

**GC-MS CHARACTERIZATION OF SULFUR SPECIES IN LOW  
TEMPERATURE DISTILLATES OF BIODIESEL FROM  
WASTE GREASE**

**by**

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**A THESIS**

**Submitted in partial fulfillment of the requirements for the degree of  
Master of Science in the Food Science and Biotechnology  
Graduate Program of Delaware State University  
DOVER, DELAWARE  
May 2017**

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## **ACKNOWLEDGEMENTS**

I would first like to thank my mother and father Michelle and Michael Hughes Sr., for without their unyielding love and support, I would not have been able to complete this project. I would also like to thank Dr. Gulnihal Ozbay, who not only served as my academic advisor after my previous advisor left the university, but also provided support both academically and motivationally. She has truly helped in achieving this milestone in my life. I would also like thank my other committee members: Dr. Victor Wyatt, a man who has been a personal mentor and role model for me over the last year, Dr. Mingxin Guo, an inspiring professor of the department, and Dr. Alberta Aryee, who despite being new to the department, happily served as a member of my committee. I must thank Dr. Mazen Shahin and Latoya Stephens of the Louis Stokes Alliance for Minority Participation (LSAMP) Bridge to Doctorate program for accepting me into the program, thereby funding my education and research. I thank Dr. Stephen Lumor and Dr. Samuel Besong for educating me in the world of food science and my classmates who supported me through my struggles in those classes: Vanessa Richards, Louis Lott, Michael Peays, Omar Melton, Prince Boakye, Immaculate Arrey, Marieme Diao, and Duchard Louis. Lastly, I would like to thank God, who has continued to bless me with these life-changing academic opportunities.

# **GC-MS Characterization of Sulfur Species in Low Temperature Distillates of Biodiesel from Waste Grease**

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## **ABSTRACT**

Biodiesel, a renewable fuel alternative, has rapidly increased in production and usage over the past decade serving as an environmentally friendly fuel source. However, dependent upon the source of its feedstock, biodiesel could contain sulfur (S) at levels that could pose significant environmental impacts. Biodiesel from waste grease (i.e., used vegetable oil), for example, usually possesses S higher than the specified quality standards for automotive fuels. In order to produce quality biodiesel from a variety of feedstocks and to continue to take steps towards the production of clean fuel, the present study aimed to identify the sulfur species in “low temperature” distillate fractions of biodiesel produced from waste grease so that strategic means to remove the S-containing impurities can be developed. Solid phase extraction (SPE) was employed to separate and concentrate S-species in industrial samples of low temperature distillates of waste grease-based biodiesels. Organic solvents with different polarities were used to effectively separate polar S-species from non-polar fatty acids and other constituents, creating concentrated sulfur samples. The samples were then analyzed for total S contents. The most S-concentrating samples were then analyzed using gas chromatography-mass spectrometry (GC-

MS) to identify individual S-containing compounds. Two sulfur species were eventually identified in the biodiesel distillates: 5-butyl-dihydro-thiophenone, and 6-propyl-tetrahydro-thiopyranone. The molecules are believed to have originally existed as the precursor molecule 4-Mercapto-octanoic acid methyl ester. The results obtained from the present study provide a base for developing effective purification methods to remove S-containing impurities from waste grease-derived biodiesel.

## TABLE OF CONTENTS

List of Tables .....	vii
List of Figures.....	viii
<b>CHAPTER 1: INTRODUCTION .....</b>	<b>1</b>
1.1 Background and Significance.....	1
1.1.1. <i>The Dangers of Sulfur</i> .....	2
1.2 Hypothesis and Objectives .....	3
1.2.1. <i>Hypothesis</i> .....	3
1.2.2 <i>Main Objective</i> .....	4
1.2.3. <i>Specific Objectives</i> .....	4
<b>CHAPTER 2: LITERATURE REVIEW.....</b>	<b>5</b>
2.1. History of the Diesel Engine.....	5
2.2 Introduction to Alternative Fuels .....	6
2.3. Biodiesel.....	7
2.3.1 <i>Production in the U.S.</i> .....	7
2.3.2 <i>Global Production</i> .....	9
2.4. Feedstock Type.....	11
2.4.1 <i>First Generation Feedstocks</i> .....	12
2.4.2 <i>Second Generation Feedstocks</i> .....	14
2.4.3 <i>Third Generation Feedstocks</i> .....	17
2.5. Limitations on Sulfur Content.....	18
<b>CHAPTER 3: MATERIALS AND METHODS.....</b>	<b>22</b>
3.1 Solid Phase Extraction.....	22
3.1.1 <i>Loading</i> .....	22
3.1.2 <i>Washing</i> .....	23
3.1.3 <i>Drying</i> .....	24
3.2 Sulfur Analysis.....	25
3.3 Gas Chromatography and Mass Spectrometry.....	26
3.3.1 <i>Gas Chromatography</i> .....	26
3.3.2 <i>Mass Spectrometry</i> .....	27

<b>CHAPTER 4: RESULTS AND DISCUSSION.....</b>	<b>28</b>
<b>CHAPTER 5: CONCLUSION.....</b>	<b>38</b>
<b>REFERENCES.....</b>	<b>40</b>

## LIST OF TABLES

Table 2.1. Properties of Diesel and Biodiesel Fuels by ASTM International.....	19
Table 4.1. Initial Masses, Volumes, and Sulfur Concentrations of Biodiesel Samples .....	29
Table 4.2A. Biodiesel Sample BD-6 fractionated by SPE .....	31
Table 4.2B. Biodiesel Sample BD-6 fractionated by SPE .....	31
Table 4.2C. Biodiesel Sample BD-9 fractionated by SPE .....	32
Table 4.3A Sulfur concentrations and mass for Biodiesel sample BD-6.....	32
Table 4.3B. Sulfur concentrations and mass for Biodiesel sample BD-8.....	33
Table 4.3C Sulfur concentrations and mass for biodiesel sample BD-9.....	33



## LIST OF FIGURES

Figure 2.1. Graph Illustrating Biodiesel/Renewable Diesel Production of the Last 10 years.....	8
Figure 2.2. Global Biodiesel Production Potential Based on Lipid Exports.....	9
Figure 2.3. Comparison of Petroleum, 1st, and 2nd generation Feedstocks .....	12
Figure 2.4. Transesterification reaction .....	13
Figure 2.5. Grease Trap Waste to Biodiesel process .....	16
Figure 3.1. Movement of Analytes during Solid Phase Extraction .....	24
Figure 3.2. Sulfur Analyzer Schematic .....	25
Figure 4.1. GC-S of Stock biodiesel .....	30
Figure 4.2A. Chromatograph of Biodiesel Sample BD-8 fraction E. ....	34
Figure 4.2B. Chromatograph of Biodiesel Sample BD-8 fraction F .....	35
Figure 4.3. Parent and daughter ions of 5-butyl-dihydro-thiophen-2-one .....	36
Figure 4.4. The Three Species.....	37

# **CHAPTER 1**

## **INTRODUCTION**

### **1.1. Background and Significance**

Environmental pollution has become one of the biggest issues facing this planet. Pollution causes several health-related disorders and it is almost impossible to prevent exposures to the pollutants. The Environmental Protection Agency (EPA) reports that over 250 million tons of municipal solid waste were produced in 2010 in the United States alone (Environmental Protection Agency, 2017). A large majority of oceans, lakes and other water sources are also polluted, with plastics being one of the largest contributors. As a result of pollution, it is estimated that approximately 663 million people worldwide do not have access to clean drinking water (World Health Organization/United Nations International Children's Emergency Fund, 2015).

Petroleum-based fuels are currently one of the leading fuel types in today's global economy; unfortunately, these fuels have devastating and lasting effects on the environment. Not only do they release harmful chemicals and greenhouse gases into the atmosphere and water supply, but also nonrenewable and as such, are limited in supply (Sundus and others, 2017). To reduce the detrimental effects of man-made pollution, many steps have been taken to limit dependence on petroleum and shift towards more beneficial fuel types (Agarwal and Dhar, 2015). One fuel, biodiesel, is environmentally friendly and has rapidly increased in popularity over the past few

years. However, biodiesel does have somewhat of a problem concerning its marketability as a fuel: its sulfur content (Ma and others, 2016).

### *1.1.1 The Dangers of Sulfur*

While elemental sulfur is non-toxic, it is reactive, and some of the compounds it forms can be quite dangerous. When industrial petroleum containing sulfur is burned in the air, it forms sulfur dioxide. These sulfur dioxide molecules, in turn, react with water and oxygen molecules to form sulfuric and sulfurous acid, the components of acid rain. When acid rain falls, it does not only cause damage to buildings and other structures, but also lowers the pH of soil and smaller bodies of water; this largely affects living organisms in the vicinity that depend on vegetation for life, including humans (Environmental Protection Agency, 2017).

Sulfur presence in petroleum can be just as detrimental to a vehicle's condition as it is to a living organism's health. As early as the 1950's, researchers began noticing that sulfur can damage various parts of an engine. In one experiment, it was found that fuel with a high sulfur content can cause varying damage, including cylinder and ring wear (Jeffrey and others, 1951.) In addition to wear and tear of engines, sulfur can also increase the production of exhaust emissions in vehicles by interfering with the proper function of the catalytic converter, a device designed to minimize toxic emissions produced by vehicles. This is done by catalyzing a redox reaction and converting pollutants into less toxic compounds. If not functioning properly, these emissions (such as deadly carbon monoxide) can be detrimental to human health. In an experiment utilizing fuels with two different sulfur contents, the reduction in sulfur concentrations was accompanied

by a decrease in the mass of the exhaust emissions (Benson and others, 1991). The Society of Automotive Engineers confirmed those suggestions in a technical paper stating that reducing sulfur content can decrease particulate emission levels (Asaumi and others, 1992). The Manufacturers of Emission Controls Association released a study stating that sulfur presence in gasoline inhibits the emission control performance of catalytic technology (MECA, 2013). An increase in vehicle production of toxic emissions will further pollute the environment and ultimately affect human health if not properly dealt with.

