

RESEARCH PROJECT REPORT

Trash to Treasure

Clean Diesel Technologies for Air Pollution Reduction

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Abstract

Alternative fuels are explored extensively in order to provide fuel options which do not use the limited resources that are present with the use of fossil fuels. Biodiesel is one of these alternative fuels that is produced through the transesterification of vegetable oil through the use of a catalyst, such as sodium hydroxide (NaOH) or sulfuric acid (H₂SO₄). In this work, a procedure will be explored which can determine how to optimize the use of a catalyst in this transesterification. Since samples of waste frying oil (WFO) have varying amounts of free fatty acids, each batch must be titrated to determine the amount of catalyst needed for the transesterification to occur. This study will look for a way to determine which transesterification method would produce the highest yield given the amount of free fatty acid present in the WFO sample. Titrations and transesterification will be performed on multiple samples of WFO of varying quality to record relationships between amounts of catalyst used and percentage of glycerol (byproduct) produced. Conclusions would be useful to companies and to the University of Cincinnati in producing biodiesel in order to minimize waste created, reaction time and cost incurred during the reaction.

Key words

Biodiesel, catalyst, free fatty acid, transesterification, waste frying oil

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1. INTRODUCTION

Biodiesel is an alternative fuel that is most commonly produced through the transesterification of an oil source as shown in figure 1. These oil sources vary from animal fats, byproducts of refining vegetable oils, inedible oil, virgin oil, to waste frying oil [1,6]. The cost of biodiesel fuel is slightly higher than petroleum-based diesel due to the majority of it being produced from virgin oils. Because the cost of WFO is estimated to be about half the price of the virgin oils, biodiesel production from lower quality oils can help reduce the price of biodiesel fuel and make it more competitive with petroleum-based diesel [3,4]. Waste frying oil can be obtained fairly easily from multiple sources however each batch of WFO can vary greatly in the amount of free fatty acid (FFA) present. The FFA percentage greatly affects the reaction yield during the production of biodiesel and must be measured before a reaction can take place.

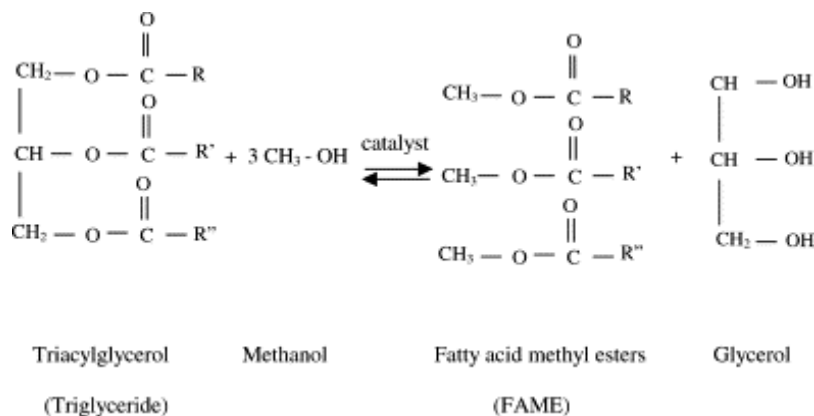


Figure 1. Representation of the transesterification of triglycerides with methanol to produce FAME and glycerol

Biodiesel fuel is environmentally friendly as it is biodegradable and non-toxic (Biodiesel Board, 2008). The EPA has identified six pollutants that are considered harmful to humans, air quality, and the overall health of the environment. Although these pollutants are found in biodiesel, there is a decreasing amount of particulate matter and carbon monoxide emissions as the percentage of biodiesel is increased in the fuel blend. This trend can be seen in figure 2 below.

