CHARACTERIZATION OF BIODIESEL

A Thesis

Presented to the faculty of the Department of Mechanical Engineering

California State University, Sacramento

Submitted in partial satisfaction of
the requirements for the degree of

MASTER OF SCIENCE

in

Mechanical Engineering

by

Michael Rowell

FALL
2017

CHARACTERIZATION OF BIODIESEL

A Thesis

by

Michael Rowell

Approved by:

____________________________________, Committee Chair
Dr. Rustin Vogt

____________________________________, Second Reader
Dr. Akihiko Kumagai

____
Date

Student: Michael Rowell

I certify that this student has met the requirements for format contained in the University format manual, and that this thesis is suitable for shelving in the Library and credit is to be awarded for the thesis.

____________________________, Graduate Coordinator ____________________
Dr. Troy Topping Date

Department of Mechanical Engineering

Abstract

of

CHARACTERIZATION OF BIODIESEL

by

Michael Rowell

Biodiesel is an alternative fuel produced by a process known as transesterification of waste cooking oil. The chemical process reacts potassium hydroxide, methanol, and triglycerides. Triglycerides are found in many feedstock oils such as waste vegetable oil. California State University Sacramento (CSUS) has a production system on campus that converts waste cooking oil into biodiesel. The university has collaborated with the Sacramento Biofuels Network (SBN) to test and produce biodiesel that adheres to ASTM D6751 standards. The ASTM characteristics focused on in this study refer to cloud point, pour point, and corrosion strip test. The SBN fuel was utilized to develop standardized tests for these characteristics and used as baseline values for future production. The corrosion strip test resulted in a standard classification number of 2a, which is below the ASTM specification. The cloud point and the pour point were found to be -3.9℃ and -9.7℃, respectively.

_______________________, Committee Chair
Dr. Rustin Vogt

____
Date

ACKNOWLEDGEMENTS

My gratitude and appreciation goes to my committee chair, Dr. Rustin Vogt, who passionately supported and guided this entire research study. Rustin was always available to answer any questions that I had. I am very grateful for the opportunity to work with Rustin throughout this project.

I would also like to thank Dr. Akihiko Kumagai for his assistance and support throughout my research and graduate studies as well as the graduate coordinator, Troy Topping.

I would like to thank Steve Bash, his enthusiasm and support for this project were truly valued. Steve has an undying passion for biodiesel and his input was exactly what pushed me to complete this thesis. Also, thanks to the Sacramento Biofuels Network for providing the biodiesel fuel that was used for testing.

A very special thank you to my parents who have always supported and pushed me through my academics. I truly appreciate all that they have done throughout the years.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Chapter 1

INTRODUCTION

1.1 Background

Over the previous decades, the idea of converting biomass (especially to liquid fuels) for sustainable energy has been gaining momentum among scientists, engineers, and policy makers. Low-carbon, sustainable biofuels will be increasingly important in the global market. Biofuels like ethanol, butanol, and biodiesel are made from organic materials making them renewable energy sources. Renewable energy sources reduce harmful greenhouse gases, such as those produced from fossil fuel, in the environment. Biofuels are considered to cause less pollution and are biodegradable. Biodiesel extracts the oils from plants to be processed, a process that reduces the viscosity of the feedstock oil to avoid flow problems. In North America, the most common plants used are soybean and canola oil. Another popular choice is used cooking oil recovered for biodiesel production. The production and use of biodiesel creates 78% less carbon dioxide air pollutants and greenhouse gases than conventional diesel [1]. In addition to being biodegradable, biodiesel is non-toxic and has a higher flash point than diesel, because of this it is safer to use and more chemically stable.

“Biofuels are biologically produced from renewable and even waste organic substrates by microorganisms, which are being explored to replace fossil fuels.” [2] Biofuels are being considered over fossil fuels “due to their renewability, biodegradability, and generating acceptable quality exhaust gases.” [2] Biofuels derive their energy from the carbon dioxide within living organisms rather than from long term geological processes. Some of the first biofuels to become widely used are ethanol fuels. These alcohol-based fuels must be distilled using fossil fuels lessening their benefits. Biodiesel is another example of a biofuel and can be produced from waste vegetable oils, resulting in a similar product to fossil fuels. Common feedstock oils used for biodiesel production are rapeseed oil, soybean oil, waste vegetable oil, animal fats, and algae. Waste vegetable oils, containing fatty acids or triglycerides, are considered among the best feedstock oil.

Biodiesel provides a good alternative to fossil fuels because it is clean burning, safe to handle, and renewable [2]. In addition, biodiesel can be produced from food processing waste (FPW). The food industry provides a wide range of products for industrial needs and human food. Inadequacies in the food industry have resulted in large quantities of FPW. Not only do FPWs have the potential to harm the environment, but their disposal is costly as well [2]. The most common method for their disposal is landfills. Waste cooking oil can be re-used multiple times or recycled, people usually will throw the used oil in the garbage. Landfills also are known to emit greenhouse gas emissions and contaminate groundwater. Converting FPW into biodiesel reduces some impacts of the food industry by lowering the energy cost of food processing.

At California State University, Sacramento (CSUS) the dining hall and campus eateries produce 200 gallons of waste oil per month [3]. In 2012 the Sustainable Technology Optimization Research Center (STORC) funded a Mechanical Engineering senior project to design a biodiesel production system converting the waste cooking oil, or fatty acids, into usable biodiesel. Following STORC's mission to facilitate, support, and house functional ongoing sustainable technology projects [3], this project would also power maintenance equipment saving the campus money while converting the FPW into a sustainable resource. In Fall of 2015 the system was revamped to produce cleaner biodiesel.

Sacramento Biofuels Network founder, Steve Bash, contacted Rustin Vogt, a professor in the Mechanical Engineering Department, about collaborating with his grassroots biodiesel group. The Sacramento Biofuels Network (SBN) works in coordination with local restaurants and commercial food services to recycle used cooking oil for biodiesel production. According to Steve, biodiesel produced locally is one solution to solving the dependence on increasingly costly and diminishing petroleum sources [4]. Another obstacle biodiesel production systems face is the resistance from the extremely powerful petroleum industry.

The CSUS biodiesel production system has three steps: filtration, reaction, and wash. The chemical process by which biodiesel is made is called transesterification. The resulting products are pure biodiesel and glycerol. The purpose of this thesis is to analyze the quality of biodiesel produced by the SBN, such as cold flow characteristics and material compatibility, to compare with the properties to biodiesel produced at CSUS. The testing methods will be developed and conducted in accordance with the American Society for Testing and Materials (ASTM) National Standards.

The cloud point and methanol content of the CSUS biodiesel were tested by a previous Mechanical Engineering Master's student, Lydia Palma, to obtain baseline values for future batches. These values will provide a guideline for verifying whether the biodiesel produced at CSUS can sufficiently meet the needs of SBN. Currently, STORC and CSUS do not have the advanced fuel analysis equipment so testing methods were developed to verify quality of future batches made on campus.

