Analysis of Biodiesel Fuel

A Major Qualifying Project Report:

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Submitted to:

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Abstract

The purpose of this major qualifying project (MQP) was to determine the optimal method to achieve lower freezing points in biodiesel fuel. The concern for using biodiesel fuels are the relatively low freezing temperatures of the fuel.This was corrected by investigating the cloud point and pour point of methanol, ethanol, iso- butanol, and iso- pentanol alcohol based biodiesels. The addition of more complex alcohols in the transesterification reaction was expected to increase carbon chains to the esters resulting in lower freezing temperatures. Prediction methods were used as well as controls to check accuracy of the data collected for cloud and pour points. The final conclusion of this project determined the validity of this experiment by showing an expected decrease in temperature. Iso-butanol was determined to be the optimal fuel for performance in lower climates, however further recommendations are provided that were not included in this project.

Acknowledgments

I would like to extend a special thanks to my advisors Professor Michael Timko and Professor Stephen Kmiotek for their guidance throughout the course of this project. I would also like to thank the Chemical Engineering Department specifically for allowing me to use the necessary equipment as well as, Tiffany Royal for assisting in lab access and ordering supplies.

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Chapter 1: Introduction

Introduction

Biodiesels were created as a solution to the depletion of fossil fuels because of the fuels'
greater availability of renewable resources. Unlike the gasoline we put in our cars, biodiesel is
made up of renewable resources such as alcohol and vegetable oil. There are a variety of ways to
make biodiesel fuels; so the resources available are relatively much greater than those of coal
burning fuels. Because of the simplicity of the reaction, any type of oil can be used, including
waste oils. The process of biodiesel production is the transesterification of fatty acids. The
alcohol is either acid or base catalyzed and then mixed with any number of oils ranging from
soybean oil to even waste oils.

However, the downside to using biodiesel is NOX emissions. In an academic article
discussing the effect of NOX vs CO2 found that, "Replacing petrol cars with diesel ones does
result in lower CO_2 emissions and climate impacts but it has clearly been worse for human
health". (Nieuwenhuis et al. 2018). and the burning of biodiesel results in NOX emissions which
are substantially worse for the environment than CO2 emissions. There are ways to reduce the
emissions of biodiesel such as adding a filler on the the exhaust pipe or changing the alcohol
used to allow less NOX emissions. Another issue with biodiesel in particular is the freezing
temperature is relatively high. Current cloud points of FFME are around 1℃ which is not a
viable option for people in colder climates.

Inorder for biodiesel to outperform fossil fuel as the leading fuel source, the freezing
point must be lowered in order to eliminate the use of antifreeze products being added to current

diesel fuels. When biodiesel freezes the fuel becomes wax like and that wax gums up the engine, corroding it. Heaters are also installed in most diesel vehicles to aid in the prevention of this corrosion. This Major Qualifying Project, focuses on the cause and effect that the complexity of the alcohol has on the freezing point of the biodiesel mixture. Once a pattern is observed through experimentation and compared to various studies then a theoretical graph can be produced to determine what alcohol mixture would be best utilized for a desired freezing point.

Biodiesel History

Biodiesel was invented by Ruldolf Diesel, who decided to attempt to create the most efficient engine based on Carnot's theorem he learned in thermodynamics. He competed with the French who were using peanut oil to power model cars. The commercialization of vegetable oil based biodiesel became marketed after World War II, Germans were using diesel as a way to make better energy efficient cars. So when the energy crisis came along in the 1990's, diesel was ready to step in as a major player. During this time period, only pure oils were being used as diesel. In 1935, a patent was published exclaiming how esters can be derived from the transesterification of free fatty acids when acid catalyzed. The fuel was then run in pubic transit in Brussels where the fuel reported ran better and was less viscous than the pure oil diesel method.(Knothe et al. 2010).

Catilization of alcohol NaOH vs KOH

In order to drive the reaction to completion, a catalyst acid or base can be used. Typically NaOH or KOH is used since base catalysts yield a less complicated reaction than the acid alternative. To determine which catalyst is optimal for this experiment, cost, separation feasibility, and product yield were considered. KOH is more expensive than NaOH as seen in figure 1 and when tested NaOH was needed in less amounts to achieve the same reaction conversion. However, the main concern is the separation of the phases. When NaOH is to be used the glycerol layer and NaOH both settle at the bottom below the esters as a solid which is difficult to remove from the mixture. KOH however, is relatively easy to use in comparison since

the glycerol remains a viscous liquid settling to the bottom. This advantage typically makes

KOH the most used catalyst in industry for recycled oils. KOH not only creates more product

yield as shown in figure 2 but also allows a better two phase separation between the esters and

glycerol layer. The limiting factor of this reaction that most affects the product yield is the

saponification of the Na- and K- with the water molecules which ultimately leads to the lower

product yield. For the purpose of this experiment, KOH will be used because of the ease of

separation. (Leung et al. 2006).