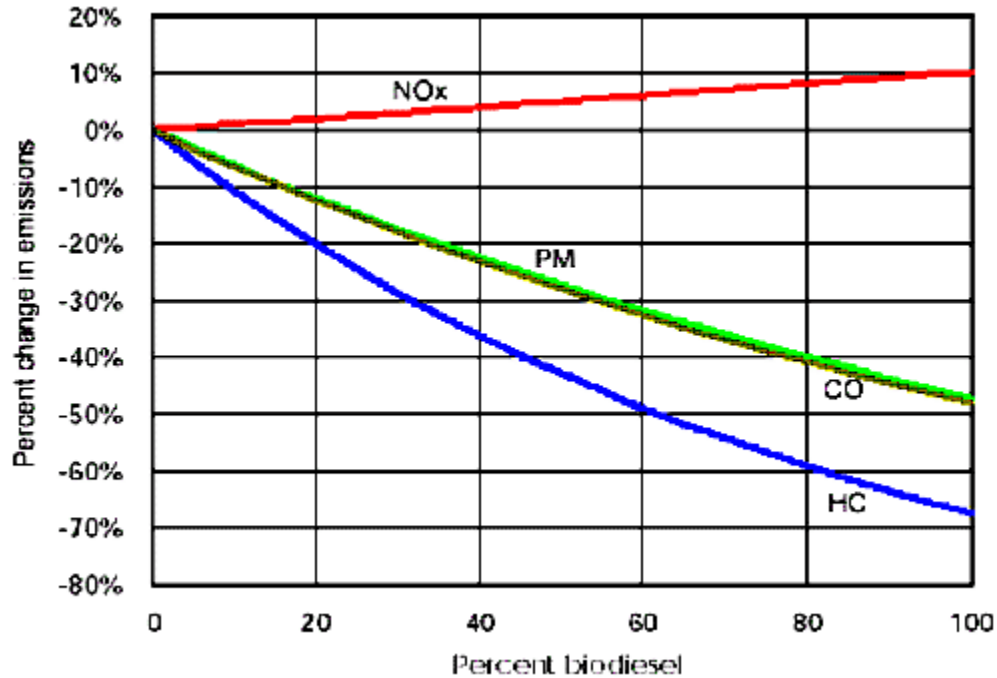


Figure 2. Average Emission Impacts on biodiesel

Because of the large range of FFAs, there are multiple methods which can be used for the production of biodiesel. Using an alkali-catalyzed system, the first of these methods, can only be used with oil sources that have less than 0.5 wt.% FFA. This system is very sensitive to FFAs and water present in the reaction. A high amount of either material will cause saponification to occur which results in the production of soap and emulsions. The soap and emulsion can lower the efficiency of separating the produced biodiesel from the glycerol byproduct of the reaction. This reaction in a laboratory setting requires a 6:1 molar ratio of alcohol (methanol) to oil to be heated to 60 °C. According to studies, anywhere from 90-98% methyl esters were converted from oil within 90 minutes of the start of the reaction. [4]

The second method which can be used for the production of biodiesel reduces the FFA content through a 2-step process by first performing an esterification reaction using an acid catalyst followed by an alkali-catalyzed transesterification. The esterification pre-treatment first lowers

the FFA percentage below 0.5 wt.% in order for the alkali-catalyzed transesterification to be effective by converting FFAs to esters [5]. Without the pre-treatment, saponification would take place instead of biodiesel production. [4] There are a couple of concerns related to the pre-treatment esterification with the biggest being the production of water. The presence of water, which is created due to the acid-catalyzed reaction of methanol and FFA, can prevent the esterification from completing, thereby working against the very purpose of the reaction. [5] The third method of transesterification (and the final method explored in this research) utilizes an acid catalyst which is most effective when the FFAs in the oil being used exceed 1%. In a study performed by Canacki and Van Gerpen [3] the yield of fatty acid methyl esters (biodiesel) was increased by increasing the methanol:oil ratio, temperature and amount of catalyst used. During their research, Zheng, Kates, Dubé, McLean used a mole ratio of 1:74:1.9 of waste oil in methanol and acid. This reaction occurred at 80 °C for over four hours had a fatty acid methyl ester yield of 99.0%. The high amount of FFAs was quickly converted into these fatty acid methyl esters as shown by their 0.5 minute sample that showed no FFAs present. One of the drawbacks to this method of transesterification is the amount of time the reaction must have to be complete. There have not been many published kinetic studies looking at this method, so it is unknown what is occurring at the various stages throughout the reaction. [3]

2. GOALS AND OBJECTIVES

The goal of this research project is to investigate methods to optimize the use of a catalyst during the transesterification of WFO into biodiesel. In order to achieve this goal we will perform multiple titrations using samples of WFO from various sources. These titrations will be used to model the transesterification reaction using both acid and alkaline catalysts. Once the reaction has occurred, the fuel will be analyzed using a gas chromatography-mass spectrometry machine

(GC-MS) and a high performance liquid chromatography machine (HPLC) to ensure the reaction has produced a quality biodiesel sample.

