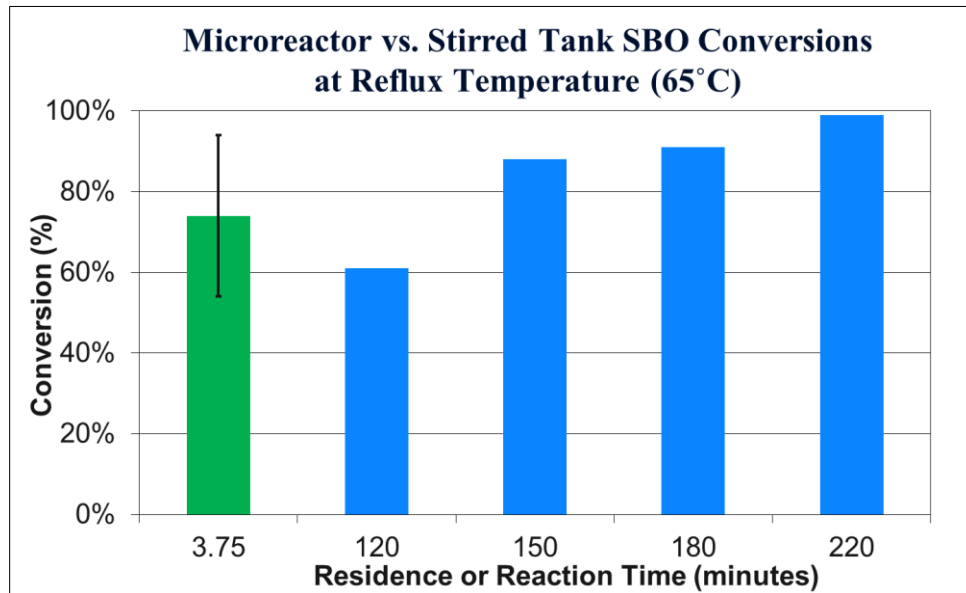


Figure 25: Comparison of Microreactor (Green) and Stirred Tank (Blue) Conversions to FAME at Reflux for SBO. Data taken from Snider.⁶

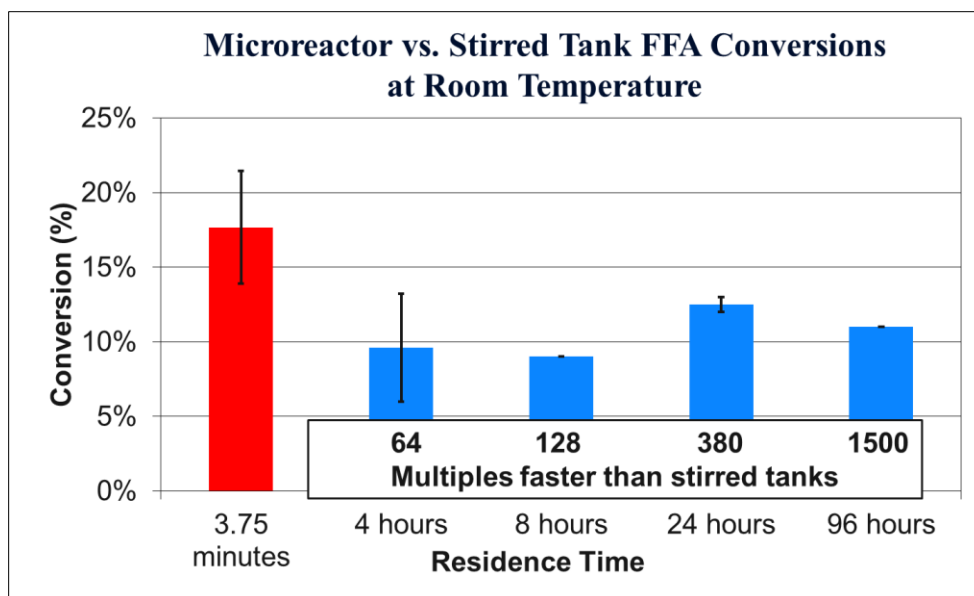


Figure 26: Comparison of Microreactor (Red) and Stirred Tank (Blue) Conversions to FAME at Room Temperature for FFA. Data taken from Snider.⁶

Furthermore, with the ability to process pure FFA with the heterogeneous catalyst, microreactors are able to produce conversions as much as 1500 times faster than the traditional stirred tank reactors using the same heterogeneous catalyst. This can be seen in Figure 26, above. The higher conversion bodes well for the implications of the single phase SBO:FFA:MeOH processing fluid.

5.2.3.1 Effect of Co-Solvent in Microreactors

Adding to the design improvements theorized in section 3.3.1, the use of FFA as a co-solvent has the potential of reducing the processing time for significant conversion to less than a minute. As the new microreactors are produced, these results will be studied.

5.2.3.2 Suggestions for Future Microreactor Design

While results from the microreactors show much potential, different problems have arisen that need to be taken into consideration in the next generation of microreactors. The first and most troublesome issue is plumbing. Ports for entering and exiting the reactor are currently attached by chemical adhesives. This method is not strong enough to withstand the pressures developed inside the reactors or the solvation by methanol vapor at or near boiling temperatures. These adhesives had to constantly be reapplied to keep the ports from losing adhesion to the glass surface. If the glass ceiling were to be doubled in thickness, it would be possible for threads to be etched into the glass in order to use threaded ports in an effort to relieve some of the pressure on the adhesive. Furthermore, the durability of the reactors needs to be considered. Silicon wafers are easily cracked, which is an issue when the reactors are being handled. 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 improving upon the catalyst coating. One way of improving the performance is sputtering on the roof of the channel. 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, thus significantly increasing reaction rates.

Secondly, the current catalyst coating on the surfaces of the microreactors has an unknown lattice structure and is assumed to be amorphous. Implementation of the

methods described in Section 3.3.1 is theorized to impact the conversion rates as well. Methods have been discovered to produce known lattice structures, using magnetron sputtering, of NiO. Three distinct crystalline structures {(111), (200), and amorphous} will be sputtered onto the channel surfaces. Further experiments will show if one structure or some combination of structures will perform best.

6.0 Conclusions

The first, and most important, goal of this project was to determine a stable single phase feedstock for biodiesel production. Multiple indefinitely stable single phase feedstocks were experimentally determined. These feedstocks will enable the reaction to overcome the phase boundaries of traditional processing.

Using these single phase feedstocks, increases in the initial reaction rates were successfully achieved. This was true for both stirred and unstirred processes. The successful increase of initial rates is more significant when reacting in unstirred reactors. The significance is due to the removal of the S-curve nature of unstirred reactions caused by the time lag from phase boundaries. Conversion begins very shortly after the reaction is started. This is beneficial when reacting using a continuous process.

Furthermore, the literature findings for design improvements in microreactors will provide means for improving the catalyst efficacy and upon further experiments determine the best lattice structure of the catalyst. Once implemented on the next generation of microreactors, the new design will result in a significantly improved continuous heterogeneous catalysis process for biodiesel production.

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