	NaOH	KOH
Price (US$/ton)	400	770

Table 1: Comparison of different catalysts prices in dollars over ton

	Ester Yield wt%	Product Yield wt%
NaOH	94.0	85.3
KOH	92.5	86.0

Table 2: Comparison of different catalysts used in the transesterification of UFO
(temperature of 70 °C, reaction time of 30 min, methanol/oil molar ratio of 7.5:1)

Reaction time

Reaction time varies for each type of alcohol used; so each alcohol will be discussed

independently. Time zero for reach reaction is considered to be when alcohol is added to

vegetable oil. Methanol based biofuel require a reaction temperature of 40-60 °C and a

minimum of 30 minutes to allow for transesterification to go to completion. The higher the

temperature the reactants are heated to, the faster the reaction will occur as long as the

temperature does not exceed the boiling point of the alcohol. (Likozar et al. 2014). Ethanol based biofuel requires a reaction temperature of 75 °C and a minimum of 2.5 hours of continuous mixing.(Anastopoulos et al. 2009). Iso-butanol based biofuels requires a reaction temperature of 72°C and a minimum of 2.5 hours of continuous mixing. For iso-pentanol based biofuel requires a reaction temperature of 105°C and a minimum of 30 minutes (Lang et al. 2006). Additional time is required for catalyst to dissolve into alcohol approximately 5-20 minutes depending on solubility of base in alcohol. Separation between layers which can take up to 12 hours.

Advantages

One advantage of using biodiesel vs fossil fuels is that biodiesel has less CO2 emissions. Cars and truck can run for longer on less fuel compared to gasoline making biodiesel ideal for commercial vehicles (Nieuwenhuis et al. 2018). Biodiesel is also relatively easy to produce and can be made from a variety of starting materials including recycled waste oil from friers.

Disadvantages

The disadvantage to using biodiesel is that the fuel freezes at 1°C because the wax can crystallize at this temperature forming a solid (Knothe et al. 2010). The current solution to this issue is to add antifreeze to the engine which is not clean burning (Antifreeze, pp.11-12). Another is to add heaters to the engine which requires time to thoroughly heat all the fuel back to a usable liquid.

Biodiesel when burned also emits NOX gas into the environment which is 4 times worse for the environment than CO2 (Nieuwenhuis et al. 2018).

Production of biodiesel With different alcohols

To combat the current freezing point of biodiesel, the addition of longer carbon chains is projected to lower freezing point by increasing the disorder of the wax crystals making them harder to freeze. ""You can reach much higher levels of renewables in fuels if you go to these longer-chain molecules," says Michelle Chang, a chemist at the University of California," (Savage, 2011).

Biodiesel refinement

Biodiesel can be purified in multiple ways. The most common being a two phase separation between unrefined esters and glycerol layers where glycerol settles to the bottom and is easily extracted. Following this step with a wash of hot water will purify the esters further. The remaining esters and water are heated so water is evaporated. This separation process is best for methyl esters; however, ethyl and longer chain esters end in a single phase so glycerol extraction by phase is no longer an option. The ideal separation for single phase unrefined complex ster groups is to use a hot water bath to boil out alcohol and condense for later use. Once excess alcohol is removed separation by phases is more attainable. Another way to seperate by unrefined biodiesel is through separation by density. This can be obtained by using a centrifuge. (Knothe et al. 2010).

Chapter 3: Methodology

The objective of this project was to:

I. Develop a procedure for producing biodiesel that can withstand colder climates by increasing carbon chain of esters.

II. Replicate objective I. by using short and long chain alcohols to produce biodiesel.

III. Identify a prediction method for determining cloud point for any biodiesel based on chain length.

The first objective was to develop a useful procedure for producing longer chain biodiesels that provided clear explanations on separation methods. For any chain longer than a methyl ester phase separation is not an option. In this case, more steps are involved for force separation by density. This was achieved by allowing either centrifuge or alcohol evaporation to drive the separation of glycerol from the esters.

The second objective was to prepare biodiesel from each alcohol type: methanol, ethanol, iso-butanol, and iso-pentanol. The goal is to have the carbon chain on the alcohol bind with the vegetable oil to form a complex ester. When complexity is increased the wax that forms from the crystallization is harder to pack together resulting in lower freezing points.

The third objective is to identify a way to predict how biodiesels will freeze. To determine this, both, experimental studies and cloud point prediction equations were referenced. This objective was tested against the data collected in this project and validated through various controls such as vegetable oil, jet-A fuel, and diesel 2D.

Methodology Introduction

For the purpose of this section, only the accurate and precise forms of biodiesel that were produced will be discussed. While more tests were completed, multiple attempts did not produce a desirable product and were discarded. Below shows the final methodologies for both driving the reaction and cloud point testing.

Chemical Reactions To Produce Esters

Figures 1-4 show the major organic reaction products that are produced through transesterification. Glycerol is not considered to be miscible in biodiesel therefore the removal of glycerol was included in the 2nd stage separation procedure. For each reaction below the increase in carbon chains can be seen. To achieve the desired biodiesel reactions from alcohol and oil a continuous stirring hot plate apparatus was used. In order to determine the differences between the four biodiesels the freezing point of each sample was tested. This was accomplished by using the standard test method for cloud point which was adapted for pour point testing as well. A convection cooling bath was prepared with ice which was temperature regulated. The apparatus is able to provide bath and biodiesel temperatures as well as visual clarity to crystallization.