3. RESEARCH STUDY DETAILS

3.1 Alkaline Catalyst

3.1.1 Materials

Multiple sources of WFO are needed to complete this research study. The samples we used were obtained from three different restaurants in surrounding areas and ranged in size from five to twenty three gallons. NaOH is also needed to act as the alkaline catalyst. Household lye (drain opener) is one possible source of NaOH. Methyl Alcohol (MeOH) is needed as the solvent that NaOH is dissolved into. Phenolphthalein was used as an indicator in one of our methods of titration.

3.1.2 Titrations

Two methods of titration were used in order to compare and confirm results. Titrations must occur for each batch of WFO used. In the first method, WFO was mixed with ethyl alcohol (EtOH) in a 1:10 ratio to allow the reaction to be visible without magnification. Two drops (0.08mL) of a 0.5% phenolphthalein solution were added to the above oil solution. A 0.05% NaOH solution was added one drop at a time until the liquid turned pink in color. The oil solution was mixed after each drop of NaOH solution. The amount of NaOH solution was recorded and used to calculate the percentage of FFAs present in the WFO. We used the following formula to calculate the % FFA: $\text{molecular weight of oil} * (\text{amount of NaOH}) / \text{molecular weight of NaOH} / \text{density of oil} * \text{volume of oil}$.

The second titration method used three varying amounts of NaOH dissolved in 2mL MeOH. Once the NaOH was dissolved, 10mL WFO were added to each of the three flasks prepared above. Each of the three samples were heated using a microwave at 30 second intervals for a total of 90 seconds. Visual inspection determined which sample yielded the

highest production of glycerol indicating that a complete reaction had taken place. This amount was then selected as the optimal amount of catalyst to be used on that oil source.

3.1.3 Fuel Analysis

After completing the transesterification, a sample of the biodiesel product was analyzed using the GC-MS machine. This analysis shows the amounts of a variety of carbon chains present in our fuel compared to a biodiesel standard. In biodiesel, C16:0, C18:0, C18:1, C18:2, C19:0 are the most prevalent carbon chains present. As seen in Figure 3, our sample is indicative of this.

