# Synthesis of Biodiesel Fuels and Pharmaceuticals Using Nano-Reactors

by

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#### Abstract

Limitations to chemical syntheses have always been present and prevented reactions from producing products effectively or even at all. The goal of this thesis is to tackle these limitations by the use of one thing; nano-reactors. These nano-reactors possess innate properties which provide viable options to improve the effectiveness of chemical reactions. The reaction that is going to be tackled is the synthesis of biodiesel fuels.

Biodiesel fuels are fatty acid-based esters that can be synthesized from used or unused cooking oils through a simple transesterification reaction<sup>1</sup>. The simplicity of the reaction, recyclable use of cooking oils, and environmental benefits of using biodiesel fuels provide a viable option to replace currently used petroleum based fuels<sup>1</sup>.

Experimental results of the one-pot reaction used to synthesize biodiesel fuels provided yields 99% plus consistently. The reaction success along with the aforementioned benefits indicate that biodiesel fuels could be a possible replacement for currently used petroleum based fuels.

## Nano-Reactors and Their use in Organic Synthesis

Organic synthesis has been successfully used to produce a plethora of organic molecules for various applications. Producing a product is not the only measure of reaction success as the ease and effectiveness of producing the product also plays a major role. Ideal reactions are cheap, require small amounts of reactants, and have high yields. This is often not the case as many reactions require excess amounts of reactants and are costly relative to the amount of product produced. When the previous conditions define a synthesis, better reaction schemes are sought after to reach high yield at a low cost. This is where this thesis is centered; finding ways to make organic syntheses more successful, specifically trying produce the profoundly desired high yield. To do this, traditional organic syntheses will be modified with the inclusion of nano-reactors to attempt to increase reaction yields.

The term nano-reactor refers to a solid, sand like substance primarily made up of bis(trimethoxysilylethyl)benzene (BTEB), a swellable organically modified silica (SOMS) compound invented by Paul L. Edminston<sup>4</sup>. The structure of BTEB is shown in Figure 1.



**Figure 1:** Chemical Structure of bis(trimethoxysilylethyl)benzene, the compound comprising the nano-reactors used to improve reaction success<sup>6</sup>.

The structure of this molecule provides it an innate ability to form a flexible, cross linked system via Si-O-Si bonds<sup>6</sup>. While doing this the aromatic center of the molecule is rather free and can interact with other aromatic centers via the pi orbitals perpendicular to the plane of the benzene ring. This interaction allows for a "stacking" of these rings and causes the crosslinked system to condense<sup>6</sup>. While interactive, this stacking is weaker than the Si-O-Si bonds and can be disrupted by the introduction of organic solvents into the system. The disruption of these interactions causes the cross-linked system to expand, opening a fillable space inside the system. Removing the solvent will cause the system to return to its condensed form and this expand-condense method can be repeated with the introduction and removal of organic solvents<sup>6</sup>. This process can be taken advantage of during chemical reactions, and therein lies the reason for the use of the nano reactors. The process can be done by combining a set of reactants, a solvent, and the nano-reactor together. The aforementioned spaces produced by the solvent induced expansion of the nano-reactors now holds the reactants. The removal of the solvent, caused by refluxing or rotary evaporation, rapidly condenses the nano-reactors, increasing the kinetic energy of the reactants and the likelihood of their contact, therefore increasing their chance of reacting<sup>6</sup>. This process can be repeated until full reaction completion. Figure 2 shows a diagram of the nano-reactor reaction process.



**Figure 2:** Mechanism of nano-reactor aided synthesis<sup>6</sup>. The nano-reactor can expand and condense with the addition and removal of solvent until the reaction makes full completion.

To prove the successful nano-reactor mechanism, previous work has been done by the research group with biodiesel fuels. A biodiesel synthesis combining cooking oil with an alcohol in an acid catalyzed reaction was performed and the percent yield was measured<sup>7</sup>. Figure 3 shows the associated data from the reactions.



**Figure 3:** Percent yield data of 10 biodiesel synthesis reactions. Yields of 95% plus were obtained in all trials<sup>7</sup>. Figure 3 shows that all biodiesel synthesis reactions performed reached yields of above 95%, supporting the theory of increased reaction yield associated with the use of the nano-reactors<sup>7</sup>.