1.2 Objectives

The objective of this thesis was to determine methods for finding the copper strip corrosion, cloud point, pour point, and CFPP of the SBN biodiesel. Following ASTM standards and prior testing done by Palma, standardized tests were designed to measure the future CSUS produced biodiesel. If the appropriate biodiesel feedstock is not selected, the fuel does not run through the fuel system properly. According to a USDA study the cloud point for biodiesel made from animal fat or waste vegetable oils have a higher cloud point compared to other feedstocks [10].

One important course the Engineering students take at CSUS is engineering materials. The students perform various labs looking at the microscopic characteristics that give materials their macroscopic properties. The course studies the effects of corrosion on different materials and how those effects can be prevented. The copper strip corrosion test was incorporated into the curriculum for Engineering Materials. This proved to be a cost-effective way to get the corrosive effects of the biodiesel for future production batches. Detailed procedures were developed to assist the students in performing the experiments described in this thesis.

1.3 Biodiesel Production

The most common method for producing biodiesel is transesterification. The chemical process involves triglycerides react with an alcohol. The products are fatty acid methyl esters (FAME) and glycerol. A triglyceride is made up of a glycerin molecule base with three fatty acid chains. The nature of the fatty acids can change the characteristics of the biodiesel depending on the type of bonds, saturated or unsaturated [2]. Triglycerides can be found in vegetable oils, recycled grease, and algae. A catalyst, such as Potassium Hydroxide (KOH) must be added for the reaction to occur. The amount of catalyst will vary depending on the acid constituents in the triglycerides. To determine the acid contents of the triglycerides a titration is needed.

Once a titration is done, a balanced chemical equation can be formulated. The previous CSUS biodiesel system used a balanced equation of 1-part triglycerides (1000 kg) with 3-part methanol (107.5 kg) and a catalyst [3].

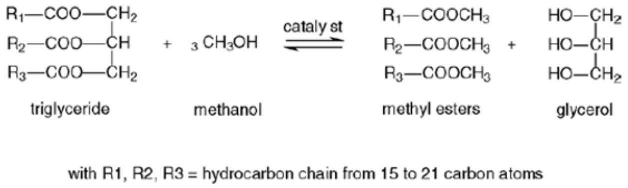


Figure 1.1 Transesterification [7].

These are mixed together in a reactor for approximately 1 hour at 333 K and the products are biodiesel fuel and glycerol. Once settled the biodiesel fuel and glycerol are easily separated because biodiesel has a lower density than glycerol, 0.8746 g/cm^3 compared to 1.26 g/cm^3. After the glycerol gets drained from the reactor the biodiesel must go through the final step: washing. The water is mixed with the biodiesel to remove soaps, leftover glycerol drops, and excess methanol. The soaps are a side reaction that occurs while the excess methanol is needed to ensure a complete reaction. The methanol may be recovered for subsequent production batches. Recovering the methanol removes a toxic and flammable substance from the biodiesel. Heating the biodiesel to approximately 75℃ turns the liquid methanol into methanol vapor. The methanol vapor exits the heating tank and is pumped into a condenser, where it is returned to a liquid state for later use. Studies have been done to determine the best way to use the excess glycerol, but the in most cases it is refined to pure glycerin and used in many different applications.

Reaction temperature, methanol to fat ratio, and reaction time have profound impacts on transesterification. Optimization studies have been done to determine the ideal reaction process. In a study by Zheng et al. [5] the ideal reaction consisted of a pretreatment to convert free fatty acids into biodiesel, acid-catalyzed esterification was performed at

75℃, a methanol to fat ratio of 8:1, and reaction time of 1 hour, to decrease the acid value. The mixture was then poured into a separation tank. The biodiesel was then process using alkaline-catalyzed reaction was done with a methanol to fat ratio of 6:1, 08%NaOH, at 65℃ for 30 minutes. Finally, the biodiesel was purified at 80℃ to remove residual methanol.

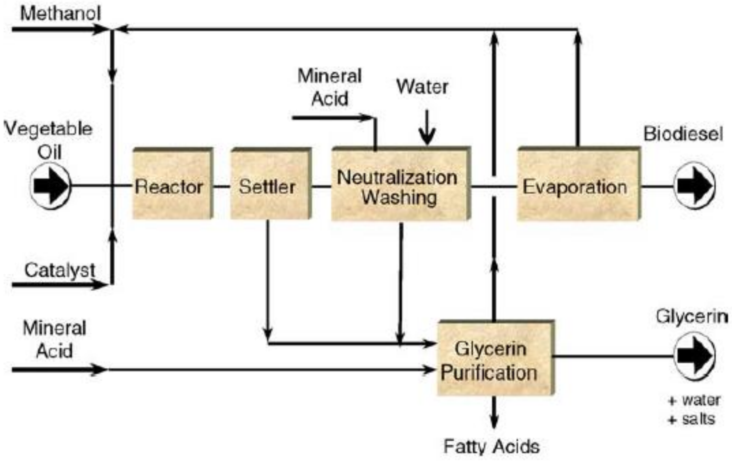


Figure 1.2 A typical schematic of a biodiesel process [7].

Any biodiesel fuel that is to be sold in the market must meet certain specifications. In the United States, the fuel must meet the ASTM standard, D6751 for biodiesel. The standard in Europe is defined by EN 14214. Using biodiesel that does meet these specifications may have adverse effects such as filter plugging, engine seizure, and poor tailpipe emissions [8]. The specifications listed by the ASTM are for B100 meaning 100% pure biodiesel. Depending on the feedstock and washing process, the resulting fuel properties will be different.

Producing fuel for the SBN market would also require the biodiesel to meet the ASTM standards. Steve Bash of SBN stated that major factors hinder the use of biodiesel. The three major issues Steve cited were cold flow, cleaning effect, and material compatibility [9].

The fuel’s cleaning effects are due to biodiesel being a solvent. The fuel cleans out the fuel system it passes through. If the fuel system has previously run on petroleum diesel, then the sediment or residues are removed. The sediment causes engine failure once it clogs the fuel filter. Fuel filters remove contaminants that may cause damage to important engine components such as fuel lines and injectors. Most contaminants in diesel fuel come from improper storage or mixing. Some common contaminants come are water, fungus, and asphaltenes [10].

Water is a common contaminant in diesel fuel. It may be introduced during fueling when warm, moisture filled air condenses on the walls of the fuel storage tanks. Water can cause damage to injector components and reduce the lubricity of the fuel. It can also cause seizure of components with low tolerances as those found in fuel pumps. In-line filters can separate out water from the diesel fuel. Fungus and bacteria feed on hydrocarbons in the diesel [10]. These bacteria can quickly clog a fuel filter once removed from fuel lines by the biodiesel fuel. Asphaltenes are by products of oxidized diesel. They create a black, tarry substance on the filter media. The tiny particles pass through the filter and stick to individual fibers within the fuel filter. Acting as a solvent the biodiesel removes these impurities further damaging fuel filters and fuel lines. This should be taken into consideration when fueling with biodiesel after using petroleum diesel in an engine.

