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A Novel Application of Ozone Chemistry for Biodiesel Improvement: Product Development and Characterization

presented by

Tylisha Marie Baber

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A NOVEL APPLICATION OF OZONE CHEMISTRY FOR BIODIESEL IMPROVEMENT: PRODUCT DEVELOPMENT AND CHARACTERIZATION

By

Tylisha Marie Baber

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering and Materials Science

ABSTRACT

A NOVEL APPLICATION OF OZONE CHEMISTRY FOR BIODIESEL IMPROVEMENT: PRODUCT DEVELOPMENT AND CHARACTERIZATION

By

Tylisha Marie Baber

Although there are numerous benefits to utilizing biodiesel as an alternative fuel, several challenges still remain, including poor oxidative stability, viscosity, volatility, and low-temperature flow properties. These research challenges are due to the structural properties of biodiesel. The specific goal of this research study was to modify biodiesel using ozone chemistry to improve its overall fuel quality. The oxidative cleavage of a mixture of alkenes in biodiesel was conducted at room temperature in a gas washing bottle-type reactor equipped with a fritted disc. Methanol was used as a reactant in a 2:1 alcohol to fuel molar ratio; and calcium carbonate was used as the catalyst at 10 wt% of the starting fuel amount.

FTIR and GC/MS analysis confirmed that the double bonds in methyl soyate were successfully cleaved by ozone-mediate oxidation. The total amount of double bonds in the mixture was reduced by more than 90% after three hours of ozonolysis. FTIR and ¹H NMR indicated the presence of hydroperoxides and ozonides in the ozonated fuel. However, these products thermally decomposed during the GC/MS analysis, producing additional methyl esters. Hydroperoxide formation may have been the result of water, a by-product in the conversion of both the hemiacetal and hydroperoxide intermediates to methyl esters, reacting with the secondary ozonide. Another possible route for hydroperoxide production is the reaction of the carboxyl oxide intermediate with methanol. Ozonide formation was most likely due to the steric hindrance in the biodiesel

molecule. GC/MS analysis also confirmed that three of the five expected esters for the ozonolysis of methyl soyate- methyl hexanoate, nonanoate, and azelate-were formed during the ozonation experiments. Two derivative forms of dimethyl malonate were detected in the volatile fraction.

Similar products were formed in the ozonation and autoxidation of methyl soyate. It was also found that the amount of double bond degradation was significantly lower when ozone was not the primary oxidant. Thus, it can be deduced that ozone was simultaneously inducing lipid oxidation (ozone-induced oxidation) and oxidatively cleaving the alkene moiety (ozonolysis) of biodiesel.

According to TGA analysis, the volatility of methyl soyate became comparable to that of No. 2 diesel fuel after 3 hours of ozone-mediated oxidation. Two maximums occurred for the rate of weight loss during TGA of ozonated methyl soyate. The first maximum occurred at 210°C from the presence of the long, hydrocarbon chains of the starting esters and the second maximum occurred at 145°C from the presence of more volatile products formed after ozonation. One broad maximum occurred at about 150°C for No. 2 diesel fuel. The DSC cooling thermograms for methyl soyate exhibited two major exothermic regions: region 1 between -10° C and -15° C and region 2 under -65° C. There was a slight increase in both T_{C1} and T_{C2} after a reaction time of 60 mins. This observation was most likely due to the presence of monomeric and polymeric ozonides in the product mixture. Selected low-temperature flow properties were evaluated for methyl soyate. It was concluded that these properties were not enhanced for the ozonated fuel due to the presence of ozonides.

DEDICATION

This dissertation is dedicated to MY PEOPLE-from ancestral, slavery, civil rights movement, to now. They sacrificed their lives for the future generations, like me, to have an equal educational opportunity.

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Chapter 1

Introduction

1.1 Research Rationale & Motivation

Economic development and growth in the 20^{th} century was driven by the use of crude oil, coal, and natural gas as raw materials for chemical, material, and energy production. Gasoline and diesel fuel power almost all vehicles, while plastics made from petroleum or natural gas are used to make clothes, food packaging, car parts, and building materials. Most chemicals, even toiletries and pharmaceuticals, are petrochemically derived. However, a new revolution spurred by the expanded use of renewable biobased products and bioenergy will have a significant impact in the 21st century. A new, sustainable economy based on biomass feedstocks will bring numerous economical, environmental, and societal benefits to the United States, encompassing the sustainable development initiative, illustrated in Figure 1.1. The mitigation of imported petroleum with biorenewable resources will help strengthen national security by reducing our nation's dependence on foreign resources and becoming self-sufficient in energy production. Biobased products will improve environmental quality by reducing pollutant emissions, like sulfur, heavy metals, and greenhouse gases, reducing soil erosion, sequestering carbon, protecting water supplies and quality, and increasing the diversity of agricultural crops and products. Finally, biobased products will revitalize rural communities by introducing innovative crops and markets to the agricultural economy.



Figure 1.1 Sustainable Development Initiative Diagram Adopted from Ref. [1]

Biomass feedstocks consist of any plant-derived organic matter, including grain, oilseeds, waste and residue crops, herbaceous and woody crops, and animal wastes. In terms of biorefinery, these constituents are chemically processed to a host of valuable and marketable chemicals, materials, and energy, while generating minimal toxic emissions and waste. A biorefinery is, thus, analogous to a petroleum refinery in that raw materials are converted to both high-volume, commodity and high-value, specialty products. A biobased economy cannot fully replace huge volumes of or eliminate the need for petrochemicals. However, as existing biorefining technologies are being improved and innovative technologies are being developed, biobased products will mitigate the use of competing petroleum-derived products, making the 21st century an increasingly sustainable, domestic, and environmentally responsible one.

1.2 Vegetable Oil Chemistry

Fats and oils derived from plants serve a vital function both in the U. S. and world economics for food and nonfood applications. Provided only with the simplest and most inexpensive inputs of carbon dioxide, sunlight, water, and minerals, plants are efficient and diverse chemical factories that serve as basic chemical blocks for the production of sophisticated chemical molecules with many structural features [2]. Vegetable oils and animal fats are triacylglycerols, also called triglycerides, consisting of three fatty acids attached to a glycerol molecule. Many naturally occurring fats and oils are made up of saturated and unsaturated fatty acids with a chain length greater than 12 carbon atoms, with the vast majority having more than 16 carbon atoms. For the unsaturated moiety, the double bonds are non-conjugated, or are interrupted by a methylene group (-CH₂-), and are in the *cis* configuration.

From a chemical perspective, triglycerides have two reactive sites, the double bonds of the unsaturated fatty acid chain (-R), and the carbonyl group (C = O), linking the fatty acid to the glycerol, shown in Figure 1.2. With regard to product development, the majority of derivatization reactions are carried out at the carbonyl group (>90%); whereas oleochemical reactions involving the alkyl chain, or double bonds, represent less than 10% [3]. On the industrial level, the most extensively applied reactions of the double bonds are hydrogenation and epoxidation. Other reactions also include polymerization, hydroxylation, metathesis, carboxylation, radical addition, and oxidative cleavage. Reactions involving the carbonyl functional group include hydrolysis, transesterification, and amine synthesis.



Figure 1.2 Basic Structure of a Triglyceride Molecule with Major Reactive Sites

As a consequence of the two reactive sites, five core classes of oleochemicals, including acids, alkyl esters, alcohols, amines, and glycerol, constitute the fundamental chemical building blocks for the oleochemical industry, depicted in Figure 1.3. In fact, about 30% of vegetable oils that are produced today are used by the oleochemical industry for non-food products and applications [2]. Thus, chemical modification of vegetable oils is an important route to obtain industrial products using renewable feedstock. There is still a research need and challenge to develop new efficient and environmentally friendly reaction pathways leading to new products and to find new applications for already existing oleochemicals.



Figure 1.3 Five Chemical Building Blocks for the Oleochemical Industry Adopted from Ref. [4]

1.3 Biodiesel Fuel Research & Development

The use of vegetable oils as fuel for diesel engines is not a new concept.

Dr. Rudolf Diesel first developed the Diesel engine in 1895 with the full intention of

running it on a variety of fuels, including vegetable oil. Diesel showed his engine at the

World Exhibition in Paris in 1900 using peanut oil as fuel. In 1912 Diesel stated,

"The fact that fat oils from vegetable sources can be used may seem insignificant today, but such oils may perhaps become in course of time of the same importance as natural mineral oils and the coal tar products are now. One cannot predict what part these oils will play in the Colonies in the future. In any case, they make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted." -Dr. Rudolph Diesel [5, 6]

Dr. Diesel's words are truer today than ever before.

Biodiesel is a domestic, renewable fuel for diesel engine use, comprised of mono-

alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, which

meets the ASTM D6751 fuel quality standard. Biodiesel is produced by the

transesterification of vegetable oils or animal fats with an alkyl alcohol to product alkyl

esters and glycerol, a valuable by-product. The most common type of biodiesel produced is methyl esters, mainly because methanol is an inexpensive alcohol. Biodiesel is biodegradable and non-toxic, being just as biodegradable as sugar and less toxic than table salt. Studies have shown biodiesel to biodegrade up to four times faster than petroleum diesel fuel, with up to 98% biodegradation in 3 weeks [7]. Moreover, no engine modifications are needed to use biodiesel in a diesel engine.

Biodiesel is one of the most thoroughly tested alternative fuels on the market. It is the first alternative fuel in the country to have a complete evaluation of emission results and potential health effects submitted to the U.S. Environmental Protection Agency (EPA) under the Clean Air Act Section 211 (b) [8]. These evaluations include the most stringent emission testing protocols ever required by the EPA for certification of fuels and fuel additives. The data gathered complete the most thorough inventory of the environmental and human health effects attributes that current technology will allow. Biodiesl's exhaust is essentially free of lead, sulfur and its derivatives, halogens, and has reduced particulates, unburned hydrocarbons, carbon monoxide, and carbon dioxide. Also, petroleum-derived diesel contains 20-40% (vol) of aromatic compounds, which increase emissions of particulate matter and nitrogen oxides, NO_X. On the other hand, biodiesel is essentially non-aromatic. EPA has surveyed the large body of biodiesel emissions studies and averaged the Health Effects testing results with other major studies. These results are listed in Table 1.1.

| Emission Type | B100 | B20 ^a |
|--|-------|------------------|
| Regulated | | |
| Unburned Hydrocarbons | -67% | -20% |
| Carbon Monoxide | -48% | -12% |
| Particulate Matter | -47% | -12% |
| Non-regulated | | |
| Sulfates & Sulfur Oxides | -100% | -20% |
| PAH (Polycyclic Aromatic Hydrocarbons) | -80% | -13% |
| nPAH | -90% | -50% |
| _ | | |

 Table 1.1 Average Biodiesel Emissions Compared to Conventional Diesel

Source: Ref. [8]; ^a20% biodiesel blended with 80% petroleum diesel, by volume

Due to the large amount of soybean production in the U. S., biodiesel research and development is focused on biodiesel derived from soybean oil, commonly referred to as methyl soyate. In fact, soybean oil accounts for about 75% of the nation's crop oil production [2]. The soybean contains high quality protein (38-42%), oil (18-22%), and meal (36-44%), which are recovered by hexane extraction [4]. Soybean meal is primarily used as animal feed, but can also be a feedstock for manufacturing biobased products. The oil is mainly used in food applications, often after partial hydrogenation, as salad oil, cooking oil, and frying oil and in margarines and shortening. Non-food uses are based mainly on the high levels of unsaturation and include coatings, epoxidized oil, and dimer acids.

At present, the high cost of biodiesel is a major obstacle to its commercialization. Roughly 75 to 90% of the cost of biodiesel is the raw materials. The current use and price of food-grade soybean oil as the feedstock for biodiesel has caused the price for the fuel to be about \$2.50/gal. Thus, reducing the cost of the feedstock is necessary for biodiesel's long-term commercial viability. One way to reduce its cost is to use less expensive feedstocks like waste cooking oil and rendered animal fats, which will also help solve the problem of waste oil disposal. However, the cost difference between

biodiesel and petrodiesel is already shrinking due to rising petroleum costs, new EPA rules requiring reduced sulfur content in diesel, and improvement in the biodiesel industry such as building larger plants with more efficient production technology and expanding the glycerol by-product market. In fact, the cost of gasoline reached a record-high price of \$2.06/gallon on average across the U. S. in June 2004; and in October of that same year, U.S. light crude hit \$55.67 a barrel, the highest level in 21 years of recorded oil prices [9]. Thus, it's a fairly safe assumption that if demand remains strong and reserves and production capacity remain limited, there will be a general upward trend in petroleum prices in the years to come. While some oil industry analysts insist that current high prices are just a temporary situation, others have stated that oil prices possibly have reached a new plateau and may not come down much at all, and that further price increases are inevitable [9]. Therefore, assuming that petroleum prices remain high and that the recently passed tax incentive for biodiesel will boost its industry, the future of biodiesel in the U. S. is very promising.

1.4 Research Problem Description

Although there are numerous benefits to utilizing biodiesel as an alternative fuel, several challenges still remain, including poor oxidative stability, low-temperature flow properties, like viscosity, and volatility. These research challenges are inherent in the structural properties of biodiesel.

Oxidative Stability

Oxidation is a major source of biodiesel contamination and is an area of great concern in biodiesel research. Unsaturated fatty acid esters are subjected to oxidation, an irreversible reaction of atmospheric oxygen with organic compounds. This reaction is

autocatalytic in nature, meaning that the rate of oxidation is slow at the beginning and increases as the reaction progresses. Illustrated in Figure 1.4, the free radical chain theory postulated by Farmer et al. [10] has been the generally accepted mechanism for lipid oxidation. In the initiation step, a "quantum" of energy from an initiator, I, like heat or light, catalyze the abstraction of an allylic hydrogen atom from an alkene functional group. The resulting free radical, R•, readily reacts with oxygen to form a peroxyl free radical, ROO. The peroxyl free radical is highly reactive and, thus, can abstract an allylic hydrogen atom from another unsaturated lipid molecule, propagating the cyclic chain reaction to yield hydroperoxides. Oxygen can attack at each end of the allylic system, producing a mixture of peroxyl radicals and yielding different positional hydroperoxides. Hydroperoxides are the unstable primary products of lipid oxidation. They decompose to stable secondary products, like aldehydes, ketones, alcohols, hydrocarbons, esters, and polymers. It has been established that the oxidative stability of fatty esters is directly related to the number of double bonds present in the molecule [11]. Thus, the rate of oxygen absorption is much higher in fatty esters containing multiple double bonds than those containing single or no double bonds. In fact, the relative autoxidation rate of methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate was found to be 1:11:114:170, respectively, at comparable temperatures [12]. It was further concluded that the rate of oxidation of non-conjugated polyunsaturated fatty esters is the fastest because of the high activation energy of methylene groups between the double bonds [10]. Therefore, since biodiesel is produced from highly unsaturated oils (85% by weight), it oxidizes more rapidly than diesel fuel. Although saturated fatty esters are also susceptible to degradation by oxidation, the autoxidation is much slower.





The oxidative instability of biodiesel is of particular concern because it contributes to long-term storage and engine/fuel systematic problems, having a negative impact on its fuel quality. The products of oxidation adversely affect fuel storage life and contribute to deposit formation in tanks and engine fueling systems. Furthermore, hydroperoxides, the primary products of oxidation, can induce polymerization of the esters, forming insoluble gums and sediments, which can cause fuel filter plugging. In fact, the Engine Manufacturers Association (EMA) [13] has recently issued a warning against using over 5% (vol) biodiesel in petrodiesel fuel because the poor oxidative stability of biodiesel can cause a variety of engine performance problems, including filter plugging, injector coking, piston ring sticking and breaking, and severe degradation of engine lubrication. The Fuel Injection Equipment manufacturers have also expressed a concern that fuel blends containing more than 5% (vol) biodiesel can cause reduced product service life and injection equipment failure [14]. As for storage issues, the EMA statement concluded that the poor oxidation stability of biodiesel fuels could result in long-term storage problems due to deposit formation in tanks, fuel systems, and filters. Many researchers have studied the oxidative stability of biodiesel from a variety of feedstocks [15-20]. The major findings from these studies were that biodiesel should be stored in darkness, at low temperatures, and under anaerobic conditions in order to

guarantee a consistent quality of the fuel. It was further recommended that the storage period should not be longer than one year. Thus, improving the oxidative stability of biodiesel is an important guide to product quality and performance.

Low-Temperature Flow Properties

In spite of biodiesel's many advantages, performance during cold weather may affect its year-round commercial viability in moderate temperature climates. Structural features of biodiesel that affect its low-temperature properties include the degree of saturation, chain length, and degree of branching. Saturated fatty acids, which contain only single carbon-carbon bonds, are chemically less reactive than the corresponding fatty acids of the same chain length with one or more double bonds. Since they do not contain any double bonds, saturated molecules can pack closely together. Therefore, saturated fatty acids are solids at room temperature and have high melting points, which increase with chain length. Biodiesel contains about 15% (wt) saturates, including methyl palmitate and stearate. This rather high level of saturation causes biodiesel to be less useful with decreasing temperature and major engine and flow problems during the winter season can be experienced. Although field studies of biodiesel performance in cooler weather are scarce, there is evidence that using the soybean methyl ester form of biodiesel raises performance issues when ambient temperatures approach 0-2°C [21]. As overnight temperatures fall into this range, the saturated methyl esters nucleate and form solid crystals. If the fuel is left unattended in cold temperatures for a long period of time, these crystals plug or restrict flow through fuel lines and filters during start-up and can lead to fuel starvation and engine failure. All biodiesel fuels exhibit poor cold-flow properties with cloud and pour points 15-20°C higher than those of petrodiesel fuel [22].

In particular, methyl soyate exhibits a cloud point near the freezing temperature (0°C) compared to petroleum's cloud point of about -16°C [23]. Similarly, the pour point of methyl soyate is around -2°C compared with -27°C for petrodiesel [23]. These values are relatively high when compared to winter ambient temperatures, making the use of biodiesel limited in areas like Canada, the northern U.S., and much of Europe.

Possible solutions to the low-temperature flow problems of biodiesel have been investigated, including blending biodiesel with petrodiesel fuels, additives, winterization, and the use of branched-chain esters. The most common application of vegetable oil esters in the U.S. is their use in blends of conventional diesel fuel [24]. Methyl esters from transesterified soybean oil were studied as neat fuels and in blends with petrodiesel [23]. This research showed that blending methyl esters with conventional diesel fuel significantly improved its low-temperature flow properties. However, results from the pour point, cloud point, and low-temperature filterability studies demonstrated significant limitations of blending esters with petroleum fuel to improve cold-flow operability because the methyl ester contents are held at relatively low blend ratios. Additives have been reported to reduce the pour points of biodiesel fuels; however, they do not reduce the cloud point nor improve the filterability of biodiesel [25]. A "winterization kit" was then suggested as a solution for warming-up the fuel in cold weather [26]. A three-step winterization process involves mixing in additives, chilling, equilibrating the fuel at a temperature between its cloud and point points, and filtering out the saturated precipitates. This process leaves behind a liquid phase with an enhanced concentration of unsaturated methyl esters. Consequently, the liquid product should demonstrate improved cold-flow properties. In a study conducted by Lee et al. [26], winterization of

neat methyl soyate produced a crystallization onset temperature (T_{co}) of -7.1°C, compared to 3.7°C for the unwinterized methyl soyate. However, it was concluded that winterization was not an efficient way of removing saturated methyl esters or reducing the T_{co} , due to the poor separation of the liquid phase from the crystalline fraction, resulting in very low yields.

Crystallization involves the arrangement of molecules in an orderly fashion. When branches are introduced into linear, long-chain esters, intramolecular associations should be attenuated and crystallization temperatures reduced [27]. Thus, the crystallization temperature of biodiesel should be improved by replacing the methyl or ethyl ester with a branched moiety such as isopropyl. Indeed, isopropyl and 2-butyl esters of soybean oil showed a lower T_{co} by 7-11°C and 12-14°C, respectively, than the corresponding methyl esters [27]. Both the cloud and pour points were also lowered by the branched-chain esters. Reducing chain length and/or increasing chain branching can improve cold-flow fuel properties. One way to alter the chain length and degree of branching is through chemical processing of the biodiesel to cleave certain double bonds or to form branched isomers. Very little practical research has been done in the chemical processing area in terms of modifying the chemical structure of biodiesel. Thus, the cold-flow properties of biodiesel fuels are clearly an area in need of considerable research.