The above data also supports the reusability of nano-reactors. All of the biodiesel trials shown above were run using the same nano-reactors, with methanol washes to clear the system after each trial. The consistent high yield of each reaction also supports the reusability of the nano-reactors along with the increased reaction yields further proving their viability<sup>7</sup>.

While showing the reaction success, the results omit the time required to reach high yields. A separate test was run to determine how long the reaction took to reach maximum yield<sup>7</sup>. Reaction rates were measured using "closes," a term that refers to a single expansion and condensing of the nano-reactor. The time of a close depends mainly on the solvent used in the reaction. For example, a close using dichloromethane takes a matter of seconds in a rotary evaporator while using methane would take far longer<sup>9</sup>. A biodiesel reaction was run with a nano-reactor while a small sample of product was analyzed for conversion after each close. Figure 4 shows the progression of the reaction yield.



**Figure 4:** Percent conversion of cooking oil to biodiesel measured after each close of the nano-reactor<sup>7</sup>. Figure 4 shows that only 13 closes were needed to reach nearly 100% conversion of cooking oil into biodiesel<sup>7</sup>. The small time required to reach full conversion again supports the viability of the use of nano-reactors.

Bringing it all together, manipulating the closure method of nano-reactors to perform organic syntheses can increase reaction yield with reactions reaching full completion in a short amount of time while the same nano-reactors can be reused with continued success between syntheses. With the success of nano-reactor enhanced reactions proven, their use can be applied to more fields. The field that will be focused on here will be a continuation into the synthesis of biodiesel fuels.

# **Synthesis of Biodiesel Fuels**

## Introduction

Biodiesel is an alternative fuel source often produced from renewable resources such as vegetable oils and animal fats<sup>1</sup>. Most biodiesel products are synthesized from cooking oil, which is chemically composed of triglycerides, or three fatty acids connected via an ester bond to glycerol, providing a 3:1 molar ratio of fatty acids to glycerol<sup>1</sup>. Figure 5 shows the structure of a general triglyceride molecule containing three fatty acids bonded to the glycerol backbone.



**Figure 5:** Chemical structure of a triglyceride molecule<sup>2</sup>. R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> represent carbon chains of varying length and hydrogen saturation on the three fatty acid groups. Carbon chains can be the same or different depending on the triglyceride<sup>2</sup>. The three fatty acid groups allow for biodiesel to be produced simply from the triglyceride because of their structural similarities to biodiesel.

The environmental and safety benefits of biodiesel are far better than petroleumbased diesel fuels significantly increasing the interest in biodiesel research<sup>1</sup>. Biodiesel possesses chemical characteristics that allow for better safety standards than conventional fuels. The benefits of biodiesel include improved safety for the user in both handling and manufacturing, positive effects on the engine using the fuel, and reduces environmental pollution<sup>1</sup>. Biodiesel has a significantly higher flashpoint of 130 °C than the 52 °C flashpoint for petroleum-based fuels<sup>1</sup>. The higher flashpoint of biodiesel makes it far less likely to combust than petroleum-based fuels allowing for significantly safer storage and transport.

Petroleum-based fuels also affect the environment in many negative ways. When spilled, petroleum-based fuels can cause significant damage to the environment and the wildlife by inhibiting animal activity by toxicity and pollution<sup>1</sup>. This is not the case with biodiesel fuels as they are synthesized with plant and animal products so the damage they cause on the environment is far less severe when spilled. Environmental harm is also caused by the release of gas, specifically carbon dioxide, into the environment when petroleumbased fuels is combusted<sup>1</sup>. Biodiesel still produces carbon dioxide, but compared to petroleum based fuels, the release is much smaller in quantity. Analysis by the Argonne National Laboratory indicates carbon dioxide emissions of biodiesel were reduced by 74% in comparison to petroleum-based fuels<sup>1</sup>.

Biodiesel also has a positive effect on the state of the engine using it. Fuel lubricity is an important characteristic of fuel used in engines that measures how much a fuel breaks down an engine overtime, eventually leaving it inoperable<sup>1</sup>. Biodiesel has a better fuel lubricity than petroleum-based fuels and therefore is better at maintaining the state of the engine. Even blending biodiesel with petroleum-based fuels improved lubricity with as little as 1% of biodiesel in the blend<sup>1</sup>.