Because of its potential to cause long-term damage to vehicles, many laws exist to regulate sulfur content. If biodiesel is to remain a contender in the fight to reduce the use of petroleum diesel, the sulfur content must be significantly reduced to increase its marketability. Researchers at the United States Department of Agriculture (USDA) Eastern Regional Research Center (ERRC) have theorized that one possible way to reduce sulfur content would be to first identify the various sulfur compounds present within biodiesel, then subsequently removed from the fuel based on chemical composition.

## **1.2 Hypothesis and Objectives**

### *1.2.1 Hypothesis*

Sulfur species found in the light fractional distillate (LFD) of biodiesel samples will be successfully identified using solid phase extraction (SPE), sulfur analysis, and mass spectrometry (MS).

### *1.2.2 Objective*

The main objective of this study is to utilize a variety of analytical techniques to identify the specific sulfur species found in LFD biodiesel for removal, thereby maximizing engine capability and minimizing environmental damage.

### *1.2.3 Specific Objectives*

- Concentrate the sulfur species found in LFD of biodiesel.
- Analyze the concentrated samples for approximate sulfur content.
- Identify the various species found within LFD of biodiesel using mass spectrometry.

## **CHAPTER 2**

### **LITERATURE REVIEW**

Production of biodiesel serves as a means of creating a renewable fuel source and lowering toxic emissions associated with traditional petroleum diesel (Barik and Paul, 2017). Around the world, many nations are conducting more research, including feedstock studies in hopes to discover a cost-effective, environmentally-friendly source of biodiesel. One feedstock type that is among those being considered for biodiesel production is waste grease from restaurants (Kemper, 2009); these wastes are rapidly produced and serve no other purpose other than occupying space in landfills. These wastes have excellent lipid contents and possess great potential to serve as biodiesel feedstock, but cannot and will not be utilized unless they meet standards set by the American Society for Testing Materials. The following sections provide information on biodiesel as a whole, global production rates, various feedstock types, biodiesel standards, and a means of adhering to those standards.

#### **2.1 History of the Diesel Engine**

Petroleum begins as crude oil present beneath the earth's surface, where it is removed and refined to meet fuel standards, and sold to the public (Math Pro Inc., 2011). Today, many engines utilize petroleum diesel as a preferred type of fuel, however the first diesel engines were actually powered by vegetable oil. The diesel engine in use today was first designed by Rudolf Diesel in 1890. Diesel was inspired by Nicholas Carnot, a French physicist behind the design of

today's modern combustion engine, and sought to improve the engine's efficiency. Diesel's initial engine, powered by peanut oil, was first completed in 1893. Diesel continued his work, modifying his design and steadily improving upon its flaws up until his death in 1913 (The Editors of Encyclopædia Britannica, 2012). Rudolph diesel not only revolutionized the diesel engine but also had a hand in one of the earliest attempts at an alternative fuel source when he chose to use peanut oil in his engine. Unfortunately, in later designs, the oil from peanuts and other vegetables were incompatible with the engines due to their viscosity (Pacific Biodiesel, n.d.). In 1937, it was discovered that the process known as transesterification would give vegetable oils the necessary viscosity to be of use in diesel engines, paving the way for modern biodiesel production (Pacific Biodiesel, n.d.).

## **2.2 Introduction to Alternative Fuels**

With crude oil reserves quickly depleting, global warming concerns growing, and gas prices on the rise, attention has once again been shifted towards the use of renewable fuel sources, also known as biofuels. Biofuels are, by definition, any fuel produced from a biological source. The term is commonly used to refer to liquid fuels produced from some type of biomass (Agarwal, 2015). A number of different biofuel types are used today, including ethanol, methanol, biobutanol and biodiesel (Biofuels: What are they, 2017). Ethanol, methanol, and biobutanol are all alcohols and are produced during the fermentation of plant biomass (Agarwal and others, 2015); these fuels have lower energy than traditional fuels and can be a challenge to use. Biodiesel is produced through transesterification, has a comparable energy to traditional petroleum diesel and produces far less environmentally-damaging compounds (Leung and others, 2010).

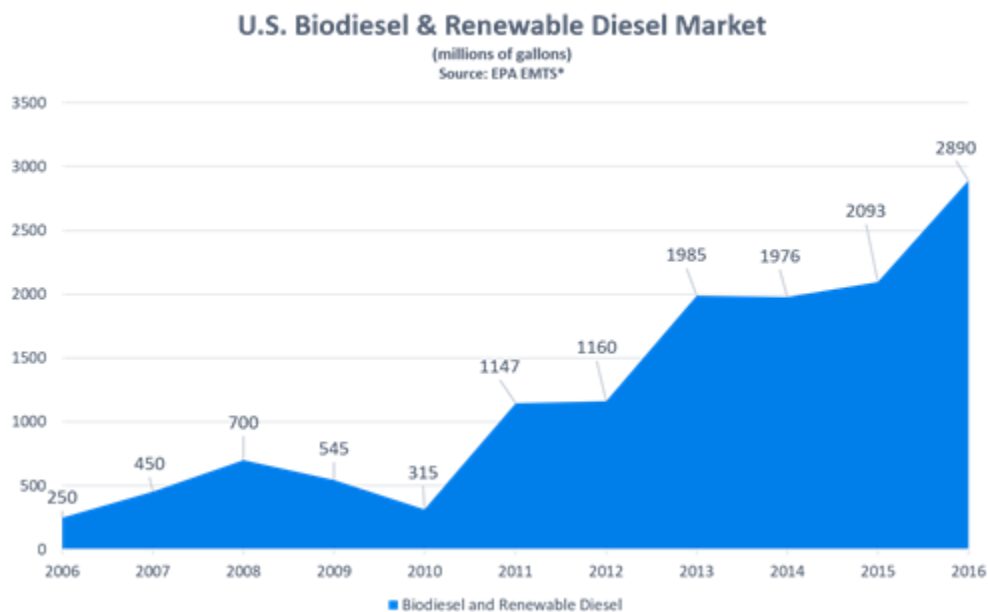
## **2.3 Biodiesel**

### *2.3.1 Production in the U.S.*

Biodiesel is a renewable fuel alternative to traditional petroleum diesel fuel (Lim and others, 2010). Defined by the National Biodiesel Board as “a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751” (Biodiesel.org, 2016), biodiesel is what some consider to be the next generation of fuel products. The production of biodiesel is an attempt to not only alleviate the United States’ dependence on foreign fuel sources, but to also alleviate the detrimental effect traditional petroleum fuels have on our environment. Biodiesel can be produced from a wide variety of feedstocks (Lee and Lavoie, 2013) and is held to a very strict set of guidelines in order to meet proper fuel quality standards. According to the National Biodiesel Board of the U.S, biodiesel production has increased from 25 million to 2.1 billion gallons from the early 2000’s to late 2015 (Figure 2.1). The United States’ production of biodiesel continues to climb as the years go by; in 2011, 1 billion gallons were produced for the first time, marking a historic milestone. In 2015, history was made, with over 2 billion gallons being produced. (Biodiesel.org, 2016.) As of September 2016, U.S. production of biodiesel was 135 million gallons (7 million less than August 2016), the majority of which occurred in the Midwest and sold as B100 (100% biodiesel) and blends. Soybean oil continues to be the largest feedstock with over 243,000 metric tons (537 million pounds) consumed in September 2016 (US Energy Information Administration, 2017).



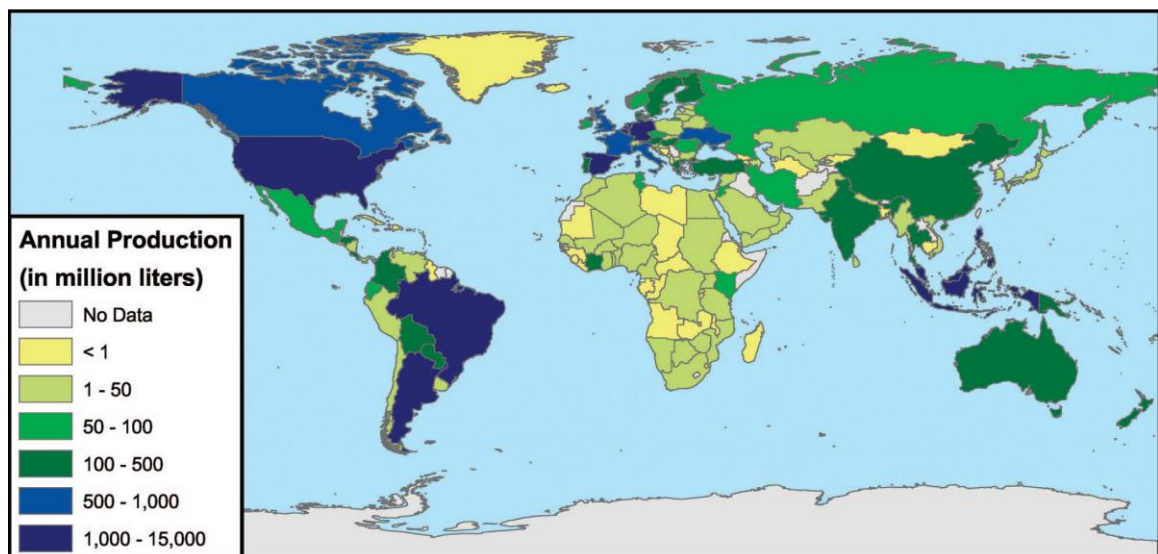
In 2013, such a sufficient quantity of biodiesel was produced, that the Environmental Protection Agency (EPA) listed biodiesel as “the only EPA-designated advanced biofuel approved for commercial production.” The U.S. industry aims to produce 10% of the nation’s diesel fuel by 2022. This not only holds positive effects for the environment, but also has the potential to significantly improve the U.S. economy. Continued production of biodiesel allows for a reduced dependence on foreign oil, freeing citizens from the ever-changing prices of the oil market. An increased production of biodiesel also provides an increase in the number of jobs; the industry currently supports over 48,000 jobs in a variety of departments, including manufacture, transportation, and agriculture. (Biodiesel.org, 2016.)



**Figure 2.1.** Graph Illustrating Biodiesel/Renewable diesel production of the last 10 years (Biodiesel.org "Production Statistics", 2016).