The material compatibility happens because the fuel corrodes certain materials. The materials must be carefully chosen to ensure corrosion will not transpire. Steve recommends polyurethane over rubber components [9]. The ASTM standards associated with material compatibility are the copper strip corrosion test and acid number. The acid number specifies the acidity of the fuel. The test measures the amount of potassium hydroxide needed to neutralize, or fully react with, 1 gram of fuel [8]. The washing process adds acidic water to neutralize the catalyst, potassium hydroxide, and some residual acids remain afterwards. Pure biodiesel does not have high acid numbers, but the freshness of the fuel or washing methods can cause the acidity to rise. The water used to neutralize the catalyst leaves residual. The acid number is higher for fuels that have oxidized or absorbed water during storage. The copper strip corrosion (CST) standard classifies biodiesel fuel from 1 to 4 based on comparison with the ASTM Copper Strip Standards. The CST estimates the fuels compatibility with brass, copper, and bronze indicating the corrosive fuel’s corrosive properties.

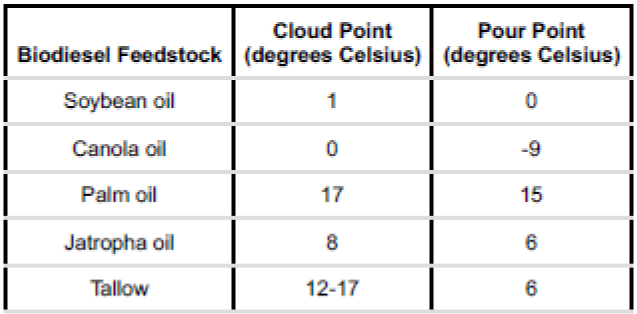
Cloud point, pour point, and cold filter plugging point (CFPP) all characterize the fuel’s cold weather characteristics and directly relate to cold flow. When the biodiesel has completely gelled, or froze, then it will not move through the fuel system properly. The actual temperatures for each property will vary depending on the type of oil or fat from which it was made. The cloud point and pour point differ significantly for petroleum diesel, but for biodiesel these values are similar. Biodiesel intended for use in colder climates needs modifications, such as anti-gel additives or No. 1 diesel fuel, to prevent the filters from clogging. Additives are not always effective, but lower blends of biodiesel, B2 or B5, perform the same as diesel in cold weather [11].

Chapter 2

COLD WEATHER CHARACTERISTICS

2.1 Overview of ASTM Standards

Cloud point, pour point, and cold filter plugging point are the ASTM tests that can be used to describe the cold weather characteristics of biodiesel. ASTM works to develop standards that are used to improve product quality, increase safety, and ensure customer satisfaction. The ASTM requirements related to biodiesel fuel are found in the standard D6751. The biodiesel properties are measured to ensure long term engine performance, fuel longevity, safety, and environmental impact [3]. While the testing standards are specified in the ASTM requirements CSUS does not have the equipment to do traditional testing for cloud point, pour point, and cold filter plugging point. It is critical to develop quantitative correlations to ensure the operability of biodiesel in cold weather [12]. Testing methods were previously developed by Palma for the CSUS biodiesel. Since the SBN fuel was compared to the previous cloud point values of CSUS biodiesel similar testing methods were used to determine cloud point for this thesis. Before discussing the experimental procedure, an understanding of the cold weather characteristics is necessary. While the cloud point and pour point do not have specific ASTM standard values, they must be reported to the consumer for proper fuel operation temperature ranges. Common cloud point and pour point values can be seen in Table 2.1.



Biodiesel Feedstock	Cloud Point (degrees Celsius)	Pour Point (degrees Celsius)
Soybean oil	1	0
Canola oil	0	-9
Palm oil	17	15
Jatropha oil	8	6
Tallow	12-17	6

Table 2.1 Cloud point and pour point for different feedstock oils [13].

2.2 Mechanism of Cold Flow Properties

At low temperatures the fuel gels, which results from the molecules forming crystals inside the liquid, leading to an increased viscosity. All diesel fuels contain wax crystals and as temperatures decrease, the wax crystallizes. This occurs when intermolecular forces of interaction are strong enough to generate thermodynamic forces, caused when reducing the temperature below its melting point [14]. Nucleation and crystal growth are the mechanisms by which crystallization occurs. First, nucleation occurs when the molecules come together to form crystal lattices. Crystal growth involves the expansion of the crystal lattices. New layers form upon the existing ones creating larger crystals. Continuous networks of crystal lattices inhibit fuel flow, leading to incomplete combustion.

2.3 Cloud Point

In colder regions, major concerns among biodiesel arise due to its unfavorable cold flow characteristics. Because of the increased viscosity the biodiesel fuel tends to gel at much higher temperatures than petroleum diesel. The cloud point is the temperature when small, dissolved wax crystals form in the liquid phase as the fuel cools. Once the temperature is below the cloud point, obvious clusters of crystals grow in multiple directions; for example, a ring of crystals may form around the bottom of the jar as the temperature decreases, but the cloud point is defined as the first appearance of crystals [15]. Because of this the engine may still operate at temperatures below the cloud point.

Petroleum diesel has a cloud point around -15℃ whereas the previous CSUS biodiesel had a cloud point of -2.78℃ [3] [12]. In many cases the fuel is blended with petroleum diesel to enable use in colder climates. A blend of biodiesel fuel with petroleum diesel fuel can be designated by BXX, where XX is the volume % of biodiesel [16].

Other methods to lower the cloud point and improve biodiesel performance are using fuel-line heaters, insulating the fuel filters and fuel lines, and by storing the diesel equipment in heated buildings while not in use. “Winterization” is a process that reduces the cloud point by removing saturated methyl esters. The fuel is cooled until crystallization occurs, then the high melting components are separated by filtration [12]. According to Lopes et al [17] the main factor in determining cloud point is the amount of saturated methyl esters because they have a higher melting point than the unsaturated esters. They derived equations to predict cloud point based on the carbon number of the biodiesel. Other research studies have correlated that increased chain lengths will increase intermolecular forces causing the cloud point values to increase. On the other hand, double bonds reduce the attractive forces between the molecules and the cloud point decreases [18]. However, winterization is considered an inefficient solution due to significant amounts of biodiesel removed.