Viscosity & Volatility

Viscosity and volatility are two key fuel properties of diesel fuel relating to the satisfactory performance of the fuel injection equipment. In the diesel engine, fuel is injected as finely atomized spray into the combustion chamber, where it mixes with the hot compressed air and ignites. Thus, viscosity and volatility affect the atomization of a

fuel upon injection into the combustion chamber, and thereby, the formation of engine deposits.

For edible fats and oils, viscosity increases with increasing degree of saturation. and decreases with decreasing carbon-chain hydrocarbon chain lengths that have lower molecular weights. This holds true for the alcohol moiety because viscosity of ethyl esters is slightly higher than that of methyl esters. Factors, such as double-bond configuration, influence viscosity (*cis* double-bonds give a lower viscosity than *trans*); whereas the position of the double bonds has a lesser affect on viscosity. Moreover, branching in the ester moiety has little or no influence on viscosity. Viscosities of neat vegetable oils are nearly 10 times that of No. 2 diesel fuel [28, 29]. The molecular weight of an ester molecule is roughly 1/3 that of the parent triglyceride molecule, resulting in a viscosity about twice that of petrodiesel. Due to the presence of high molecular weight constituents and a high level of unsaturation, biodiesel fuel has a lower volatility than its petrodiesel counterpart. High viscosity and very low volatility lead to poor atomization of the fuel, incomplete combustion, coking of the fuel injectors, ring carbonization, and accumulation of fuel in the lubricating oil, resulting in serious engine deterioration. Lubricating oil contamination is a result of the unsaturated fraction of the fuel polymerizing, causing the oil to gel and requiring frequent oil changes.

1.5 Ozone Chemistry

Ozone, the triatomic allotrope of oxygen, has the formula O_3 , and generally exists as a relatively unstable, reactive gas. In gaseous form, ozone is colorless, whereas liquid ozone is almost non-transparent and bluish-black and its crystals are violet-blue. Ozone exists naturally in large quantities in the upper atmosphere, where it absorbs ultraviolet

light and acts as a screen to prevent this radiation from penetrating to the earth's surface. Ozone can be represented as a combination of its two most stable Lewis structures, depicted in Figure 1.5.



Figure 1.5 Resonance Structure of Ozone

Overall, ozone is a neutral but polar molecule. The high electronegativity of oxygen makes ozone a powerful electrophile. In fact, ozone is a much more powerful oxidizing agent than oxygen. Thus, it undergoes a remarkable reaction with alkenes in which the C-C double bonds are cleaved. No other oxidizing agent is capable of cleaving double bonds in such a fast, clean, and selective way to yield carbonyl compounds [30]. Due to its low cost and availability, ozone is one of the most attractive reagents for carrying out oxidative cleavage of unsaturated fatty materials to give an array of products. The reaction between ozone and olefinic compounds occurs by the well-known Criegee mechanism [31]. The mechanism consists of an electrophilic attack of ozone, or a 1,3-dipolar cycloaddition, at the carbon-carbon double bond, producing1,2,3trioxolane. This primary ozonide is a very unstable five-membered ring structure and decomposes immediately by selective cleavage of the single C-C bond and one O-O bond leading to a carbonyl intermediate and the "zwitterion" carbonyl oxide intermediate. The latter is a very reactive molecule that can react in the following ways: (1) recombines with the carbonyl intermediate to give the Criegee secondary ozonide, 1,2,4-trioxolane. In an aqueous medium, this secondary ozonide reacts with water to generate carbonyl compounds and hydrogen peroxide; (2) reacts with protic solvents to produce

hydroperoxides; (3) undergoes chemical reduction in the presence of a metallic reducing agent, like zinc, and water to yield ketones and aldehydes; (4) reacts with itself to generate polymeric peroxides; (5) rearranges to form carboxylates. The Criegee mechanism is depicted in Figure 1.6.



Figure 1.6 Criegee Mechanism for the Ozonolysis of the Alkene Functional Group

Commercially, large quantities of ozone are produced in specially engineered electric-discharge generators. Electric discharge technology is the only convenient and economical industrial method for ozone synthesis [32]. Figure 1.7 depicts a typical generator cell, which consists of two metallic electrodes separated by a gas-filled gap and a dielectric material. Oxygen gas flows through the discharge gap while high voltage (8-

10kV) is applied to the electrodes. Ozone is produced as a direct result of power dissipation in the generator. The major part of the energy applied during the electrical discharge is transformed into heat. This heat must be evacuated from the discharge space to maintain correct ozone generator performance. Thus, cooling water circulates between the stainless steel dielectric tube and the cooling jacket to dissipate the heat generated.

Water cooled Low Voltage electrode



High Voltage electrode

Figure 1.7 A Typical Electric Discharge Ozone Generator

Although there are a number of mechanisms that may contribute to ozone formation in a generator, one particular reaction path is considered dominant [33]. The reaction is initiated when free, energetic electrons dissociate oxygen molecules:

$$e^{-} + O_2 \longrightarrow 2O + e^{-}$$
 (1.1)

Following this, ozone is formed by a three-body collision reaction:

$$O + O_2 \longrightarrow O_3$$
 (1.2)

At the same time, however, atomic oxygen and electrons also react with ozone to form oxygen:

$$O + O_3 \longrightarrow 2O_2$$
 (1.3)

 $e^{\cdot} + O_3 \longrightarrow O_2 + O + e^{\cdot}$ (1.4)

Ozone-oxygen mixtures are explosive over a wide range of ozone concentrations (~ 20-100%, vol). Working with ozone at concentrations of 0 to 15% (vol) is considered to be safe because explosive decomposition of ozone does not occur in this range. However, because of the competing reaction of ozone decomposing back to oxygen, ozone is generally synthesized at low concentrations, typically between 2-5% (vol) [34].

1.6 **Research Hypothesis**

Marshall *et al.* [35, 36] described experimental findings on the direct conversion of certain olefins to methyl esters by treatment with ozone in methanolic sodium hydroxide or sodium methoxide with dichloromethane as a co-solvent at -78°C. The results were consistent with a reaction pathway in which the aldehyde and carbonyl oxide intermediate, derived from the primary ozonide in the Criegee mechanism, react with methanol to afford hemiacetal and hydroperoxide, respectively. The hemiacetal undergoes base-assisted hydride abstraction by ozone to produce methyl ester, while generating oxygen and water as by-products. The hydroperoxide dehydrates, liberating a water molecule and producing a methyl ester. The reaction mechanism is shown in Figure 1.8. This reaction scheme has been applied to a number of allylic ethers having terminal double bonds and to several olefins with internal double bonds. For example, methyl oleate was converted to a separable mixture of methyl nonanoate and dimethyl azelate in 78% and 77% yields, respectively.



Figure 1.8 Mechanism for the Direct Conversion of Olefins to Esters Via Ozonolysis Source: Ref. [35]

Applying the work of Marshall *et al.* [35, 36], the oxidative cleavage of a mixture of alkenes was employed by the ozonolysis of methyl soyate under basic methanolic conditions. Reaction conditions were chosen based on engineering scale-up considerations: the reaction temperature was chosen to be room temperature, rather than -78°C; to minimize toxic waste disposal, dichloromethane, a carcinogen, was not used as a co-solvent; and for ease of product separation, a heterogeneous catalyst was employed. The expected products from this reaction are shown in Figure 1.9 and their properties are listed in Table 1.2. Unlike with the other chemical modification techniques described in the next chapter, it is expected that eliminating the double bonds will enhance the thermal and oxidative properties of biodiesel. Moreover, a methyl ester functionality at the terminal position is expected to enhance the cold-flow properties and should prevent wax-like crystallization and precipitation. The cleavage of the fatty acid residues at the double bond will lower the molecular weight of biodiesel by generating shorter, fragmental esters, decreasing its viscosity and increasing its volatility to be comparable to that of diesel fuel. It is expected that this treatment will negate the need for blending biodiesel with petroleum-based diesel.



Figure 1.9 Expected Ester Products from the Ozonolysis of Methyl Soyate

| Methyl Ester | Molecular Structure | Molecular Weight | Melting Point (°C) | Boiling Point (°C) |
|-----------------------|---|---------------------|--------------------------|--------------------------|
| Initial Esters | | | | |
| Methyl Palmitate | | 270 | 30 | 136 |
| Methyl Stearate | | 298 | 40 | 181 |
| Methyl Oleate | | 296 | -20 | 218 |
| Methyl Linoleate | | 294 | -35 | 215 |
| Methyl Linolenate | | 292 | below -35 | 182 |
| Expected Pro | oduct Esters | | | |
| Methyl Propionate | | 88 | -88 | 80 |
| Methyl Hexanoate | | 130 | -71 | 151 |
| Methyl Nonanoate | | 172 | -40 | 214 |
| Dimethyl Azelate | $\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array}$ | 216 | -20 | 156 |
| Dimethyl Malonate | | 132 | -62 | 181 |

 Table 1.2 Properties of the Initial and Expected Product Esters

1.7 Specific Goal & Research Objectives

The specific goal of this research study was to chemically modify biodiesel using ozone chemistry in order to improve its overall fuel quality. To achieve this goal, the following experiments were conducted on the ozonated biodiesel fuel:

• Structural characterization (FTIR, NMR, GC, GC/MS): analyzed the product mixture of the ozonated fuel to monitor the degradation of double bonds and the formation of the expected esters, based on the mechanism proposed by Marshall *et al.* [35].
• Thermal characterization (TGA, DSC, Low-Temperature Flow Properties): analyzed the volatility and oxidative stability of the ozonated fuel; measured key low-temperature properties, including cloud point, pour point, cold filter plugging point, onset crystallization temperature, and viscosity.

Biodiesel derived from soybean oil was chosen due to its crop abundance and availability in the U.S. Low-saturated (low-sat) biodiesel contains half the amount, by weight, of the saturated components contained in regular biodiesel. Low-sat biodiesel is of particular interest due to its reduced saturation level, making it more appealing than regular biodisel for low-temperature applications. Thus, experiments were conducted with both low-sat and regular biodiesel fuels for comparative studies.

1.8 Organization of Dissertation

This dissertation is divided into six chapters. The current chapter explains the significance of this work, provides background information on vegetable oil chemistry, biodiesel research, and ozone chemistry; and states the problem to be investigated and the proposed solution to solve it. Chapter 2 reviews the four common chemical modification techniques- pyrolysis, dilution, microemulsion, transesterification- used to improved biodiesel fuel quality. Chapter 3 explains the analytical techniques used in this work, including a brief description of the theory of operation and the experimental parameters used. Chapters 4 and 5 provide the experimental results and detailed discussions on the structural and thermal characterization of ozonated biodiesel fuel, respectively. Finally, Chapter 6 reviews the major experimental findings, gives recommendations for future work, and provides other considerations relating to biodiesel research.

Chapter 2

Literature Review

There have been many problems associated with using neat vegetable oil in diesel engines, including (1) coking and trumpet formation on injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices, (2) carbon deposits, (3) oil ring sticking, and (4) thickening and gelling of the lubricating oil as a result of contamination by vegetable oils [37]. Other major disadvantages include their high viscosity, causing poor flow and atomization characteristics within diesel engines. Furthermore, vegetable oils solidify at intermediate temperatures, which is impractical for low-temperature use and applications. Four chemical/physical modification techniques have been investigated towards solving these challenging problems, including pyrolysis, dilution, microemulsion, and transesterification. This chapter reviews the fuel preparation of neat vegetable oils by these four processes and their effect on fuel properties and engine performance.

2.1 Pyrolysis

Pyrolysis, or thermal cracking, is the catalytic thermal decomposition of vegetable oil at high temperatures (300-800°C) in the absence of air. This process involves cleavage of C-C chemical bonds to yield smaller molecules of all possible fragments, including alkanes (paraffins), alkenes (olefins), alkadienes, carboxylic acids, aromatics and small amounts of gaseous products, to achieve high yields of liquid fuels. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids, and methyl esters of fatty acids [37]. In most research studies, the pyrolysis of vegetable oil use metallic salts as catalysts to obtain products structurally similar to those present in

petroleum sources. Thermal cracking of fats and oils has been investigated for more than 100 years, especially in countries where there is a shortage of petroleum deposits [38]. In 1888, the first pyrolysis of vegetable oil was conducted by Engler in an attempt to synthesize petroleum from vegetable oil [39]. Since World War I, many researchers [29, 40-49] have studied the thermal cracking of vegetable oils to obtain products suitable for fuel, using different reaction conditions and methods.

Schwab *et al.* [40] thermally decomposed refined soybean oil using the ASTM standard method for distillation of petroleum products. Typical breakdown of the distillates found from the pyrolysis of safflower and soybean oil using GC/MS analysis is listed in Table 2.1. The carbon-hydrogen ratio in the distillates showed about 79% and 12%, respectively, indicating considerable amounts of oxygenated compounds.

| | Percent by Weight | | | | |
|------------------------|--------------------------|------|-----------------------|----------|--|
| | High Oleic Safflower Oil | | Soybean Oil | <u>.</u> | |
| | N ₂ Sparge | Air | N ₂ Sparge | Air | |
| Alkanes | 37.5 | 40.9 | 31.3 | 29.9 | |
| Alkenes | 22.2 | 22.0 | 28.3 | 24.9 | |
| Alkadienes | 8.1 | 13.0 | 9.4 | 10.9 | |
| Aromatics | 2.3 | 2.2 | 2.3 | 1.9 | |
| Unresolved Unsaturates | 9.7 | 10.1 | 5.5 | 5.1 | |
| Carboxylic acids | 11.5 | 16.1 | 12.2 | 9.6 | |
| Unidentified | 8.7 | 12.7 | 10.9 | 12.6 | |

 Table 2.1 Compositional Data of Pyrolyzed Oils^a

^aSource: Ref. [40]

The fuel properties of the pyrolyzed soybean oil were improved substantially compared to the unpyrolyzed soybean oil. The cetane number of the pyrolyzed soybean oil was enhanced to 43 from 37.9, exceeding the ASTM minimum value of 40. The viscosity was reduced from 32.6 cSt to 10.2 cSt, a two-thirds reduction, but still exceeded the ASTM specified value of 7.5 cSt. The pyrolyzed vegetable oil had acceptable amounts of

water and sediment, sulfur and copper corrosion values; but unacceptable ash, carbon residue amounts and pour point. Niehaus *et al.* [50] also thermally cracked refined soybean oil and obtained similar fuel properties. The fuel properties of thermally cracked soybean oil are compared with the fuel properties of neat soybean oil and No. 2 diesel fuel in Table 2.2.

| Soybean Oil | | <u>Cracked</u> Soybean Oil | | No. 2 Diesel Fuel | |
|-------------|-------------------------|---|--|---|---|
| | b | a | b | а | Ь |
| 2.6 | 32.6 | 10.2 | 7.74 | 1.9-4.1 | 2.82 |
| 12 | +12.2 | +7 | +4.4 | -7 max. | -6.7 max. |
| 7.9 | 38.0 | 43.0 | 43.0 | 40.0 | 51.0 |
| 9.6 | 39.3 | 40.3 | 40.6 | 45.5 | 45.6 |
| | | | | | |
| | 2.6 12 7.9 9.6 | $ \begin{array}{r} b \\ 2.6 & 32.6 \\ 12 & +12.2 \\ 7.9 & 38.0 \\ 9.6 & 39.3 \\ \end{array} $ | $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ |

 Table 2.2 Comparative Fuel Properties of Soybean Oil and Diesel Fuel

^aSource: Ref [40], ^bSource: Ref. [50]

Catalytic cracking of two tropical vegetable oils, copra and palm oils, at 450° C over a SiO₂/Al₂O₃ catalyst to produce liquid biofuels with lower molecular weights has also been studied [51]. The chemical composition and physical properties of the thermally cracked vegetable oil fractions were close to that of fossil fuel. However, the formation of water, coke and tar made up about 15 wt% of the pyrolyzed products.

Dandik and Aksoy [42, 52, 53] performed a series of studies in the pyrolysis of used vegetable oil using a fractionating pyrolysis reactor equipped with a packed column. They studied the effects of reaction temperature (400°C and 420°C), catalyst type (sodium carbonate and HZSM-5), catalyst amount (1, 5, 10, and 20 wt% of the oil mass) and column length (180, 360 and 540 mm) on the thermal cracking of vegetable oils. In all three studies, conversion was found to increase with an increase in reaction temperature and decrease with an increase in the column length. Moreover, an increase in the reaction temperature increased the amount of acid phase, liquid hydrocarbons, and gaseous products but decreased the amount of aqueous phase. Also, an increase in the column length decreased the amount of liquid hydrocarbons and acid phase and increased the amount of coke-residual oil. An increase in both catalyst content and temperature increased the formation of both liquid hydrocarbons and gaseous products and decreased the formation of the aqueous phase, acid phase, and coke-residual oil. The reaction products leaving the fractionating column were separated into liquid (organic and aqueous phases) and gaseous fractions, which were analyzed by gas chromatography. In all three investigations, the pyrolyzed oil consisted of gaseous and liquid hydrocarbons, carboxylic acids, CO, CO_2 , H_2 , water, and coke. The liquid hydrocarbon fraction consisted mainly of alkanes, alkenes and their isomers, and aromatics. The gaseous fraction contained CO, CO_2 , H_2 , and saturated/unsaturated hydrocarbons mostly in the C_1 - C_3 range. Depending upon the experimental conditions, coke-residual oil made up between 4-60 wt% of the product composition.

The pyrolysis of a mixture of methyl esters derived from rapeseed oil, called methyl colzate, was studied in a tubular reactor between 550 and 850°C [54]. The major products were olefins, paraffins, aromatics and saturated/unsaturated methyl esters. The effect of temperature on conversion was studied and it was observed that the amount of methyl colzate converted at 550°C was about 6 wt% and increased nonlinearly up to 850°C. Starting at 750°C, conversion increased more slowly as it approached 100 wt%, with 96.6 wt% conversion at 850°C. Coke was a minor by-product and its amount of formation seemed to be independent of temperature. Other research studies [41, 55-57]

on the pyrolysis of methyl esters produced the hydrocarbons normally produced in conventional diesel fuel.

Mechanisms for the thermal decomposition of triglycerides are complex because of the many structures and multiplicity of possible reactions of mixed triglycerides. In general, thermal decomposition of these molecules proceeds through either a free-radical or carbonium ion mechanism [47, 58]. Alencar [47] proposed a scheme for the thermal decomposition pathway of saturated moieties of triglycerides during pyrolysis, which follows the Rice free-radical theory modified by Kossiakoff and referred to as the RK theory [59]. Carboxylic acids formed during pyrolysis is most likely a result from the cleavage of the glyceride moiety, as suggested by Nawar [41].

Very little research has been conducted on diesel engine combustion of pyrolyzed oils. To investigate their ignition delay and combustion behavior, Shihadeh and Hochgreb [60] conducted experiments with two biomass pyrolyzed oils and No. 2 diesel fuel in a direct injection diesel engine. If was found that while the indicated thermal efficiency of both pyrolysis oils equaled that of diesel fuel, they exhibited excessive ignition delays. The longer ignition delay time observed was associated with the chemical composition of the pyrolyzed fuel. Also, neither pyrolyzed oil could ignite without a moderate degree of combustion air preheating at 55°C. Niehaus *et al.* [50] tested thermally cracked soybean oil on a diesel engine. The oil produced slightly less power than diesel fuel and produced lower levels of nitrogen oxide and higher levels of hydrocarbons than diesel fuel. The engine testing was limited to short-term tests.

The equipment for pyrolysis is expensive for modest throughputs and this thermal cracking process consumes a lot of energy due to high reaction temperatures. Although

the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel [37]. Pyrolyzed oils contain significant quantities of moisture (~15-25 wt%), particulates, nitrogen, alkali, and tar, and are generally more dense and viscous than No. 2 diesel fuel [60].

2.2 Dilution

Dilution or blending is simply mixing diesel fuel with vegetable oil. Numerous performance tests in a diesel engine for various diesel/vegetable blends have been researched. A long-term performance test was conducted on a 3:1 (vol) fuel blend of unrefined mechanically expelled soybean oil and diesel fuel, respectively [61]. The viscosity of the expelled soybean oil was about 13.5 times as viscous as diesel fuel at 40°C. By blending it with 25 vol% diesel fuel, the viscosity was reduced by half. However, this blended viscosity was still 7.3 times as viscous as diesel fuel at 40°C. The 200-hr screening test for alternative fuels set forth by the Engine Manufacturer's Association (EMA) was used to evaluate the performance of the test engine when burning the blended fuel. A test failure occurred 90-hr into the screening test due to a dramatic 670% increase in the lubricating oil viscosity. After the oil was changed, the test was allowed to continue to see if any further deterioration occurred. At the 159-hr point, the engine no longer maintained a constant load and the screening test was terminated. After the testing, abnormal carbon buildup/deposits and wet, gummy substances were found on all injector tips and all the engine parts of the combustion chamber. Schlick et al. [62] conducted the same EMA engine testing on mechanically

expelled, unrefined soybean oil blended with No. 2 diesel fuel in a 3:1 volume ratio and observed similar results.