### 2.3.2 Global Production

Biodiesel production has also seen an increase in production globally; with one of the most recent booms in popularity occurring in the early 1990's (Johnston and Holloway, 2007). A number of nations have begun to recognize biodiesel's true environmental worth. Europe produced 2 billion liters from soy, rapeseed, mustard seed, and waste vegetable oils in 2004 compared to the 100 million in the U.S. (The Worldwatch Institute, 2005). At the time, both the U.S. and European Union accounted for over 95% of the world's biodiesel demand, while South Africa, Japan, Brazil, China, India, and many other industrious nations were developing their own biodiesel programs (Figure 2.2). A study conducted by Johnston and Holloway (2007) identified countries with the potential to rapidly increase their biodiesel programs, Malaysia, Indonesia, Argentina, The United States, and Brazil were listed as the top five. The five were selected in part due to the nations' ability to grow two popular feedstock plants (soybeans and palm).



**Figure 2.2.** Global biodiesel production potential based on lipid exports (Johnston and Holloway, 2007).

In 2007, Nigeria, a very populated African nation, created its own biofuel program prompted by the Federal Government of Nigeria in 2005 (Abila, 2012.) Nigeria began shifting towards clean-burning energy sources in an effort to adhere to the United Nations' Sustainable Development Goals. Nigeria potentially has a huge amount of biofuel available in the form of palm oil, Jatropha, and soy beans. These fuel options and many others are currently under investigation for utilization and mass production (Giwa and others, 2017).

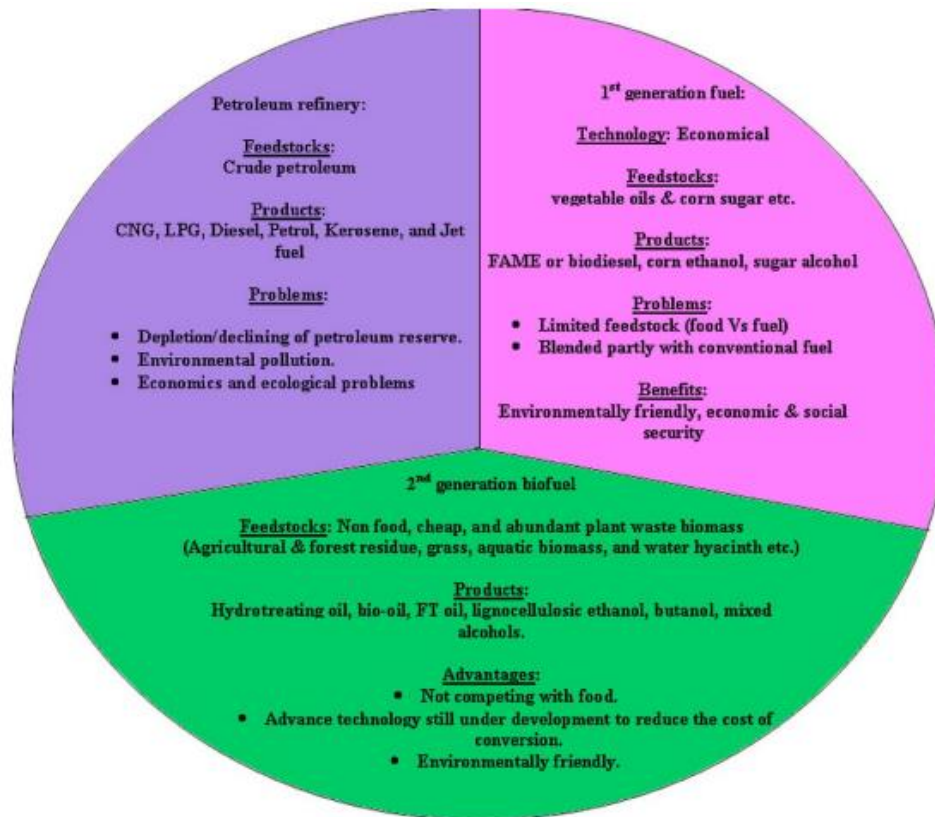
The United Kingdom has also begun increasing the use of biofuels over the last few years, as a means of reducing carbon dioxide emissions. Though current engine tests indicate somewhat of a loss of power as more biodiesel was incorporated into a fuel blend, current research is being conducted to optimize fuel efficiency; land capacity for growth of biofuel feedstock plants and lifecycle impacts of biodiesel are also being studied (Hammond and others, 2008). Since a biofuel is not considered beneficial if its production harms the environment at a greater rate than petroleum diesel, UK researchers must weigh the options and find an ideal way to incorporate biodiesel into the mainstream fuel industry while meeting agricultural and environmental standards (Hammond and others, 2008).

Many Latin American countries have begun establishing biofuel programs in response to the successes of similar programs in Brazil, the European Union, and the United States (Janssen and Rutz, 2011). Colombia, Guatemala, Venezuela, and Costa Rica utilize bioethanol while Argentina has shifted towards using biodiesel. In 2008, Argentina became one of the five largest biodiesel producers in the world (Janssen and Rutz, 2011). Biofuels in Latin America are

produced primarily from plant oils, which has caused some concerns in expansion of the biofuel programs, mainly deforestation and land use (Janssen and Rutz, 2011). In order to meet the demand ever-expanding market for biodiesel, land must be set aside to grow these biofuel crops, which has its own environmental implications. Many feel as though forests and grasslands should not be destroyed to produce fuel (albeit, a clean-burning fuel) (Janssen and Rutz, 2011).

## **2.4 Feedstock Type**

When comparing biodiesel production across the nations, one thing is certain: selection of a proper feedstock is critical to the program's success. An ideal feedstock should be inexpensive to harvest and convert into biodiesel, produce a clean burning and efficient fuel, and have as little effect as possible on the environment (Barik and Paul, 2017). In today's biodiesel market, there are several different types of feedstock in use, and can be grouped into three different classifications: first, second and third generation (Lee and Lavoie, 2013). First generation feedstocks are typically defined as a biomass (organic matter) that is more than often, edible at the time of fuel production. Second generation feedstocks include a wide variety of feedstocks, ranging from lignocellulosic biomass (dried plant matter) to waste cooking oils. What distinguishes second generation feedstocks from first generation feedstocks is that they are incapable of being consumed as food for humans or animals (Figure 2.3). Second generation feedstocks typically have been consumed to the point where only waste (or what would be considered waste) is remaining. Third generation feedstocks are defined as fuels produced from algal source (Lee and Lavoie, 2013).

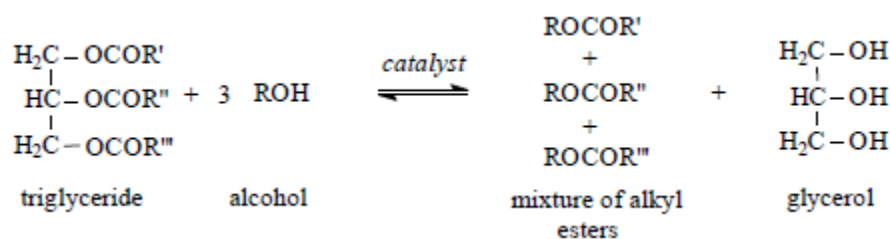


**Figure 2.3.** Comparison of petroleum, 1st, and 2nd generation feedstocks (Naik and others, 2009).

#### 2.4.1 First Generation Feedstocks

When producing biodiesel using first generation feedstocks, the oils from the selected feedstock plant must be extracted (Schuchardt and others, 1998) and subjected to a chemical reaction known as “transesterification” (Figure 2.4). During transesterification, the triglycerides of the plant/seed oil are reacted with an alcohol (typically in excess) and typically utilizing a strong acid or base as a catalyst. Other catalysts including enzymes (such as lipase) and waste-derived catalysts (such as egg shells) have also been used in the production of biodiesel (Talha and others, 2016). The released free fatty acids form ester bonds with the alkyl group(s) and

(typically) become fatty acid monoesters (FAME) while the glyceride backbone combines with the hydroxyl groups to form glycerol, a harmless by-product of biodiesel (Schuchardt and others, 1998). First generation feedstocks are commonly used in developing biodiesel programs internationally. Soybean oil is one of the most popular choices for biodiesel production due to its wide availability in quantities that are sufficient enough to support a national demand (Canakci and others, 2003), though some argue that soybean oil as a feedstock is counterproductive to the pro-environmental purpose of biodiesel production. In one study, biodiesel production using soybean oil required 27% more energy than the biodiesel product produced (Pimentel and others, 2005). In addition, soybean oil is highly valued as a food product and thus, makes it difficult to produce biodiesel from while remaining as cost-effective as it is in the food industry (Canakci and Van Gerpen, 2001.) As mentioned previously, growing the amount of soybeans necessary to satisfy fuel industry needs requires large amounts of open land, which can result in deforestation and other forms of environmental damage (Janssen and Rutz, 2011). Soybean oil can be rather costly when compared to other oils; in 2012, it was priced at \$1,180 per ton, whereas palm oil was priced at \$931 per ton, canola oil at \$1180 per ton, and Jatropha oil ranging from \$350-500 per ton (Lee and Lavoie, 2013.) As a result, many nations who utilize first-generation feedstocks are shifting to other plant oils.



**Figure 2.4.** Transesterification reaction (Schuchardt and others, 1998).

In Malaysia, Jatropha oil has the potential to be an excellent biodiesel feedstock. Over 1.5 million hectares (~ 9656.064 kilometers) of land are available for agricultural development, with some of the land having already been dedicated to Jatropha cultivation. Jatropha is also inedible so it does not have to compete with demand from the food industry (Syamsuddin and others, 2015.) In India, a study by Tiwari and others (2007) was conducted to improve the yield of biodiesel from Jatropha oil. After optimization of the reaction, transesterification of Jatropha can yield over 99% biodiesel, which had functional properties similar to that of conventional petroleum diesel and adhered to American/European biodiesel standards (Tiwari and others, 2007).

Canola oil-based biodiesel has been shown to reduce carbon monoxide and unburned hydrocarbon emissions, but was found to raise nitrogen oxide emissions and slightly reduce engine performance (Ozsezen and others, 2009). Rubber seed oil is being considered as a potential non-edible feedstock for biodiesel in Nigeria (Ikwuagwu and others, 2000). Careful testing showed that rubber seed oil biodiesel has a FAME content of 97.7%, a lower water content than palm oil biodiesel and meets European standards for biofuels. Rubber seed is also relatively inexpensive in Thailand, making it a proper candidate for biodiesel production (Roschat and others, 2017).