CH2-COOR1
|
HOCH3 + CH-COOR2 $\xrightarrow{\text{KOH}}$ 3 R-C-OCH3 + Glycerol
| ‖
CH2-COOR3 O
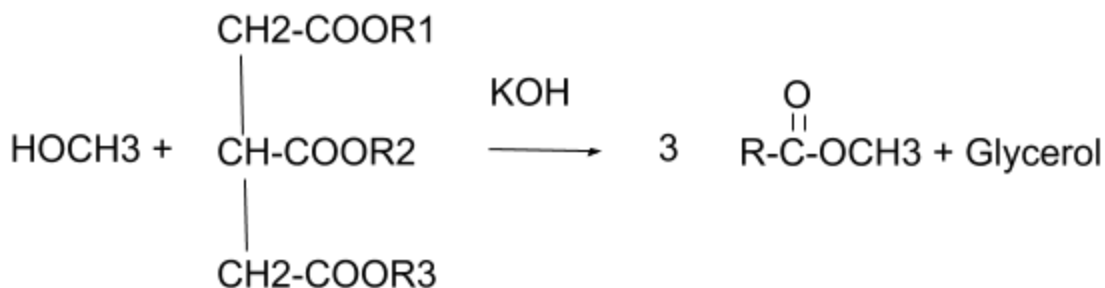
Figure 1: Transesterification reaction of methyl esters from methanol and soy oil

CH2-COOR1
|
HOCH2CH3 + CH-COOR2 $\xrightarrow{\text{KOH}}$ 3 R-C-OCH2CH3 + Glycerol
| ‖
CH2-COOR3 O
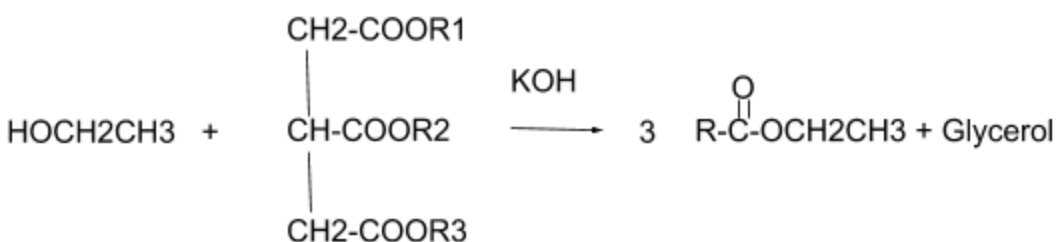
Figure 2: Transesterification reaction of ethyl esters from ethanol and soy oil

CH2-COOR1
|
HOCH2CH(CH3)2 + CH-COOR2 $\xrightarrow{\text{KOH}}$ 3 R-C-OCH2CH(CH3)2 + Glycerol
| ‖
CH2-COOR3 O
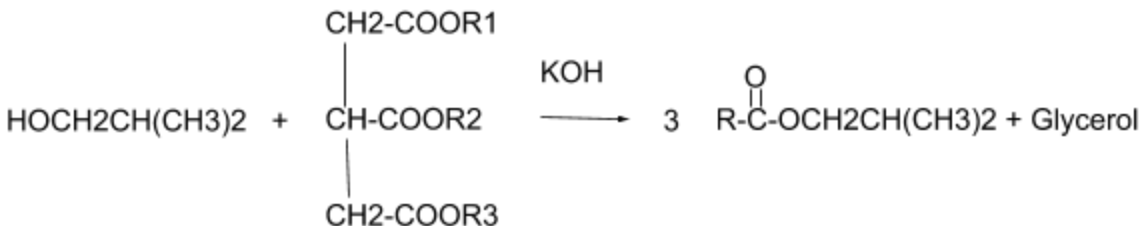
Figure 3: Transesterification reaction of iso-butyl esters from iso-butanol and soy oil

CH2-COOR1
|
HOCH2CH2CH(CH3)2 + CH-COOR2 $\xrightarrow{\text{KOH}}$ 3 R-C-OCH2CH2CH(CH3)2 + Glycerol
| ‖
CH2-COOR3 O
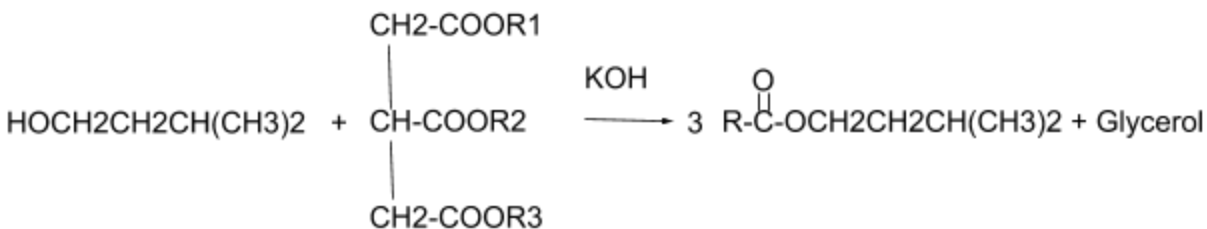
Figure 4: Transesterification reaction of iso-pentyl esters from iso-pentanol and soy oil

Procedure for preparing first stage transesterification of biodiesel

1. Measure out 6:1 equivalent amounts of vegetable oil to alcohol

2. Dissolve 1.5 wt.% KOH in alcohol

3. Heat vegetable oil to 75℃ on a stir plate

4. Slowly pour alcohol into heated vegetable oil

5. Stir evenly for 2.5 hours

6. Repeat steps 1-5 for all methanol, ethanol, and isobutanol alcohol based biodiesel

7. Repeat steps 1 and 2 for iso-pentanol but heat vegetable to 105℃ on a stir plate proceed to step 4 and stir evenly for half an hour.