In a paper by Adams *et al.* [63], mixtures of degummed soybean oil with No. 2 diesel fuel in the volume ratios of 1:2 and 1:1, respectively, were tested for engine performance and crankcase lubricant viscosity in a John Deere 6-cylinder, directinjection engine. The 200-hr EMA engine testing was conducted on both sets of blends. The results indicated that a lubricating oil contamination problem resulting in an unacceptable thickening and a potential for gelling occurred with the 1:1 blend. Moreover, the results of a 400-hr endurance run on the 1:2 blend showed that carbon deposits accumulated on the injector tips, intake valves, pistons, and the exhaust area.

Other vegetable oil blends with diesel fuel have also been studied. Ziejewski *et al.* [8] studied the effects of using a 1:3 (vol) blend of alkali-refined sunflower oil and diesel fuel in a direct-injection diesel engine and compared its engine performance with non-blended diesel fuel. The viscosity of the blended fuel was reported to be 4.88 cSt at 40°C, moderately less than that of the neat sunflower oil; but still above the maximum specified ASTM value of 4.0 cSt at 40°C. Problems such as early deterioration of injection nozzle performance, piston ring groove carbon filling, heavy carbon on the piston lands, and heavy carbon build-up on the cylinder liners were observed. These problems would result in premature engine failure. Thus, the 1:3 fuel blend was not recommended for long-term use in a direct-injected diesel engine. A comparable blend with high-oleic safflower, replacing sunflower oil, had a viscosity of 4.92 cSt at 40°C and passed the 200-hr EMA test [64]. The different results were attributed to the degree of unsaturation of the vegetable oil. The more unsaturated oil is highly reactive and tends to

oxidize and polymerize, and the accumulation of such products leads to thickening of the lubricant. Thus, frequent replacement or change of the lubricant oil becomes necessary.

Direct use of vegetable oils and/or the use of blends of the oils has generally been considered to be unsatisfactory and impractical for both direct and indirect diesel engines [37]. The high viscosity, acid composition, free fatty acid content, carbon deposits and lubricating oil thickening, as well as gum formation due to oxidation and polymerization during storage and combustion, are all challenging problems.

2.3 Microemulsion

Microemulsification was amongst the first solutions pursued to solve the high viscosity problem of vegetable oils [65]. Schwab and Pryde [66] defined a microemulsion as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1 to 150 nm range formed spontaneously from two normally immiscible liquids and one or more amphiphile. They can be composed of diesel fuel, vegetable oil, an alcohol, a surfactant, and a co-surfactant. Microemulsions can be classified as nonionic or ionic, usually depending on the amphiphile or surfactant present. Microemulsions with solvents, such as methanol, ethanol, 1-butanol and ionic or non-ionic surfactants, have been studied.

Hybrid fuels based on vegetable oils without combination with conventional diesel fuel are among the most widely studied formulations [24]. Hybrid fuels of special interest are water-in-oil type microemulsions in which the vegetable oil is the continuous phase and an aqueous alcoholic solvent forms the dispersed phase [67]. For example, Ziejewski and Kaufman [8] prepared a nonionic sunflower oil-aqueous ethanol microemulsion composed of 53.3 vol% alkali-refined, winterized sunflower oil, 13.3

vol% ethanol and 33.4 vol% 1-butanol. This nonionic emulsion was characterized by a viscosity of 6.31 cSt at 40°C, cetane number of 25, and had an ash content of less than 0.01 wt%. These and other fuel properties are listed in Table 2.3. In a EMA 200-hr screening test, no significant deterioration in performance was observed; however, heavy carbon deposits, premature injection-nozzle deterioration (irregular needle sticking), incomplete combustion, and an increase of the lubricating oil viscosity were all problems experienced while operating with the microemulsion. Therefore, the tested microemulsion was not recommended for long-term use in a direct-injection diesel engine.

Goering and Fry [68] used soybean oil instead of sunflower oil in a microemulsion. The nonionic fuel was composed of 50 vol% No. 2 diesel fuel, 25 vol% degummed, alkali-refined soybean oil, 5 vol% ethanol, and 20 vol% 1-butanol. The fuel properties are also summarized in Table 2.3. Both the hybrid fuel and No. 2 diesel fuel completed the engine screening test without difficulty; but the hybrid burned more efficiently over the entire speed range. Furthermore, no substantial changes were observed in the viscosity of the lubricating oil when burning either No. 2 diesel or hybrid fuels. The better performance can be attributed to the solvent action and cooling effect of the alcohol in keeping the injector needles and orifices clean. Similar results were also reported by Goering [67] in the study of two (ionic and nonionic) hybrid fuels.

| Property | No. 2 Diesel Fuel ^a | NonionicShippSunflowerOil-AqueousEthanol ^a Fuel ^b | | Hybrid Fuels ^c | |
|----------------------------|--------------------------------------|---|------|---------------------------|----------|
| | | - | | <u>Ionic</u> | Nonionic |
| Viscosity, cSt, 40°C | 2.37 | 6.31 | 4.03 | 8.77 | 6.77 |
| Pour Point, °C | -29 | a* | | c* | c* |
| Cetane Number | 50.1 | 25 | 34.7 | 29.8 | 25.1 |
| Flash Point, °C | 51.7 min. ^c | 27 | 28.3 | 22.2 | 27.8 |
| Heat of Combustion (KJ/kg) | 45, 422 | 36, 393 | 41 | | |

Table 2.3 Fuel Properties of Microemulsions

^aSource: Ref. [8], ^{a*} The sample separated into two phases at 2°C. The lower layer solidified at -29°C and the upper layer was still liquid at -65.0°C; ^bSource: Ref.[68]; ^cSource: Ref. [67], ^{c*}The fuel separated into two layers at 0°C.

In a paper by Masjuki *et al.* [69], engine evaluation was conducted on a diesel engine fueled with emulsions of Malaysian palm oil diesel or conventional diesel, containing 5% and 10% of water by volume, to determine the engine performance and wear characteristics. If was found that palm oil diesel emulsified with water did not present any obstacles in the operation of diesel engine during steady state engine tests. In fact, the main conclusion was that the engine performance and fuel consumption for palm oil diesel and its emulsions were comparable with those of conventional diesel fuel.

To select candidate fuels, potential formulations are characterized by physical characteristics such as phase equilibrium and miscibility limits [29]. Schwab *et al.* [29] used the ternary phase equilibrium diagram and the plot of viscosity versus solvent fraction to determine the emulsified fuel formulations. All microemulsions with butanol, hexanol and octanol met the maximum viscosity requirements for No. 2 diesel. Mixtures of hexadecane, 1-butanol and 95 wt% ethanol also formed microemulsions [70]. Furthermore, Schwab and Pryde [66] demonstrated the use of 2-octanol as an effective surfactant in the micellar solubilization of methanol in triolein and soybean oil. Thus, by

microemulsion formation, it is possible to prepare alternative diesel fuels completely free of petroleum.

2.4 Transesterification

Transesterification, also called alcoholysis, is a reversible reaction of fats or oils with alcohol to form alkyl esters and glycerol. This process is by far the most common method for reducing the viscosity of vegetable oils. The general scheme of the transesterification reaction is shown in Figure 2.1. According to the chemical equation, the stoichiometry of this reaction requires a 3:1 molar ratio of alcohol to triglyceride to produce 1 mole of glycerol and 3 moles of fatty acid alkyl esters. Moreover, the molecular weight of an ester molecule is roughly one-third that of its parent vegetable oil molecule and has a viscosity approximately twice that of diesel fuel instead of 10 to 20 times, as is the case for the neat vegetable oils [71]. The most commonly prepared esters are methyl esters, largely because methanol is the least expensive alcohol. It has been reported the yield of alcohol esters was the highest for methanol, as methanol is the shortest-chain alcohol and more reactive, with the added advantage of alkaline catalysts being easily soluble in it because of its polarity [38].



Figure 2.1 Transesterification Reaction of Vegetable Oil

The transesterification of various animal fats, oils and waste oils has been extensively studied for the past 20 twenty years, particularly in the 1980's. In fact, several reviews concerning the production of biodiesel by transesterification have been published [37, 72-79]. The main factors influencing the yield and purity of biodiesel include purity of the feedstocks, alcohol/vegetable oil molar ratio, catalyst type, reaction time, reaction temperature, and mixing.

2.4.1 Mechanism & Kinetics

Transesterification consists of a number of consecutive, reversible reactions [29, 80]. Thus, a catalyst and excess alcohol are used to increase the rate of reaction and to shift the equilibrium to the right, respectively. As depicted in Figure 2.2, the triglyceride is converted stepwise to diglyceride, monoglyceride, and finally to glycerol. A mole of ester is liberated at each step. The mechanism of base-catalyzed transesterification of vegetable oils is illustrated in Figure 2.3. The mechanism was formulated as four steps [81, 82]. The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst (A). The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (B), from which the alkyl ester and the corresponding anion of the diglyceride are formed (C). The latter deprotonates the catalyst, thus regenerating the active species (D), which is able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. The mechanism of an acid-catalyzed transesterification is similar in that the tetrahedral intermediate is formed. However, carboxylic acids can be formed by the reaction of a carbocation intermediate with water present in the reaction mixture. This

suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduces the yield of alkyl esters.

1. Triglyceride (TG) + R'OH
$$\xleftarrow{\text{Catalyst}}$$
 Diglyceride (DG) R'-O-C-R₁
2. Diglyceride (DG) + R'OH $\xleftarrow{\text{Catalyst}}$ Monoglyceride (MG) R'-O-C-R₂
3. Monoglyceride (DG) + R'OH $\xleftarrow{\text{Catalyst}}$ Glycerol (GL) R'-O-C-R₃



$$ROH + B \rightleftharpoons RO^{-} + BH^{-} \qquad (A)$$

$$R_{1}COO - CH_{2}$$

$$R_{2}COO - CH + CH_{3} + COR \rightleftharpoons R_{1}COO - CH_{2}$$

$$R_{2}COO - CH + H_{2}C - OC - R_{3} = H_{2}C - O - C - R_{3} = (B)$$

$$R_{1}COO - CH_{2} + CH_{3} + COO - CH_{2}$$

$$R_{2}COO - CH + R_{3} + R_{1}COO - CH_{2} + R_{2}COO - CH + ROOCR_{3} = (C)$$

$$H_{2}C - O - C - R_{3} + H_{2}C - O - CH_{2} + R_{2}COO - CH_{3} + COO - CH_{4} + COO + CH_{4} + COO -$$

Figure 2.3 Mechanism of Base-Catalyzed Transesterification of Vegetable Oils Source: Adopted from Ref. [77]

Surprisingly, little is known about the kinetics of the transesterification of vegetable oils. The reason might be the complexity of the reaction itself, which runs through two intermediates, in addition to the analytical problem in simultaneously quantifying mono-, di-, and triglycerides as well as methyl esters [83]. Freedman et al. [80] were one of the first researchers to study the transesterification kinetics of soybean oil. With acid or alkaline catalysis, the forward reaction followed pseudo-first-order kinetics for a 30:1 molar ratio of butanol:soybean oil. However, for a molar ratio of 6:1 in the alkaline-catalyzed study only, the forward reaction followed consecutive secondorder kinetics. The reaction kinetics of methanol with soybean oil at a 6:1 molar ratio with 0.5% (w/w) sodium methoxide at 20-60°C was a combination of second-order consecutive and fourth-order shunt reactions. A shunt reaction is a reaction in which all three positions of the triglyceride react virtually simultaneously to give three alkyl ester molecules and glycerol. Reverse reactions of both acid and alkaline catalysis appeared to be second-order. For both forward and reverse reactions, the rate constants for the alkaline-catalyzed reactions were significantly larger than those for the acid-catalyzed reactions. Also, the rate constant increased with an increase in the amount of catalyst used.

The transesterification kinetics of soybean oil with methanol was also investigated by Noureddini *et al.* [84]. The effect of mixing and temperature on the reaction rate was studied while the molar ratio of alcohol to oil and concentration of catalyst were held constant. The experimental results revealed that the effect of mixing is most significant during the slow rate region of the reaction. As methyl esters are formed, a single phase is established and mixing became insignificant while the reaction temperature primarily

influenced the reaction rate. Thus, the experimental results clearly demonstrated an initial mass transfer-controlled region, followed by a kinetic-controlled region. The data for the latter region fitted well into a second-order kinetic mechanism.

2.4.2 Effects of Moisture & Free Fatty Acids

Wright et al. [85] noted that the starting materials used for alkaline-catalyzed transesterification of vegetable oils must meet certain specifications. The triglyceride should have an acid value less than 1 and all materials should be anhydrous. If the acid value is greater than 1, more sodium hydroxide is required to neutralize the free fatty acids, which results in the production of soap. Water can also cause soap formation, which consumes the catalyst and reduces its efficiency. The resulting soaps cause an increase in viscosity or formation of gel, lower the yield of ester, and the separation of ester and glycerol during water washing becomes difficult. As little as 0.3% water in the reaction mixture reduces ester yields by catalyst consumption [86]. Other researchers have also stressed the importance of oils being dry and free of free fatty acids [87, 88]. Freedman et al. [86] also reported that ester yields were significantly reduced if the reactants did not meet these specifications. In his study, prolonged contact with air diminished the effectiveness of both sodium hydroxide and sodium methoxide through interaction with moisture and carbon dioxides. In the presence of water or moisture, the esters produced from transesterification can undergo saponification to produce fatty salts, also referred to as soap, as depicted in Figure 2.4. While, shown in Figure 2.5, hydrolysis of the triglyceride can occur to produce free fatty acids. These free fatty acids, and the free fatty acids originally present in the vegetable oil, can undergo further chemical reaction via saponification generating additional water, illustrated in Figure 2.6. Thus,

the absence of moisture and free fatty acids in the vegetable is important in order to maximize product yield and enhance product purity.

Figure 2.4 Saponification of Ester

Figure 2.5 Hydrolysis of Triglyceride

$$\begin{array}{c} O \\ \parallel \\ R - C - OH \end{array} + NaOH \xrightarrow{Heat} \qquad \begin{array}{c} O \\ \parallel \\ R - C - O \end{array} + H_2O$$
Free Fatty Acid Metallic Alkoxide Salt Water

Figure 2.6 Saponification of Free Fatty Acid

The effects of free fatty acids and water on transesterification of beef tallow with methanol were investigated [89]. This study reported that the presence of both free fatty acids and water had a synergistic negative effect on the reaction. Thus, in order to obtain maximum conversion, the water content of beef tallow should be kept below 0.06% (w/w) and the free fatty acid content should be kept below 0.5% (w/w). This maximum content of free fatty acids confirmed the research results of Bradshaw and Meuly [88] and Feuge and Grose[87].

2.4.3 Effect of Molar Ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride [37]. Stoichiometrically, transesterification of vegetable oil requires three moles of alcohol and one mole of triglyceride to produce three moles of fatty acid ester and one mole of glycerol. Based on the Le Chatelier's principle, excess amount of alcohol is generally used to shift the reaction equilibrium far to the right. Thus, high alcohol to vegetable molar ratios result in greater ester conversion than the stoichiometric molar amounts.

Bradshaw and Meuly [88] stated that a molar ratio of 4.8:1 of methanol to vegetable oil led to an ester yield of 97-98%, depending on the quality of the oil. They also noted that a molar ratio greater than 5.25:1 interfered with the gravitational separation of glycerol and added more cost to the separation process due to the excess amount of residual alcohol. Freedman et al. [86] studied the effect of molar ratio on ester conversion with four vegetable oils. Soybean, sunflower, peanut, and cottonseed oils behaved similarly and achieved highest conversions to esters (93-98%) at the 6:1 molar ratio. It was also noted that ratios greater than 6:1 did not increase yields, but rather complicated ester and glycerol recovery and increased the cost of alcohol recovery. In the ethanolysis of peanut oil, a 6:1 molar ratio liberated significantly more glycerol than a 3:1 molar ratio [87]. In the transesterification of cynara cardunculus L. oil, molar ratios of ethanol to cynara were studied [90]. With a stoichiometric amount of alcohol, the conversion to esters was about 62% after 2 hours. The ester yields increased as the molar ratio increased up to a value of 12:1. The best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete; and for a molar

ratio of 15:1, the separation of glycerol was difficult and the apparent yield of esters decreased because part of the glycerol remained in the biodiesel phase. Tanaka *et al.* [91], in his novel two-step transesterification of oils and fats such as tallow, coconut oil and palm oil, used 6:1-30:1 molar ratios with alkali-catalysis to achieve a conversion of 99.5%.

2.4.4 Effect of Catalyst Type

Catalysis commonly used in the transesterification of vegetable oil are alkaline and acid. The effectiveness of the catalyst is determined by the molar ratio of the reactants and the quality of the vegetable oil. Alkaline metal alkoxides are the most effective alcoholysis catalysts because they give very high ester yields in short reaction times at low molar concentrations [92]. However, alkaline metal hydroxides, like sodium hydroxide, are cheaper and are, thus, a good alternative because they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2%, based on the mass of the oil. For acid-catalysis, the acids that can be used include sulfuric, phosphoric, hydrochloric or organic sulfonic acids. Transmethylations occur approximately 4000 times faster in the presence of an alkaline catalyst than those catalyzed by the same amount of acidic catalyst [93]. Even at ambient temperatures, the alkaline-catalyzed reactions proceeds rapidly, whereas acid-catalyzed reactions commonly require reaction temperatures above 100°C [82]. Because alkaline catalysts are less corrosive to industrial equipment than acid catalysts and the reaction rate is significantly faster, most commercial transesterifications are conducted with this type of catalysis. However, if the vegetable oil has a high free fatty acid and water content, an

acid-catalyzed pre-treatment is employed because free fatty acids deactivate an alkaline catalyst.

The catalysts sodium hydroxide (NaOH) and sodium methoxide (NaOCH₃) were compared at a 6:1 and 3:1 molar ratio of methanol to vegetable oil [86]. Ester conversion at a 6:1 molar ratio for 1% (w/w) sodium hydroxide and 0.5% (w/w) sodium methoxide were essentially identical after 60 minutes. However, at the 3:1 molar ratio, the methoxide catalyst was superior to the hydroxide catalyst during the entire 60-minute reaction time. Ma *et al.* [89] noticed that, comparing these catalysts for the methanolysis of beef tallow, sodium hydroxide was significantly better than sodium methoxide. Maximum yields with 0.3% (w/w) sodium hydroxide and 0.5% (w/w) sodium methoxide were 60% and 54%, respectively. Encinar *et al.* [90] studied the ethanolysis of cynara cardunculus L. oil, by comparing the effectiveness of sodium hydroxide and potassium hydroxide in a concentration range of 0.25 to 1.5% (w/w). Of these two catalysts, sodium hydroxide gave a slightly high ethyl ester yield. The optimum concentration for both catalysts was 1% (w/w), resulting in a conversion of >90%.

The acid-catalyzed transesterification of soybean oil with methanol, ethanol, and butanol were compared using 1% (w/w) concentrated sulfuric acid [86]. Conversions to esters were unsatisfactory with both 6:1 and 20:1 molar ratios at 3 and 18 hours, respectively. Instead, a 30:1 molar ratio resulted in a high conversion to the methyl ester. However, at this particular ratio, the hours needed to obtain high a conversion were 3, 22, and 69, for the butyl, ethyl and methyl esters, respectively. Ikwaguagwu *et al.* [94] transesterified palm oil with 3% sulfuric acid at a 23:1 molar ratio of sulfuric acid to palm oil, which gave a maximum yield of 78% methyl esters.

2.4.5 Effect of Reaction Time

Ma *et al.* [89] studied the effect of reaction time on the transesterification of beef tallow with methanol and 0.3% (w/w) sodium hydroxide as the catalyst. From 1 to 5 minutes, the apparent yield surged from 1% to 38%. Then, the production of beef tallow methyl ester slowed down and reached a maximum value at about 15 minutes. The initial delay was due to the mixing and dispersion of methanol into beef tallow. Freedman *et al.* [86] transesterified peanut, cottonseed, sunflower and soybean oils at a 6:1 molar ratio and in the presence of 0.5% (w/w) sodium methoxide at 60°C. For soybean and sunflower oils, an approximate yield of 80% was observed after 1 minute; similar to the results of the ethanolysis of peanut oil, in which about 80% of the esters were formed in the first five minutes [87]. However, ester conversions after 1 minute with peanut and cottonseed oils were distinctly lower. After 1 hour, the conversions were almost the same for all four oils, 93-98%.