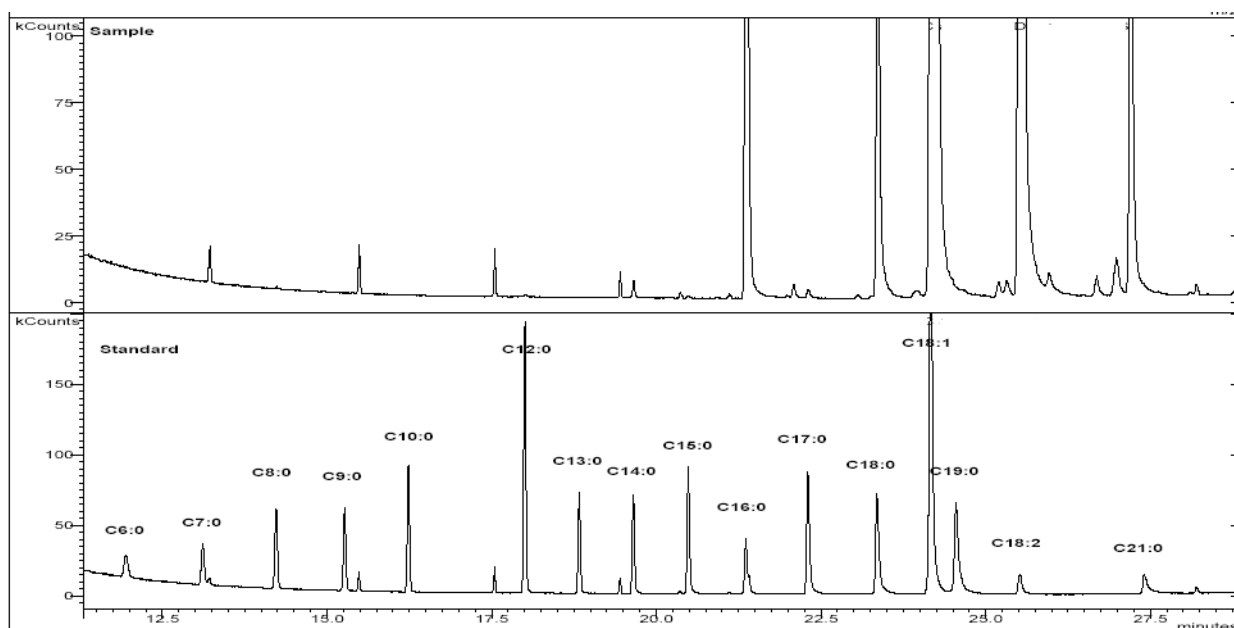


Figure 3. Fuel Analysis using GC-MS

3.2 Acid Prewash

After performing a titration on a sample procured from a local restaurant, we found the FFA content to be 4.47%, which is significantly higher than the average which ranges between 0.2-2%. Attempts at transesterification resulted in producing glycerol and soap mixtures that had no biodiesel present. An increased amount of NaOH catalyst would make transesterification possible, however the increased cost prohibits this method. An additional

method was researched using an acid esterification pretreatment to lower the FFA amount so that biodiesel could then be produced from this source.

3.2.1 Materials

Oil containing an increased amount of FFA is needed for this method. Sulfuric acid (H_2SO_4) was used during the esterification pretreatment phase. This esterification also required the use of a heat source that had the capabilities to mix for an extended period of time. MeOH is used in the esterification as well as the transesterification processes. After the esterification phase is complete, NaOH is added according to the titration results.

3.2.2 Titrations

To begin the esterification reaction the high FFA oil was heated to 35 C while being continually mixed. MeOH was added at an 8% by volume ratio to the oil. This solution was mixed for five minutes and formed a murky suspension due to methanol being a polar compound and oil being a non-polar compound. After the suspension was formed, H_2SO_4 was added in a rate of 1mL per L oil. While maintaining the temperature at 35 C, the solution was continually stirred for one hour. Heat was then discontinued but stirring continued for an additional one hour. The mixture created was left to sit overnight.

Believing our solution to be similar to previous batches we had processed we performed the transesterification as usual. The resulting product was soap. We repeated the acid pretreatment using the same source of oil. At the completion of the esterification, a titration was performed using the phenolphthalein method to determine the amount of acid still present in our oil. Because of the use of H_2SO_4 catalyst, the acid concentration was still elevated but was lower than the original FFA percentage. Four varying amounts of NaOH were chosen based on the titration results and were used to determine the optimal amount of catalyst necessary for the transesterification reaction to completely react. Using 100mL oil, 20mL

MeOH was mixed with .454g NaOH, .552g NaOH, .656g NaOH, .766gNaOH to create our four samples. These were heated for a total of 90 seconds, were mixed and were allowed to settle. Upon visual inspection, it was determined the sample using .656g NaOH yielded to highest amount of glycerol, indicating a complete transesterification reaction had occurred. This sample was then prepared for a fuel analysis using the GC-MS machine.

3.2.3 Fuel Analysis

After completing the acid pre-treatment and alkaline catalyst transesterification, the biodiesel produced was washed and prepare for analysis at a dilution rate of 1:12,500. Our results are shown in figure 4 below.