Procedure for preparing second stage transesterification of biodiesel

Methyl esters

1. Allow unrefined biodiesel to phase separate over 12 hours

2. Remove bottom glycerol layer and wash esters 5 times with hot distilled water

3. Drain water out in between washes and when done heat to above 55℃

Ethyl esters

1. Add unrefined biodiesel to a bulbed glass connected to a hot water bath at the temperature of the alcohols boiling point. Evaporate out alcohol from mixture and condense back into a liquid using dry ice and a vacuum

2. Allow unrefined biodiesel to phase separate over 12 hours

3. Remove bottom glycerol layer

4. Pump de-ethylated unrefined biodiesel into a resin funnel

5. Collect bottoms from funnel

6. Repeat steps 1-5 for iso-butanol

Iso-pentyl esters

1. Extract equal amounts of unrefined biodiesel into two capped tubes

2. Centrifuge biodiesel at 2500 rpm for 15 minutes

3. Extract out top layer into a separate container

Figure 5: Heating of vegetable oil prior to the addition of alcohol

Figure 6: first stage transesterification process of methanol based biodiesel

Figure 7: Second stage transesterification separation of methyl esters and glycerol

Cloud Point Test Procedure:

1. Measure out 3 ml of purified biodiesel into a glass tube

2. Plase glass tube in the larger container

3. Insert a corked thermometer into the small glass tube and another thermometer into the ice bath.

4. Record bath temperature at the start

5. Record every -1℃ change of the 3 ml of purified biodiesel and look for clouding

6. For iso-butyl and iso-pentyl esters modify step 3 to a dry ice bath to allow for colder freezing temperatures.

Pour Point Test Procedure:

1. Measure out 3 ml of purified biodiesel into a glass tube

2. Plase glass tube in the larger container

3. Insert a corked thermometer into the small glass tube and another thermometer into the ice bath.

4. Record bath temperature at the start

5. Record every -1°C change of the 3 ml of purified biodiesel and look for solidification

6. Record when fluid is no longer able to be poured

7. For ethyl, iso-butyl, and iso-pentyl esters modify step 3 to a dry ice bath to allow for colder freezing temperatures.
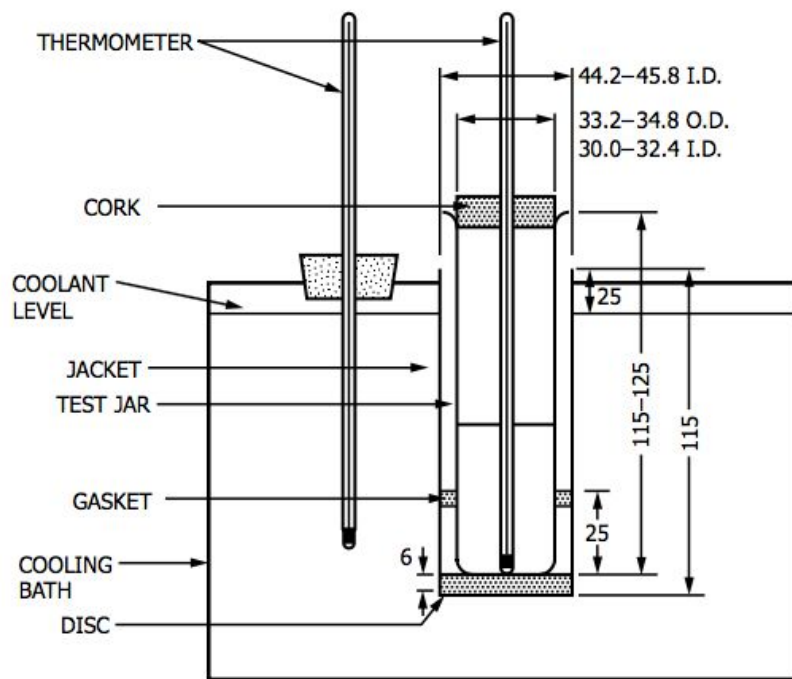

Figure 8: ASTM D5551 apparatus schematic for cloud point test methods

Figure 9: Cooling bath used to conduct cloud and pour point tests on fuel samples

Figure 10: Biodiesel refinery apparatus used to recover excess alcohol and purify esters

Chapter 4: Results & Discussion

Theoretical:

To determine the effect that carbon chains have on ester groups freezing points a prediction system was implemented. Cooling points can be predicted by understanding the structures of the free fatty R-esters, thermodynamic models, and freeze point depreciation factors (Dunn, 2008). In this section four different prediction methods are discussed, however only one was used to fit data prediction for this particular data set.