2.4.6 Effect of Temperature

The rate of reaction is strongly influenced by the reaction temperature. Generally, transesterification is conducted near the boiling point of the alcohol at atmospheric pressure, although the reaction may be carried out at room temperature. Given enough time, transesterification can proceed satisfactorily at ambient temperatures in the case of alkaline catalysis. The methanolysis of refined soybean oil at 60°C, 45°C and 32°C was studied at a 6:1 methanol/soybean oil molar ratio and using 1% (w/w) sodium hydroxide [86]. After 0.10 hr, the ester yields at 60°C, 45°C, and 32°C were 94, 87 and 64%, respectively, showing the influence of temperature on ester conversion. After 1 hour, ester formation was identical for the 60°C and 45°C runs, and only slightly lower for the

32°C run. After 4 hours, the ester conversion for the 32°C experiment slightly exceeded that of the other two reaction temperatures. A study by Kusy [95] showed similar results, using temperatures from 32°C to 83°C. It was concluded from both of these papers that a time of 1 hour at 60°C was equivalent to 4 hours at 32°C in terms of ester conversion efficiency. Encinar *et al.* [90] studied the ethanolysis of refined cynara cardunculus oil at 75°C, 50°C, and 25°C. In all experiments, an ethanol/oil molar ratio of 9:1 and 1% (w/w) sodium hydroxide were used. After 2 minutes, esters present in the 75°, 50° and 25°C runs were 79%, 76.5%, and 75.5%, respectively. However, after 2 hours, ester formation was basically identical for the three runs at 93.1%, 92.5%, and 91.6%, respectively.

2.4.7 Effect of Mixing

A factor of particular importance in the transesterification process is the degree of mixing between the alcohol and triglyceride phases. Triglyceride and alcohol phases are not miscible and initially form two liquid layers. This miscibility phenomenon results in a lag time in the formation of methyl esters. Thus, mixing is normally applied to increase the contact between the reactants, resulting in an increase in mass-transfer rate. The effect of mixing on the rate of reaction was studied by Noureddini [84]. It was discovered that the reaction was initially controlled by diffusion, in which poor diffusion between the phases resulted in a slow rate. As methyl esters formed, they acted as a mutual solvent for the reactants and a single-phase system was formed. The mixing effect was most significant during the slow rate region of the reaction. As the single phase was established, mixing became insignificant and the reaction temperature primarily influenced the reaction rate. Boocock *et al.* [96, 97] have addressed the

problem of the mass-transfer limitations by the use of non-reactive co-solvents, like simple ethers.

2.4.8 Engine Performance

Clark *et al.* [98] burned methyl and ethyl soybean esters in a direct-injection, turbocharged diesel engine. They found that engine performance during the EMA 200-hr test with the soybean esters did not differ greatly from that of diesel fuel. Emissions for both methyl and ethyl esters, as well as No. 2 diesel fuel, were essentially the same. Hydrocarbon emissions from the esters were slightly less than those from No. 2 diesel fuel while NO_x emissions were slightly greater for the esters. Measurements of engine wear and fuel-injection system tests showed no abnormal characteristics for any of the three fuels after the 200-hr tests. Deposit formation was comparable in amount; however, the methyl ester engine experienced greater piston carbon deposits. It was also concluded that the methyl and ethyl esters of vegetable oils could be used as alternative fuels on a short-term basis, provided certain fuel quality standards are met. Table 2.4 compares fuel properties of some soybean esters.

| Fuel | Viscosity, 40°C (mm ² /s) | Cetane No. | Heat of Combustion (KJ/kg) | Cloud Point (°C) | Pour Point (°C) |
|----------------------|---|---------------|----------------------------------|---------------------|--------------------|
| Methyl soyate | 4.08 | 46.2 | 39, 800 | 2 | -1 |
| Ethyl soyate | 4.41 | 48.2 | 40, 000 | 1 | -4 |
| Butyl soyate | 5.24 | 51.7 | 40, 700 | -3 | -7 |
| No. 2 Diesel Fuel | 2.07 | 47.0 | 45, 343 | -15 | -33 |

Table 2.4 Fuel Properties of Soybean Esters^a

^aSource: Refs. [98] and [29]

Sims [99] used a tractor powered by a direct-injection engine for evaluating the performance of tallow ester as an alternative diesel fuel. He concluded that the fuel properties of methyl tallow esters were remarkably similar to diesel fuel. It was observed that a blend of diesel fuel and tallow ester gave improved combustion characteristics.

2.5 Summary of the Physicochemical Processes

There has been extensive research in the area of the physicochemical modification of triglycerides for utilization in diesel engines. Each of the four processes discussed give improved fuel properties over those of unprocessed, neat vegetable oils. However, the viscosity of chemically modified vegetable oils is still about twice that of No. 2 diesel fuel. Moreover, fuel properties, such as low-temperature flow properties and oxidative/storage properties, are still in need of further enhancement. Thus, alternative chemical processes must be developed in order to achieve better fuel properties of vegetable oil-derived fuels and, in turn, their quality as an alternative diesel fuel.

Chapter 3

Materials & Methods

3.1 Chemicals

Refined and bleached (RB), regular and low-sat, soybean oils [8001-22-7] were generously provided by Zeeland Farm Soya (Zeeland, MI). Premium No. 2 diesel fuel [68334-30-5] was provided by the Michigan State University Service Garage (East Lansing, MI). High-purity HPLC water [7732-18-5], analytical grade methanol [67-56-1], petroleum ether [8032-32-4], and potassium iodide [7681-11-0] were purchased from Mallinckrodt Baker, Inc (Phillipsburg, NJ); sodium hydroxide [1310-73-2] and sodium sulfate (purified and anhydrous) [7778-18-9] from Spectrum Quality Products, Inc. (Gardena, CA); concentrated hydrochloric acid [7647-01-0] from Columbus Chemical Industries, Inc. (Columbus, WI); and calcium carbonate [471-34-1] from Jade Scientific (Canton, MI).

Nine fatty acid methyl ester (FAME) standards used in the quantitative GC analysis, methyl propionate (propionic acid, methyl ester, [554-12-1]), methyl hexanoate (hexanoic acid, methyl ester, [106-70-7]), methyl nonanoate (nonanoic acid, methyl ester, [1731-84-6]), methyl undecanoate (undecanoic acid, methyl ester, [124-10-7]), methyl palmitate (hexadecanoic acid, methyl ester, [112-39-0]), methyl stearate (octadecanoic acid, methyl ester, [112-61-8]), methyl oleate (*cis*-9-octadecenoic acid, methyl ester, [112-62-9]), methyl linoleate (*cis*,*cis*-9,12-octadecadienoic acid, methyl ester, [112-63-0]) and methyl linolenate (*cis*,*cis*-9,12,15-octadecatrienoic acid, methyl ester, [301-00-8]), were all chromatographically >99% pure and purchased from Nu-Chek Prep, Inc. (Elysian, MN). Two additional reference standards, dimethyl azelate (nonanedioic acid, dimethyl ester, [1732-10-1]) and dimethyl malonate (propanedioic acid, dimethyl ester, [108-59-8]), were purchased from TCI America (Portland, OR), each having a 98% purity. Unless noted, all chemicals were used as received.

3.2 Transesterifcation of Soybean Oil

The transesterification reaction was carried out in a 3-neck, 2000-mL capacity, round-bottom flask, equipped with an adjustable speed mechanical stirrer, condenser, thermometer, and a heating mantle for temperature-controlled heating. Approximately 850 grams of RB soybean (low-sat or regular) was added to the reaction vessel and preheated to 60°C. To achieve a 9:1 molar ratio of alcohol to vegetable oil, 280 grams of methanol was premixed with 8.50 grams of sodium hydroxide (1 wt% of the vegetable oil) and agitated. The methanol/catalyst solution was added to the reaction vessel and the mechanical stirrer was powered on. The transesterification reaction was allowed to proceed for 2 hours at a reaction temperature of 70°C. The experimental apparatus for the transesterification of RB soybean oil is illustrated in Figure 3.1.



Figure 3.1 Experimental Apparatus for the Transesterification of RB Soybean Oil

Once the reaction was complete, the contents of the reaction vessel were transferred to a 2000-mL capacity glass separatory funnel and allowed to cool to room temperature. About 35 mL of a 10 M aqueous, concentrated hydrochloric acid solution was added to neutralize the catalytic base to sodium chloride salt. The aqueous phase was then discarded and the organic phase was further purified. Glycerol and excess methanol were removed by rinsing the organic phase with three cycles of 500 mL of warm water (~60°C), and the aqueous layer was discarded after each cycle. In order to completely remove any residual catalyst and glycerol, 1000 mL of petroleum ether was added and the aqueous layer was again discarded. The resultant solution was dried over anhydrous sodium sulfate via vacuum filtration. Petroleum ether and residual methanol in the ester layer were removed on a rotary evaporator under vacuum at 70°C. The ester product was dried over anhydrous sodium sulfate and filtered for further purification. This high-purity methyl soyate product was characterized for fatty acid methyl ester content and composition using GC analysis.

One transesterification reaction generated about 400 mL of methyl soyate. Thus, ten batches of soybean oil were transesterified to methyl soyate. All batches were collected together in a 4-L amber glass container.

3.3 Ozonolysis of Methyl Soyate

A solution of methyl soyate (100 g), methanol (74 g), and calcium carbonate (10 g) was added to a reaction vessel equipped with a fused fritted glass disc. Methanol was used in excess at a methyl soyate to methanol molar ratio of about 1:4 (theoretical is 1:2) and the amount of catalyst was chosen to be 1 wt% of methyl soyate. A heterogeneous catalyst was chosen for easy separation of the products via filtration. The reaction

temperature was maintained at ambient conditions by immersing the reaction vessel into a temperature-controlled water bath. Ozone was produced by passing oxygen through high voltage electrodes in a Praxair Trailigaz OZOBLOC Model OZC-1001 ozone generator (Cincinnati, OH). This silent electric-discharge technology is the only convenient and economical industrial method for ozone synthesis [32]. With tygon tubing, the exit port of the ozone generator was connected to the inlet port of the bubbling reactor, which was located underneath the reactor. The gaseous oxygen/ozone mixture was delivered to the reaction solution through the fused fritted disc at a flow rate of 0.35 ft^3 /sec, ozone concentration of 6 wt%, and the generator was maintained at a pressure of 12 psi. A 400-mm condenser was attached on top of the bubbling reactor to reflux methanol and other volatile compounds. Via tygon tubing, the exhaust outlet from the condenser was connected to a 250-mL capacity, round-bottom, flask, which was immersed in a dewar filled with dry-ice. The purpose of the dry-ice trap was to collect any unreacted methanol and volatile compounds produced during the ozonolysis reaction. A 1000-mL capacity, Erlenmeyer flask containing ~850 mL of a 2% KI aqueous solution was placed in series of the dry ice trap. The purpose of this solution was to trap and rapidly decompose any unreacted ozone. After the specified reaction time, the generator was shutdown and the reaction products were flushed for 10 minutes with oxygen to remove excess ozone. The reaction products were separated from the heterogeneous catalyst via vacuum filtration and stored in a cool environment for further characterization. The ozonolysis reaction was conducted in a fume-hood environment, ensuring that ozone was always contained within the reaction system. For kinetics studies, ozonolysis was conducted in reaction time intervals of 30, 60, 90, 120, 150, and

180 minutes, each as a separate and single experiment. To study the effect of catalysis, ozonolysis was also conducted under non-catalytic conditions. A schematic of the process flow design is illustrated in Figure 3.2.



Figure 3.2 Process Flow Design for the Ozonolysis of Methyl Soyate

3.4 Structural Analysis

3.4.1 Fourier Transform Infra-Red

Fundamental Theory of Operation

Infrared spectroscopy measures the intensity of the absorption of various frequencies in the infra-red region of the electromagnetic spectrum by a sample. This analytical technique takes advantage of the fact that almost every carbon-containing molecule strongly absorbs IR radiation, making IR spectroscopy a useful and powerful tool for identifying molecular structures within chemical compounds. In fact, the majority of common organic functional groups absorb infrared radiation between 4000 and 400 cm⁻¹. When a beam of infrared radiation is directed at a sample, some light passes through (transmitted) and some light is absorbed by the molecules at specific frequencies, causing them to vibrate by the bending and stretching of chemical bonds. The precise frequency of the absorbed radiation, or energy, depends on the functional group in the molecule. Thus, the absorption intensity as a function of frequency generates an infrared spectrum of the sample. The infra-red spectrum provides a "fingerprint" of the molecular chemical bonds present in the sample because no two unique molecular structures absorb light at the same precise frequency.

The main component of a Fourier-Transform Infra-Red spectrometer is the Michelson interferometer, an optical device that contains a fixed mirror, a movable mirror, and a beamsplitter. As shown in Figure 3.3, the incident radiation is split into two optical beam paths by the beamsplitter. One path travels to a mirror at a fixed distance, while the other beam travels to a moving mirror whose position varies uniformly with time. The two beams recombine back to the beamsplitter by reflecting off of these mirrors, and are then directed to the sample and the detector. An optical path difference is generated as the moving mirror is moved away from the beamsplitter, causing the two beams to "interfere" with each other. Thus, an interferogram is generated, in which the intensity of the beam striking the detector is measured as a function of the movable mirror position, $f(\chi)$. This signal is Fourier transformed, a mathematical technique that "decodes" the interferogram data and expresses it as a function of frequencies, f(v), generating an absorption spectrum.



Figure 3.3 A Typical Michelson Interferometer

A Perkin-Elmer model Infrared Spectrometer 1000 (Boston, MA), operating at room temperature, was used to study the degradation of double bonds in ozonated methyl soyate, with respect to reaction time, and to identify certain functional groups contained in the ozonated samples. Samples of the volatile fraction collected in the dry-ice were also examined with respect to reaction time. FTIR spectra (resolution: 2 cm⁻¹, scan: 64, frequency range: 4000-500 cm⁻¹, frequency interval: 0.5 cm⁻¹) were performed after spreading a thin film of sample between two sodium chloride plates. Sodium chloride is used because it does not absorb strongly in the infrared region. Because there needs to be a relative scale for the absorption intensity, a background reference spectrum containing no sample in the beam was also collected using identical conditions. This technique results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features that are present in the spectrum are strictly due to the sample.

3.4.2 Nuclear Magnetic Resonance Spectroscopy

Fundamental Theory of Operation

Nuclear magnetic resonance spectroscopy (NMR) is based upon the measurement of absorption of electromagnetic radiation in the frequency range of roughly 4 to 600 MHz. In contrast to ultraviolet, visible, and infrared absorption, nuclei of atoms are involved in the absorption process. The theoretical basis for NMR is that certain atomic nuclei have spin and magnetic moment properties and, as a consequence, their energy levels split when exposed to a magnetic field. Therefore, NMR is another excellent tool for determining functional groups in a pure compound or in complex mixtures.

Analysis

NMR analysis was performed at room temperature using a Varian Inova-300 MHz superconducting NMR-Spectrometer (Palo Alto, CA), operating at 300.103 MHz interfaced with a Sun Microsystems Ultra5 UNIX console. Samples were diluted in deuterated chloroform (CDCl₃).

3.4.3 Gas Chromatography

Fundamental Theory of Operation

Gas-liquid chromatography (GC) is based upon the partition of the sample components between the mobile phase and a liquid stationary phase immobilized on the surface of an inert solid. Basic components of a complete gas chromatographic system is schematically shown in Figure 3.4, which includes the carrier gas supply, flow controller, injection port, column oven, detector, and a data collection system. A small amount of liquid sample, 1.0 μ L, is injected into the injection port and is volatilized in the hot injection chamber. The sample is then transported through the column by the flow of an

inert, gaseous mobile phase and interacts with the stationary phase. The stationary phase can selectively adsorb components in a sample mixture based on volatility and/or polarity. Thus, as a consequence of the difference in mobility due to affinities for the stationary phase, sample components separate into discrete bands that can be qualitatively and quantitatively analyzed. The flame ionization detector (FID) generates a measurable electrical signal, referred to as peaks, that is proportional to the amount of analyte present. Detector response is plotted as a function of the time required for the analyte to elute from the column.



Carrier gas

Figure 3.4 Basic Components of a Gas Chromatographic System

The highest precision for quantitative chromatography is obtained by using an internal standard because the variations introduced by sample injection are avoided. In this procedure, a carefully measured quantity of an internal standard compound is added to both the standard solution and the sample, and the ratio of the analyte peak area to the internal standard peak area serves as the analytical parameter, called the response factor. Since the internal standard has a known concentration in both the standard solution and sample mixture, it can be used to correct for sample variations. With a suitable internal standard, precisions of better than 1% can be achieved [100].

For calculating the response factor, the area of a peak due to compound x in the sample is denoted by A_x . In order to relate this area to the area of compound x in the standard solution, sample variations must first be corrected for to arrive at a "corrected area," denoted $A_{C, x}$, which can be calculated using equation 3.1.

$$\left[A_{C,X}\right]_{Sample} = \left[A_{X}\right]_{Sample} \cdot \left[\frac{A_{I.S.}}{C_{I.S.}}\right]_{Standard Solution} \cdot \left[\frac{C_{I.S.}}{A_{I.S.}}\right]_{Sample}$$
(3.1)

where A, C, and I.S. denote peak area, concentration, and internal standard, respectively. Note that the internal standard signal area is proportional to the mass of analyte passing through the detector. Since mass is equal to the concentration of the internal standard times the volume, the ratio of A/C is equal to the volume times a proportionality constant. Equation 3.1 results in a cancellation of the proportionality constant, and can be rewritten as,

$$A_{C,X} = A_X \cdot \frac{(InjectedVolume_{I.S.})_{S \tan dardSolution}}{(InjectedVolume_{I.S.})_{Sample}}$$
(3.2)

to emphasize the importance of the internal standard in correcting for sample volume. The resulting $A_{C, X}$ is an area that has been corrected to give a volume equivalent to what would be expected if the internal standard peaks had identical areas in the sample and standard chromatograms. From the corrected peak areas, the concentration of component x in the sample mixture can be calculated using equation 3.3,

$$\begin{bmatrix} C_X \end{bmatrix}_{\text{Sample}} = \begin{bmatrix} A_{C,X} \end{bmatrix}_{\text{Sample}} \cdot \begin{bmatrix} \frac{C_X}{A_X} \end{bmatrix}_{\text{Standard Solution}}$$
(3.3)

Equation 3.3 reflects the fact that the properly corrected area of compound x in the sample can be compared with its area in the standard solution, whose concentration is known.

In this research study, the aforementioned internal standard calibration method was used to determine the concentration of selected esters in ozonated methyl soyate samples. Methyl undecanoate (C_{11} methyl ester) was chosen as the internal standard because of its predictable retention time and non-interference with the peak areas from all the components in the sample mixture. Two samples were analyzed for each reaction time interval, the oil fraction (reaction vessel) and the volatile fraction (dry ice trap). The oil fraction samples were diluted with methanol to a 1:100 dilution prior to injection. On the contrary, volatile fraction samples were not diluted because they were already heavily diluted with unreacted methanol. Thus, two standard solutions were prepared, one diluted with methanol and one not diluted with methanol. Since the amount of internal standard that was added to the standard solutions was the same, then equation 3.4,

$$\left[\frac{C_{I.S.}}{A_{I.S.}}\right]_{\text{Oil Fraction Standard}} = \left[\frac{C_{I.S.}}{A_{I.S.}}\right]_{\text{Volatile Fraction Standard}}$$
(3.4)

is validated. The C/A ratio between the oil fraction and volatile fraction standard solutions were experimentally within 99.5% of each other. Thus, the injected volume of these standard solutions was assigned 1.0 μ L as a reference.

Analysis

A SGE (Austin, TX) BPX70 capillary column (70% cyanopropyl phenyl, 60-m length, 0.25-mm i.d., 0.25- μ m thickness) was used. The BPX70 is a phase specifically designed to aid the selectivity and separation of complex mixtures of fatty acid methyl esters, including geometric and positional isomers. A Hewlett-Packard instrument (Palo Alto, CA) Model HP-5890 Series II gas chromatograph equipped with and a flameionization detector and a 3396A integrator for data acquisition was used to administer the analysis. Splitless injection was used at a sample size of 1.0 μ L. Helium was the carrier gas at a flow rate of about 10 mL/min. The flow rate of hydrogen was 35 mL/min and the flow rate of air was about 400 mL/min. The temperature of the injector and detector was 280°C and 300°C, respectively. For the column temperature programming conditions, the initial temperature was 50°C and the final temperature of 240°C was reached at a rate of 5°C/min and held isothermally for 22 minutes, giving a total run-time of 60 minutes.