Biodiesel is synthesized via a transesterification reaction, where the nucleophilic attacking alcohol creates a new carbon-oxygen ester bond with the carbonyl as the previous carbon-oxygen ester bond is broken displacing the original alcohol<sup>2</sup>. Catalysts, specifically acid catalysts in the reaction scheme used in this experimentation, can be used to increase

yield and reaction rates. Due to the three fatty acids present in the triglyceride molecule, transesterification must occur three times to completely convert all fatty acids in a single mole of triglyceride into biodiesel. Equation 1 shows the generic chemical reaction.

$$3CH_3OH + TG \to 3BD + GL \tag{1}$$

In Equation 1 TG, BD, and GL represent triglyceride, biodiesel, and glycerol respectively. A 3:1 molar ratio of biodiesel to glycerol in the products is evidenced here. The mechanism of this reaction is shown in Figure 6.



**Figure 6:** Mechanism of biodiesel synthesis from cooking oils<sup>2</sup>. The R groups are varying carbon chains specific to the oil and alcohol used. The reactants used during experimentation are explained in the experimental methods section.

Figure 6 depicts the mechanism of transesterification for biodiesel synthesis via nucleophilic acid attack<sup>2</sup>. Step A corresponds to the pronation of a single carbonyl group via acid to increase the electrophilicity of the carbon of the carbonyl group. Step B corresponds to the nucleophilic attack of the alcohol on the enhanced electrophile of the carbonyl center. Step C corresponds to the reformation of the previously broken  $\pi$  bond of the carbonyl resulting in the breaking of the ester bond to glyceride molecule. Step D corresponds to the deprotonation of the carbonyl group and the loss of the excess proton on the bonded alcohol to produce the final biodiesel product. This reaction scheme must be run twice more to release the last two fatty acid groups<sup>2</sup>. Specific reactants used in this experiment are specified in the experimental methods section.

Furthermore, during biodiesel synthesis the carbon-oxygen ester bond is severed with an alcohol to produce three biodiesel molecules and glycerol as a side product<sup>2</sup>. Figure 7 shows these products.



**Figure 7:** Chemical structure of the products of the esterification reaction<sup>2</sup>. Figure 2A depicts glycerol while 2B depicts three biodiesel molecules. R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are carbon chains of varying length and carbon

saturation.  $R^4$  is the carbon chain specific to the alcohol used synthesize the biodiesel. The final molar ratio of the reaction is 3:1 as three biodiesel molecules are produced while only one glycerol molecule is.

Figure 7 depicts the chemical structures of the products of biodiesel synthesis<sup>2</sup>. The separation of the biodiesel fuel from the glycerol is easy as glycerol and biodiesel are immiscible with different densities and can therefore be separated easily after synthesis.

The final produced products are immiscible, pure, and possess different densities, allowing for easy separation and identification after completion of the reaction<sup>2</sup>. To determine the presence of glyceride / glycerol and biodiesel the protons corresponding to the methylene group of the glyceride / glycerol molecule and the methoxy group of the biodiesel product were monitored with Proton Nuclear Magnetic Resonance Spectroscopy (<sup>1</sup>H-NMR). Figure 8 depicts the corresponding protons of interest.



**Figure 8:** Hydrogen atoms used in identification of glyceride / glycerol and biodiesel presence in reaction products via 1H-NMR. Figure  $5A_1$  depicts the methylene protons, circled, of the glyceride molecule present in unconverted cooking oil. Figure  $5A_2$  depicts the methylene protons, circled, of the glycerol molecule present in

the reaction product. Figure 5B depicts the methoxy protons, circled, of the biodiesel molecule present in the reaction product.

Figure 5 depicts the hydrogen atoms used in the identification of glyceride / glycerol and biodiesel presence in reaction products. The presence of methoxy protons in the reaction indicate the production of biodiesel while the presence of the methylene protons indicates the presence of either glyceride or glycerol. <sup>1</sup>H-NMR was used to identify the presence of the molecules by peak identification. Figure 9 and 10 show <sup>1</sup>H-NMR spectra of cooking oil and biodiesel respectively, with each peak identified.