Cloud point prediction method one:

DSC scan was required to analyze the melting onset temperature (MP), the maximum peak temperature (PH), and the enthalpy of melting (ΔHp). These parameters were used to solve the hildebrand equation X for ideal solutions. This equation is used to predict crystallization onset temperature of solute in solution within 5℃ of the actual temperature. This method was not used to calculate carbon chains longer than methyl esters but can be used for longer chains if necessary. This particular was not used for the prediction of the cooling points completed in this paper but would be a valid method for anyone with access to a DSC scan apparatus(Dunn, 2008).

Cloud point prediction method two:

Cloud point modeling based on n- alkane content. The equation X summarizes the general solid-liquid equilibrium function using the composition in both phases. The entire calculation equation X-X predicts the fluid behavior at low temperatures (Coutinho et al. 2002). UNIQUAC solid phase non- ideality was used as the predictive model. This prediction method

was derived for the use of analyzing n-alkane of a methyl ester biodiesel fuel blends. This prediction method was not used but would be ideal if n-alkane values are available.

Cloud point prediction method three:

For this method n-alkane of a methyl ester biodiesel fuel blends were predicted with set equations provided for each respective ASTM test procedure. This particular resource was beneficial in conducting ASTM testing but the equations X-X were difficult to interpret. This method would be best for determining which tests to run and providing a scope of deliverables. (Saxena et al. 2013)

Cloud point prediction method four:

Cold flow properties of biodiesel may be estimated based on total saturated fatty acid alkyl ester (Sats) concentration. Equation X was used to calculate cloud point based on the saturation point with a $\mp 2°C$ level of accuracy. Saturation values were found in The Biodiesel Handbook for each alcohol tested in this project (Knothe et al. 2010). This prediction method as seen in figure X, indicates an increase in cloud point with increasing carbon content

	Jet A	Dies el 2- D	Iso- Pent anol	Iso- Buta nol	Etha nol	Met hano l	Vege table oil
■ Series1	-40	-18	-14.7	-13.3	-1	1	1

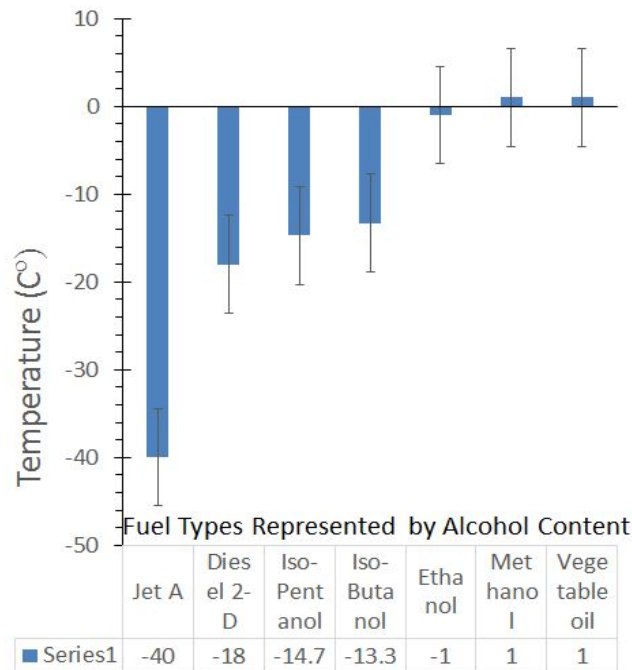*Figure 11:Theoretical cloud points for various fuels*

Pour point prediction method:

Pour point was predicticted based on previous studies results and was used to compare to experimental data. Multiple sources were used to provide the most accurate set of pour points. In the figure X theoretical pour points indicate an increase in temperature that correlates to the decreasing number of carbon chains present.

Fuel Types Represented by Alcohol Content							
	Jet A	Diesel 2-D	Iso-Pentanol	Iso-Butanol	Ethanol	Methanol	Vegetable oil
■ Series1	-47	-30	-7	-8.5	-4	-2	-7
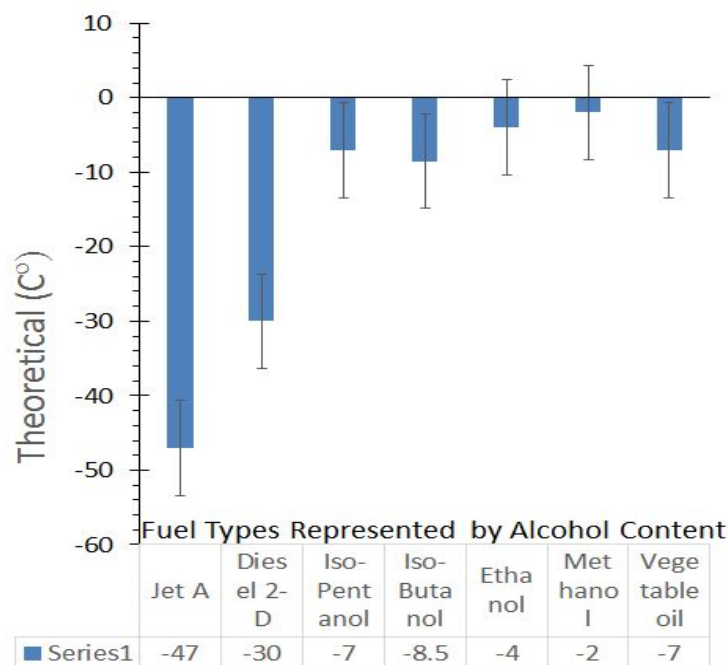
Figure 12: Theoretical Pour Points for Various Fuels

Experimental:

Using the methodology procedures above, each reaction was completed and cooling point tests were run on samples of each biodiesel type. Each sample was analyzed for cloud and pour points. The results of this data can be seen below under the respective ester carbon length in fuel.