3.4.4 Gas Chromatography/Mass Spectrometry

Fundamental Theory of Operation

In the gas chromatography/mass spectrometry (GC/MS) analytical technique, gas chromatography volatilizes and separates the components of a mixture and mass spectroscopy characterizes each of the compounds individually based on their molecular weight. In principle, the conventional mass spectrometer is an electronic, high vacuum instrument used for the analysis of gases or volatilized by means of the dissociation of molecules by electron impact ionization, chemical ionization, or field ionization bombardment and the subsequent separation of the positive ions according to their mass
to charge ratio. Thus, a mass spectrometer creates charged particles (ions) from molecules and analyzes these ions to provide information about the molecular weight of the compound and its chemical structure. Since molecules have distinctive fragmentation pattern ('fingerprint'), mass spectroscopy is useful for determining chemical and structural information about compounds.

The gaseous molecules exiting the GC are bombarded by a high-energy, typically 70 eV, beam of electrons in an ionization chamber. As a result of this collision, the energy impacted is sufficient enough to dislodge one of the molecule's electrons, as shown in equation 3.5,

A:B +
$$e^{-}$$
 \longrightarrow $(A \cdot B)^{+}$ + $2e^{-}$ (3.5)

(molecule) (electron) (molecular ion) (electron) The molecular ion produced has the same mass as the molecule from which it is formed. Electrons with energies of about 70 eV are energetic enough to, not only ionize a molecule, but also impart a large amount of energy to the resulting molecular ion, causing it to dissociate into smaller fragments. Dissociation of a cation radical produces a positively charged fragment and an uncharged fragment, depicted in equation 3.6.

$$(\mathbf{A} \cdot \mathbf{B})^+ \longrightarrow \mathbf{A}^+ + \cdot \mathbf{B}$$
 (3.6)

(molecular ion) (fragment cation) (fragment ion) The positively charged fragments are accelerated by an electric field and pass through slits to form a narrow, well-focused beam. This beam of ions then passes through an applied magnetic field. Because an accelerating ion produces its own magnetic field, an interaction with the applied magnetic field occurs, causing the trajectory of the path of ions to change. The amount of path deflection for each ion depends on its mass/charge

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ratio (m/z). Thus, the original beam splits into several beams- ions of small m/z are deflected more than those of larger m/z, causing the ions to separate. In electron impact ionization, singly charged particles are produced, so the charge, z, is one. Therefore, an ion's path will depend on its mass. Only charged particle will be accelerated, deflected and detected by the mass spectrometer. The uncharged particles are removed by a vacuum pump. The detector converts the beam of ions into an electrical signal that can be processed and records the abundance of each m/z. Scanning all m/z values give the distribution of positive ions characteristic of a particular molecule, called a mass spectrum. Therefore, the mass spectrum is essentially a fingerprint for the molecule, which is used to identify the compound or components of a mixture. A schematic representation of a mass spectrometer is shown in Figure 3.5.



Figure 3.5 A Typical Mass Spectrometer

Analysis

GC/MS analysis was performed using electronic impact (EI) ionization mode on a JEOL AX-505H double –focusing mass spectrometer (JEOL, USA, Peabody, MA) interfaced with a Hewlett-Packard 5890J gas chromatograph. A BPX70 capillary column (70% cyanopropyl phenyl , 60-m length, 0.25-mm i.d., 0.25- μ m thickness) from SGE (Austin, TX) was used for the separation of esters. A scanning rate of 5°C/min from a starting temperature of 50°C to a final temperature of 240°C was employed, holding the final temperature isothermally for 22 minutes. An ionization voltage of 70 eV over the mass scanning range of 45-750 atomic mass units was used to fragment the components. The carrier gas was helium and splitless injection at a volume of 1.0 μ L was used. Other operating conditions were injector temperature of 250°C, interface temperature of 240°C, and ion source temperature of 200°C. A NIST/EPA/NIH Mass Spectral Library, Version 2.0, was used for compound identification. Also, a ShraderTSS Pro, Version3.0, operating system (Shrader Analytical and Consulting Labs, Detroit, MI & Jeol Ltd, Peabody, MA) was used for data collection and analysis.

3.5 Thermal Analysis

3.5.1 Thermogravimetrical Analysis

Fundamental Theory of Operation

Thermogravimetry (TGA) is a technique that monitors the mass of the sample as a function of time or temperature in a controlled atmosphere. TGA can also measure the rate of change (derivative) in the weight of a material as a function of temperature or time. This analytical method is most frequently used for thermal stability studies resulting in changes of mass, including oxidative stability and thermal degradation.

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A sample is placed into a tared sample pan, which is attached to a sensitive thermobalance assembly. The sample is suspended directly from the balance beam in order to hang down into a controlled-temperature furnace. In the TGA 2950 design (TA Instruments, New Castle, DE) horizontal purge gas flow is used to ensure good interaction between the sample and purge gas, as well as rapid removal of decomposition products so that undesired recombination effects and interactions of the product gases with the sample suspension system are minimized, reducing weigh loss peak broadening. The sample may be heated or cooled at a selected heating rate (dynamic mode), or it may be maintained under isothermal conditions (static mode). The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight as heat is applied to the sample. Figure 3.6 shows a schematic for the TGA 2950 thermogravimetric analyzer.



Figure 3.6 TGA 2950 Thermogravimetrical Analyzer

Analysis

TGA volatility studies were carried out with a TA Instruments Model TGA 2950 thermobalance (New Castle, DE). The instrument was operated in the dynamic mode with a heating rate of 10°C/min, where 40°C and 350°C were the initial and final temperatures, respectively. On average, 5 mg was the initial mass of each sample analyzed. A reactive atmosphere (air purge gas) surrounding the sample was used to study the effect of air oxidation on volatility and to simulate the environmental conditions of a diesel engine combustion chamber. For oxidative stability studies, the instrument was operated in the static mode at 350°C.

3.5.2 Differential Scanning Calorimetry

Fundamental Theory of Operation

Differential scanning calorimetry (DSC) is a technique used to measure the heat flow associated with thermal transitions in materials as a function of time and temperature, while the temperature of the sample is programmed in an inert or reactive atmosphere. This technique provides qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes. DSC is the most widely used method for thermal analysis.

Figure 3.7 shows the cell compartment of a DSC instrument. A sample pan and an equivalent empty reference pan are equally positioned on identical platforms. These platforms are connected by a constantan thermoelectric disk and surrounded by a controlled temperature furnace. Purge gas is administered to both the reference and sample chamber through an orifice in the heating block wall midway between the platforms. The gas is preheated by circulation through the block before entering the

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sample chamber. This circulation process provides a uniform, stable thermal environment which assures excellent baseline flatness and exceptional sensitivity. As the furnace temperature is heated, or cooled, at a constant scanning rate, heat is symmetrically transferred to the sample and reference through the thermoelectric disk. When the cell arrangement is identical, the same amount heat flows into both the sample and reference. Thus, the differential temperature is zero. However, when this steady-state equilibrium is disturbed by a physical or chemical change of the sample, a temperature difference between the sample and the reference is produced. As a result of this transition, a differential heat flow between the sample and reference is established and measured by thermocouples welded beneath each platform. This measured differential heat flow is converted to differential power as the signal output and recorded as a peak on the thermogram. The area under the peak is directly proportional to the enthalpic change of the sample.



Figure 3.7 Cell Compartment of a Differential Scanning Calorimeter

Analysis

DSC analysis was carried out with a TA Instruments (New Castle, DE) model DSC Q1000, equipped with a 50-position auto-sampler, PC-based controller, and a refrigerated cooling system (RCS) for sub-ambient temperature scans. The TA Instruments DSC Q series are specifically designed to take into consideration extraneous heat flow effects using the advanced T_{ZERO}[™] technology (TA Instruments, New Castle, DE), accounting for the cell resistances and capacitances, as well as pan effects [101]. The DSC chamber was continuously purged with low-pressure nitrogen gas (99,9999%) purity) at a flow rate of 50 mL/min, to create a reproducible and dry atmosphere. On average, 10.0 mg samples were weighted to the nearest 0.1 mg with a microbalance and sealed in aluminum pans. An empty, sealed aluminum pan was used as a reference. For cooling scans, samples were first held isothermally at 40°C for 10 min to establish thermal equilibrium. Previous studies have shown that calorimetric properties vary significantly with temperature scanning rate [27, 102]. It was concluded that, in order to obtain thermal event temperatures close to the thermodynamic value and high accuracy measurements, slow scanning rates should be used. A scanning rate of 5°C/min is a convenient and reliable rate to use because it gives a good combination of resolution and flat baselines [27]. Therefore, after equilibration, the samples were then cooled to -90°C at a cooling rate of 5°C/min and held isothermally for 10 min, then heated back to 40°C at the same rate. Each sample was scanned three consecutive times to eliminate thermal history. The third scan of every sample was taken as the experimental data. Heat flow vs. temperature thermograms were analyzed to determine the crystallization properties of the samples. The DSC instrument was calibrated with high purity metal indium (melting point: 156.51°C, ΔH_{fusion} : 28.71 J/g)

3.5.3 Low-Temperature Flow Properties

Fundamental Theory of Operation: CP, PP, and CFPP

The petroleum industry routinely uses cloud and pour points to characterize lowtemperature properties of diesel fuels. The cloud point measures the temperature at which wax first becomes visible when the fuel is cooled, and the method is published by the ASTM with the designation D 2500 [103]. In the test, a small sample of the fuel is placed in a glass jar, cooled at a specified rate and examined at intervals of 1°C. A thermometer is immersed in the fuel to measure the temperature at the bottom of the jar, where the first waxes appear. It is a subjective test, depending on the operator's judgment that wax particles are visible. The pour point test is used to measure the temperature at which the amount of wax out of solution is sufficient to gel the fuel. It is carried out in a similar fashion and under the same controlled cooling conditions as the cloud point test, except that the thermometer is located with its bulb just below the surface of the fuel, and checks on the conditions of the fuel are made at intervals of 3°C. Checks are made by briefly removing the test jar from the cooling bath and tilting it to see whether the fuel flows. This procedure is continued until the fuel fails to move when the jar is held horizontally for 5 seconds. The pour point test method is published as ASTM D 97 [104]. The experimental apparatus for both the cloud and pour point tests are identical and is illustrated in Figure 3.8.

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Figure 3.8 General Apparatus for Cloud and Pour Point Measurement

The cold filter plugging point represents the highest temperature at which a given volume of fuel fails to pass through a standardized filtration device in a specified time when cooled. In this test, a sample of the fuel is cooled under specified conditions and, at 1°C intervals, is drawn into a pipette under a controlled vacuum through a standardized wire mesh filter. Testing is continued until the amount of wax crystals that have separated out of solution is sufficient to stop or slow down the flow so that time taken to fill the pipette exceeds 60 seconds or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C. The indicated temperature at which the last filtration was commenced is recorded as the cold filter plugging point. The most common standard method used to measure the cold filter plugging point is ASTM D 6371 [105] and the general apparatus is depicted in Figure 3.9.



Figure 3.9 General Apparatus for Cold Filter Plugging Point Measurement Analysis

The low-temperature flow properties (CP, PP, CFPP) on selected ozonated methyl soyate samples were conducted at Savant, Inc. (Midland, MI), an independent laboratory and research center that specializes in ASTM and custom tests on engine oils, transmission fluids, and other lubricants. The test methods used to measure cloud point, pour point, and cold filter plugging point were ASTM D 2500, D 97, and D 6371, respectively.

3.5.4 Viscosity Measurements

Fundamental Theory of Operation

Viscometry deals with the measurement of the flow behavior of liquids. Common instruments, capable of measuring fundamental rheological properties can be categorized as rotational type and tube type [106]. There are three types of shear-induced liquid flow models for rotational type viscometers, including flow between a cone and plate, flow between two parallel plates, and circular flow in the annular gap between two concentric cylinders. Of the three aforementioned models, the concentric cylinder rotational viscometer is a very common instrument for viscosity determination [106]. The most common design for rotational viscometers is the Searle system, illustrated in Figure 3.10. In this system, the inner cylinder, often referred to as the spindle, rotates at a specified, constant speed (n), while the outer cylinder is stationary. The rotating inner cylindrical spindle forces the liquid in the annular gap to flow, causing the sample to exert a resistance, or shear stress, to this rotational movement due to its viscosity. The spindle is operated by a synchronous motor through a calibrated torsion spring. The torque of the fluid against the spindle causes the spring to deflect. Thus, the viscometer measures the torque (Md) required to maintain a constant angular velocity of the cylindrical spindle while immersed in the sample. This measured torque is proportional to the viscosity of the sample and is dependent upon a spindle's rotational speed and geometry. The major advantages of a rotational coaxial cylinder viscometer, also called a Brookfield viscometer, are that continuous measurements can be made at a given shear rate, the dependency of viscosity on time can be readily determined, making it suitable for measuring the viscosity of Newtonian and Non-Newtonian fluids.



Figure 3.10 Searle-Type Rotational Viscometer

Shear rates and shear stresses are mathematically defined for rotational viscometers. By definition, viscosity describes the relationship between shear stress (τ) and shear rate ($\dot{\gamma}$):

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{3.7}$$

Starting with the measured values for torque (Md) and rotational velocity (n), the geometric characteristics of a particular spindle sensor system are accounted and are inherent in equation 3.7 by the spindle geometrical factors f and M. Thus, it can now be supplemented as follows:

$$\eta = \frac{f \cdot Md}{M \cdot n} \tag{3.8}$$

For cylindrical systems:

$$f = \frac{0.01}{2\pi L R_i^2}$$
 and $M = \frac{\pi}{15} \frac{R_a^2}{R_a^2 - R_i^2}$ (3.9)

where:

$$R_i$$
 = spindle radius [m]
 R_a = cup radius [m]
 n = speed of spindle [min⁻¹]

The following assumptions are made in developing the mathematical relationships: flow is laminar and steady, end effects are negligible, test fluid is incompressible, properties are not a function of pressure, temperature is constant (i.e., no increase in temperature due to viscous heating), no slip at the walls of the instrument, and radial and axial velocity components are zero [106].

Analysis

A HAAKE VT550 viscometer (Paramus, NJ) was used to measure the viscosity of selected oil samples at 10°C, 25°C, and 40°C. Spindle type "MV" for the HAAKE VT550 viscometer is primarily used for viscosity measurements of medium-viscosity liquids, such as oils, paints, and emulsions, working in the medium shear rate range. Therefore, this spindle type was used in all viscosity measurements. Table 3.1 lists the spindle's geometric parameters.

Table 3.1 Spindle Geometric Parameters

| Inner Cylinder (R | otor) | Outer Cylinder (Cu | up) | Radii Ratio R _a /R _i | 1.05 |
|-----------------------------|-------|-----------------------------|------|--|------|
| Radius, R _i (mm) | 20.04 | Radius, R _a (mm) | 21.0 | Gap Width (mm) | 0.96 |
| Height, L (mm) | 60.0 | | | Sample Volume (cm ³) | 34.0 |

Chapter 4

Results and Discussion Part I: Structural Analysis & Reaction Kinetics

4.1 FTIR Analysis

Direct structural evidence to the nature of catalytic ozonolysis can be observed from the FTIR spectra as a function of reaction time, which shows the absorption of common functional groups found in the ozonated oil at various frequencies. Figure 4.1 shows the FTIR spectra for the catalytic ozonolysis of low-sat methyl soyate, with a frequency range of 400-4000 cm⁻¹. In order to see the absorption intensities more clearly, the spectrum was divided into two separate regions, A (2400-3800 cm⁻¹) and B (400-2000 cm⁻¹), plotted in Figures 4.2 and 4.3, respectively.



Figure 4.1 FTIR Spectra for the Catalytic Ozonolysis of Low- Sat Methyl Soyate

In region A, a small broad peak is observed at around 3460 cm⁻¹, characteristic of a hydroxyl functional group, OH, and its intensity increases with reaction time. This hydroxyl peak is characteristic in alcohols, hydroperoxides, and carboxylic acids. The typical frequencies of an OH functional group attached to an oxygen atom, like in hydroperoxides, is significantly different from those of carboxylic acids and alcohols. Due to electronegativity differences, the OH stretching mode in hydroperoxides fall at a distinctly higher frequency than in alcohols, which was assigned a value of 3450 cm⁻¹ [107]. According to the GC/MS data, discussed in more detail later, no carboxylic acids are detected in the ozonated oil fraction. Moreover, methanol is being consumed as the reaction progresses, which should result in a decrease, rather than an increase, in the absorption intensity of OH. Thus, it may be deduced that the OH functionality is attributed to hydroperoxides rather than methanol or carboxylic acids. This conclusion is also consistent with the mechanism proposed by Marshall et al. for the oxidative cleavage of alkenes in the presence of methanol. In the mechanism, water is a by-product in the conversion of both the hemiacetal and hydroperoxide intermediates to methyl esters (refer to Figure 1.8). As mentioned in Chapter 1, the secondary ozonide from the combination of the carbonyl compound and carbonyl oxide intermediate, can react with water to produce carbonyl compounds and hydrogen peroxides (refer to Figure 1.6). Likewise, the carbonyl oxide intermediate can react with protic solvents, like water and methanol, to produce hydroperoxides (refer to Figure 1.6).



Figure 4.2 FTIR Spectra for the Catalytic Ozonolysis of Low- Sat Methyl Soyate: Region A

The double bonds, C=C, in the fatty esters were readily attacked and cleaved as expected, which is indicated by the disappearance of the absorbance stretching peak at around 3000 cm^{-1} , with respect to reaction time. Furthermore, the increase in peak height of the methyl group, CH₃, at 2940 cm⁻¹, suggests the formation of additional methyl groups in the ozonated oil. The additional methyl groups arise from the formation of dimethyl esters, where CH₃ is located at both terminal ends of the molecule, and methyl esters alike.

Figure 4.3 shows region B of the FTIR spectra for the catalytic ozonolysis of lowsat methyl soyate. The broadening of the carbonyl peak, C=O, at 1740 cm⁻¹ as a function of time suggests that additional carbonyl groups are formed. The C=O functional group is characteristic in carboxylic acids, ketones, aldehydes, and esters. However, based on GC/MS experimental data, the C=O functionality in the ozonated fuel is most likely due to the presence of esters and aldehydes. The formation of aldehydes may be a result of the secondary ozone, 1,2,4-trioxolane, reacting with water. Moreover, the $C - CH_3$ absorption peak at 1360 cm⁻¹ becomes more intense as the reaction time increases, indicating a high concentration of terminal alkyl hydrocarbon chains.