#### *2.4.2 Second Generation Feedstocks*

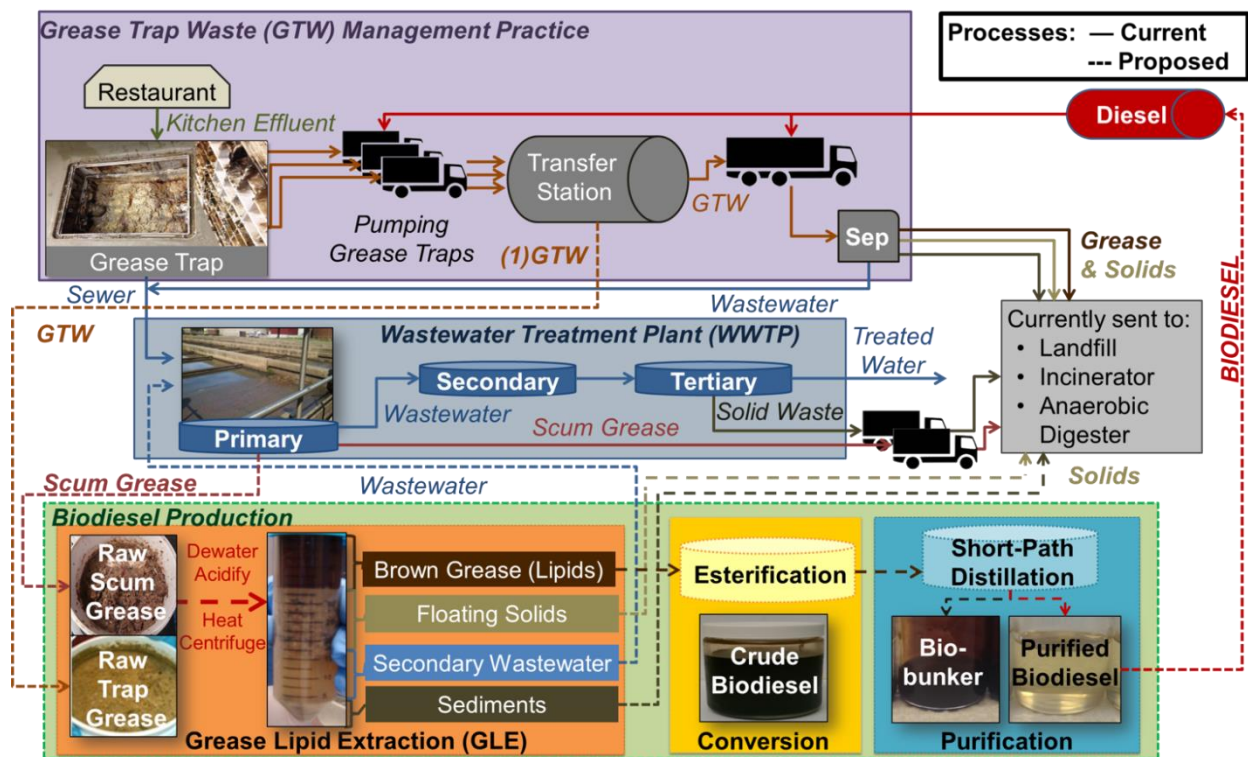
While first generation feedstocks have been proven time and again to be efficient precursors to biodiesel, they are not without their drawbacks. Plant oils can be rather expensive, particularly if

they are of any use in the food industry, and land clearing can present a political and/or environmental barrier. It is at this point that many consider second generation feedstocks. Second generation feedstocks can be further classified into three subcategories: homogenous, quasi-homogenous, and non-homogenous (Lavoie and others, 2011). Homogenous feedstocks can be somewhat expensive in comparison to quasi and non-homogenous feedstocks, with prices around \$100 per 907.185 kg. Quasi-homogenous feedstocks can range from \$60-\$80, and non-homogenous feedstocks can be close to \$0 (Lavoie and others, 2011).

Many have begun to identify food and grease waste as ideal second generation feedstocks; the biodiesel formed from used grease recovered from restaurants has been shown to burn cleaner than traditional petroleum diesel and is a fraction of the price (Mu and others, 2013). In a life cycle assessment of scum grease (home and restaurant greases that collect in water treatment facilities after they've been disposed of) to biodiesel conversion, it was found that scum grease has the least environmental impact when compared to petroleum diesel, soybean oil, and vegetable oil (Kulkarni and others, 2006). Scum sludge has also been found to contain several long chain fatty acids and a high calorific value (energy released as heat during combustion, particularly in fuels), ideal qualities when selecting a proper feedstock (Wang and others, 2016). Hundreds of thousands of tons of restaurant waste are produced annually in several countries across the globe. These wastes are inedible and account for much of landfill space; on some occasions, these wastes can form a barrier around plant roots and prevent plants from absorbing nutrients in soil and damage sewer systems (Capuano and others, 2017). Using this waste as a feedstock will address and eliminate two immediate problems: the use of landfill space for dumping of waste grease and release of dangerous gases by traditional diesel fuel (Hums and



others, 2016). In Figure 2.5, the path from waste grease to biodiesel and the alternative path to landfill are illustrated.



**Figure 2.5.** Grease trap waste to Biodiesel process (Hums and others, 2016).

Some researchers may argue that though scum grease and other second generation feedstocks are inexpensive and there can be problems with the functionality of the biodiesel produced. Because second generation feedstocks are often blends from many different sources, it is often difficult to yield a high amount of biodiesel (due to interference with the transesterification reaction by impurities), separate impurities, and meet ASTM specifications (Canakci and others, 2008). Canola oil mixed with used cooking oil was shown to meet most standards when blended at 60% with petroleum diesel. When blended at a lower ratio, however, quality decreased (Issariyakul

and others, 2008). Waste palm oil methyl esters, though excellent in reducing toxic emissions, reduced engine performance (Ozsezen and others, 2009). Other researchers have found that by experimenting with methodology, solvents, and catalysts, it is possible to utilize these clean burning feedstocks without sacrificing performance. By optimizing lipid extraction and purification, food waste can potentially serve as an ideal feedstock (Talebian-Kiakalaieh and others, 2013). According to Phan and others (2008), waste greases do somewhat decrease on engine capability when used alone, but when blended at an ideal ratio, the mixture can be used in an engine without decreasing its function. Waste fryer grease can yield over 90% biodiesel when a two stage acid and base catalysis is used over the traditional 1 stage catalysis in transesterification (Issariyakul and others, 2007). Some researchers assert that biodiesel from waste cooking oil gives better engine performance (Kulkarni and others, 2006).

#### *2.4.3 Third Generation Feedstocks*

Third generation feedstocks were once categorized alongside waste greases in second generation fuels. As time passed on and more research was conducted, it was revealed that algae can produce higher yields of biodiesel with lower input of resource (Third Generation Biofuels, 2010.) Unlike first generation feedstocks, algae are not considered food or used in traditional food items, and thus, do not need to compete with the food industry for use. While second generation feedstocks have also addressed that issue, the technology for conversion to biodiesel from these feedstocks has not yet met commercial standards (Brennan and Owende, 2010). Algae have high lipid content and are able to yield a greater amount of oil than plants, due to their higher growth rates. Algae are relatively inexpensive to harvest, biologically efficient due to their use of solar power, and can actually utilize the carbon dioxide in the atmosphere, helping

alleviate the greenhouse gas problem plaguing our society (Ahmad and others, 2011). However, as with all good benefits, there are downsides to utilizing algae as well. It can be difficult to extract lipids from the algae without completely drying them, which can be a rather expensive process. In addition, algae require water to produce biodiesel constituents, and in nations where much of the water is frozen, production becomes challenging (Lee and Lavoie, 2013).

## **2.5 Limitations on Sulfur Content**

The three generations of feedstock pose three different means of producing an alternative, renewable fuel in the form of biodiesel. Though each feedstock type is unique in composition and is environmentally friendly, it is only the second generation feedstocks that not only produce a functional biodiesel, but simultaneously recycle what would otherwise be considered waste in the process. Grease trap waste in particular, holds a massive amount of potential to be utilized as a feedstock for biodiesel; unfortunately, it cannot be made commercially available until it can meet the standards established by the American Society for Testing Materials (ASTM.)

In 1898, the American Section of the International Association for Testing Materials was established with a set of goals in mind: “the development of international standards for materials and products (The History of ASTM International. N.d.) The organization sets standards for various materials and products used across the globe including biodiesel as a means of assuring the best quality of product possible. Such specifications include, but are not limited to: fuel standard, kinematic viscosity, carbon content, hydrogen content, and sulfur content (in parts per million.) (Alleman and others, 2016). When present in fuel, sulfur can have detrimental effects

on the environment and the vehicle itself. Sulfur interferes with the oxidizing agents present in the emission control system, reducing their effectiveness and releasing dangerous toxins into the atmosphere, including hydrocarbons and carbon monoxide (Stanislaus and others, 2010). In order to secure the use of grease trap waste as a feedstock source for biodiesel, sulfur content must be reduced to 15 ppm before it can be marketed, according to specification ASTM D6751 (Table 2.1). Any biodiesel used in the United States should meet ASTM D6751 before blending (Alleman and others, 2016).

**Table 2.1.** Select properties of Typical No. 2 Diesel and Biodiesel Fuels by ASTM International (Alleman and others, 2016).

Fuel Property	Diesel	Blodlesel, No. 1-B grade
Fuel standard	ASTM D975	ASTM D6751
Higher heating value, Btu/gal	-138,490	-119,550
Lower heating value, Btu/gal	-129,488	-127,960
Kinematic viscosity, @ 40°C (104°F)	1.3 – 4.1	4.0 – 6.0
Specific gravity @ 15.5°C (60°F)	0.85	0.88
Density, lb/gal @ 15.5°C (60°F)	7.1	7.3
Carbon, wt %	87	77
Hydrogen, wt %	13	12
Oxygen, by dif. wt %	0	11
Sulfur, wt % (parts per million [ppm])	0.0015 max. (15 ppm max.)	0.0 – 0.0015 (0 – 15 ppm)
Boiling point, °C (°F)	180 – 340 (356 – 644)	315 – 350 (599 – 662)
Flash point, °C (°F)	60 – 80 (140 – 176)	100 – 170 (212 – 338)
Cloud point, °C (°F)	-35 – 5 (-31 – 41)	-3 – 15 (26 – 59)
Pour point, °C (°F)	-35 – -15 (-31 to 5)	-5 – 10 (23 – 50)
Cetane number	40 – 55	47 – 65

The standard limit of 15 ppm was first established in 2002 by ASTM international. After some minor revisions and updates, the standard was finalized and has remained the ever since (Lin and others, 2011). At this level, emissions controls systems are able to function properly without releasing dangerous toxins. Current research is already being conducted to lower the sulfur content of grease trap waste and scum grease to suitable levels. Ma and others (2016) were able to develop a method for producing low-sulfur biodiesel; by utilizing a combination of solvent extraction and acid washing as well as reflux distillation and adsorptive desulfurization, approximately 70% of the biodiesel product was formed with less than 15 ppm sulfur content.