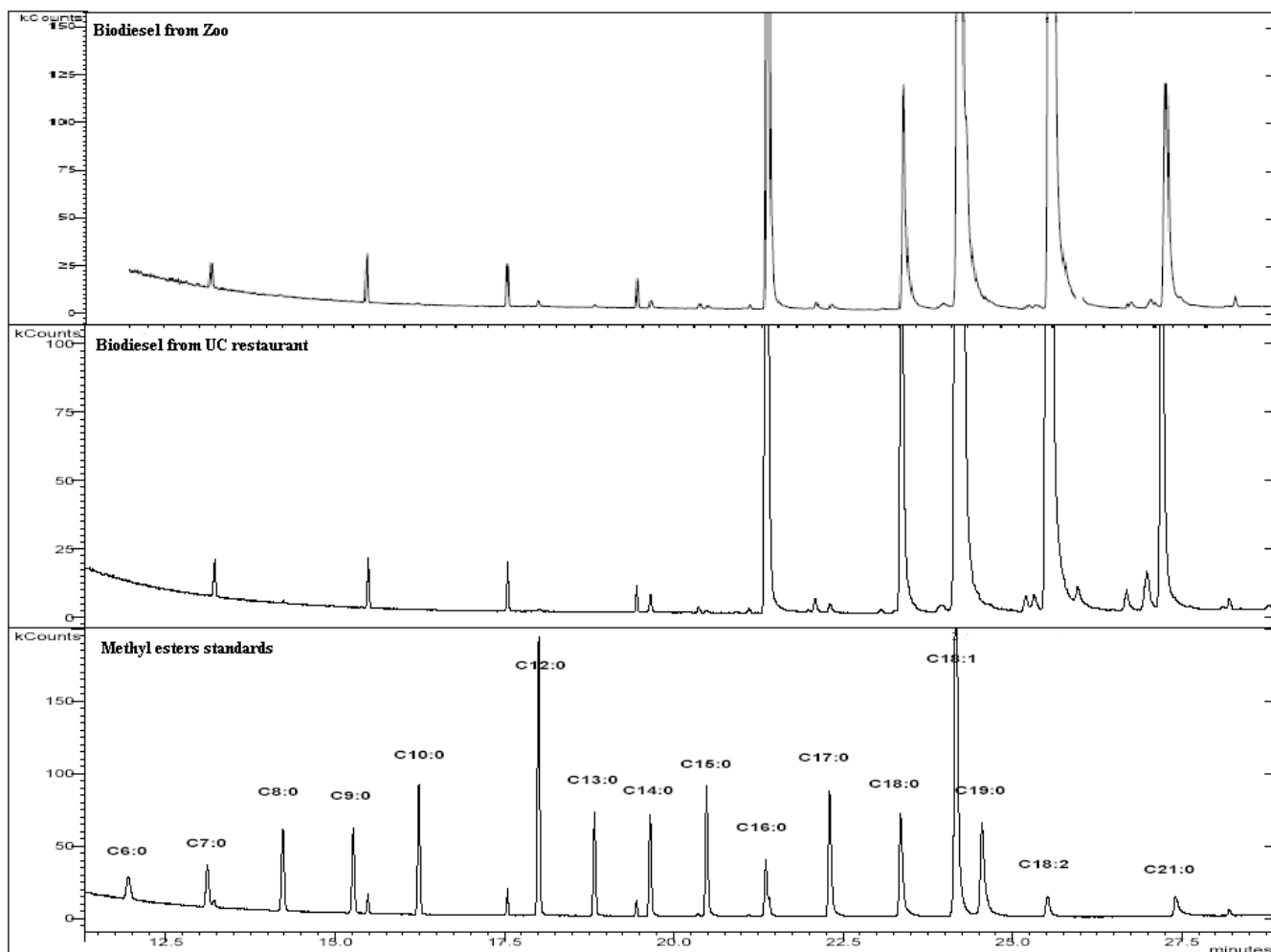


Figure 4. Fuel analysis using GC-MS

3.3 Acid Catalyst

Using the same WFO that was titrated earlier in our research and knowing its FFA content to be 4.47%, a transesterification was performed using only an acid catalyst. This reaction has been researched but it not commonly used to do the extensive amount of time required for the reaction to completely transesterify.

3.3.1 Materials

Oil containing a high % FFA is needed for this reaction to occur. A five neck flask, cooling tube and a hot plate with stirring capabilities are also needed for the acid transesterification. Methanol is needed in a 1:6 mole ratio to oil and 1 % sulfuric acid by volume was then added to the above mixture.

3.3.2 Titrations

Titration results from the acid-pretreatment method were used for this reaction because of the use of the same oil source. The oil we used contained 4.47% FFA.

3.3.3 Reaction and Fuel Analysis

In order to look at the kinetics of the acid catalyst reaction, samples of the reaction were taken at five minute intervals for thirty minutes, ten minute intervals for ninety minutes, thirty minute intervals for three hours, one hour intervals for four hours, and samples taken at the following total reaction times: 15 hours, 22 hours, 26 hours, 31 hours, 38 hours, 46 hours, and 50 hours. These samples were chilled and given 24 hours to settle. One tenth milliliter of biodiesel was taken from each sample and will be analyzed using the HPLC. The remaining sample was measured by volume to determine the amount of biodiesel, glycerol, and waste produced.