Figure 4.3 FTIR Spectra for the Catalytic Ozonolysis of Low-Sat Methyl Soyate: Region B

A distinct absorption peak at 1100 cm^{-1} is evident only after the start of ozonolysis and becomes more intense as the reaction time increases. The characteristic bands of the five-member ozonide ring usually differ from the spectra of other peroxy compounds and lie in the 950-1150 cm⁻¹ frequency range [34]. Shown from the data presented in Table 4.1, the infra-red spectra of monomeric and polymeric ozonides are essential identical. Criegee *et al.* [108] studied the infra-red absorption of 18 various types of ozonides and noted that, in the majority of them, a new strong absorption band

appeared after ozonolysis in the 1064-1042 cm-¹ frequency range. Briner and Dallwigk [109-111] confirmed this finding, and Garvin and Schubert [112] also found ozonide absorptions in this region. Thus, the 1100 cm⁻¹ absorption peak present in ozonated methyl soyate is characteristic of an ozonide moiety. Since the infra-red spectra of monomeric and polymeric ozonides are essentially identical, the ozonides formed in the ozonation of methyl soyate may be a mixture of these products. In the proposed mechanism for the conversion of alkene to esters, the extent to which the primary fragments recombine to form the secondary ozonide depends on steric effects [35]. For example, no secondary ozonide is observed with the ozonolysis of mono-substituted olefins, whereas the ozonolysis of di- and tri-substituted systems give rise to significant quantities of the secondary ozonide [35]. These results are compared in Table 4.2 and Figure 4.4. Therefore, secondary ozonides present in ozonated methyl soyate may have been formed as a result of steric effects inherent in the structure of methyl soyate, which is a mixture of long-chain saturated and unsaturated hydrocarbons.

| Compound | Structure | Absorption |
|---------------------------------------|---|-------------------------------|
| | | (C-O ring bond) |
| | | cm ⁻¹ |
| Monomeric ozonide of 1-hexene | $CH_3(CH_2)_3CH$ CH_2 | 1100; 1040; 985 ^a |
| Polymeric ozonide of 1-hexene | $ \begin{pmatrix} O - CH - OO - CH_2 \\ I \\ (CH_2)_3 CH_3 \end{pmatrix}_{X} $ | 1100; 1040; 985 ^a |
| Monomeric ozonide of methyl oelate | ⁰ −0 CH ₃ (CH2) ₇ CH CH(CH ₂) ₇ COOCH ₃ | 1109, 1110, 1109 ⁶ |

Table 4.1 Characteristic Absorption Frequencies for Several Ozonides

^aRef. [113]; ^bRef. [114]

| Reaction A | | | | | |
|---|--------------------------|-------|--------------|--------------|--|
| R ₁ | R ₂ | | A1, yield, % | | |
| CH ₃ (CH ₂) ₅ (hexyl) | CH ₃ (methyl) | | 63 | | |
| | Reacti | ion B | | | |
| Rı | R ₂ | R_3 | B1, yield, % | B2, yield, % | |
| CH ₃ (methyl) | Н | Η | 56 | 19 | |
| $CH_3(CH_2)_3$ (butyl) | Н | Η | 57 | 29 | |

 Table 4.2 Direct Conversion of Olefins to Esters: Nomenclature and Yields



Figure 4.4 Direct Conversion of Olefins to Esters Adopted from Ref. [35]

The FTIR spectra for the volatile fraction of ozonated low-sat methyl soyate under catalytic conditions is depicted in Figure 4.5. Based on GC/MS data, the OH absorption peak, 3340 cm⁻¹, is mainly due to the presence of excess or unreacted methanol and trace amounts of carboxylic acids. The C-O absorption peak characteristic of an ozonide, 1026 cm⁻¹, is more prevalent in the volatile fraction than in the oil fraction, confirming that ozonides are being condensed and collected in the dry-ice trap before unreacted ozone is decomposed in the KI destruction unit. The C-O peak, 1100 cm⁻¹, due to the presence of esters, is also distinct in the volatile fraction spectra.



Figure 4.5 FTIR Spectra for the Catalytic Ozonolysis of Low-Sat Methyl Soyate: Volatile Fraction

The FTIR spectra for the non-catalytic ozonolysis of low-sat methyl soyate, noncatalytic and catalytic ozonolysis of regular methyl soyate, were all analogous to that of the catalytic ozonolysis of methyl soyate. The difference in their spectra is the absorption intensities. Table 4.3 lists the theoretical and experimental frequencies of the functional groups present in both the oil and volatile fractions of ozonated methyl soyate.

Table 4.3 Theoretical and Experimental Absorption Frequency Ranges forCommon Functional Groups Present in Ozonated Methyl Soyate

| | Stretching Mode | | Bending Mode | |
|---------------------------------|------------------------|-----------------------|------------------------|-------------------------|
| | Theoretical | Experimental | Theoretical | Experimental |
| Functional | Frequency ^a | Frequency | Frequency ^a | Frequency |
| Group | cm ⁻¹ | cm ⁻¹ | cm ⁻¹ | cm ⁻¹ |
| <u>Alkanes</u> | | _ | • | |
| CH ₃ | 2850-2950 | 2940 | | |
| C – CH ₃ | | | 1370-1380 | 1365 |
| CH ₂ | 2900-2940 | 2925 | 1445-1485 | 1430-1460 1400-1440* |
| (CH ₂) ₄ | | | 750-720 | 720 |
| СН | 2850-2970 | 2850 | 1240-1470 | |
| Alkenes | • | • | • | |
| c=c | 3010-3040 | 3000 | | |
| Hydroxyl | | | | |
| OH _{alcohol} | 3280-3450 | 3340* | 1260-1350 | |
| OH _{carboxlyic} acid | 3500-3600 | 3340* | | |
| OH _{hydroperoxide} | 3450-3650 | 3450 | | |
| Carbonyl | · | • | | • |
| $C = O_{ester}$ | 1717-1750 | 1740 | | |
| $C = O_{aldehyde}$ | 1660-1740 | 1740 | | |
| C – O | 1025-1300 | 1170-1190 1100* | | |
| <u>Ozonides</u> | 1042-1064 | 1100 1026 * | | |

^aSource: Ref. [115], *Denotes the frequencies for the volatile fraction

4.2 NMR Analysis

Selected ozonated methyl soyate samples of both low-sat and regular were analyzed by ¹H NMR to confirm the existence of ozonides and hydroperoxides. In general, the proton in the 1,2,4-trioxolane ring resonated at about δ 5.15 ppm. The aldehydic proton is also detected at both δ 9.75 and δ 9.63 ppm, while δ 5.55 ppm is the olefinic signal from hydroperoxides. These specific resonances were absent in nonozonated methyl soyate. The ¹H NMR spectra for non-ozonated and ozonated low-sat methyl soyate are depicted in Figures 4.6 and 4.7, respectively. The experimental findings were consistent with those found in the literature, based on the ozonation of various pure esters and vegetable oil. The ¹H NMR spectrum of methyl linoleate ozonation in ethanol showed multiplets between δ 5.10 and δ 5.3, attributed to the Criegee ozonide signal, and a triplet at $\delta 9.75$ from the aldehydic proton [116]. Ozonolysis of sunflower oil in the absence and presence of water was monitored by ¹H NMR [117]. The NMR analysis showed that products in both cases included aldehydes, δ 9.75, and ozonides with 1,2,4-trioxolane ring, δ 5.17. Diaz et al. [118] conducted spectroscopic characterization experiments for the ozonation of sunflower oil. Ozonation products of sunflower oil were identified by ¹H, ¹³C, and two-dimensional ¹H NMR. The virgin sunflower oil and ozonated sunflower oil showed very similar ¹H NMR spectra; except for the resonances at δ 9.74 and δ 9.63 ppm, both corresponding to aldehydic protons, δ 5.60 ppm, the olefinic signal from hydroperoxides, and δ 5.15 ppm, proton from ozonides.



Figure 4.6 ¹H NMR Spectra for Non-Ozonated Low-Sat Methyl Soyate



Figure 4.7 ¹H NMR Spectra for the Catalytic Ozonated Low-Sat Methyl Soyate

4.3 GC Analysis

Transesterification

Transesterification reaction experiments were carried out for both regular and low-sat RB soybean oil. The fatty acid composition, shown in Table 4.4, for both transesterified oils (methyl soyate) was determined by GC, using the internal standard quantification method described in Chapter 3. The fatty acid composition of regular methyl soyate was comparable to other published data [98, 119]. Low-sat methyl soyate contained about half of the amount of saturation contained in regular methyl soyate. Figures 4.8 and 4.9 show the chromatograms for low-sat and regular methyl soyate, respectively. The peak that eluted at a retention time of about 29 minutes is methyl undecanoate, the chosen internal standard.

 Table 4.4 Fatty Acid Composition of Transesterified, RB Soybean Oils

Low-Sat Soybean Regular Soybean Weight Weight Component **Retention Time Retention Time** mins (%) mins % 10.25 Methyl Palmitate 39.586 3.93 39.638 Methyl Stearate 43.665 3.75 43.570 4.89 Methyl Oleate 44.302 24.76 44.207 24.36 Methyl Linoleate 45.420 51.89 45.529 58.86 Methyl Linolenate 46.646 8.70 46.572 8.61



Figure 4.8 Chromatogram of Transesterified Low-Sat Soybean Oil



Figure 4.9 Chromatogram of Transesterified Regular Soybean Oil

Ozonolysis & Reaction Kinetics

The reactor system for the ozonolysis of methyl soyate was modeled as a semibatch reactor. The semi-batch reactor is typically used for two-phase reactions in which a gas is usually bubbled continuously through a liquid [120]. For a constant-volume batch system, the mass balance for component i is

$$-r_{i} = \frac{dC_{i}}{dt}$$
(4.1)

Thus, the rate of reaction of any component is given by the rate of change of its concentration. For a constant-volume reactor, it is assumed that the reactor is perfectly mixed so that the concentration of the reacting species is spatially uniform. In this study, the concentration of selected reaction components was quantified using the internal

standard method from the GC data. Both the differential and integral methods were used to determine the reaction order, α , and the reaction rate, k, for each specified reactant component of the methyl soyate mixture.

Integrating equation 4.1 with $C_i = C_{iO}$ at t = 0, and setting r_i equal to the reaction constant, k_i , for a zero-order reaction,

$$C_i = C_{i0} - k_i t$$
 (4.2)

Thus, a plot of the concentration of component *i* as a function of time is linear with slope k. Methyl palmitate, stearate, and oleate all fit a zero-order equation for the ozonolysis of regular and low-sat methyl soyate, under both catalytic and non-catalytic conditions alike. Figure 4.10 shows the kinetic data for these three constituents in the catalytic ozonolysis of low-sat methyl soyate. Each data point represents a single ozonolysis reaction. The reaction rate constants for methyl palmitate, stearate, and oleate for the ozonolysis of low-sat and regular methyl soyate, are compared in Tables 4.5 and 4.6, respectively. In general, the rate of reaction was slightly faster in the presence of the alkaline catalyst, as expected. For methyl palmitate, the reaction rate for ozonated regular methyl soyate was nearly twice that for ozonated low-sat methyl soyate. Regular and low-sat methyl soyate are comprised of about 85 wt% and 92% unsaturates, respectively. So, the starting concentration of double bonds is less for regular methyl soyate, which may result in an increase in the reactivity of methyl palmitate. Moreover, the reaction rate constants for low-sat methyl stearate and oleate are slightly higher than that of regular methyl stearate and oleate. This observation may be due to less steric hindrance, or steric effect arising from the crowding of molecules, in low-sat methyl soyate because of the reduced amount of saturated molecules. Therefore, these

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experimental findings suggest that the kinetics of methyl soyate is influenced by both the amount of double bonds and steric effects inherent in its molecular structure.



Figure 4.10 Kinetics for the Catalytic Ozonolysis of Low-Sat Methyl Soyate: Methyl Palmitate, Methyl Stearate, Methyl Oleate Constituents

*Data is on the secondary y-axis

| Table 4.5 | Reaction Rate | Constants for t | he Ozonolysis | of Low-Sat | Methyl Soyate: |
|-----------|----------------------|-----------------|---------------|------------|----------------|
| Methyl Pa | lmitate, Steara | te, Oleate Cons | tituents | | |

| Catalytic | | | | | |
|------------------|---|-----------|---------------------|----------------|--|
| Component | Estimate of k | Standard | 95% Confidence | R ² | |
| - | $(mg/\mu L) \ge 10^3 \cdot min^{-1}$ | Error | Level | | |
| Methyl Palmitate | -0.0353 | ±0.00295 | (-0.0428, -0.0277) | 0.966 | |
| Methyl Stearate | -0.0476 | ±0.00556 | (-0.0619, -0.0333) | 0.936 | |
| Methyl Oleate | -0.710 | ±0.0429 | (-0.820, -0.560) | 0.982 | |
| | Non-C | Catalytic | | | |
| Component | Estimate of k | Standard | 95% Confidence | R ² | |
| | $(mg/\mu L) \times 10^3 \cdot min^{-1}$ | Error | Level | | |
| Methyl Palmitate | -0.0257 | ±0.00789 | (-0.0460, -0.00539) | 0.679 | |
| Methyl Stearate | -0.0426 | ±0.00241 | (-0.0488, -0.0364) | 0.984 | |
| Methyl Oleate | -0.704 | ±0.0455 | (-0.821, -0.587) | 0.980 | |

 Table 4.6 Reaction Rate Constants for the Ozonolysis of Regular Methyl Soyate:

 Methyl Palmitate, Stearate, Oleate Constituents

| Catalytic | | | | | |
|------------------|--|------------------|----------------------|----------------|--|
| Component | Estimate of k | Standard | 95% Confidence | R ² | |
| | $(mg / \mu L) \ge 10^3 \cdot min^{-1}$ | Error | Level | | |
| Methyl Palmitate | -0.0754 | ±0.0138 | (-0.111, -0.0400) | 0.857 | |
| Methyl Stearate | -0.0268 | ±0.0101 | (-0.0527, -0.000833) | 0.585 | |
| Methyl Oleate | -0.650 | ±0.0549 | (-0.791, -0.509) | 0.966 | |
| | <u>Non-C</u> | <u>Catalytic</u> | | | |
| Component | Estimate of k | Standard | 95% Confidence | R ² | |
| | $(mg/\mu L) \ge 10^3 \cdot min^{-1}$ | Error | Level | | |
| Methyl Palmitate | -0.0606 | ±0.0133 | (-0.0948, -0.0265) | 0.806 | |
| Methyl Stearate | -0.0241 | ±0.00932 | (-0.0481, -0.000142) | 0.572 | |
| Methyl Oleate | -0.636 | ±0.0479 | (-0.759, -0.513) | 0.972 | |

Shown in Figure 4.11, the concentration-time data for the polyunsaturated methyl esters, linolenate and linolenate, fit very well to 2nd-order polynomials. This observation holds true for ozonated low-sat and regular methyl soyate under both catalytic and non-catalytic conditions. Therefore, the differential method for rate analysis was used to analyze the kinetics of these two constituents. In the this method of rate data analysis, it is assumed that the rate law is of the form

$$-r_i = kC_i^{\alpha} \tag{4.3}$$

where α is the reaction order [120]. Combining equation 4.1 and 4.3 and taking the natural logarithm,

$$\ln\left(-\frac{dC_i}{dt}\right) = \ln k_i + \alpha \ln C_i \qquad (4.4)$$

Thus, the slope of plot $\ln(-dC_i/dt)$ versus (\ln/C_i) is the reaction order, α , and the yintercept is the natural logarithm of the rate constant, k, depicted in Figure 4.12. The kinetic data for the ozonolysis of low-sat and regular methyl soyate containing the polyunsaturated constituents are compared in Tables 4.7-4.10. For the methyl linoleate constituent, the rate of reaction was slightly faster under catalytic conditions. As previously mentioned, there is less steric hindrance in the low-sat mixture because the bulky long-chain saturated hydrocarbons are reduced to half the amount compared to that of regular methyl soyate. Moreover, the starting amount of polyunsaturates is greater for low-sat methyl soyate, increasing the reactivity of these compounds due to the presence of double bonds. Thus, the rate of reaction is faster when both linoleate and linolenate are comprised in the low-sat mixture. It appears that, for methyl linolenate, the presence of the catalyst has no effect on the reaction rate. Moreover, the degradation of methyl linolenate was approximately three times faster than that of methyl linoleate. This observation suggests that the rate of ozonolysis is heavily dependent on the number of double bonds in the mixture, as predicted. For example, in lipid oxidation, the relative autoxidation rate of methyl linoleate to methyl linolenate was found to be about 1:1.5 [12].





*Data is on the secondary y-axis



Figure 4.12 Linear Relationship of the Kinetics for the Catalytic Ozonolysis of Low-Sat Methyl Soyate: Methyl Linoleate, Linolenate Constituents

Table 4.7 Reaction Rate Constant for the Ozonolysis of Low-Sat Methyl Soyate: Methyl Linoleate, Linolenate Constituents

| | Catalytic Ozor | nolysis | | |
|-------------------|--|-----------|----------------|----------------|
| Component | Estimate of ln k | Standard | 95% Confidence | R ² |
| | $[(mg/\mu L) \times 10^3]^{1-\alpha} \cdot min^{-1}$ | Error | Level | |
| Methyl Linoleate | -2.22 | ±0.0804 | (-2.43, -2.01) | 0.996 |
| Methyl Linolenate | -3.30 | ±0.214 | (-3.89, -2.70) | 0.963 |
| | Non-Catalytic Oz | conolysis | | |
| Component | Estimate of ln k | Standard | 95% Confidence | R ² |
| | $[(mg/\mu L) \times 10^3]^{1-\alpha} \cdot min^{-1}$ | Error | Level | |
| Methyl Linoleate | -2.77 | ±0.294 | (-3.53, -2.02) | 0.964 |
| Methyl Linolenate | -3.36 | ±0.152 | (-3.78, -2.94) | 0.981 |

Table 4.8 Reaction Rate Constant for the Ozonolysis of Regular Methyl Soyate: Methyl Linoleate, Linolenate Constituents

| Catalytic Ozonolysis | | | | | |
|----------------------|--|-----------|----------------|----------------|--|
| Component | Estimate of ln k Standar | | 95% Confidence | R ² | |
| | $[(mg/\mu L) \times 10^3]^{1-\alpha} \cdot min^{-1}$ | Error | Level | | |
| Methyl Linoleate | -2.95 | ±0.524 | (-4.29, -1.60) | 0.886 | |
| Methyl Linolenate | -2.87 | ±0.0736 | (-3.07, -2.66) | 0.992 | |
| | Non-Catalytic Oz | conolysis | | | |
| Component | Estimate of ln k | Standard | 95% Confidence | R ² | |
| | $[(mg/\mu L) \times 10^3]^{1-\alpha} \cdot min^{-1}$ | Error | Level | | |
| Methyl Linoleate | -2.11 | ±0.194 | (-2.61, -1.61) | 0.971 | |
| Methyl Linolenate | -2.68 | ±0.118 | (-3.00, -2.35) | 0.976 | |

Table 4.9 Reaction Order Constant for the Ozonolysis of Low-Sat Methyl Soyate: Methyl Linoleate, Linolenate Constituents

| Catalytic Ozonolysis | | | | |
|----------------------|----------------------|-------------------|-------------------------|----------------|
| Component | Estimate of α | Standard Error | 95% Confidence Level | R ² |
| Methyl Linoleate | 0.576 | ±0.0164 | (0.534, 0.618) | 0.996 |
| Methyl Linolenate | 0.725 | ±0.0713 | (0.527, 0.923) | 0.963 |
| | Non-Catalytic (| Dzonolysis | | |
| Component | Estimate of α | Standard | 95% Confidence | R ² |
| | | Error | Level | |
| Methyl Linoleate | 0.684 | ±0.0594 | (0.531, 0.836) | 0.964 |
| Methyl Linolenate | 0.739 | ±0.0511 | (0.598, 0.881) | 0.981 |

 Table 4.10 Reaction Order Constant for the Ozonolysis of Regular Methyl Soyate:

 Methyl Linoleate, Linolenate Constituents

| Catalytic Ozonolysis | | | | | |
|----------------------|----------------------|------------------|----------------|----------------|--|
| Component | Estimate of α | Standard | 95% Confidence | R ² | |
| | | Error | Level | | |
| Methyl Linoleate | 0.715 | ±0.115 | (0.420, 1.01) | 0.886 | |
| Methyl Linolenate | 0.605 | ±0.0266 | (0.531, 0.679) | 0.992 | |
| | Non-Catalytic Oz | <u>zonolysis</u> | | | |
| Component | Estimate of α | Standard | 95% Confidence | R ² | |
| | | Error | Level | | |
| Methyl Linoleate | 0.539 | ±0.0417 | (0.431, 0.646) | 0.971 | |
| Methyl Linolenate | 0.528 | ±0.0414 | (0.413, 0.643) | 0.976 | |

Figure 4.13 shows the relative amounts of degradation for each of the unsaturated constituents. Nearly all of the double bonds of methyl linolenate were decomposed after 3 hours of ozonolysis, with more than a 98% reduction . Likewise, methyl linoleate and oleate had over 94% and 80% reduction in double bonds, respectively. Thus, the total amount of double bonds in the mixture were reduced by more than 90% after three hours of ozonolysis .



Figure 4.13 Relative Amounts of Double Bond Degradation for the Unsaturated Moieties

The concentration of selected products was also determined by GC. Methyl hexanoate, nonanoate, and dimethyl azelate were the predicted compounds formed based on the original hypothesis, confirming the direct conversion of olefins to esters via ozonolysis. The amount of these compounds produced was higher for catalytic ozonolysis than for non-catalytic ozonolysis. Figure 4.14 shows the amount of these compounds produced in the catalytic ozonolysis of low-say methyl soyate. Initially, more dimethyl azelate is formed than methyl nonanoate; but after a reaction time of 120 mins, more nonanoate is formed. Similar observations were also found for the ozonolysis of regular methyl soyate.