**Figure 9:** <sup>1</sup>H-NMR spectra of vegetable oil before the reaction. The boxed peaks correspond to the methylene protons of the glyceride and glycerol molecules, circle on molecule.



**Figure 10:** <sup>1</sup>H-NMR spectra of biodiesel. The boxed peak corresponds to the methoxy proton, shown in the molecule above, present in the biodiesel produced from the reaction.

Figures 10 depicts the <sup>1</sup>H-NMR spectra of canola oil with the methylene peaks indicated. These peaks decrease in size as the vegetable oil is converted into biodiesel because the biodiesel spectrum loses methylene protons. The full loss of the methylene peaks indicates the full conversion of the vegetable oil into biodiesel. Other peaks correspond to separate protons on the triglyceride but are not pertinent in molecule identification.

#### Methods

A reaction scheme designed by the Shaw Research Group was used to synthesize biodiesel from used cooking oils<sup>7</sup>. To a round bottom flask 4.0 M HCl (423  $\mu$ L, 1.7 mmol), methanol (6.0 mL, 0.15 mol), cooking oil (0.5000 g, ~0.5758 mmol), and the nano-reactor (2.000 g) were added. The exact amount of these reactants was not important, but the ratio of each reactant to each other needed to be precise. The amount of methanol was also varied to insure complete encompassing of the nano-reactor and other reactants. Methanol was chosen since it provided the least possible steric hindrance from the alcohol. The approximation in the moles of cooking oil was due to the fact that the exact composition, and therefore molecular weight, was not known for each oil used. The flexing process previously described was used to perform the reaction and take advantage of the properties of the nano-reactor. The reaction was run overnight to insure complete conversion of the cooking oils. <sup>1</sup>H-NMR was used to determine the completion of the reaction by identifying the presence, or lack thereof, of the methylene and methoxy hydrogen. If methylene peaks were still present, the reaction was allowed to run until the peaks were completely removed, indicating the complete formation of biodiesel.

Once the methylene peaks were completely removed, indicating the complete conversion of glyceride into biodiesel, the product was vacuum filtered with methanol to remove all product from the nano-reactor and separate the nano-reactor from the biodiesel. The biodiesel, glycerol, and methanol mixture was then put on a Heidolph Hei-VAP rotary evaporator to remove all the methanol. Once all the methanol was removed, the corresponding biodiesel-glycerol product separated due to density differences between the products. When put into a separation funnel, biodiesel composed the top layer and glycerol composed the bottom layer. This was confirmed by <sup>1</sup>H-NMR. The biodiesel layer was used to determine the percent conversion of the glyceride molecule.

## Results

Data used to determine the presence of biodiesel, glyceride, and glycerol was obtained using <sup>1</sup>H-NMR. Integrations of the peaks were used to precisely determine exactly how much of the vegetable oil was converted into biodiesel. Figure 11 and 12 show the 1H-NMR spectra for biodiesel produced from new and used cooking oils respectively and the peaks used for conversion calculations.



**Figure 11:** <sup>1</sup>H-NMR spectrum after the biodiesel synthesis reaction with unused cooking oil was run overnight. Box A corresponds to the methylene peaks of glycerol and glycerides. Box B corresponds to the methoxy peaks of the biodiesel molecule. Data from this spectrum corresponds to sample number 1 in Table 1.

Figure 11 depicts the <sup>1</sup>H-NMR spectrum of biodiesel synthesized from canola oil. Box A corresponds to the methylene peaks of glyceride and glycerol. Box B corresponds to the methoxy peaks of the synthesized biodiesel. The small integration values of the methylene peaks in comparison to the methoxy peak indicate that much more biodiesel was present than glycerides or glycerol. Data from this spectrum corresponds to sample number 1 in Table 1. All other spectra for each unused cooking oil run are not shown, but the same method for data analysis was used.



**Figure 12**: 1H-NMR spectrum after the biodiesel synthesis reaction with used cooking oil was run overnight. Box A corresponds to the methylene peaks of glycerol and glycerides. Box B corresponds to the methoxy peaks of the biodiesel molecule. Data from this spectrum corresponds to sample number 1 in Table 2.