This project employs biodiesel that has been subjected to vacuum distillation in a Wiped Film Evaporator (WFE.) Through the WFE process, researchers are able to reduce sulfur content from 200-500 ppm to 80-250 ppm, however that alone is not sufficient enough to create marketable biodiesel from scum grease. This project is designed to identify an adequate strategy in identifying sulfur species and potentially hold the key to more efficient removal of sulfur from biodiesel. Researchers in the past, though skillful in their ability to yield a large quantity of biodiesel, have struggled with a means of reducing sulfur content to below 15 ppm. Bi and others (2015) were able to produce a quality biodiesel product but were unsuccessful in developing an optimized method of sulfur removal. A previous study conducted by Ma and others (2016) uses a combination of heptane extraction, reflux distillation, and adsorptive desulfurization to remove sulfur species from biodiesel, yet were unable to reduce sulfur concentration to below the ASTM standard for most of the samples. The researchers in the study noted that some of their removal methods may have been ineffective due to sulfur being present as an organosulfur species. With the ability to identify these species down to their molecular structures, removal methods could be

modified to include a wider variety of sulfur species such as organosulfur, thus removing the species and yielding a better biodiesel product.

## **CHAPTER 3**

### **MATERIALS AND METHODS**

All biodiesel samples used throughout the experiment were obtained from the laboratory of Dr. Richard Cairncross of Drexel University, Department of Chemical and Biological Engineering (Philadelphia, PA.). Samples of biodiesel began as trap grease of Philadelphia metropolitan-area restaurants collected at wastewater treatment facilities and subjected to distillation by wiped film evaporator at Drexel University.

#### **3.1 Solid Phase Extraction**

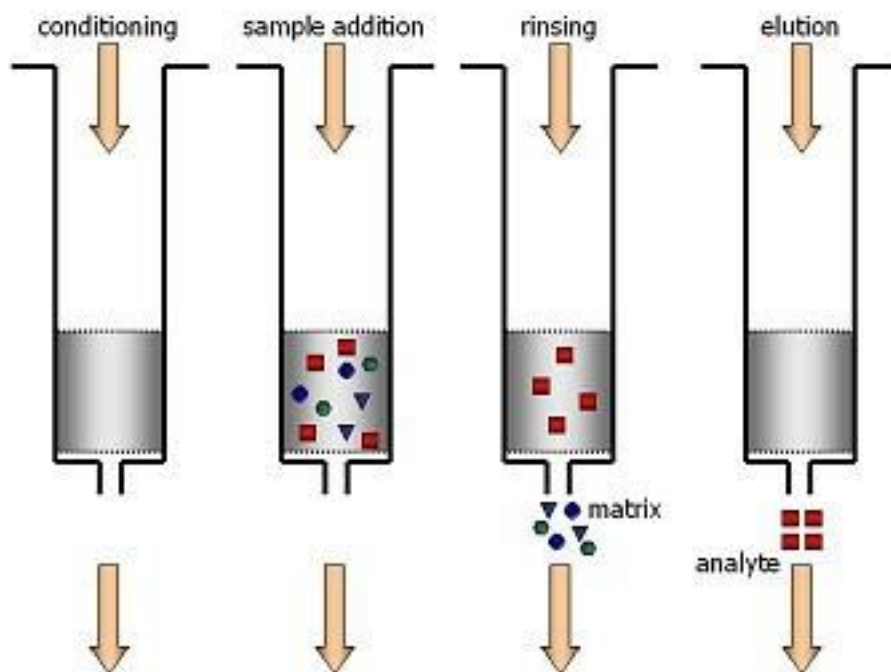
##### *3.1.1 Loading*

SPE was performed using a Visiprep™ SPE Vacuum Manifold standard (St. Louis, MO) 12-port model and Thermo Scientific™ 10 g silica SPE cartridges (Waltham, MA). The SPE cartridge was conditioned, first using 10 ml of ethyl acetate (allowing for the solvent to completely flow through the column) then hexane mixed with methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) in a 9:1 ratio. This ensures that the polar silica column in the cartridge will be able to properly adsorb the polar species. Three low temperature distillate fractions, designated B6, B8 and B9 were analyzed. Approximately 20 g of each biodiesel sample was weighed and loaded onto the column. A vacuum may be applied to expedite the elution process if the biodiesel samples do not efficiently elute through the cartridge.

### 3.1.2 *Washing*

Upon completion of the loading step, the column was washed. Using six solvents ranging from lowest to highest in elution strength, the analytes were extracted from the stationary column in an increasing concentration, with the final solvent removing the highly polar sulfur species desired. In this experiment, the solvents of choice (listed in terms of increasing polarity) include a 9:1 hexane-CH<sub>2</sub>Cl<sub>2</sub> solution, a 1:1 hexane-CH<sub>2</sub>Cl<sub>2</sub> solution, 100% CH<sub>2</sub>Cl<sub>2</sub>, ethyl acetate, methanol (MeOH), and acetone. To begin, 10 ml of the 9:1 hexane-CH<sub>2</sub>Cl<sub>2</sub> solution were added to the same cartridge used in the loading step. While the solvent moved through the column (can be expedited with a vacuum pressure not to exceed 20 mmHg,) more polar analytes bonded to the column are removed and were collected in a sample tube. This step is repeated with the solvents in increasing elution strength, with each eluent being collected in its own sample vial. Upon completion, the cartridge is removed and discarded. The collected elution samples were then prepped for the final drying stage.





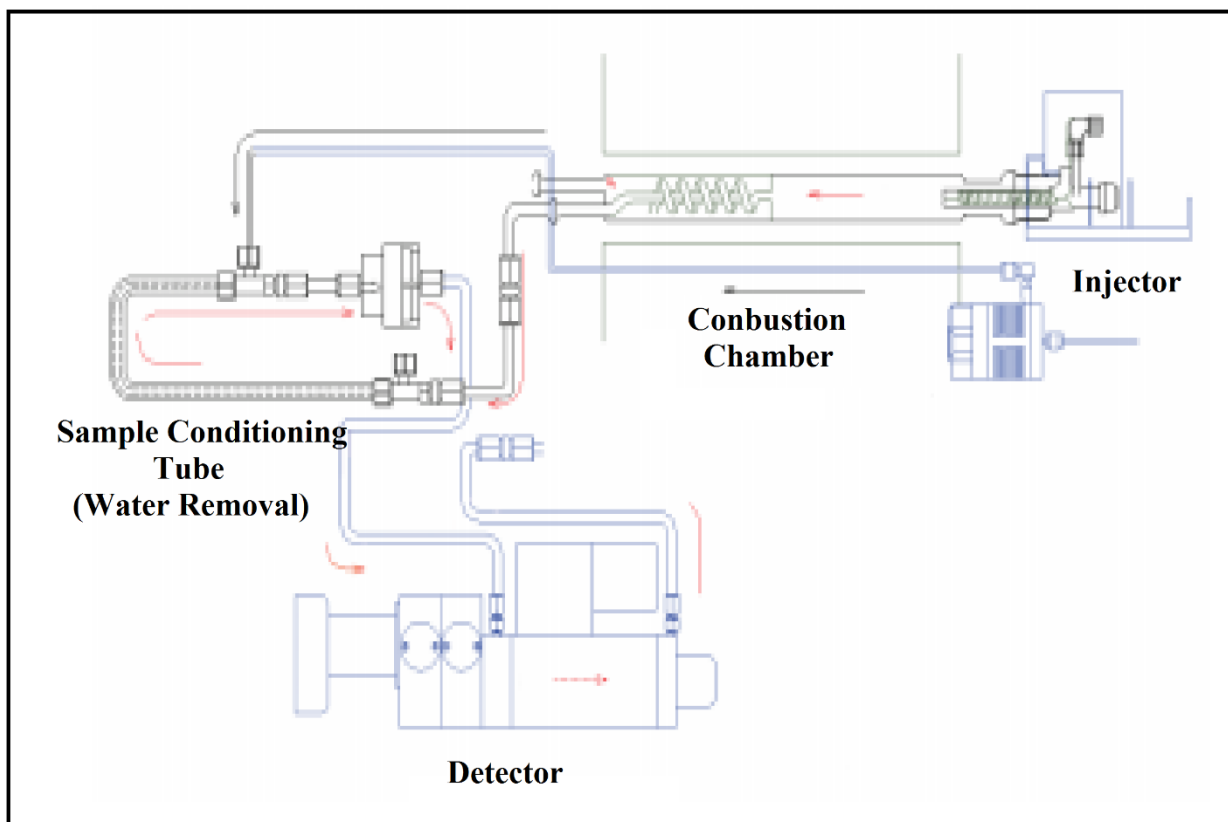
**Figure 3.1.** Movement of analytes during Solid Phase Extraction (Lucci and others, 2012).

### 3.1.3 Drying

All elution samples must have all solvent completely removed before they can be analyzed for the sulfur content. This was done for approximately 2 hours utilizing The Meyer N-evap nitrogen blower (Berlin, MA) at the USDA Eastern Regional Research Center. Tubes were placed in a hot water bath of 30°C to aid in solvent evaporation.