Methyl ester

Methanol based biodiesel resulted in a 2 phase separation between glycerol and methyl ester layers. Because of the ease of glycerol removal the remaining esters were able to be washed to yield a higher purity level of methyl esters based on the reaction mechanics. 3 ml of biodiesel were sampled for cloud point and pour point data collection shown below.

	Bath Temp ℃	Cloud Point ℃	Pour Point ℃
Run 1	-8.5	-3	-4.5
Run 2	-4.5	-3.5	-5

Table 3: Experiment results for cloud point sample tests for methanol based biodiesel

 Ethyl ester

Troubleshooting

Ethanol based biodiesel took multiple attempts to produce. The limiting factor for this reaction was the inability of separation between layers. One of the ways that was attempted to drive separation was to add 10 ml additional glycerol to the unrefined solution and shake vigorously. The added glycerol was meant to drive the layers to separate by density. For this particular trial added glycerol made no difference however the study who's process was repeated seemed to have success. Another attempt made was to separate by using freezing points. The idea was to have the glycerol freeze and leave behind liquid biodiesel. The problem that occured was that the freezing did not drive glycerol to sink to a bottom layer but instead froze the solution as whole. Therefore, the prediction that the freezing would provide separation by density was also disproved. The last attempt made to separate before reaching the optimal separation technique was to add excess NaCl to try to force layer separation through solubility. Unfortunately, NaCl was not very soluble in the solution so phase separation was unable to be achieved.

Ethyl ester optimal separation and cooling results

Separation of glycerol from biodiesel occured in both methods used. The first was through centrifuge at 3000 rpm and 15 minutes. This particular extraction method was not used in the final sample collected. The separation method used was a biodiesel refinery apparatus shown in figureX. Having extracted the desired de-ethylanol reined biodiesel cloud and pour points were able to be tested on a 3ml sample. Results for both CC and PP are represented in the table below.

	Bath Temp °C	Cloud Point °C	Pour Point °C
Run 1	-50	-6	-8.5
Run 2	-50	-6.5	-8.5

Table 4: Experiment results for cloud point sample tests for ethanol based biodiesel

2- butyl ester

Troubleshooting

This particular sample was unable to produce a successful sample because of the outcome of the reaction. One of the by-products of the transesterification reaction is water. The issue is that saponification reactions can occur if too much water is present during the reaction. Some water was not entirely dried from the glassware resulting in a saponification reaction. The final product can be seen in the figure below.
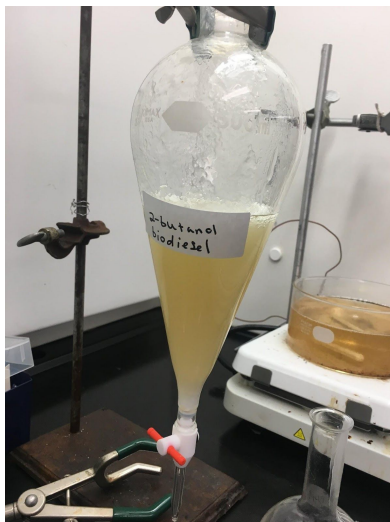
Figure 13: Saponification of 2-butanol with vegetable oil and KOH

Iso- butyl ester

Iso-butanol based biodiesel was not successful in phase separating using the biodiesel refinery method so a centrifuge at 2500 rpm was used for 15 minutes. The amount of alcohol evaporated was not recorded due to inadequate sealing of the apparatus. The top layer of the solution was extracted out and 3ml were sampled for cloud point and pour point data collection shown below.

	Bath Temp ℃	Cloud Point ℃	Pour Point ℃
Run 1	-50	-8	-14
Run 2	-50	-9	-14

Table 5: Experiment results for cloud point sample tests for iso-butanol based biodiesel

Iso-pentyl ester

Iso-pentanol base biodiesel was the longest carbon chain tested adding and additional 5 carbons to the chain. Separated occured by the use of a centrifuge at 2500 rpm was used for 15 minutes.

The top layer of the solution was extracted out and 3ml were sampled for cloud point and pour point data collection shown below.

	Bath Temp ℃	Cloud Point ℃	Pour Point ℃
Run 1	-50	-7	-11.5
Run 2	-50	-7.5	-13

Table 6: Experiment results for cloud point sample tests for iso-pentanol based biodiesel

Controls

Diesel 2D

Diesel 2D was used as a control to validate the cloud point and freeze point test methods. 3ml were sampled for cloud point and pour point data collection shown below.

	Bath Temp ℃	Cloud Point ℃	Pour Point ℃
Run 1	-50	-21	-30
Run 2	-50	-21	-30

Table 7: Experimental results for cloud point sample tests for diesel 2D

Jet A

Jet A was used as a control to validate the cloud point and freeze point test methods. 3ml were sampled for cloud point and pour point data collection shown below.