The standard test method for cloud point in petroleum diesel is issued under the fixed designation of D 2500. The purpose of cloud point testing is to notice the presence of wax crystals in the fuel; however, if the fuel has not been properly washed, trace amounts of water and other compounds may exist. The test method should not monitor the phase transition of the water, but rather capture the temperature at which the fuel contains two phases, liquid and solid [16]. ASTM D2500 requires the cloud point temperature to be measured by means of a cloud point instrument, or controlled cooling environment. CSUS does not have this equipment, thus a method was developed by Palma using a driver, Type T thermocouples, and Labview. For this thesis, a method using an infrared thermometer was constructed to simplify the cloud point testing. The visual inspection of cloudiness in the specimen was done with a GoPro camera.

2.4 Pour Point

An engine may still run once the biodiesel fuel has reached its cloud point, but once the fuel has completely gelled, or reached its pour point, then the engine will not run. Viscosity is an important fuel property of biodiesel as well as petroleum diesel. The ASTM standard D445 describes kinematic viscosity. It has been shown that kinematic viscosity increases with the chain length of either the fatty acid in a fatty ester. The viscosity depends on nature and quantity of the double bonds present in the unsaturated fatty compounds [19]. The hydrocarbons in petroleum diesel exhibit lower viscosity in a smaller range than the fatty esters in biodiesel. The pour point denotes the temperature where there is movement of the fuel if the container is tipped. The pour point and cloud point have a much smaller range than petroleum diesel [11].

Based on the ASTM definitions for cloud point and pour point, it would be expected that the pour point will always be lower than the cloud point, but how they are reported the pour point may be higher. The cloud point test requires reporting at intervals of 1℃ whereas the pour point at every 3℃. As the temperature is lower, the surface movement is examined every 3℃ when the container is tipped. If no movement transpires, the temperature is lowered 3℃ until no movement is seen. Therefore, if a cloud starts to cloud at -11℃ and completely solidifies at -11℃, the cloud point is reported at -10℃, and the pour point at -9℃ [11]. The pour point temperature was recorded using a similar set up to the cloud point test. An infrared thermometer was used to measure the temperature while the container was tipped roughly every 3℃ that the temperature dropped. Once there was no movement in the sample, the pour point was recorded.

2.5 Cold Filter Plugging Point

The testing methods for cloud point and pour point are simple, and are commonly used to approximate the cold filter plugging point(CFPP). The CFPP is the temperature where the crystallization, or gelling, of the biodiesel fuel plugs the fuel filter. The engine cannot operate at temperatures below the CFPP and engine failure will occur. The CFPP testing can be expensive and monotonous because each test would result in ruining an engine, therefore, a temperature range at which the fuel will plug the engine is more widely used. The CFPP is reported at the lowest temperature a sample volume still passes through a pipette, or another standardized filtration device in a specified time when cooled [18]. The standard test method for CFPP is described in ASTM D6371. In accordance with D6371 a specimen of the sample is cooled under controlled conditions, and at each degree Celsius, the fuel is drawn into a pipet through a standardized wire mesh filter. The procedure is repeated as the specimen cools until the amount of wax crystals is sufficient to stop the flow into the pipet. If filling the pipet to more than 20 mL takes longer than 60s, or the fuel fails to return to the test jar before the fuel has cooled by another 1℃, then the temperature shall be recorded as the CFPP [20]. For this study, the cold filter plugging point was estimated based on the cloud point and pour point tests.

Chapter 3

CORROSIVE CHARACTERISTICS OF BIODIESEL

3.1 Corrosion

Corrosion can be defined as the destruction or deterioration of a material due to reacting with its environment, or the destruction by means other than straight mechanical [21]. For corrosion to occur an ionic solution, or electrolyte, is needed to accept ions as well as a reaction to consume the ions. In metallic corrosion, an electrochemical change of a metal to its positive ion takes place. For example, a copper specimen would lose two electrons as shown below:

$$Cu \rightarrow\ Cu^{2+} + 2e^{-}$$

Or more generally can be stated as,

$$M \rightarrow\ M^{2+} + ne^{-}$$

Where e^- represents an electron and M represents a metal. A reaction in which electrons are released describes an oxidation reaction whereas those that consume electrons are reduction reactions [21]. Oxidation takes place at the anode and reduction at the cathode. The electrolyte, either a liquid or solid, initiates the ion transfer and a physical path transfers electrons between the anode and cathode. A galvanic cell is made up of these four components: electrolyte, physical path, anode, and cathode. Corrosion effects the anode. The biodiesel fuel acts as an electrolyte that facilitates the reaction between coper and oxygen, from water added during the washing process, in the fuel.

3.2 Mechanism of Biodiesel Corrosion

A study by Weng Jiaqing [22] showed the corrosion of biodiesel on engine wear, and the results demonstrated that the water, acid, and other impurities are the source of corrosion. The better the washing process, the less impurities will result in the final biodiesel fuel. In petroleum diesel, corrosion is mainly caused by sulfur [23], while biodiesel does not contain any sulfur. The sulfur content for biodiesel must not be higher than 15ppm, but most biodiesel fuels average 3-4 ppm [24].

Corrosion due to biodiesel occurs in two ways. The first is biodiesel oxidizes because it has oxygen in it. Organic acids result from the oxidation reaction accelerating corrosion. Biodiesel also contains many double bonds, which also cause oxidation, and the metal degrades the double bonds into aldehydes, ketones, and other corrosive substances [23]. The other corrosive reaction occurs when hydroxyl in the monoglycerides, diester, and triester combine with metal atoms.

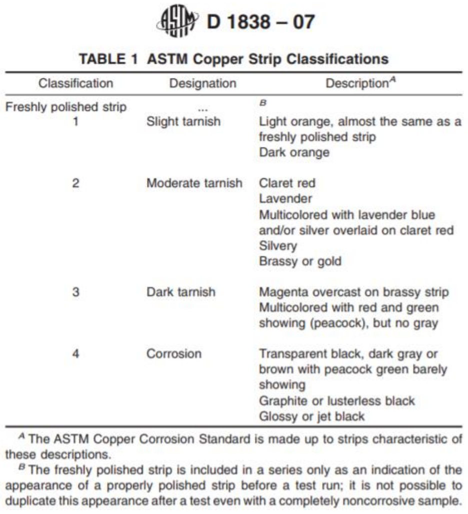
Biodiesel will dissolve elastomers as well as tank deposits leading to filter and injector plugging [25]. The fuel removes aromatics and additives from the elastomers that are added to prevent cracking. Common automotive seal and gasket materials, such as trilobutyldiene and nitrile rubber, are also known to swell when used in biodiesel systems

[26]. Therefore, using polyurethane in the fuel system is preferred as well as stainless steel and aluminum materials. Stainless steel and aluminum are less likely to oxidize biodiesel versus bronze, copper, lead, tin, and zinc, which have been reported to cause oxidation.

3.3 Copper Strip Corrosion

Copper strip corrosion is defined as a qualitative method that determines corrosive properties of fuels. In the copper strip test, a polished copper is submersed in the fuel and its effects examined [27]. It detects the presence of acids. The presence of acids determines the fuel's compatibility with copper, brass, or bronze parts. The higher the copper strip corrosion value the more likely the fuel is to corrode engine components.