4. ANALYSIS; RESEARCH RESULTS

After completing the three methods of transesterification, our findings are consistent with previous research that has been conducted. Upon completion of each reaction, the % yield was

calculated in order to find the most completely reacted sample. Figures 5 and 6 show the % yield for each of the methods previously described.

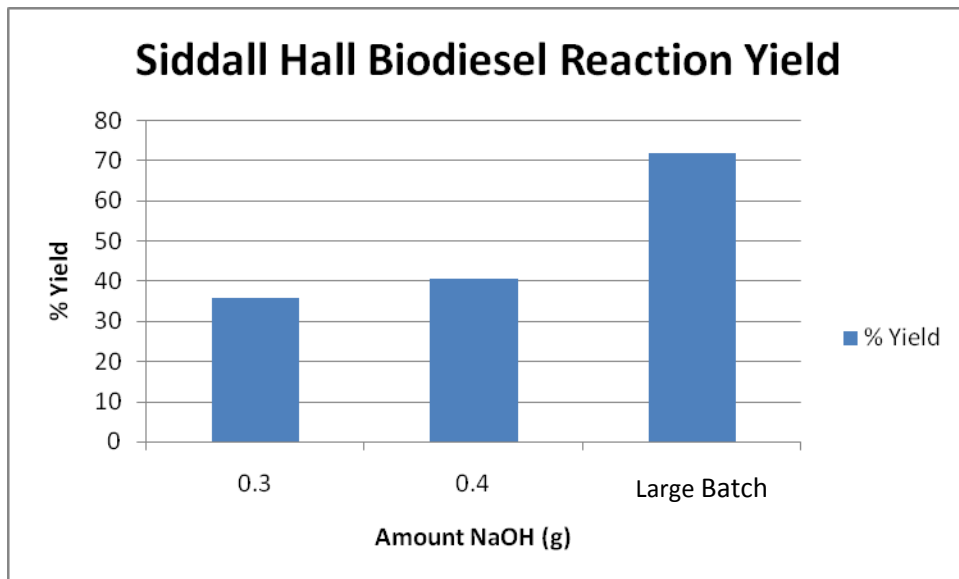


Figure 5. % Yield Siddall Hall WFO

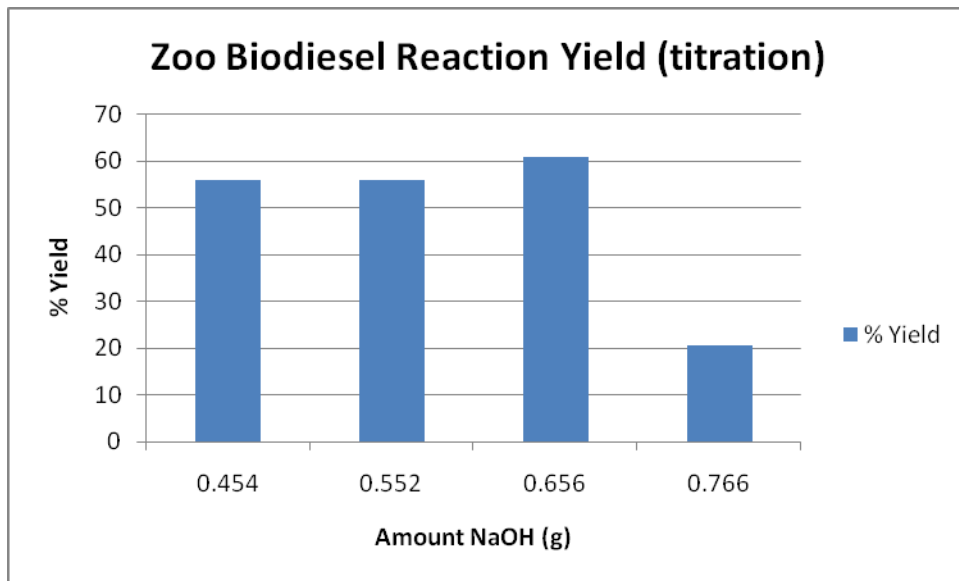


Figure 6. Zoo Oil % Yield using Acid Pre-treatment

Table 1 Fuel Analysis Comparison

Methyl ester	Griffin Industry		Biodiesel from UC Siddall Hall		Biodiesel from Zoo	
	weight%	Relative %	weight%	Relative %	weight%	Relative %
C8:0	0%	0%	0%	0%	0%	0%
C10:0	0%	0%	0%	0%	0.027%	0.03%
C12:0	0%	0%	0.017%	0.02%	0.090%	0.09%
C13:0	0%	0%	0%	0%	0.050%	0.05%
C14:0	0.58	0.60%	0.027%	0.03%	0.075%	0.08%
C14:1	0.18	0.19%	0%	0%	0%	0%
C15:0	0%	0%	0%	0%	0.046%	0.05%
C16:0	14.17	14.66%	3.113%	3.31%	7.080%	7.31%
C16:1	1.27	1.31%	0.118%	0.13%	0.088%	0.09%
C16:2	0.24	0.25%	0.717%	0.76%	0%	0%
C17:0	0.17	0.18%	0.039%	0.04%	0.060%	0.06%
C17:1	0	0.00%	1.947%	2.07%	0.025%	0.03%
C18:0	8.19	8.47%	74.40%	79.10%	5.526%	5.71%
C18:1	48.2	49.88%	11.56%	12.29%	36.08%	37.24%
C18:2	22.19	22.96%	1.899%	2.02%	42.91%	44.30%
C18:3	1.45	1.50%	0.206%	0.22%	4.808%	4.96%
C20:0	0%	0%	0.717%	0.76%	0%	0%
C22:0	0%	0%	0%	0%	0%	0%
sum	96.64%	100%	94.06%	100%	96.85%	100%

Table 2 UC Waste Fryer Oil Inventory

Restaurant	Waste oil (gallon per week)		Supplier	Price	Current disposal method	Cost	Diner
	Summer	Other					
Gold star chill	6	8			Griffin Industry		
Burge King	Not open, estimate a little more than Gold star chill		NA	NA	NA	NA	
Mick&Mack's/Quick Mick's	8	10	Frywise	\$0.88/lb	Supplier pick-up	Included	100
Catering	8	10	Frywise	\$0.88/lb	Supplier pick-up	Included	100
Center courts	closed	15	Frywise	\$0.88/lb	Supplier pick-up	Included	5500
MarketPointe@Siddall	12	16	RTI	\$1.09/lb	Supplier pick-up	Included	5500
Other restaurants	Not use fry oil						