Figure 4.14 Kinetics for the Catalytic Ozonolysis of Low-Sat Methyl Soyate: Methyl Hexanoate, Nonanoate and Dimethyl Azelate Ester Products

4.4 GC/MS Analysis

All major products of ozonated methyl soyate were identified based on molecular weights using GC-MS. Since GC analysis confirmed that the same products were formed for both ozonated regular and low-sat methyl soyate under catalytic and non-catalytic conditions, only the catalytic ozonolysis of low-sat methyl soyate will be discussed in further detail from this point onward. Figures 4.15 and 4.16 show chromatograms of non-ozonated and ozonated low-sat methyl soyate for 180 minutes, respectively. For each scan, a mass spectrum was generated and each peak was identified by molecular weight. The statistical probability of the match between the experimental and theoretical mass spectrums for all identified peaks was above 75%. This number represents the likelihood of the identified peaks based on the NIST library database of mass spectrums. Identification of the majority of peaks and their structure are listed in Table 4.11. Unlabeled peaks in Figure 4.16 indicate that they were unidentifiable by the library database.



Figure 4.15 Chromatogram of Non-Ozonated Low-Sat Methyl Soyate *Internal Standard



Figure 4.16 Chromatogram of Ozonated Low-Sat Methyl Soyate at a Reaction Time of 180 mins *Internal Standard

Table 4.11Peak Identifications and Their Structures for Ozonated Low-Sat MethylSoyate at a Reaction Time of 180 mins

| Peak | Component | Functional | Structure | Statistical |
|------|----------------------------|------------|---|-------------|
| | | Group | | Match |
| Α | Hexanal | aldehyde | $\sim \sim _0$ | 93.3% |
| В | Methyl Hexanoate | ester | | 94.1% |
| С | Methyl Octanoate | ester | | 90.6% |
| D | Nonanal | aldehyde | | 87.8% |
| E | 4-Nonenal | aldehyde | ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ | 85.2% |
| F | Methyl Nonanoate | ester | | 91.9% |
| G | Methyl 3- Nonenoate | ester | | 87.7% |
| Н | Methyl Decanoate | ester | | 78.7 |
| *1 | Methyl Undecanoate | ester | | 88.1% |
| I | Methyl 10- Undecanoate | ester | | 85.1% |
| 2 | Methyl Palmitate | ester | | 89.4% |
| J | Dimethyl Azelate | ester | | 92.7% |
| К | Methyl 9-Oxo- Nonanoate | ester | ~0 ~~~~~~ 0 | 92.2% |
| 3 | Methyl Stearate | ester | | 84.2% |
| 4 | Methyl Oleate | ester | | 92.6% |
| 5 | Methyl Linoleate | ester | | 91.5% |
| 6 | Methyl Linolenate | ester | | 87.7% |

*Internal Standard
Three of the expected esters from the oxidative cleavage of low-sat methyl soyate by ozone were detected. These products include methyl hexanoate, nonanoate, and methyl azelate. Figures 4.17-4.19 show the experimental mass spectra (top) for these esters and their corresponding theoretical mass spectra (bottom) that was generated by the NIST/EPA/NIH mass spectral library.



Figure 4.17 Mass Spectra of Methyl Hexanoate

Three of the expected esters from the oxidative cleavage of low-sat methyl soyate by ozone were detected. These products include methyl hexanoate, nonanoate, and methyl azelate. Figures 4.17-4.19 show the experimental mass spectra (top) for these esters and their corresponding theoretical mass spectra (bottom) that was generated by the NIST/EPA/NIH mass spectral library.



Figure 4.17 Mass Spectra of Methyl Hexanoate







Figure 4.19 Mass Spectra of Dimethyl Azelate

Since the internal standard solution contained only selected esters, the area percent GC quantification method was used to estimate the amount of all the identifiable components in the catalytic, ozonated low-sat methyl soyate mixture that are listed in Table 4.11. This method assumes that the detector responds identically to all compounds. However, due to the complexity of the structures in the product mixture, this assumption is not valid. Thus, this method provides a rough estimate of the amounts of analytes present. To calculate the area percent, the peak area of an analyte is divided by the sum of all the peak areas. This value represents the percentage of an analyte in the sample. The peak area percent divided by 100 is roughly equal to the mass fraction. The area percents for all components were automatically calculated by the GC integrator. Since methanol (area percent = 86.72634) and the internal standard (area percent = 1.97269) were not in the original product mixture, the area percent for the major identifiable components was normalized. The total sum of the peak area percentages for methanol, internal standard, and the major compounds was about 98%. The final mass of the ozonated mixture after a reaction time of 180 mins, minus the mass of the catalyst, was determined to be about 141 grams by gravimetrical means. Thus, a rough mass estimate for each product component can be determined, as shown in Table 4.12.

Table 4.12 Mass Estimation for the Major Components in the Catalytic, Ozonated Low-Sat Methyl Soyate at a Reaction Time of 180 mins

| Peak | Component | Peak Area | Normalized Peak | Component Mass |
|------|---------------|-----------|-----------------|----------------|
| | | Percent | Area Percent | in Mixture |
| | | | | (grams) |
| Α | Hexanal | 0.67235 | 7.34231 | 10.35266 |
| В | Methyl | 0.29255 | 3.19475 | 4.50460 |
| | Hexanoate | | | |
| C | Methyl | 0.35690 | 3.89748 | 5.49545 |
| | Octanoate | | | |
| D | Nonanal | 0.03059 | 0.33405 | 0.47101 |
| E | 4-Nonenal | 0.06597 | 0.72042 | 1.01579 |
| F | Methyl | 0.79361 | 8.66651 | 12.21978 |
| | Nonanoate | | | |
| G | Methyl 3- | 0.63805 | 6.96774 | 9.82451 |
| | Nonenoate | | | |
| Н | Methyl | 0.07138 | 0.77950 | 1.09910 |
| | Decanoate | | | |
| Ι | Methyl 10- | 0.07553 | 0.82482 | 1.16300 |
| | Undecanoate | | | |
| 2 | Methyl | 0.80435 | 8.78380 | 12.38516 |
| | Palmitate | | | |
| J | Dimethyl | 0.60593 | 6.61698 | 9.32994 |
| | Azelate | | | |
| K | Methyl 9- | 2.19400 | 23.95923 | 33.78251 |
| | Oxo- | | | |
| | Nonanoate | | | |
| 3 | Methyl | 0.55520 | 6.06299 | 8.54882 |
| | Stearate | | | |
| 4 | Methyl Oleate | 1.12714 | 12.30878 | 17.35538 |
| 5 | Methyl | 0.83324 | 9.09929 | 12.82999 |
| | Linoleate | | | |
| 6 | Methyl | 0.04041 | 0.44129 | 0.62222 |
| | Linolenate | | | |

Unlike in the FTIR and NMR analysis, which were conducted at room temperatures, no hydroperoxides or ozonides were detected by GC or GC/MS in the ozonated oil. Most hydroperoxides become unstable at temperatures above 70°C [34]. Due to the GC column temperature increasing at a scanning rate of 5°C/min from an initial temperature of 50°C up to a final temperature of 240°C, the hydroperoxides and ozonides present in the ozonated fuel were most likely thermally decomposed during the GC/MS analysis. The main decomposition products include aldehydes and carboxylic acids. For ozonides, the driving force for its decomposition is the cleavage of the energy-rich O-O bond and the release of conformational strain present in the trioxolane ring [34].

Components present in the corresponding volatile fraction were also identified by GC/MS. Figure 4.20 shows the chromatogram for the volatile fraction of ozonated lowsat methyl soyate, which corresponds to the oil fraction presented in Figure 4.16. Table 4.13 lists the identified compounds and their corresponding structures. The statistical probability of the match between the experimental and library database mass spectrums for all identified peaks was above 70%. Unlabeled peaks in Figure 4.20 indicate that they were unidentifiable by the library database. The aldehydes formed were also the volatile products formed in the ozonation of sunflower oil [121]. Moreover, 1,1,3,3-Tetramethoxy-Propane (peak 1) and Methyl, 3-3-Dimethoxy-Propionate (peak 7) are the derivative forms of dimethyl malonate that were present in the volatile fraction. Dimethyl malonate is one of the predicted esters that is theoretically formed from the oxidative cleavage of methyl linoleate and linolenate.



Figure 4.20 Chromatogram of Ozonated Low-Sat Methyl Soyate at a Reaction Time of 180 mins: Corresponding Volatile Fraction

| Peak | Component | Functional | Structure | Statistical |
|------|-------------------------------------|------------|---|-------------|
| | | Group | | Match |
| 1 | 1,1,3,3-Tetramethoxy- Propane | acetal | | 70% |
| 2 | Hexanal | aldehyde | | 89.6% |
| 3 | 1,1-Dimethoxy- Hexane | acetal | | 82.7% |
| 4 | Methyl Hexanoate | ester | | 93.1% |
| 5 | 1,1-Dimethoxy- Heptane | acetal | | 83.6% |
| 6 | 1,1-Dimethoxy- Octane | acetal | | 81.4% |
| 7 | Methyl,3,3- Dimethoxy-Propionate | ester | ~0 ~0 ~0 0 | 77.8% |
| 8 | 1,1-Dimethoxy- Nonane | acetal | | 75.7% |
| 9 | Methyl Nonanoate | ester | | 88.3% |
| 10 | Methyl Decanoate | ester | | 73.7% |
| 11 | Hexanoic acid | acid | | 77.1% |
| 12 | Methyl Undecanoate | ester | | 88.5% |
| 13 | Phenol | alcohol | ОН | 84.1% |
| 14 | Methyl Palmitate | ester | | 76.1% |
| 15 | Dimethyl Azelate | ester | $\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array}$ | 88.1% |
| 15 | Methyl Stearate | ester | | 85.6% |

 Table 4.13 Peak Identifications and Their Structures for Ozonated Low-Sat Methyl

 Soyate at a Reaction Time of 180 mins: Volatile Fraction

Many of the major products present in the volatile fraction were acetals. One possibility of their formation is the reaction of aldehydes with methanol under acid catalytic conditions. The overall reaction mechanism, illustrated in Figure 4.21, proceeds in four stages. The hemiacetal is formed in the first stage by nucleophilic addition of the alcohol to the carbonyl group (1). Under the acidic conditions of its formation, the hemiacetal is converted to an acetal by way of a carbocation intermediate (2). This carbocation is stabilized by electron release from its oxygen substituent (3). Finally, nucleophilic capture of the carbocation intermediate by an alcohol molecule leads to an acetal (4). Hexanoic acid, a carboxylic acid, was formed in the volatile fraction. Thus, it may serve as the acid that catalyzed the reaction of acetal formation. This carboxylic acid may have been formed by the hydrolysis of the secondary ozonide (refer to Figure 1.6); or by ester hydrolysis, shown in Figure 4.22.



Figure 4.21 Overall Reaction Mechanism for Acetal Formation



Figure 4.22 Hydrolysis of Ester

Similar products formed in the ozonation of methyl soyate were also formed in the autoxidation of pure methyl oleate, linoleate, and linolenate [122, 123]. The volatile by-products produced during the autoxidation of methyl oleate, linoleate, linolenate, under the influence of metallic promoters was studied [122]. The components of the byproducts were separated and identified by GC/MS. Air or oxygen was bubbled through the methyl esters containing the desired amount of promoter via a gas washing bottle at 20°C for 10 hours. The volatile by-products were collected in a cryogenic trapping system. Table 4.14 lists some of the autoxidation volatile by-products derived from the three esters. In a similar study conducted by Frankel *et al.* [123], pure hydroperoxides from autoxidized methyl oleate, linoleate, and linolenate were thermally decomposed and the major volatile products were identified. The GC/MS analysis of volatile compounds from thermally decomposed hydroperoxides are presented in Table 4.15. This work also supports the fact that hydroperoxides of ozonated methyl soyate were thermally decomposed during GC/MS analysis, based on the similarity in product distribution.

| Table 4.14 | Products Formed | During the | Autoxidation | of Methyl | Oleate, Linol | eate, |
|-------------------|------------------------|-------------------|-------------------------------|-----------|---------------|-------|
| and Linole | nate in the Present | t of Metallic | Promoters ^a | | | |

| Methyl Oleate | Methyl Lino | leate | Methyl Linolenate | | |
|---------------|-------------|------------------|-------------------|------------------|--|
| Cobalt/lead | Cobalt/lead | Cobalt/Aluminum | Cobalt/lead | Cobalt/aluminum | |
| propanal | hexanal | hexanal | propanal | propanal | |
| hexanal | 2-hexenal | methyl hexanoate | methyl | methyl octanoate | |
| | | | octanoate | | |
| octanal | hexanoic | methyl | 2-pentenal | 2-pentenal | |
| | acid | heptanoate | | | |
| nonanal | methyl | methyl octanoate | | | |
| | octanoate | | | | |

^aSource: Ref. [122]

 Table 4.15 Volatile Compounds of the Thermally Decomposed Pure Hydroperoxides

 from Autoxidized Methyl Oleate, Linoleate, and Linolenate^a

| Methyl Oleate | | Methyl L | inoleate | Methyl Linolenate | |
|---------------|----------|-----------|----------|-------------------|----------|
| Compound | Weight % | Compound | Weight % | Compound | Weight % |
| octanal | 11 | hexanal | 15 | propanal | 7.7 |
| nonanal | 15 | 2-nonenal | 1.4 | decatrienal | 14 |
| methyl 9-oxo- | 15 | methyl 9- | 19 | methyl 9-oxo- | 13 |
| nonanoate | | oxo- | | nonanoate | |
| | | nonanoate | | | |
| methyl | 5 | methyl | 15 | methyl | 22 |
| octanoate | | octanoate | | octanoate | |
| methyl | 1.5 | | | 2,4- | 9.3 |
| nonanoate | | | | heptadienal | |
| methyl 10- | 12 | | | | |
| oxo-decanoate | | | | | |

^aSource: Ref. [123]

Based on these studies, major products formed in the ozonolysis of methyl soyate may be attributed to autoxidation from oxygen in the O₃/O₂ gaseous mixture. To confirm this hypothesis, regular biodiesel, in the presence of methanol and calcium carbonate as the catalyst, was oxidized with oxygen for 180 mins, using the same experimental set-up and conditions employed in the ozonolysis experiments. The GC chromatogram of the oxidized oil is illustrated in Figure 4.23. The double bond decomposition comparison between the autoxidation and ozonolysis of biodiesel is depicted in Table 4.16. Like in the ozonolysis experiments, the volatile products of autoxidized methyl soyate were collected and analyzed. Figure 4.24 shows the chromatogram of the volatile fraction from autoxidized regular methyl soyate, where Table 4.17 lists the compounds and structures for each identifiable peak. Indeed, many of the same products from the ozonation experiments were formed in the autoxidation experiments. The amount of double bond decomposition was significantly lower when ozone was not used as the

primary oxidant. Thus, it may be deduced that ozone was simultaneously inducing lipid oxidation (ozone-induced oxidation) and oxidatively cleaving the alkene moiety (ozonolysis) of biodiesel during the oxidation experiments. In fact, in addition to the use of ozone as the primary oxidant in the synthesis of a range of oxygen-containing functional groups, there are many applications in which ozone serves only as a catalyst or initiator for another oxidant, usually oxygen [124-126].



Figure 4.23 Chromatogram of the Autoxidation of Regular Methyl Soyate at a Reaction Time of 180 mins

 Table 4.16 Double Bond Decomposition Comparison Between the Autoxidation and

 Ozonolysis of Regular Methyl Soyate

| Component | C/Co | C/Co | |
|-------------------|--------------|------------|--|
| | Autoxidation | Ozonolysis | |
| Methyl Oleate | 0.8253 | 0.2184 | |
| Methyl Linoleate | 0.8031 | 0.0764 | |
| Methyl Linolenate | 0.6703 | 0.0259 | |



Figure 4.24 Chromatogram for the Autoxidation of Regular Methyl Soyate at a Reaction Time of 180 mins: Volatile Fraction

| Table 4.17 | Peak Identifica | tions and Their | · Structures for | r the Autoxidation | of |
|-------------------|------------------------|-----------------|------------------|--------------------|----|
| Regular M | ethyl Soyate at a | a Reaction Time | e of 180 mins: ` | Volatile Fraction | |

| Peak | Component | Functional Group | Structure | Statistical Match |
|------|--------------------------|---------------------|-----------|----------------------|
| 1 | Hexanal | aldehyde | | 88.3% |
| 2 | 1,1-Dimethyoxy Hexane | acetal | | 87.2% |
| 3 | 1,1-Dimethoxy Nonane | acetal | | 74% |
| 4 | Methyl Decanoate | ester | | 72% |
| 5 | Methyl Undecanoate | ester | | 91.1% |
| 6 | Methyl Palmitate | ester | | 85.6% |
| 7 | Methyl Oleate | ester | | 74.2% |
| 8 | Methyl Linoleate | ester | | 73.4% |

Chapter 5

Results & Discussion Part II: Thermal Analysis

5.1 TGA Analysis

Volatility is one of the most fundamentally important qualities of fuel in engines because it has a major affect on the vapor-air ratio in the cylinder and, therefore, influences the ignition quality of the fuel. The TGA profiles of ozonated low-sat methyl soyate, at various reaction time intervals, and No.2 diesel fuel are illustrated in Figure 5.1. It is clearly evident that as the reaction time increases, the volatility of the ozonated biofuel approaches that of the No. 2 diesel fuel. In general, the boiling points of methyl esters increase with the length of the hydrocarbon tail, or with molecular weight. Methyl soyate has a rather low volatility due to the presence of both C16 and C18 hydrocarbons. However, its volatility becomes comparable to No. 2 diesel fuel after ozone-mediated oxidation, as the heavy, long chain, unsaturated and saturated components are fragmented to shorter, lighter, components. Also, as in the GC/MS experiments, the hydroperoixdes and ozonides present in the ozonated fuel were thermally decomposed during the TGA experiments as the analysis temperature reached a maximum at 350°C. Thus, the decomposition products of hydroperoxides and ozonides seemed to improve the volatility of ozonated methyl soyate. Table 5.1 lists the available boiling points [127] and molecular weights of the products present in ozonated methyl soyate. Methyl palmitate and stearate have the highest boiling points due to their degree of saturation and the length of their hydrocarbon tails. Likewise, the unsaturated constituents also have relatively high boiling points compared to the formed products.



Figure 5.1 TGA Profiles of Ozonated Low-Sat Methyl Soyate and No. 2 Diesel Fuel

| Product | Molecular Weight | Boiling Point °C | Product | Molecular Weight | Boiling Point °C |
|---------------------------|---------------------|---------------------|----------------------------|---------------------|---------------------|
| Methyl Stearate | 298.50 | 443 | Nonanal | 142.26 | 191 |
| Methyl Palmitate | 270.45 | 417 | Methyl Linolenate | 292.46 | 182 |
| Methyl 10- Undecenoate | 198.30 | 248 | Dimethyl Azelate | 216.28 | 156 |
| Methyl Decanoate | 186.29 | 224 | Methyl Hexanoate | 130.19 | 150 |
| Methyl Oleate | 296.49 | 219 | Hexanal | 100.16 | 131 |
| Methyl Linoleate | 294.48 | 215 | 4-Nonenal | 140.22 | N/A |
| Methyl Nonanoate | 172.27 | 214 | Methyl 3- Nonenoate | 170.25 | N/A |
| Methyl Octanoate | 158.24 | 193 | Methyl 9-Oxo- Nonenoate | 186.25 | N/A |

| Table 5.1 Boling Pol | int Data for C | Compounds l | Present in (| Ozonated 1 | Methyl Soyate |
|----------------------|----------------|-------------|--------------|------------|---------------|
|----------------------|----------------|-------------|--------------|------------|---------------|

The derivative weight loss, or the maximum rate of weight change, versus temperature data for ozonated methyl soyate and No. 2 diesel fuel is illustrated in Figure 5.2. For non-ozonated methyl soyate (0 mins), one maximum peak occurs at around 210°C, which is due to the presence of the starting methyl esters. As the reaction time increases, however, a second maximum develops at around 145°C, which corresponds to the production of the lower-molecular weight esters and aldehydes. Moreover, the peak at 210°C decreases as a function of reaction time, supporting the fact that the starting methyl esters are being cleaved during ozonolysis. One broad maximum peak occurs at around 150°C for No. 2 diesel fuel. Thus, after 3 hours of ozonation, the derivative weight loss vs temperature profile of ozonated methyl soyate is comparable, almost identical, to that of No. 2 diesel fuel.



Figure 5.2 Plot of Derivative Weight Loss vs Temperature for No. 2 Diesel Fuel and Ozonated Methyl Soyate

TGA experiments were conducted with ozonated regular methyl soyate to compare its TGA profile with that of ozonated low-sat methyl soyate. Figure 5.3 shows the results of these experiments. As expected, the peak area of the first peak is greater in regular methyl soyate than in low-sat methyl soyate. This observation can be explained by the fact that the amount of saturation in low-sat methyl soyate is about half of that in regular methyl soyate.