The polished copper strip is suspended in 30 mL of fuel. The strip is then removed and classified based on a scale that ranges from 1 to 4 as specified in the ASTM copper strip corrosion standard in Table 3.1. A test jar with the fuel and copper strip are placed in a thermostatically controlled water bath at depths per ASTM requirements. The maximum temperature the bath is elevated to is around 105℃ [28].



D 1838 – 07

TABLE 1 ASTM Copper Strip Classifications

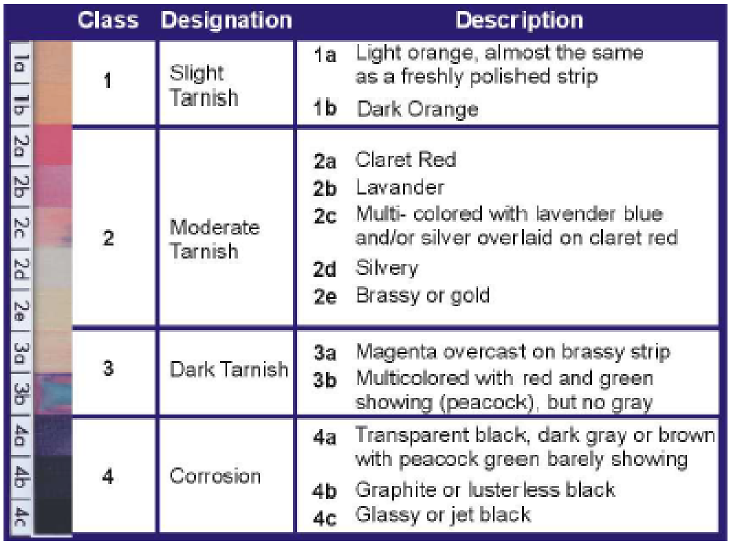
Classification	Designation	Description^A
Freshly polished strip	...	^B
1	Slight tarnish	Light orange, almost the same as a freshly polished strip Dark orange
2	Moderate tarnish	Claret red Lavender Multicolored with lavender blue and/or silver overlaid on claret red Silvery Brassy or gold
3	Dark tarnish	Magenta overcast on brassy strip Multicolored with red and green showing (peacock), but no gray
4	Corrosion	Transparent black, dark gray or brown with peacock green barely showing Graphite or lusterless black Glossy or jet black

^A The ASTM Copper Corrosion Standard is made up to strips characteristic of these descriptions.

^B The freshly polished strip is included in a series only as an indication of the appearance of a properly polished strip before a test run; it is not possible to duplicate this appearance after a test even with a completely noncorrosive sample.

Table 3.1 ASTM Copper Strip Classifications [29].

The testing apparatus specified in the ASTM requirements was not used for this study. The test method and equipment is described in the Experimental Procedure. Figure 3.1 shows the classifications of ASTM Standard D130.



	Class	Designation	Description
1a 1b	1	Slight Tarnish	1a Light orange, almost the same as a freshly polished strip 1b Dark Orange
2a 2b 2c 2d 2e	2	Moderate Tarnish	2a Claret Red 2b Lavander 2c Multi- colored with lavender blue and/or silver overlaid on claret red 2d Silvery 2e Brassy or gold
3a 3b	3	Dark Tarnish	3a Magenta overcast on brassy strip 3b Multicolored with red and green showing (peacock), but no gray
4a 4b 4c	4	Corrosion	4a Transparent black, dark gray or brown with peacock green barely showing 4b Graphite or luster less black 4c Glassy or jet black

Figure 3.1 D130 Standard Classifications [29].

Chapter 4

CLOUD POINT TESTS

4.1 Experimental Procedure

ASTM describes the cloud point of a fuel as the temperature of the specimen when the smallest observable clusters of hydrocarbon crystals first appear during cooling. The clusters of wax look like patches of milky clouds, which is where the name for the test comes from. Commonly, the crystals form at the lower circumferential wall of the test jar where temperature is lower [15]. Some clusters may be easily observable, while others are much harder to detect.

The first step is placing the test jar in a cool area while inspecting the fuel sample for when cloudiness begins. The previous method developed by Palma was used as a guideline for determining cloud point in this testing set up. National Instruments LabView Data Acquisition Assistant recorded temperature data. Type T (copper and copper nickel) thermocouples were used with National Instruments 9211 driver to monitor temperatures in the test jar. These components are shown in Figure 4.1.

Figure 4.1 Testing apparatus used to monitor temperature for Palma method [3].

A Sentry ST650 and OEM infrared thermometers were used to monitor temperature for the cloud point determination. The thermometer is pictured below in Figure 4.2.

Figure 4.2 Sentry ST650 Infrared Thermometer

A freezer set at a constant temperature was used for the controlled cooling environment. The camera video recorded time while the infrared thermometers measured temperature at various increments throughout the test. The biodiesel fuel was placed in the freezer and a gopro camera observed the sample for cloudiness as shown in figure 4.3.

The fuel used for testing was supplied by Sacramento Biofuels Network. The cloud point must be reported to the nearest 1℃ once any clouding is observed within the test jar. At each test thermometer reading that is a multiple of 1℃, inspection for clouding was done using a GoPro camera. To prepare the specimen, bring the fuel to a temperature at least 14 ℃ above the estimated cloud point. Excess moisture may be removed using a dry lintless filter paper until the oil is perfectly clear [15]. 50 mL of biodiesel was used for both tests.

4.1.1 Test 1

The biodiesel sample was placed in a freezer and the temperature was recorded approximately every five minutes using the infrared thermometer. A thermometer was also used to measure the temperature of the cooling environment. In test 1 an open container with the fuel was placed in the freezer. A GoPro camera was set up to observe clouding and record time.

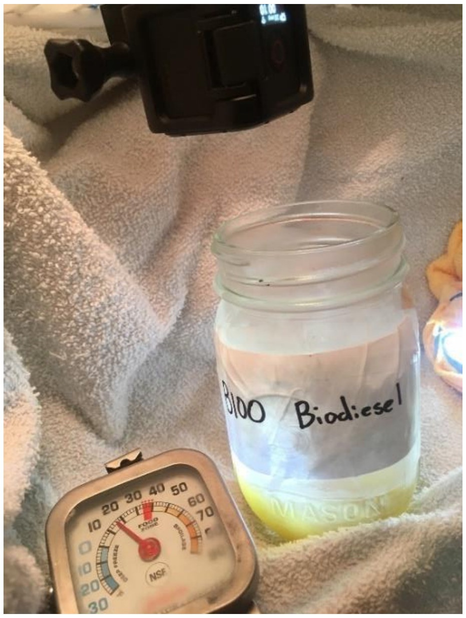


Figure 4.3 Test set up for cloud point testing

4.1.2 Test 2

The biodiesel sample was placed in a freezer and the temperature was monitored using the infrared thermometer. Time data was taken using a stopwatch. A thermometer was also used to measure the temperature of the cooling environment. In test 2 a closed container of fuel was placed in the freezer.