Table 3 Cost of biodiesel production using an alkaline catalyst

	Unit price	Unit	10 gallons of biodiesel		unit cost in euro/kg	30 gallons of biodiesel		35 gallons of biodiesel		50 gallons of biodiesel	
			labor	cost per gallon		labor	cost per gallon	labor	cost per gallon	labor	cost per gallon
used oil	0.00	\$/gallon	0.00	1.00		0.00	1.00	0.00	1.00	0.00	1.00
MeOH	4.33	\$/gallon	8.65			25.96		30.29		43.27	
NaOH	0.01	\$/g	1.56			4.68		5.46		7.81	
filtration	0.09	\$/filter	0.90	0.50		2.69	1.00	2.69	1.00	4.48	1.50
electricity (5 hour heating + 10 hour pump)	0.80	\$/kWh	8.74			8.74		8.74		5.44	
purification (water)	0.80	\$/1,000 gallon	0.04	2.50		0.12	5.00	0.14	5.00	0.20	7.50
subtotal			19.89	1.99	0.60	42.20	1.41	47.32	1.35	61.19	1.22
Labor	10.00	\$/hour	80.00			120.00		120.00		150.00	
total			99.89	9.99		162.20	16.22	167.32	16.73	211.19	21.12

5. CONCLUSIONS

Although sources of WFO can vary greatly in their FFA content, multiple methods can be used in order to convert this oil into quality biodiesel fuel. As seen through the above research, these methods vary greatly in the amount of time required for the reaction to completely occur. This significantly impacts the production cost. When looking at the feasibility of the University of Cincinnati producing biodiesel from on-campus sources, the price of production is examined. While overall production cost, including labor, is higher than No. 2 diesel, production of

biodiesel with on-campus WFO provides the university with an opportunity to move towards a green campus and become more sustainable, setting an example for universities around the nation.

6. RECOMMENDATIONS

Further research could be conducted regarding the optimization of reaction time using an acid catalyst for WFOs with a high % of FFAs. This could be accomplished by further researching the kinetics of the reaction conducted at various temperatures and amounts of MeOH.

7. ACKNOWLEDGEMENTS

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