Figure 12 depicts the <sup>1</sup>H-NMR spectrum of a biodiesel synthesis with used cooking oil run overnight. Box A corresponds to the methylene peaks present in glycerol and glycerides. Box B corresponds to the methoxy peak of the synthesized biodiesel. The integration of the peaks was used in determining the amount of each molecule left after the reaction. The methylene peaks were still present, but with such smaller integration in comparison to the methoxy peak. The much higher integration values from the methoxy peak indicates that biodiesel is much more prominent than the triglyceride. Data from this spectrum corresponds to sample number 1 in Table 2. All other samples used the same method of analysis via <sup>1</sup>H-NMR.

**Table 1:** Chemical shift and integration measurements of canola oil biodiesel samples from

 <sup>1</sup>H-NMR

Sample Number	Peak Type	Chemical Shift	Integration
		(ppm)	
1	Methylene	4.13	0.0195
	Methoxy	3.65	1.00
2	Methylene	4.14	1.00
	Methoxy	3.64	641
3	Methylene	4.12	1.00
	Methoxy	3.65	66.2
4	Methylene	4.11	1.00
	Methoxy	3.65	19400

**Table 2:** Chemical shift and integration measurements of used cooking oil biodiesel samples

 from <sup>1</sup>H-NMR

Sample Number	Peak Type	Chemical Shift	Integration
		(ppm)	
1	Methylene	4.11	0.0366
	Methoxy	3.66	2.34
2	Methylene	4.15	1.00
	Methoxy	3.65	112
3	Methylene	4.14	1.00
	Methoxy	3.64	1170
4	Methylene	4.11	1.00
	Methoxy	3.64	109

Table 2 depicts the chemical shift and integration of peaks corresponding to the methylene and methoxy protons for four samples of used cooking oil biodiesel. Chemical shift and integration values were determined from the <sup>1</sup>H-NMR spectrum of the biodiesel product. Peak type corresponds to the labeled protons in Figure 9 and 10.

Integration values from Table 1 and Table 2 were used to determine the percent conversion of the cooking oil to biodiesel. Equation 2 depicts the formula for the determination of percent conversion<sup>8</sup>.

Percent Conversion

$$=\frac{\frac{Methoxy Peak Integration}{3}}{\left(\frac{Methoxy Peak Integration}{3} + \frac{Methylene Peak Integration}{4}\right)} * (100\%)$$
(2)

Equation 2 showed that the percent conversion of cooking oil into biodiesel was dependent on the ratio of the integrations of methoxy peak and the methylene peak. There were 3 methoxy protons on each biodiesel molecule and 4 methylene protons on each triglyceride molecule. The ratio of these two would not provide conclusive data when analyzed since the number of protons on each was not the same. A ratio of how each individual methoxy proton was related to the total amount of chemically unique protons would provide information about how much of the total protons were from the synthesized biodiesel and therefore tell us how much of the triglyceride had been converted.

This equation was specifically used because the percent conversion was not directly measurable based on a single peak. While the decrease in size of a single peak would indicate the conversion of that peak, it alone was not enough to determine the percent conversion in comparison to other spectra. The integration of a peak depends on how many protons are associated with that peak and the concentration of the sample measured. Higher concentrations produce larger peaks, have more area under the curve, and therefore a larger integration. The ratio between the integrations was still the same, so the change in integration value did not change the number of protons producing the signal. And with more protons on an atom, a bigger integration value would be obtained. Since the concentration of each <sup>1</sup>H-NMR sample was not constant, Equation 2 was used to account for this. Equation 2 also accounted for only the conversion of glyceride into biodiesel and not any side products. This assumes perfect conversion of triglyceride into biodiesel, which is not the case. Tables 3 and 4 show the percent conversions of the canola oil and used cooking oil samples.