### 3.2 Sulfur Analysis

The presence of sulfur in each sample was determined with a TS 3000 Total Sulfur Analyzer (Waltham, MA) connected to a TS-UV module and an Archie autosampler. The autosampler was calibrated using four AccuStandard (New Haven, CT) biodiesel standards at 0, 15, 30 and 75 ppm. Standards were used to confirm accurate ppm and establish a calibration curve. The dried samples were transferred into 1.5 ml vials along with 1 ml of ethyl acetate per sample and loaded onto the autosampler platform. Then, 20 microliters ( $\mu\text{l}$ ) samples were injected into the analyzer. The analyzer injected each biodiesel sample in triplicate and averaged the sulfur concentration for each sample.



**Figure 3.2.** Sulfur analyzer schematic (TS 3000 Product Sheet).

### 3.3 Gas Chromatography and Mass Spectrometry

#### 3.3.1 Gas Chromatography

Two types of GC detectors were used: a Flame Ionization Detector (FID) and a Pulsed Flame Photometric Detector (PFPD) for sulfur species.

1. Using the FID, 1 $\mu$ l of SPE column fractions were analyzed on a capillary column (Phenomenex ZB-5ht, 30 m x 0.25 mm x 0.25  $\mu$ m film using an Agilent 6890 GC (Agilent Technologies, Palo Alto, CA, USA) fitted with a flame ionization detector. Column flow was set at 1.0ml/min using helium as carrier gas. A gradient temperature program starting at an initial temperature of 100°C, held for 2 min before increasing to 190°C at 30°C per min after injection, then ramped to 210°C at a rate of 1°C per min followed by holding for 5 min provided separation of the components in 30 min. The injector was held at a temperature of 300°C and operated in the split mode with a flow of 10.0ml/min. The detector was held at 250°C and fueled by hydrogen and air gases at 30 ml/min and 350 ml/min respectively.
2. Using the PFPD, 1 $\mu$ l of SPE column fractions were analyzed on a capillary column (Phenomenex ZB-5ht, 30 m x 0.25 mm x 0.25  $\mu$ m) film using an HP 5890 series II GC (Agilent Technologies, Palo Alto, CA, USA) fitted with an 5380 pulse flame photometric detector (O I Analytical, Collese Station, TX, USA). Column flow was set at 1.0ml/min using helium as carrier gas. A gradient temperature program starting at an initial temperature of 100°C, held for 2 min before increasing to 190°C at 30°C/min after injection, then ramped to 210°C at a rate of 1°C/min followed by holding for 5 min provided separation of the components in 30 min. The injector

was held at a temperature of 300°C and operated in the split mode with a flow of 10 ml/min. The detector was held at 250°C and fueled by hydrogen and air gases optimized per the manufacturers specifications. A BG-12 purple optical filter and R1925 photomultiplier tube, specific to sulfur emissions were used. Carbon and sulfur gate parameters were 1 to 3 ms and 6 to 24 ms respectively.

### *3.3.2 Mass Spectrometry*

During MS, 1 µl of SPE column fractions were analyzed on a capillary column (Phenomenex ZB-5ht, 30 m x 0.25 mm x 1.0 µm) film using an Agilent 7890 GC (Agilent Technologies, Palo Alto, CA, USA) coupled with an Agilent 5975 mass selective detector (MSD). Column flow was set at 1.0 ml/min using helium as carrier gas. A gradient temperature program starting at an initial temperature of 100°C, held for 2 min before increasing to 190°C at 30°C/min after injection, then ramped to 250°C at a rate of 2°C/min followed by holding for 5 min provided separation of the components in 40 mins. The injector was held at a temperature of 300°C and operated in the split mode with a flow of 10 mins. The mass transfer line was heated to 300°C. The MSD source and quadrapole were heated to 250°C and 150°C respectively. The ion scan range was 45 to 700 m/z. In the chemical ionization mode, methane was used as the reagent gas.

## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

This project focused on identifying the sulfur species in lightweight fractions of biodiesel for extraction. Solid phase extraction (SPE) has been used as a means of concentrating sulfur species present in biodiesel. Solvents ranging from least to most polar were used to effectively separate polar sulfur species from non-polar fatty acids and other constituents, creating a concentrated sulfur sample. Then, the samples were analyzed using a TS 3000 Total Sulfur Analyzer connected to a TS-UV module to determine sulfur concentration in parts per million. Finally, the specific sulfur molecules were determined using mass spectrometry. The identities of possible sulfur-bearing compounds in waste grease biodiesel have been determined. Typically, three major temperature profiles were used to collect fractions separated by WFE. These temperature profiles can be described, in general, as low, middle and high temperature distillates. In this project, we studied the low temperature fraction which was subsequently evaluated by total sulfur analysis, SPE and GC-MS.

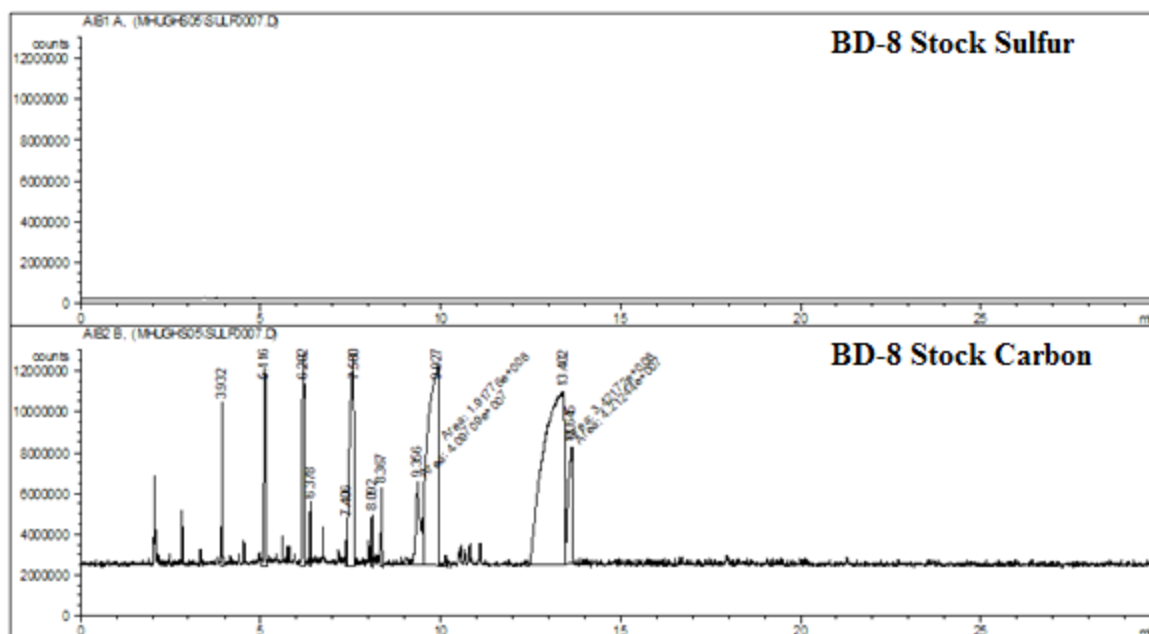
Table 4.1 shows the initial mass, volume and sulfur concentrations of three different low temperature biodiesel fractions distilled by WFE. These samples were shown to have an average of 42.34 ppm sulfur, which corresponds to an average of 1.06 mg of sulfur. After proving that sulfur-bearing species exist in the samples, a systematic approach to identifying those species was employed. To first evaluate the identity of the S-bearing species, it was imperative to determine if they could be separated chromatographically from other compounds. To do this,

GC-S detection was used. To detect sulfur species on GC, the molecules must be present in as little as 10 PPM. Therefore, the sulfur concentrations for all three low temperature WFE distillates were eligible for GC-S analysis.

Figure 4.1 shows that, although sulfur is present in the sample, according to total sulfur analysis, there are no peaks that correspond to sulfur detected by GC-S. The reason for this could be that the value for total sulfur is the combination of many different types of sulfur bearing compounds or that the concentration of sulfur-bearing compounds is below the detection limit of the GC-S detector. In either case, the amplification of the sulfur species is necessary; hence, the samples were subjected to solid phase extraction.

**Table 4.1.** Initial Masses, Volumes, and Sulfur Concentrations of Biodiesel Samples

	<b>BD-6 Stock</b>	<b>BD-8 Stock</b>	<b>BD-9 Stock</b>	<b>Average</b>
<b>Mass (g)</b>	25.13	25.58	24.20	24.97 ( $\pm 0.51$ )
<b>Volume (ml)</b>	28.23	28.70	27.19	28.04 ( $\pm 0.57$ )
<b>[S] PPM</b>	58.16	33.95	34.92	42.34 ( $\pm 10.54$ )
<b>S mass (mg)</b>	1.46	0.87	0.85	1.06 ( $\pm 0.27$ )



**Figure 4.1.** GC-S of Stock biodiesel.

Tables 4.2A-4.2C show the results of the SPE performed on three different low temperature distillate biodiesel fractions. Each sample was extracted separately. The expectation was that the sulfur-bearing species would bond to the stationary phase of the polar silica column while the nonpolar constituents (typically fatty acid methyl esters, or FAME) would elute. Subsequently, the column was washed with 6 solvents to concentrate the sulfur-bearing species on the basis of polarity. The non-polar fractions accounted for  $89.97(\pm 0.78)\%$  of the solid fractions.