Figure 5.3 Plot of Derivative Weight Loss vs Temperature for Regular and Low-Sat Methyl Soyate

5.2 DSC Analysis

Thermograms of low-sat methyl soyate and ozonated low-sat methyl soyate at various reaction times are compared in Figure 5.4. The cooling curves for both fuels display two major exothermic regions: region 1 between -10°C and -15°C, and region 2 less than -65°C. This behavior is consistent with mixtures of fatty compounds, such as unsaturated and saturated methyl esters [128]. The length of the hydrocarbon chains and their degree of unsaturation strongly influence the phase transitions of fatty mixtures. Components with short-chain hydrocarbons will crystallize at a lower temperature than components with long-chain hydrocarbons because the intermolecular forces are weaker between the shorter fatty tails. Intermolecular forces among neighboring hydrocarbon tails increase as the tails get longer, enhancing the tendency to crystallize. In terms of saturation, saturated components are flexible since every carbon-carbon bond is free to rotate, forming closely packed and well-ordered crystals. Because rotation around the double bond is hindered, the presence of *cis* double bonds produces a distinct bend in the hydrocarbon chain. This bend prevents the formation of closely packed, well-ordered crystals and, hence, decreases the intermolecular forces amongst the hydrocarbon chains. Consequently, *cis* unsaturated fatty esters have much lower freezing points than saturated fatty esters. Thus, unsaturation present in methyl esters has a pronounced lowering effect on freezing points, and polyunsaturation more so than monounsaturation [129]. For thermograms of low-sat methyl soyate and ozonated methyl soyate, the higher temperature region (region 1) is the freezing transition of the high molecular weight, long-chain saturated methyl esters, and the lower temperature region (region 2) is the freezing transition of the unsaturated and low-molecular weight methyl esters. The

available freezing point data [127] for compounds found in ozonated methyl soyate is presented in Table 5.2.



Figure 5.4 DSC Cooling Thermograms for Low-Sat Methyl Soyate

| Product | Molecular Weight | Freezing Point °C | Product | Molecular Weight | Freezing Point °C |
|----------------------|---------------------|-------------------------|----------------------------|---------------------|-------------------------|
| Methyl Stearate | 298.50 | 40 | Methyl 10- Undecenoate | 198.30 | -28 |
| Methyl Palmitate | 270.45 | 30 | Dimethyl Azelate | 216.28 | -20 |
| Methyl Hexanoate | 130.19 | -71 | Methyl Oleate | 296.49 | -20 |
| Hexanal | 100.16 | -56 | Methyl Decanoate | 186.29 | -18 |
| Methyl Octanoate | 158.24 | -40 | Nonanal | 142.26 | N/A |
| Methyl Linolenate | 292.46 | below -35 | 4-Nonenal | 140.22 | N/A |
| Methyl Linoleate | 294.48 | -35 | Methyl 3- Nonenoate | 170.25 | N/A |
| Methyl Nonanoate | 172.27 | -30 | Methyl 9-Oxo- Nonenoate | 186.25 | N/A |

Figure 5.5 shows the onset crystallization temperatures for regions 1 and 2 of ozonated low-sat and regular methyl soyate and Table 5.3 list these values. The onset crystallization temperature, T_{C1} , was defined as the intersection of a line tangent to the scan at the point of sharpest slope and a line tangent to a baseline segment on the "hot" side of the onset crystallization peak. Similarly, the onset freezing temperature, T_{C2}, was defined as the point where a line tangent to the scan at the point of sharpest slope on the "hot" side of the freezing peak intersects a line across the base of the region. The regular methyl soyate thermogram, $T_{C1} = 3.79$ °C, is comparable to that of unwinterized methyl soyate, $T_{C1} = 3.7^{\circ}$ C, of Lee *et. al.*[130]. It is clearly evident that T_{C2} has been significantly reduced from about -62°C (for methyl soyate) to a minimum temperature of about -87°C. This phenomenon occurred because of the cleavage of the double bonds, which reduced the length of the hydrocarbon tail, into smaller fragments and the formation of methyl and dimethyl esters at the terminal position, as predicted. Also, the size of the peak diminished due to the reduction of the unsaturated portion of the oil. After 180 min of reaction time, there was nearly no phase transition occurring in region 2. Also, as expected, the onset crystallization properties in region 1 is lower for low-sat methyl soyate that for regular methyl soyate.

Note that there was a slight increase in both T_{C1} , and T_{C2} starting at a reaction time of 60 min. This observation may be due to the presence of monomeric and polymeric ozonides from the ozonated unsaturated moieties of methyl soyate. In general, monomeric and polymeric ozonides are oily, viscous liquids with a characteristic odor, which rapidly decompose at temperature above 70°C; at room temperature most of them are quite stable [34]. Moreover, depending on the structure of the initial olefin and the

reaction conditions, monomeric and polymeric ozonides can be viscuous and Vaselinelike (ozonides of normal olefine), rubber-like (ozonides of cyclo-olefins), or powder form (ozonides of naphthalene, phenanthrene). Olefin ozonides have not been studied very thoroughly and, thus, physicochemical properties have been described only for individual representatives. A comparison of the physicochemical properties of the monomeric and polymeric ozonides of cyclohexane is presented in Table 5.4.



Figure 5.5 Onset Crystallization Temperatures for Regions 1 and 2 as a Function of Reaction Time

| Table 5.3 Onset C | rystallization | Temperatures | for | Methy | yl So | yate |
|-------------------|----------------|--------------|-----|-------|-------|------|
|-------------------|----------------|--------------|-----|-------|-------|------|

| Reaction Time | Low-Sat, T _{C1} | Low-Sat, T _{C2} | Regular, T _{C1} | Regular, T _{C2} |
|---------------|--------------------------|--------------------------|--------------------------|--------------------------|
| (mins) | (°C) | (°C) | (°C) | (°C) |
| 0 | -9.40 | -61.75 | -3.79 | -62.24 |
| 30 | -9.06 | -72.44 | -4.72 | -76.24 |
| 60 | -8.57 | -87.91 | -3.56 | -86.55 |
| 90 | -7.42 | -83.98 | -2.60 | -83.73 |
| 120 | -5.66 | -82.41 | -1.23 | -81.88 |
| 150 | -5.37 | -80.94 | 1.30 | -80.42 |
| 180 | -5.50 | -78.91 | 1.87 | -79.08 |

| Ozonide | Monomeric | Polymeric | |
|---------------------------|---|-------------------------|--|
| Structure | | (_0-0,) | |
| | -CH ₂ CH ₂ CH CHCH ₂ CH ₂ - | CH2CH2CH CHCH2CH2 | |
| Appearance | colorless liquid | white elastic substance | |
| Freezing Point, °C | -38 | 72 | |
| Boiling Point | 32 | not volatile | |
| IR-Spectrum Absorption | 1110 | 1110 | |

Table 5.4 Physicochemical Properties of Cyclohexene Ozonides

5.3 Low-Temperature Flow Properties

5.3.1 Cloud, Pour, and Cold Filter Plugging Point Measurement

Selected low-temperature flow properties were evaluated for low-sat methyl soyate and ozonated low-sat methyl soyate. Shown in Table 5.5, these measurement values were compared to literature measurements of regular methyl soyate and No. 2 diesel fuel. The properties for low-sat methyl soyate were lower than regular soyate, as expected. However, the cold-properties for the ozonated fuel were not enhanced, probably due to the presence of viscous, oil polymeric and monomeric ozonides. Thus, further product purification must be considered in order to separate out the ozonides from the product mixture. Eliminating the ozonides should significantly improve the cold-temperature flow properties.

| | Methyl | Low-Sat | Low-Sat Ozonated | No. 2 |
|--------------------|---------------------|---------------|------------------|---------------------|
| | Soyate ^a | Methyl Soyate | Methyl Soyate | Diesel ^a |
| Cloud Point, °C | 0 | -4 | 3 | -16 |
| Pour Point, °C | -2 | -6 | 0 | -23 |
| Cold Filter | -3 | -10 | 9 | -27 |
| Plugging Point, °C | | | | |
| | | | | |

Table 5.5 Low-Temperature Flow Properties of Methyl Soyate and No. 2 Diesel Fuel

^aSource: Ref. [131]

5.3.2 Viscosity Measurement

The dynamic viscosity of selected oil samples were measured as a function of shear rate and temperature. All oil samples exhibited Newtonian-like behavior, in which the plot of shear stress (Pa) vs. shear rate (1/s) was linear with a slope equal to the viscosity, illustrated in Figure 5.6. Table 5.6 lists the viscosity of selected samples at 25°C with the corresponding coorelation coefficient (R²) from the linear plot. The viscosity of methyl soyate is about 1.6, or approximately ~2, times the viscosity of No. 2 diesel fuel, which is comparable to literature data. The viscosity of ozonated methyl soyate has about the same viscosity as its parent triglyceride and is about 14 times more viscous than No. 2 diesel fuel. Figure 5.7 shows the dependence of viscosity on temperature for low-sat methyl soyate. The viscosities decrease with rising temperature as expected and follow an exponential behavior. However, the viscosity of the ozonated methyl soyate is significantly higher than that of methyl soyate. Thus, the presence of viscous/oily ozonides has a profound effect on the viscosity of the ozonated fuel.

| Oil/Fuel | Viscosity Pa•s | R ² |
|--------------------------------|-------------------|----------------|
| Low-Sat Soybean Oil | 0.0503 | 0.9997 |
| Low-Sat Methyl Soyate | 0.0060 | 0.9927 |
| Ozonated Low-Sat Methyl Soyate | 0.0519 | 0.9993 |
| No. 2 Diesel Fuel | 0.0038 | 0.9909 |

Table 5.6 Dynamic Viscosity Values of Selected Oils at 25°C



Figure 5.6 Shear Stress Versus Shear Rate for Selected Fuels *Data on secondary y-axis



Figure 5.7 Dynamic Viscosity as a Function of Time for Low-Sat and Ozonated Low-Sat Methyl Soyate

Chapter 6

Conclusions, Future Work & Biodiesel Research Considerations

6.1 Conclusions

Important current trends in the chemical industry are intensification of production processes and reduction of the volume of by-products, and of harmful liquid-gas discharge. In chemical manufacturing, the various oxidation operations are common in which gaseous oxygen or inorganic oxidants are employed as the oxidizing agent. One of the promising methods for manufacturing many products of industrial importance is utilization of ozone as the oxidizing agent. Ozone reacts more energetically than any other oxidizing agents and, moreover, it excludes formation of large amounts of inorganic waste matter, whose separation from the reaction products and subsequent utilization involve sizable additional costs. Ozone's most characteristic and, at the same time, very important use in the chemical industry and preparative chemistry, results from its specific effect on the olefinic double bond. Ozonolysis reactions are also frequently employed during a synthetic pathway, as ozone reacts under remarkably mild conditions and displays a high level of selectivity, making ozonolysis an extremely valuable synthetic entity. The first ozonolysis process commercialized was the production of azelaic and nonanoic acids from oleic acid, which was introduced by Emery Industries [132].

6.1.1 Structural Analysis

FTIR and GC/MS analysis confirmed that the double bonds in methyl soyate were successfully cleaved by ozone-mediate oxidation. The total amount of double bonds in the mixture was reduced by more than 90% after three hours of ozonolysis. The degradation rate of methyl linolenate was approximately three times faster than that of

methyl linoleate. Methyl palmitate, stearate, and oleate all fit zero-order reaction kinetics. The kinetic studies also suggest that the rate of ozone-mediated oxidation of biodiesel is influenced by the amount of double bonds and steric effects inherent in its molecular structure.

FTIR and ¹H NMR confirmed the presence of hydroperoxides and ozonides in the ozonated fuel. However, they thermally decomposed during the GC/MS analysis, leading to the production of additional methyl esters. Hydroperoxide formation may be the result of water, a by-product in the conversion of both the hemiacetal and hydroperoxide intermediates to methyl esters, reacting with the secondary ozonide. This particular reaction readily occurs without the necessity of a catalytic acid or base. Another possible route for hydroperoxide production is the reaction of the carboxyl oxide intermediate with the protic solvent. Thus, there are several competing reactions occurring during the ozonation of methyl soyate. Ozonide formation is most likely due to the steric hindrance of the methyl soyate molecule, which is composed of long-hydrocarbon chains. Based on the FTIR absorption intensities, the ozonide was more concentrated in the volatile fraction than in the oil fraction. The volatile fraction of the ozonated fuel were collected in a dry-ice collection trap and characterized by FTIR and GC/MS. The majority of the volatile by-products were acetals. Acetal formation can occur by the reaction of alcohol with an aldehyde under acidic conditions. Small amounts of carboxylic acids, like hexanoic acid, could have served as the acidic medium.

Three of the five expected esters, methyl hexanoate, nonanoate, and azelate, were formed during the ozonation experiments. Two derivative forms of dimethyl malonate were detected in the volatile fraction. Methyl propionate was not detected in the GC

analysis. Since methyl propionate is a very volatile compound, it may have eluted off the GC column with the solvent peak, making it undetectable. These results demonstrate that a co-solvent, like dichloromethane, and very low reaction temperatures are not needed to form the expected esters, which is a huge advantage from an engineering point of view.

Similar products were formed in the ozonation and autoxidation of methyl soyate. It was also found that the amount of double bond degradation was significantly lower when ozone was not the primary oxidant. Thus, it was concluded that ozone was simultaneously inducing lipid oxidation (ozone-induced oxidation) and oxidatively cleaving the alkene moiety (ozonolysis) of methyl soyate. In fact, in addition to the use of ozone as the primary oxidant in the synthesis of a range of oxygen-containing functional groups, there are many applications in which ozone serves only as a catalyst or initiator for another oxidant, usually oxygen [124-126].

6.1.2 Thermal Analysis

According to TGA analysis, the volatility of methyl soyate became comparable to that of No. 2 diesel fuel after 3 hours of ozone-mediated oxidation. The heavy, long chain, esters were fragmented to shorter, lighter, saturated components, shifting its TGA profile towards diesel fuel. Also, as in the GC/MS experiments, the hydroperoixdes and ozonides present in the ozonated fuel were thermally decomposed during the TGA experiments as the analysis temperature reached a maximum at 350°C. Thus, the decomposition products of hydroperoxides and ozonides seemed to improve the volatility of ozonated methyl soyate. Two maxima occur for the rate of weight change data of ozonated methyl soyate The first maximum occurred at 210°C from the presence of the

long, hydrocarbon chains of the starting esters and the second maximum occurred at 14°5C from the presence of more volatile products formed after ozonation. One broad maximum occurred at about 150°C for No. 2 diesel fuel. Therefore, after 3 hours of ozonation, the derivative weight loss vs. time profile of ozonated methyl soyate was comparable, almost identical, to that of No. 2 diesel fuel.

The DSC cooling curves for methyl soyate exhibited two major exothermic regions: region 1 between -10C and -15C and region 2 under -65C. The higher region (1) is the freezing transition of the high, molecular weight, long-chain saturated methyl esters and the lower temperature region (2) is the freezing transition of the unsaturated and lowmolecular weight methyl esters. There was a slight increase in both T_{C1} and T_{C2} beginning at a reaction time of 60 mins. This observation may be due to the presence of monomeric and polymeric ozonides in the fuel, which are generally viscous/oily and stable at room temperature. Furthermore, TC_1 is lower for low-sat methyl soyate than for regular methyl soyate.

Selected low-temperature flow properties- cloud point, pour point, cold filter plugging point, viscosity-were evaluated for methyl soyate. However, these properties were not enhanced for the ozonated fuel because of the presence of ozonides in the product mixture. Thus, separation techniques must be developed for their removal from the product mixture. Eliminating the ozonides should significantly improve these properties.

6.2 Future Work

6.2.1 Ozonide Analysis

Common techniques used to analyze ozonides are TLC and HPLC [114]. It is recommended that HPLC/MS be used to identify and quantify ozonides present in the product mixture. One advantage of using HPLC over GC is that the analysis is conducted at room temperature, thus thermal decomposition of the ozonides is avoided. Also, it is recommended that separation techniques be developed to isolate the ozonide from the product mixture and reevaluate the structural and thermal properties.

6.2.2 Process Development and Mass Transfer Studies

There are two techniques in which ozone is delivered to a solution during ozonolysis: diffuser and venture injector. A bubble diffuser, which was used in the ozonation of methyl soyate, works by emitting ozone through hundreds of bubbles beneath the solution surface. This results in low ozone mass transfer rate, typically around 10-15%. Conversely, a venturi injector works by forcing the reaction solution through a conical body which initiates a pressure differential between the inlet and outlet ports. This creates a vacuum inside the injector body, which initiates ozone suction through the suction port. The venture injector system allows very high ozone mass transfer rate, up to 90%. The increased mass transfer efficiency provided by the venturi injector, combined with the closed nature of the contactor, allows for more precise ozone dosing and reduces the volume requirements of the contactor. The ozone gas actually becomes a part of the reaction solution at the venturi, traveling through the contactor without exposure to air or atmospheric pressure. This adds to the efficiency of the system by allowing for greater ozone saturation.

It is recommended that a venturi injector assembly be designed and used for the deliver of ozone during ozonation experiments. Comparative ozone mass transfer studies between the two different deliver systems should be conducted to understand the effects of diffusion on the overall rate of reaction.

6.2.3 Quality Assurance Testing for Reliable Vehicle Operation

A precondition for the successful use of plant oil methyl ester as an alternative fuel for car and commercial vehicle diesel engines is that they must run just as reliably as on diesel fuel. If this alternative fuel is to have a long-term future on the market, it must be able to fulfill the same requirements currently met by standard commercial diesel fuel, i.e. it must supply a high quality product. It is recommended that, after further research in product and process development, the properties comprised in the ASTM D 6751 fuel standard (Table 6.1) should be evaluated for ozonated biofuel. Engine performance and emission tests should also be conducted

| Property | ASTM Method | Limits | Units |
|--------------------|-------------|------------|----------------------|
| Flash Point | D93 | 130 min. | C |
| Water & Sediment | D2709 | 0.050 max. | % vol |
| Kinematic | D445 | 1.9-6.0 | mm ² /sec |
| Viscosity, 40C | | | |
| Sulfated Ash | D874 | 0.020 max. | % mass |
| Sulfur | D5453 | 0.050 max. | % mass |
| Copper Strip | D130 | No. 3 max | |
| Corrosion | | | |
| Cetane Number | D613 | 47 min. | |
| Cloud Point | D2500 | Report | C |
| Pour Point | D97 | Report | C |
| Carbon Residue | D4530 | 0.050 max. | % mass |
| Acid Number | D664 | 0.80 max | mg KOH/g |
| Free Glycerin | D6584 | 0.020 max. | % mass |
| Total Glycerin | D6584 | 0.240 max | % mass |
| Phosphorus Content | D4951 | 0.001 max. | % mass |

| Table 6.1 A | ASTM D | 6751 | Fuel S | pecifications. |
|-------------|--------|------|---------------|----------------|
|-------------|--------|------|---------------|----------------|

6.3 Other Uses of Biodiesel Fuel

In addition to serving as fuels, esters of vegetable oils and animal fats can be utilized for numerous other purposes. Methyl esters can serve as intermediates in the production of fatty alcohols from vegetable oils [133]. Fatty alcohols are used in surfactants and cleaning supplies. Branched esters of fatty acids are used as lubricants, in which their improved biodegradability makes them environmentally attractive. Biodiesel can also be used as a substitute for home heating oil [134].

Over the past few years, industry knowledge and awareness of methyl soyate as an alternative industrial solvent has grown tremendously. Methyl soyate possesses good solvent properties, which is demonstrated by its use as a medium for cleaning beaches contaminated with crude oil [135-137]. It offers natural cleaning and degreasing characteristics with low volatile organic compounds (VOCs), low hazardous air pollutants, low toxicity, high flash point, and it is readily biodegradable. The solvent strength of methyl soyate is also demonstrated by its high Kauri-Butanol value (relating to the solvent power of hydrocarbon solvents), which makes it similar or superior to many conventional organic solvents. The only physical disadvantages of methyl soyate may be slow evaporation and water insolubility, which can be improved by formulation with surfactants and co-solvents to meet desired performance requirements. The good technical attributes of methyl soyate, in combination with the regulatory pressures on the traditional chlorinated and petroleum solvents, present good opportunities for use of methyl soyate as a solvent.

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