	Bath Temp ℃	Cloud Point ℃	Pour Point ℃
Run 1	-50	-35	-
Run 2	-50	-36	-

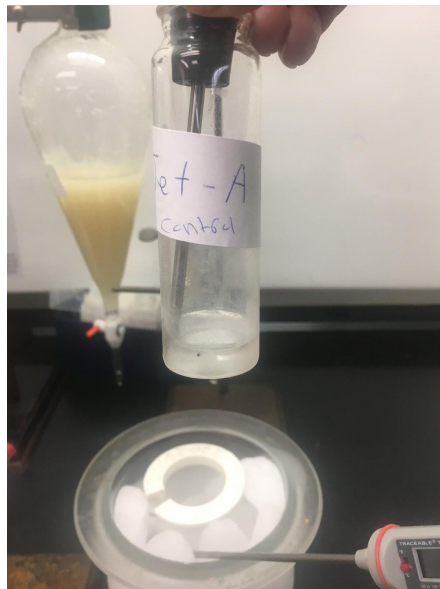*Table 8: Experiment results for cloud point sample tests for jet A*

Figure 14: Cloud point of Jet A fuel sample

Cloud point

Each sample was compared on a graph against the cloud point temperature in decreasing order of carbon length. Jet A and Diesel 2D were used as controls and their actual cloud points are -40℃ and -18℃, respectively found on figure 11. For the cloud points collected Jet A and Diesel 2D were recorded at -36℃ and -21℃, respectively. The error for this experiment was expected to be ± 4℃. Iso-butanol based biodiesel had the lowest cloud point of -8.5℃ while methanol based biodiesel had the highest cloud point of -3℃. In figure 15 an increase in cloud point with increasing carbon content is seen.
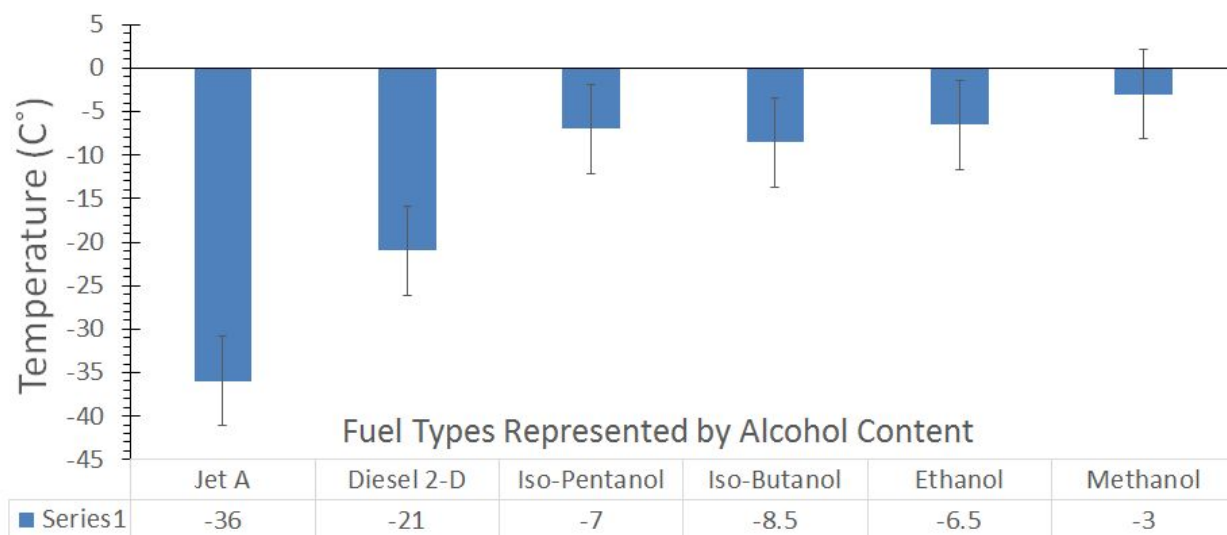
Figure 15: Experimental cloud points for various fuels