4.2 Results

The fuel sample was placed in a controlled cooling environment and the clarity was viewed using a camera while temperature data was taken at various points throughout the tests. The two tests were done using an open and closed container. In both tests the wax crystals began forming near the bottom circumference of the jar as expected.

4.2.1 Test 1 Results

The biodiesel reached its cloud point. The open container fuel sample showed signs of crystallization at 18 minutes inside the cooling environment. The cloud point was recorded at -5.3℃ after being placed in a freezer at roughly 10 ℃ and held at that temperature until clouding was observed. The first signs of clouding are shown in figure 4.4 from a screenshot of the test video.

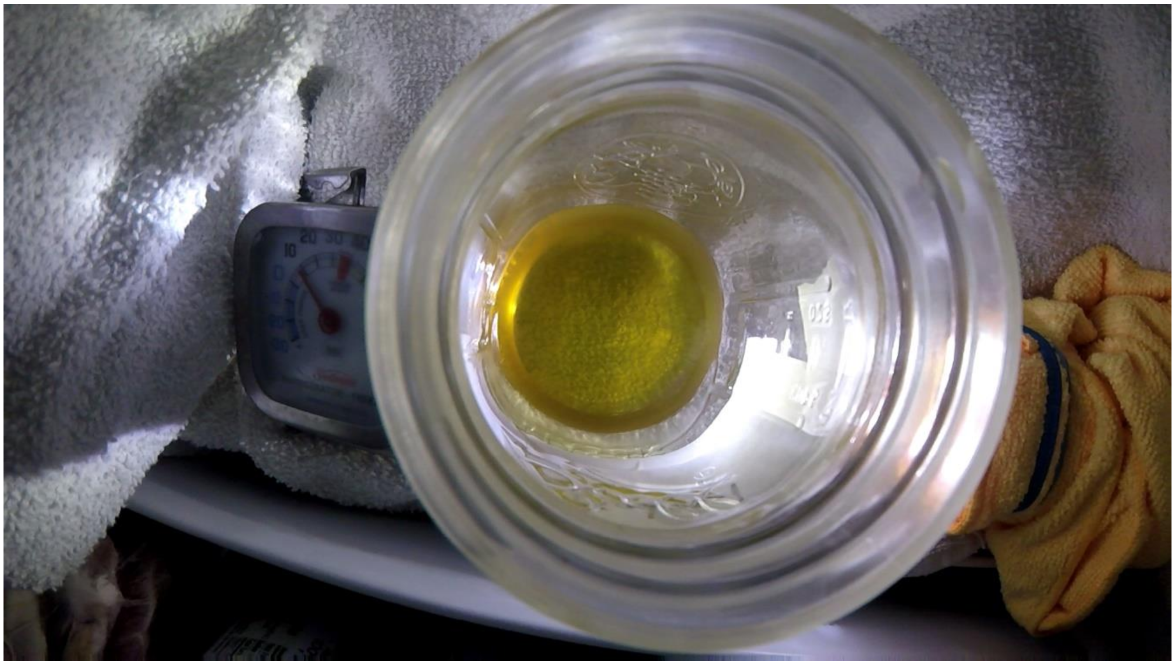


Figure 4.4 Cloud Point test 1 showing wax crystal formation in fuel.

The experimental results from test 1 were compared to Palma's data of the fresh biodiesel, washed, unwashed, and old washed biodiesel.

Sample	Cloud Point °F	Cloud Point °C
Fresh Biodiesel, Washed	27	-2.78
Fresh Biodiesel, Unwashed	30	-1.11
Old Biodiesel, Washed	34	1.11
SBN Biodiesel Test 1	22.46	-5.3
SBN Biodiesel Test 2	24.98	-3.9

Table 4.1 Experimental results from cloud point test

In the Sacramento region temperatures do not drop below 32°F often. Blending with petroleum diesel fuel can prevent clouding, if concerned about proper engine operation during winter months. These cloud point values are lower than the expected values for waste vegetable feedstocks that are listed in Table 2.1 at 12-17℃. The cloud points for the CSUS fresh, washed biodiesel are close to the values for the SBN biodiesel.

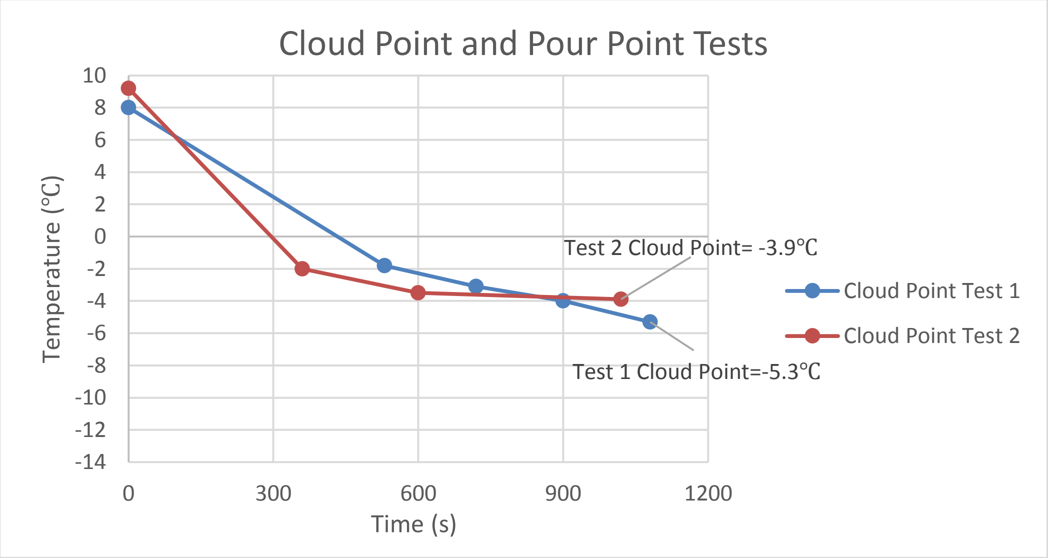


Figure 4.5 Temperature vs. time of Cloud Point Test 1 and Cloud Point Test 2

4.2.2 Test 2 Results

The second test was done with a closed container. The test showed that a closed container caused a higher cloud point. The cloud point for the second test was -3.9℃. This value is closer to the value of the CSUS biodiesel. Therefore, the fuel produced at CSUS proves to be well within the quality specifications of SBN. The improved production system should provide a cleaner fuel that has a cloud point close to the SBN fuel. The temperature vs. time graph showed a similar temperature decrease between the open and closed container tests as described in figure 4.5.