**Table 4.2A.** Biodiesel Sample BD-6 fractionated by SPE.

<b>Fraction Designation</b>	<b>BD-6</b>	<b>Tube Mass (g)</b>	<b>Tube+Elution mass (g)</b>	<b>elution mass (g)</b>	<b>Tube+Dry Mass (g)</b>	<b>Dry Mass (g)</b>	<b>Fraction of total mass (%)</b>
<b>A</b>	Load	13.246	34.457	21.211	28.0546	14.8086	59.3%
<b>B</b>	Hex/CH <sub>2</sub> Cl <sub>2</sub> 9:1	13.303	26.72	13.417	20.673	7.37	29.5%
<b>C</b>	CH <sub>2</sub> /Cl <sub>2</sub> 1:1	13.243	23.518	10.275	14.4077	1.1647	4.7%
<b>D</b>	CH <sub>2</sub> Cl <sub>2</sub>	13.228	24.414	11.186	13.7875	0.5595	2.2%
<b>E</b>	Et. Ace	13.299	26.525	13.226	14.0659	0.7669	3.1%
<b>F</b>	MeOH	13.204	25.347	12.143	13.486	0.282	1.1%
<b>G</b>	Acetone	13.304	25.727	12.423	13.336	0.032	0.1%
<b>TOTAL</b>						<b>24.9517</b>	<b>100%</b>

**Table 4.2B.** Biodiesel Sample BD-8 fractionated by SPE.

<b>Fraction Designation</b>	<b>BD-8</b>	<b>Tube Mass (g)</b>	<b>Tube+Elution mass (g)</b>	<b>elution mass (g)</b>	<b>Tube+Dry Mass (g)</b>	<b>Dry Mass (g)</b>	<b>Fraction of total mass (%)</b>
<b>A</b>	Load	13.264	35.443	22.179	29.0258	15.7618	62.1%
<b>B</b>	Hex/CH <sub>2</sub> Cl <sub>2</sub> 9:1	13.204	25.822	12.618	20.3868	7.1828	28.3%
<b>C</b>	CH <sub>2</sub> /Cl <sub>2</sub> 1:1	13.307	22.268	8.961	14.5035	1.1965	4.7%
<b>D</b>	CH <sub>2</sub> Cl <sub>2</sub>	13.097	21.78	8.683	13.4862	0.3892	1.5%
<b>E</b>	Et. Ace	13.177	26.047	12.87	13.7845	0.6075	2.4%
<b>F</b>	MeOH	13.277	25.91	12.633	13.536	0.259	1.0%
<b>G</b>	Acetone	13.254	24.546	11.292	13.288	0.034	0.1%
<b>TOTAL</b>						<b>25.3968</b>	<b>100%</b>



**Table 4.2C.** Biodiesel Sample BD-9 fractionated by SPE.

<b>Fraction Designation</b>	<b>BD-9</b>	<b>Tube Mass (g)</b>	<b>Tube+Elution mass (g)</b>	<b>elution mass (g)</b>	<b>Tube+Dry Mass (g)</b>	<b>Dry Mass (g)</b>	<b>Fraction of total mass (%)</b>
<b>A</b>	Load	13.178	33.959	20.781	27.4955	14.3175	59.3%
<b>B</b>	Hex/CH <sub>2</sub> Cl <sub>2</sub> 9:1	13.269	25.535	12.266	20.8488	7.5798	31.4%
<b>C</b>	CH <sub>2</sub> /Cl <sub>2</sub> 1:1	13.29	23.297	10.007	14.6069	1.3169	5.5%
<b>D</b>	CH <sub>2</sub> Cl <sub>2</sub>	13.256	23.242	9.986	13.7016	0.4456	1.8%
<b>E</b>	Et. Ace	13.228	27.284	14.056	13.66	0.432	1.8%
<b>F</b>	MeOH	13.221	23.161	9.94	13.2831	0.0621	0.3%
<b>G</b>	Acetone	13.2	23.754	10.554	13.2279	0.0279	0.1%
<b>TOTAL</b>						<b>24.1539</b>	<b>100%</b>

The fractions were then analyzed for sulfur concentration in PPM and recorded in Tables 4.3A-4.3C. Based on the mg of S (Table 4.1) present in each of the stock solutions, only 54.97(±10.18)% of the S could be accounted for in the eluted samples based on mass balance. This could be the manifestation of experimental error or a lot of the sulfur-bearing species could remain on the column. In all three biodiesel samples, elutions E and F contained the highest concentration (ppm) of sulfur and were, therefore, the best candidates for analysis by GC-S.

**Table 4.3A.** Sulfur concentrations and mass for Biodiesel sample BD-6.

<b>Fraction Designation</b>	<b>[S] Dry PPM</b>	<b>based on dry mass (mg)</b>	<b>based on dry volume (mg)</b>	<b>% of initial S</b>
<b>A</b>	12.13	0.179628318	0.20183	12.29%
<b>B</b>	13.01	0.0958837	0.107734	6.56%
<b>C</b>	24.62	0.028674914	0.032219	1.96%
<b>D</b>	34.84	0.01949298	0.021902	1.3%
<b>E</b>	248.4	0.19049796	0.214043	13.0%
<b>F</b>	233.56	0.06586392	0.074004	4.5%
<b>G</b>	55.51	0.00177632	0.001996	0.1%
		0.580041792	0.651732	<b>39.69%</b>

**Table 4.3B.** Sulfur concentrations and mass for Biodiesel sample BD-8.

<b>Fraction Designation</b>	<b>[S] Dry PPM</b>	<b>based on dry mass (mg)</b>	<b>based on dry volume (mg)</b>	<b>% of initial S</b>
<b>A</b>	14.17	0.223345	0.250949	25.72%
<b>B</b>	15.01	0.107814	0.121139	12.42%
<b>C</b>	20.72	0.024791	0.027856	2.85%
<b>D</b>	20.41	0.007944	0.008925	0.9%
<b>E</b>	128.83	0.078264	0.087937	9.0%
<b>F</b>	179.51	0.046493	0.052239	5.4%
<b>G</b>	12.61	0.000429	0.000482	0.0%
		<b>0.488651</b>	<b>0.549046</b>	<b>56.27%</b>

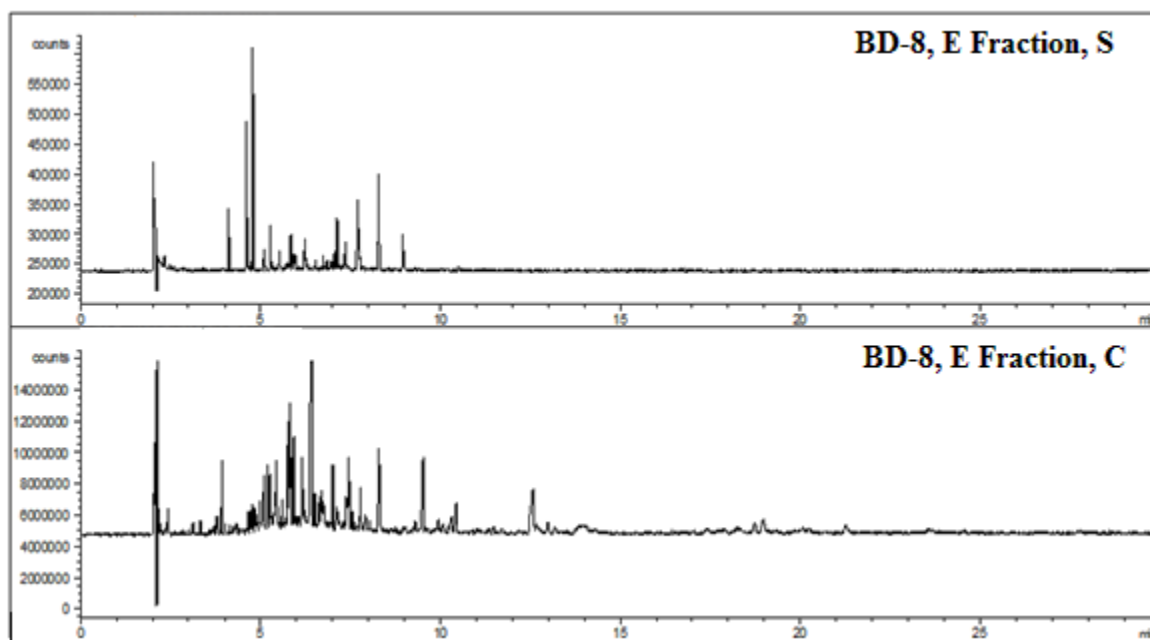
**Table 4.3C.** Sulfur concentrations and mass for biodiesel sample BD-9.

<b>Fraction Designation</b>	<b>[S] Dry PPM</b>	<b>based on dry mass (mg)</b>	<b>based on dry volume (mg)</b>	<b>% of initial S</b>
<b>A</b>	22.94	0.328443	0.369038	38.86%
<b>B</b>	22.45	0.170167	0.191198	20.13%
<b>C</b>	20.2	0.026601	0.029889	3.15%
<b>D</b>	14.88	0.006631	0.00745	0.8%
<b>E</b>	107.39	0.046392	0.052126	5.5%
<b>F</b>	71.22	0.004423	0.004969	0.5%
<b>G</b>	5.31	0.000148	0.000166	0.0%
	<b>TOTAL</b>	<b>0.583</b>	<b>0.655</b>	<b>68.94%</b>

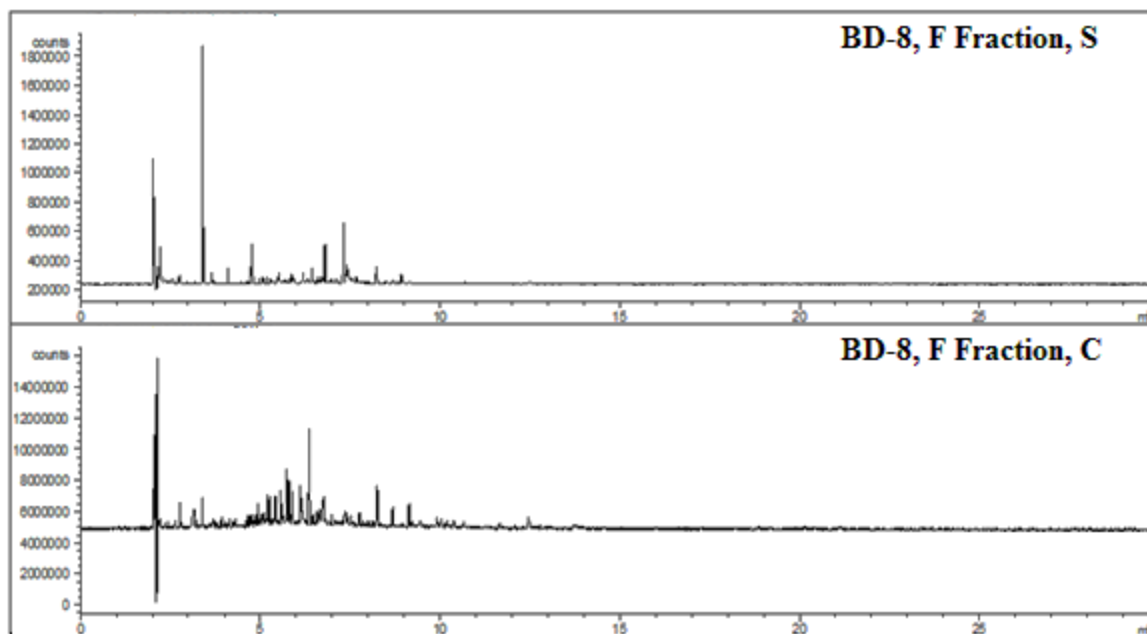
The samples were first analyzed by GC-FID for method development and to validate that the samples were correlated with expected and known chromatograms for biodiesel. The samples were then transferred to the GC-S detector where peaks correlating to sulfur-bearing species were detected (Figures 4.2A and 4.2B). There appeared to be approximately 6 peaks representative of sulfur-bearing species present in the sample.