Sample Number	Percent Conversion (%)
1	98.56
2	99.88
3	98.88
4	100.0
Average	99.33

**Table 3:** Percent conversion of canola oil triglyceride to biodiesel over complete reaction

Table 3 depicts the percent conversion data of four unused cooking oil biodiesel samples. Percent conversion data was determined using the final <sup>1</sup>H-NMR spectrum obtained and Equation 2. **Table 4:** Percent conversion of used cooking oil triglyceride to biodiesel over complete

 reaction

Sample Number	Percent Conversion (%)
1	98.84
2	99.34
3	99.94
4	99.32
Average	99.36

Table 4 depicts the percent conversion data of four used cooking oil biodiesel samples. Percent conversion data was determined using the final <sup>1</sup>H-NMR spectrum obtained and Equation 2.

## **Discussion and Future Work**

The average percent conversion for both biodiesel samples was calculated and compared using percent difference. Table 5 shows this data.

Table 5: Percent conversion of both cooking	oils to biodiesel over complete reaction
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Oil Type	Average Percent Conversion (%)	
Unused Cooking Oil	99.33	
Used Cooking Oil	99.36	
Percent Difference of Percent Conversions	0.0279%	

Table 5 shows that the reaction samples showed very high percent conversion indicating that nearly all the starting triglyceride was converted into biodiesel. The very high percent conversion that was consistently obtained proves that the reaction scheme used for the synthesis of biodiesel was very successful and valid. Almost none of the cooking oil used in the creation of the fuel was wasted.

Both the unused and used cooking oils provided very high percent conversion indicating that very little cooking oil was wasted and that this was a very successful and viable reaction scheme. A percent difference of less than 0.1% between the biodiesel samples percent conversion indicated that the points were nearly identical. Since both points were almost the same this indicated that the triglycerides in both used and unused cooking oils were converted equivalently. This indicated that the reaction was viable for both types of oils. While used cooking oils had high percent conversions, they had the problem of other side products in the final biodiesel sample. These side products included fatty acid chains that can harm the engines in which the biodiesel would be used. A method to remove these fatty acid chains needs to be developed to provide usable biodiesel fuels.

Experimentation proved that the synthesis of biodiesel at high conversion was consistently obtained with our reaction. The problem with this reaction was the yield of biodiesel, while high in percent conversion, was low in volume of biodiesel produced. So, a lot of oil was converted into biodiesel, but the amount of oil was too small to produce a usable amount biodiesel. In order for a successful transition from petroleum-based fuels to biodiesel for engine use, large quantities of biodiesel must be produced by cheaper and easier production in comparison to petroleum-based fuels. In order to produce more biodiesel product, the entire reaction must be scaled up. Further experimentation determined that the reaction could be scaled up by five times the initial reaction size and successfully produce biodiesel, but much larger yields still must be produced. The upscaling was done by increasing the amount of each reactant, including the nano-reactor, by the same factor. Using this same relationship, the reaction would need to be scaled up by an extreme amount to synthesize a useable amount biodiesel for even a single engine. This scaling up would require a much larger reaction chamber and would also cost a significant amount of money. To combat this, a way to either lower the price on the reactants or to find a cheaper way to produce the biodiesel would be needed.

### Conclusion

Nano-reactors provide an innate functionality that may be used in improve reaction success of organic syntheses with traditionally low or no yield. The structure of these nano-reactors provides an ability to expand and condense with the introduction and removal of solvent respectively which can be manipulated to improve the yield as mentioned above<sup>6</sup>. The advantages of these nano-reactors were used to improve the success of the synthesis of biodiesel fuels.

A reaction scheme for the synthesis of biodiesel fuels from cooking oils by the use of nano-reactors was proposed and determined to be effective. The effectiveness of the reaction was quantified using percent conversion of triglycerides to biodiesel. The reaction samples

showed very high percent conversions, with an average percent conversion of 99.33% and 99.36% for unused oil and used cooking oil respectively. The high percent conversion indicated a very effective pathway in the synthesis of biodiesel fuels. While used cooking oil provided a high conversion into biodiesel, it had the issue of having side products other than biodiesel in the final sample. Some side products are fatty acids that can harm engines using the produced biodiesel. Future work includes finding a way to remove these side products from the final biodiesel samples. To become commercially viable, a much higher amount of biodiesel must be produced, but this reaction scheme only produces a small amount of a biodiesel product. Future work would involve significantly scaling up the current biodiesel reaction and determining ways to decrease the price of the commercial scale reaction.

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