Chapter 5

POUR POINT

5.1 Experimental Procedure

The pour point can be defined as the lowest temperature at which the fuel moves within its test container. At the temperature at which wax crystal structures or increased viscosity, or both, stop movement of the surface of the test specimen is called the no-flow point [31]. The no-flow point occurs when observation no longer perceives movement. The previous observation temperature at which flow was observed, is recorded as the pour point. The pour point estimates the lowest temperature the fuel can be used effectively. The cold flow properties are important for the proper operation of fuel systems.

The pour point test was done simultaneously with the cloud point testing. The camera and infrared thermometer continued monitoring temperature vs. time once the cloud point was reached. At approximate intervals of 1℃, the test jar was tilted and inspected for any signs of movement. This testing was continued until the test jar was held in the horizontal position for 5s and there was no movement. It is important that the tilting of the jar does not take longer than 30s, or the fuel sample will rise in temperature.

5.1.1 Test 1

Once the cloud point was reached the sample was cooled to the no flow point. The specimen showed no signs of movement at 30 minutes, but before the 5s were finished, movement occurred. The testing continued until the temperature dropped further and no movement was shown.

5.1.2 Test 2

The cloud point was reached for the closed container specimen at 35 minutes. The test was performed using the same B100 fuel as the second cloud point test. The specimen showed no signs of movement below the cloud point.

5.2 Results

The fuel sample was cooled below the cloud point and tested for movement at each degree Celsius. Visual inspection for movement was used to monitor the increased viscosity of the fuel. Both samples reached their pour point.

5.2.1 Test 1 Results

The pour point for the open container sample was -9.7℃. This value was below the theoretical value of 6℃ listed in Table 2.1. The sample was tilted at -8.8℃ and held for 4s before movement occurred. The solidified fuel sample is shown in figure 5.1.

Figure 5.1 B100 biodiesel at -9.7℃

5.2.2 Test 2 Results

The second sample reached the pour point at 37 minutes. The pour point temperature was lower for the closed container compared to open container test. The pour point for test 2 was -12.7℃.

Chapter 6

COLD FILTER PLUGGING POINT

6.1 Experimental Procedure

The cold filter plugging point occurs when the wax crystals stop flow through a filter causing engine failure. Since the cloud point is when the wax crystals first begin to nucleate and the pour point when the crystals are solidified, the cold filter plugging point will occur between these values. Between the range values determined for the cold filter plugging point engine operation will begin to decrease in efficiency. Operation will still occur at temperatures below the cloud point, but as it gets closer to the pour point, engine failure can occur. The ranges were estimated from the test data.

6.1.1 Results

The cold filter plugging point values were determined from the cloud point and pour point tests. A bracketed range for the temperatures at which proper engine operation occurs was estimated from the test data. The first test resulted in cloud point and pour point temperatures of -5.3°C and -9.7°C, respectively. The cold filter plugging point for the first test is -5.3°C to -9.7°C.

The second test resulted in a cloud point of -3.9°C and the pour point at -12.7°C. Therefore, the cold filter plugging point for the second test is -3.9°C to -12.7°C.

Both tests were done on the same fuel. Any significant errors could cause incorrect usage of the biodiesel. The range for both tests must be considered when estimating the range for the cold filter plugging point. Therefore, the cold filter plugging point of the fuel was calculated from both tests. The second test showed signs of crystallization earlier so the higher value of cold filter plugging point was taken from the second test. At temperatures below the cloud point engine failure may occur. The first test displayed no movement at a higher temperature than the second test, thus the value for cold filter plugging point was taken from this test.

The cold filter plugging point for the SBN B100 biodiesel is between -4℃ and -9℃. At temperatures within this range engine failure may occur. These numbers are lower than expected for biodiesel showing that the washing process used by SBN is effective and the CSUS system must ensure high quality fuel from their production system.

Chapter 7

COPPER STRIP TEST

7.1 Experimental Procedure

The copper strip test was developed for this study in accordance with California State University policy and ASTM requirements. The copper strip test covers the detection of components of the fuel that may be corrosive. The test evaluates the degree to which corrosion will occur in copper containing materials such as bronze and brass. The ASTM requirements state that the results are reported as compared to the standard chart in Table 3.1. The test specimen was removed of all surface blemishes using steel wool. It is important to polish the whole surface uniformly to obtain proper results. If the initial edges show wear, they will be more likely to corrode.

The fuel must be placed in a test jar along with the copper strip. The test jar is to be immersed in a water bath maintained at 50℃ ± 0.5℃ for 3 hr ± 5 min. The exposed strip is removed and compared with the ASTM Copper Strip Corrosion standards. The test strip and the standard must be held so that light reflects off them both at an approximate angle of 45°. Test duration and test temperature must also be reported. A sentry infrared thermometer and stopwatch were used to monitor the test’s temperature and time.

7.1.1 Test

The copper strip was polished using grade 00 steel wool to remove surface blemishes. A water bath was preheated to 50℃ using a Thermolyne Type 1900 hot plate. The copper strip and 40 mL of fuel were placed in a test jar, and then set in the water bath for 3 hours. The Sentry ST 650 monitored the temperature throughout the test to keep it at a consistent temperature. The test was continued after 3 hours at a higher temperature to test for corrosion properties close to engine temperatures. The test set up is shown in figure 7.1.

	Test 1	**Test 2**
Avg. Temperature (℃)	49.7	64
Maximum Temperature Reached (℃)	54	89
Time (hr)	3	1.33
Classification	1b	2a

Table 7.1 Test information for the copper strip testing

Figure 7.1 Copper sample after copper strip test showing slight tarnish

Figure 7.2 Corrosion strip test set up

7.2 Results

The copper strip test was performed using a closed test jar with 40 mL of biodiesel and a copper sample. The strip was first polished and immediately placed into the test jar. After 3 hours as specified in the ASTM requirements, the copper sample was removed and compared to the D130 classifications shown in figure 3.1. Table 7.1 shows the testing values that were implemented for the two tests.

7.2.1 Description of Results

The sample was removed from the test jar and showed only a slight tarnish from the corrosion strip test. The ASTM standards require that the classification number is below a value of 3. Both tests resulted in values below the ASTM requirements. The sample after testing is shown in Figure 7.2. The fuel provided by SBN showed little corrosive properties. The test was done at standard pressure values. Manufacturing a pressure vessel to reach engine operating pressures would improve the accuracy of the corrosion strip copper test.

Chapter 8

CONCLUSION

The test methods developed for this thesis are practical options for determining the cloud point, pour point, and corrosiveness of the biodiesel produced on campus. These tests can be easily implemented in various courses to increase the student's understanding of key concepts associated with Mechanical Engineering. For more accurate results related to material compatibility, development of a standardized corrosion test is recommended. A project dedicated to creating the proper testing apparatus, including a pressure vessel that meets ASTM requirements, would be necessary to determine the fuel's corrosive properties with regards to other materials. The cloud point and pour point values of the SBN demonstrate a quality production system. These values are lower than expected values for biodiesel fuel made with waste vegetable oil. To produce fuel that meets the needs of SBN, the improvements made to the CSUS washing process must generate high quality biodiesel. With the guidance of Steve Bash and Rustin Vogt, CSUS has the capability to meet the needs of SBN and supply their buyer's group.