Transferring the sample from the GC-S to GC-MS proved more problematic than originally expected. During MS analysis, samples were injected into the instrument, ionized, and

fractionated. The instrument detects the ionized species and suggests structural matches from the MS library. However, the MS detector is not as sensitive as the GC-S and, therefore, some of the smaller sulfur bearing molecules could not be analyzed by MS with confidence. Of the SPE fractions analyzed by GC, the most promising peak was eluted at 4.8 mins. This peak was present in all 3 of the low temperature distillate samples studied in this project.



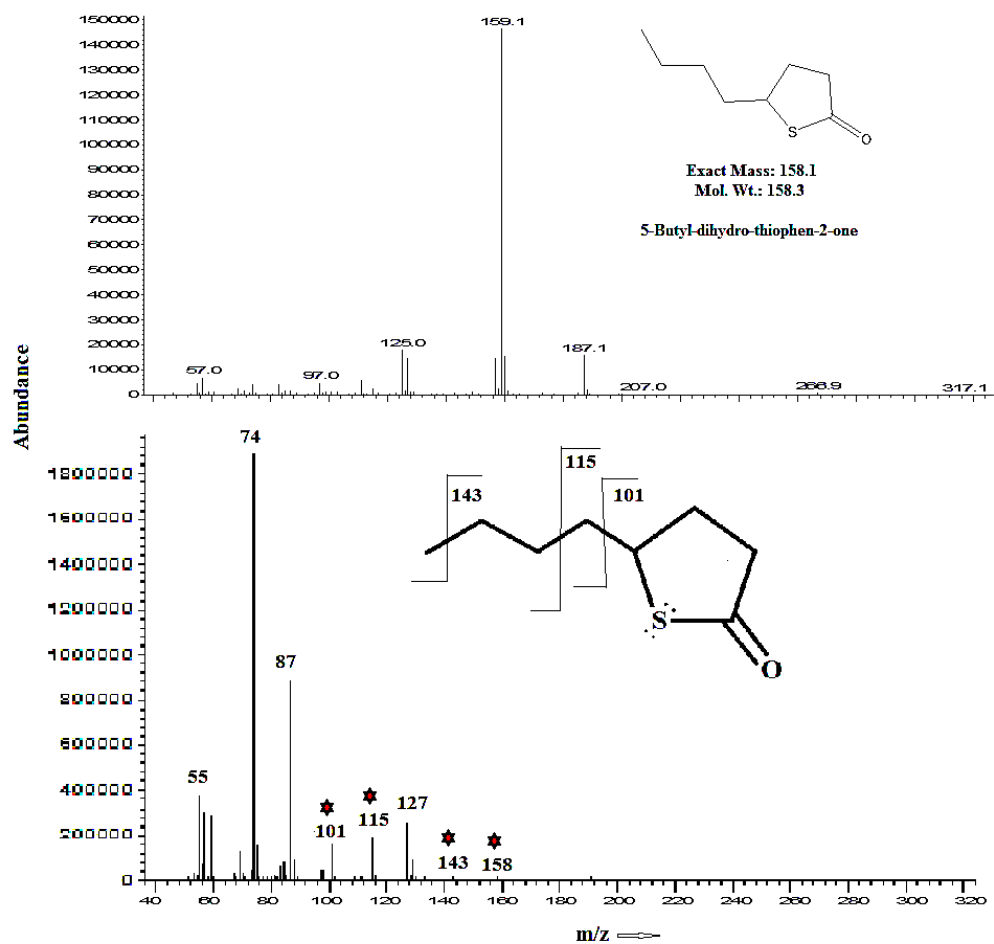
**Figure 4.2A.** Chromatograph of Biodiesel Sample BD-8 fraction E. The top chromatograph shows sulfur peaks while the bottom shows carbon peaks.



**Figure 4.2B.** Chromatograph of Biodiesel Sample BD-8 fraction F. The top chromatograph shows sulfur peaks while the bottom shows carbon peaks

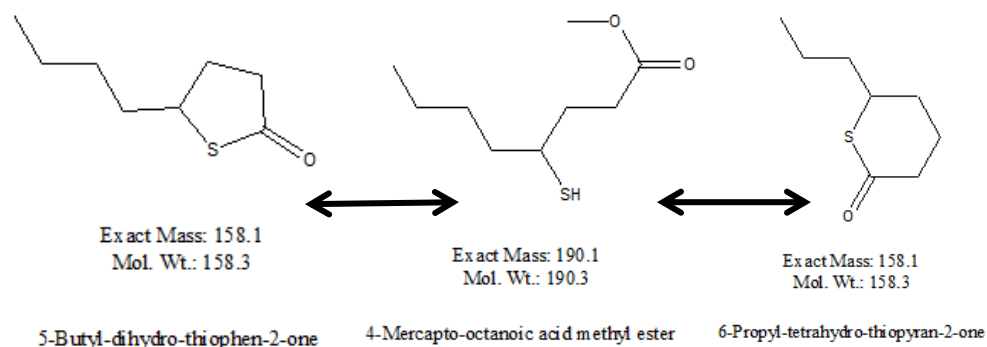
Attempts to determine the structural identity of the molecule that eluted at 4.8 mins by GC analysis was performed by two type of mass spectroscopy techniques: Chemical ionization (CI) and Electron Ionization (EI). CI is an ionization technique is a lower energy process than electron EI, yielding less or, sometimes, no fragmentation. As a result of the low degree of fragmentation, a typical CI spectra has an easily identifiable protonated molecule peak  $[M+1]^+$  which allows for determination of molecular mass of the parent compound. Conversely, when EI is employed, the energy from the bombarding electrons is so great that the entire molecule is fragmented, leaving little chance for identifiable molecular ion peak. However, extensive fragmentation that results from EI is useful for the structure determination of unknown compounds. Figure 4.3 shows the results of the MS spectra for CI (top) and EI (bottom) techniques. In the CI spectra, 159.1 and represents the protonated molecular weight  $[M+1]$  of the sulfur-bearing species. The EI spectra shows only a small peak for at 158 because very little

of the molecular ion still exists. Instead, it shows other molecular weights that represent ionated fractions of the molecule that have been used theoretically identify the molecule as 5-butyl-dihydro-thiophen-2-one.



**Figure 4.3.** Parent and daughter ions of 5-butyl-dihydro-thiophen-2-one (as determined by top chemical ionization and bottom electron ionization mass spectroscopy).

Figure 4.4 is a proposed mechanism for the formation of the two sulfur bearing species via the intramolecular formation of a thioester. It is reasonable to assume that fatty acid species in various forms exist in all restaurant waste grease products. 4-Mercapto-octanoic acid methyl ester is an ester of a short chain fatty acid that is likely formed from the chemical degradation of a longer polyunsaturated fatty acid. Sulfur is theoretically added to unsaturated fatty acid by reacting with subterranean hydrogen sulfide ( $H_2S$ ) gas or by chemical exchange with the sulfur atoms indigenous to foods such as onions and garlic that are likely present in trap grease. Therefore, 4-Mercapto-octanoic acid methyl ester is believed to be the precursor to either 5-butyl-dihydro-thiophen-2-one or 6-Propyl-tetrahydro-thiopyran-2-one dependent on the position of the SH group along the hydrocarbon backbone.



**Figure 4.4.** The three species: 5-butyl-dihydro-thiophen-2-one, 4-Mercapto-octanoic acid methyl ester, and 6-Propyl-tetrahydro-thiopyran-2-one were found to be the molecules represented by the peaks found in GCMS.

## **CHAPTER 5**

### **CONCLUSION**

The information provided in this study has not only shed a bit of light on the methodology used in sulfur analysis, but has also highlighted a few sulfur species that could potentially be found in many other biodiesel fuels. Data concerning identification of specific compounds containing sulfur is relatively new to the biodiesel industry, with little to no available information in the area. By being able to successfully characterize just a small number of compounds, my research has paved the way for a multitude of experiments regarding sulfur removal and yielding a cleaner biodiesel product.

Though sulfur species were found on the biodiesel as intended by the experiment, some difficulties were encountered. Using the N-evap nitrogen blower to completely dry out the samples after SPE proved to be somewhat of a challenge, as a sample with solvent remaining can skew the results of the sulfur analysis stage. The availability of low temperature biodiesel distillate was also an obstacle encountered. Often times, there was only enough sample to perform 1 replicate of SPE, making it difficult to duplicate and confirm results with that particular sample.

In future experiments of a similar nature, researchers aim to minimize the number of solvents used in solid phase extraction and obtain a larger quantity of the sulfur containing fractions. SPE, though an effective process, can still be optimized. A method should be developed to eliminate the use of methanol, acetone, and the hexane/methylene chloride 1:1

mixture, as these steps do not contribute as much to the concentration of sulfur species as the other solvents used. The solvents also have a tendency to produce unnecessary peaks during GC, making interpretation of chromatographs a bit more difficult. Though gas chromatography utilizes a small injection size, a larger stock would allow for a greater quantity of biodiesel to undergo solid phase extraction, which in turn provides a greater volume of the polar fractions containing sulfur. This larger fraction will in theory, have a higher sulfur concentration and produce a greater signal during GCMS.

It is the hope of the researchers in this lab that through the identification of sulfur species found in biodiesel samples, we will be able to develop a more efficient method for sulfur removal that is expected to be species-specific. By targeting individual species such as thioesters and thiols, the removal will occur quickly, effectively, and at as low of a cost as possible. The method that is developed should also utilize as little solvent as possible, as a greater amount of chemical use allows for error and contamination of the final product. Ideally, this method of sulfur removal will not affect the yield of biodiesel product, improve the marketability of biodiesel and further increase its usage over traditional petroleum diesel.



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