Pour point

Each sample was cooled using the methodology procedure above. Jet A was not included in this experiment because the fuel was not able to freeze in the bath conditions. Diesel 2D was used as the control in this experiment with a recorded pour point of -30℃ matching the actual pour point of the fuel exactly. The the same error for cloud point was used for this experiment. Iso-butanol had the lowest pour point and methanol had the highest pour point. An increase in pour point with increasing carbon content can be seen in figure 16.
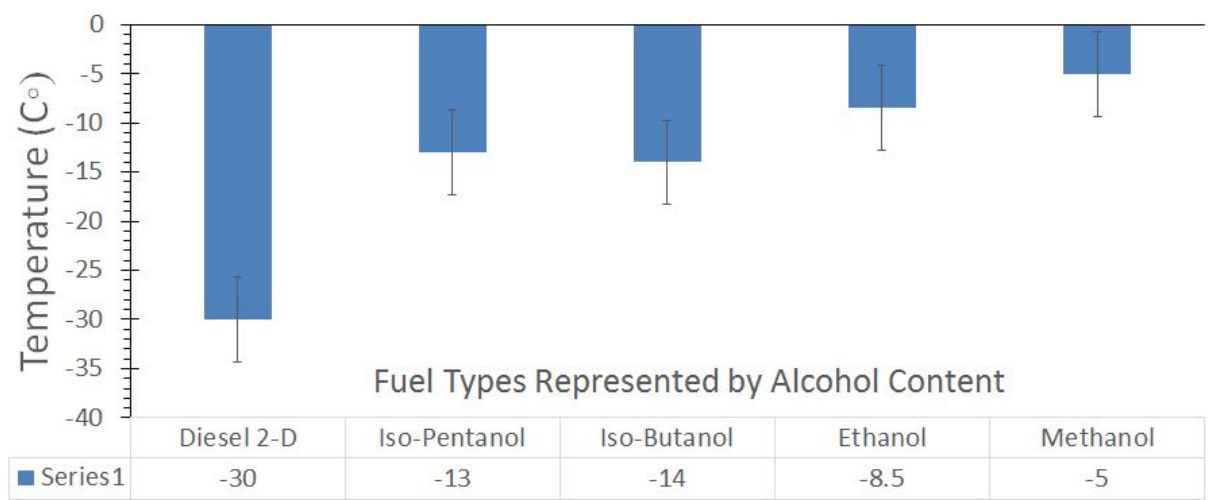
	Diesel 2-D	Iso-Pentanol	Iso-Butanol	Ethanol	Methanol
■ Series1	-30	-13	-14	-8.5	-5

Figure 16: Experimental Pour Points for Various Fuels

Chapter 5: Conclusion & Recommendations

The purpose of this experiment was to determine if the lengthening of the carbon chain in bio-fuels would decrease cloud points. Through experimentation, the cloud point was able to be lowered as the addition of carbon increased. Iso-butanol had the lowest cloud point of -8.5℃ followed by iso-pentanol -7℃, ethanol -6.5℃, and methanol -3℃. The cloud point test was verified by the controls of shell diesel and jet-A fuel. Iso-butanol was found to be the optimal fuel for colder climate conditions. Compared to the cloud point and pour point prediction analysis the methyl ester biodiesel fell into the ± 2℃ difference as expected.

As theoretical data predicted, iso-pentanol based biodiesel was supposed to yield the lowest cloud and pour points out of all of the samples. There are potential errors that occurred during experimental methods that could have caused this. Iso-pentanol base biodiesel was shown to be less successful than iso -butanol base biodiesel however, this could be because there was excess alcohol and impurities in the final product which would have affected freezing results. To improve the quality of this experiment, it is recommended to evaporate out excess alcohol during refinement as well as to wash all final products to make sure the quality of esters is as pure as possible.

For future replications of this experiment an improved prediction analysis of pour point would be beneficial in determining the accuracy of the data collected. Another recommendation was to use the data provided in this experiment and use the optimal alcohol length iso-butanol based biodiesel as a blend. Combining diesel fuel with a lower cooling point biodiesel would yield more desirable freezing points that would be more competitive with petrol fuels.

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Appendix

Biodiesel can be produced through the transesterification of an alcohol and oil catalyzed but an acid or base compound.

Equations

Cold flow properties of biodiesel may be estimated based on total saturated fatty acid alkyl ester (Sats) concentration. The following correlation was based on results from SME (Dunnet al., 1997):

Equation 1:

CP=1.44*[Sat]-24.8

Used to calculate cloud point based on the saturation point with a $\mp 2°C$ level of accuracy.

Cloud point modeling based on n- alkane content

The below equation summarizes the general solid-liquid equilibrium function using the composition in both phases.

Equation 2:

$$\left(\ln \frac{s\, \gamma^s}{x\, \gamma^l} = \frac{\Delta h_m}{RT_m}\left(\frac{T_m}{T} - 1\right) + \frac{\Delta h_{tr}}{RT_{tr}}\left(\frac{T_{tr}}{T} - 1\right)\right)_i$$

Equation 3:

$$\frac{g^E}{RT} = \sum_{i=1}^{n} x_i \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{Z}{2} \sum_{i=1}^{n} q_i x_i \ln\frac{\theta_i}{\Phi}$$

$$- \sum_{i=1}^{n} x_i q_i \ln\left[\sum_{j=1}^{n} \theta_j \exp\left(-\frac{\lambda_{ji} - \lambda_{ii}}{q_i RT}\right)\right]$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

Equation 4:

$$\lambda_{ii} = -\frac{2}{Z}\left(\Delta h_{sblm_i} - RT\right)$$

CFPP is a cold flow plugging point where the minimum temperature required to filter 20 ml through 45 um wire mesh under 0.02 atm vacuum within 60 sec is found.

CFPP=0.438[Sats]-8.93

(Dunn, 2008)

Equation 5:

$$\ln(x) = -\frac{\Delta H_{fus}}{R_g}\left[\frac{1}{T_f} - \frac{1}{MP}\right]$$

x= Solute mole fraction

Rg= gas constant

Equation 6:

CP=18.134Nc-0.79UFAME

Nc=weighted average number of carbon atoms

UFAME=composition of fames in bio-diesel