References

[1] Biodiesel. (n.d.). Retrieved November 3, 2017, from http://www.fueleconomy.gov/feg/biodiesel.shtml

[2] Z. Zhang, I. M. O'Hara, S. Mundree, B. Gao, A. S. Ball, N. Zhu, Z. Bai, and B. Jin, "Biofuels from food processing wastes," *Current Opinion in Biotechnology*, vol. 38, 97–105, 2016.

[3] L. Palma, "Biodiesel: A Look into Testing and Quality Standards," 2015.

[4] S. Bash, "Sac Cooking Oil Recycling Campaign in the news," *Sacramento Biofuels Network*. [Online]. Available: http://sacbiofuels.org/. [Accessed: 31-Oct-2017].

[5] L. Zheng, Q. Li, J. Zhang, and Z. Yu, "Double the biodiesel yield: Rearing black soldier fly larvae, Hermetia illucens, on solid residual fraction of restaurant waste after grease extraction for biodiesel production," *Renewable Energy*, vol. 41, pp. 75–79, 2012.

[6] Biodiesel Engineering. (n.d.). Retrieved November 4, 2015, from http://www.chmltech.com/biodieseltech.htm

[7] L. Bournay, D. Casanave, B. Delfort, G. Hillion, and J. Chodorge, "New heterogeneous process for biodiesel production: A way to improve the quality and value of the crude glycerin produced by biodiesel plants," *Catalysis Today*, vol. 106, no. 1-4, pp. 190–192, 2005.

[8] D. Shrestha, J. Thompson, and J. Nowatzki, "Biodiesel Fuel Quality," *eXtension*. [Online]. Available: https://articles.extension.org/pages/27998/biodiesel-fuel-quality. [Accessed: 18-Nov-2017].

[9] M. D. Rowell and S. Bash, “Biodiesel Challenges,” 08-Sep-2017.

[10] “Diesel Fuel Contamination and Fuel Filter Plugging,” *Hastings Filter*, Oct-2007. [Online]. Available: http://www.hastingsfilter.com/Literature/TSB/95-1R2.pdf. [Accessed: 24-Nov-2017].

[11] J. Nowatzki, D. Shrestha, A. Swenson, and D. P. Wiesenborn, “Biodiesel Cloud Point and Cold Weather Issues,” *eXtension*. [Online]. Available: http://articles.extension.org/pages/26611/biodiesel-cloud-point-and-cold-weather-issues. [Accessed: 02-Nov-2017].

[12] Y.-C. Su, Y. A. Liu, C. A. D. Tovar, and R. Gani, “Selection of Prediction Methods for Thermophysical Properties for Process Modeling and Product Design of Biodiesel Manufacturing,” *Industrial & Engineering Chemistry Research*, vol. 50, no. 11, pp. 6809–6836, 2011.

[13] B. R. Moser, “Influence of Blending Canola, Palm, Soybean, and Sunflower Oil Methyl Esters on Fuel Properties of Biodiesel†,” *Energy & Fuels*, vol. 22, no. 6, pp. 4301–4306, 2008.

[14] Pressman, A. (2007). *Biodiesel use, handling, and fuel quality*. Butte, Montana: National Sustainable Agriculture Information Service.

[15] “D 2500: Standard Test Method for Cloud Point of Petroleum Products,” Vol. D2500, West Conshohocken, PA: ASTM International, 2005.

[16] J. C. A. Lopes, L. Boros, M. A. Krähenbühl, A. J. A. Meirelles, J. L. Daridon, J. Pauly, I. M. Marrucho, and J. A. P. Coutinho, “Prediction of Cloud Points of Biodiesel,” *Energy & Fuels*, vol. 22, no. 2, pp. 747–752, 2008.

[17] H. Tang, S. Salley, and K. Simonng, “Fuel properties and precipitate formation at low temperature in soy-, cottonseed-, and poultry fat-based biodiesel blends,” *Fuel*, vol. 87, no. 13-14, pp. 3006–3017, 2008.

[18] Dwivedi G, Jain S, Sharma MP. Impact analysis of biodiesel on engine performance—a review. Renewable Sustainable Energy Rev 2011.

[19] G. Knothe and K. R. Steidley, “Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components.,” *Fuel*, vol. 84, p. 87, Feb. 2005.

[20] “Standard Test Method for Cloud Filter Plugging Point of Petroleum Products,” Vol. D6371, West Conshohocken, PA: ASTM International, 1999.

[21] Holl, S., “Corrosion Background Unit”, Sacramento, CA: CSUS, 2004.

[22] W. J. Qing, Y. Z. Xue, “The corrosion wear of biodiesel on diesel engine and its mechanism analysis,” *Lubrication Engineering*, vol. 33, no. 8, pp. 54–57, August 2008.

[23] Y. Su, F. Chen, Z. Wu, and H. Wang, “Corrosion characteristics of biodiesel in storage,” *2013 International Conference on Materials for Renewable Energy and Environment*, 2013.

[24] B. B. He, J. H. V. Gerpen, and J. C. Thompson, “Sulfur Content in Selected Oils and Fats and their Corresponding Methyl Esters,” *Applied Engineering in Agriculture*, vol. 25, no. 2, pp. 223–226, 2009.

[25] R. Baranescu, “Biodiesel research—engine warranty policy,” Presented at

Commercialization of Biodiesel: Establishment of Engine Warranties, University of Idaho National Center for Advanced Transportation Technology, pp. 102–106, 1994.

[26] K. Koontz, "Biodiesel research—engine warranty policy-Cummins", Presented at *Commercialization of Biodiesel: Establishment of Engine Warranties*, University of Idaho, National Center for Advanced Transportation Technology, pp. 107–124, 1994.

[27] "Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test," Vol. D130, West Conshohocken, PA: ASTM International, 2012.

[28] "What is Copper Strip Corrosion? - Definition from Corrosionpedia," *Corrosionpedia*. [Online]. Available: https://www.corrosionpedia.com/definition/328/copper-strip-corrosion. [Accessed: 12- Nov-2017].

[29] "Standard Test Method for Copper Strip Corrosion by LP Gases," Vol. D1838, West Conshohocken, PA: ASTM International, 2007.

[30] "Standard Test Method for Pour Point of Petroleum Products," Vol. D5949, West Conshohocken, PA: ASTM International, 2001.

[31] "Standard Test Method for Pour Point of Petroleum Products" Vol. D97, West Conshohocken, PA: ASTM International, 2005.