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EFFECTS OF AGING ON CARBON RESIDUE OF BIODIESEL FUELS

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## **Abstract**

Biodiesel fuels have long been known to experience changes in fuel characteristics and quality as it ages and oxidizes. Due to several chemical factors of the fuel, notably the unsaturated nature of the hydrocarbon chains, this oxidation readily takes place under typical storage conditions of the fuel. As a large amount of biodiesel fuel is already present in our fuel supply and its usage is poised to grow in the near future, it is important to have a full understanding of the fuel's lifespan and storability.

Focusing specifically on the effects of oxidation on carbon deposition characteristics of biodiesel fuels, two experiments were carried out utilizing the Ramsbottom test to determine carbon residue. The first tested several types of biodiesel fuels and standard ultra low-sulfur diesel fuel before and after a storage period of several months. During the storage period, the fuels were stored at room temperature in small glass vials with adequate air space for autoxidation. The results of this testing did not show a conclusive change in the Ramsbottom carbon residue of any of the fuels tested, however the diesel fuel did have a significant decrease in carbon residue. The biodiesel did generate lower levels of carbon residue than the diesel fuel.

The second experiment carried out tested a specific biodiesel fuel over time as it oxidized. A high-quality, commercially-made biodiesel fuel with an antioxidant additive package was tested to simulate what a consumer would purchase from a large

manufacturer. The fuel was artificially oxidized in a heated sealed reaction chamber with a constant flow of oxygen through the device. The fuel was tested before, during, and after a 24 hour period in the reaction chamber. Testing results showed that the fuel did not experience any significant changes in Ramsbottom carbon residue. This indicates that long-term storage would not create a problem for carbon depositions when using a high-quality, chemically treated biodiesel fuel.

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## List of Symbols and Abbreviations

ASTM .....	American Society for Testing and Materials
AV .....	Acid Value
B20 .....	20% Biodiesel, 80% Diesel Fuel Blend
B100 .....	100% Biodiesel, or Neat Biodiesel
BSFC.....	Brake-Specific Fuel Consumption
CME .....	Canola Methyl Ester
CN.....	Cetane Number
CO.....	Carbon Monoxide
EIA .....	Energy Information Administration
HC.....	Total Unburned Hydrocarbons
HV.....	Heating Value
PAH.....	Polynuclear Aromatic Hydrocarbons
PM .....	Particulate Matter
PV .....	Peroxide Value
RIT .....	Rancimat Induction Time
SG .....	Specific Gravity
SME .....	Soy Methyl Ester
ULSD .....	Ultra Low Sulfur Diesel (No. 2-D S15)
v.....	Kinematic Viscosity

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# Introduction

## *Biodiesel Use and Future Potential*

As supply, cost, environmental, and political impacts of our use of petroleum-based fuels become a greater issue of concern, alternative sources of energy and fuels are a growing topic of concern. One existing technology that has shown feasibility and merit is the use of biodiesel fuels to power both on-road and off-road transportation. Although the use of biodiesel is not new, it has become more prevalent recently. Biodiesel fuels can be produced in areas that do not have access to geologic petroleum reserves, they have shown a marked reduction in many pollutant emissions, and they can readily be applied using our current vehicles and fueling infrastructure.

Biodiesel consumption in the United States has been on the rise for the last several years. The Energy Information Administration (EIA) [1] estimated that the U.S. consumed about 260 million gasoline-equivalent gallons of biodiesel in 2006. While this is a significant amount, it is less than 0.6% of the total diesel fuels used in the U.S. for that year, and less than 0.15% of the total fuel consumption. However, the percent share of biodiesels has grown significantly over the last few years; the EIA reported that in 2003 biodiesel was only 0.04% of the total diesel fuel consumption.

While current growth is significant, biodiesel is not a viable replacement for all diesel fuels. The EIA [1] projects that bio-derived fuel production in the US will grow from 0.5 million barrels per day in 2007 to 2.3 million barrels per day by the year 2030, but total liquid fuel consumption will be about 20 million barrels per day. Furthermore,

biodiesel will only represent a small portion of the 2.3 million barrels per day, with the majority being ethanol. Because of these limitations of scale, biodiesel is seen as a blending fuel to displace some diesel fuel rather than a neat fuel to replace all diesel fuel. Many locations already offer B20, which is a blend of 20% biodiesel and 80% petroleum diesel, rather than B100, which is neat, 100% biodiesel fuel.

### ***Motivation for Research***

Although biodiesel will continue to be an important fuel source in the future, there are several areas of concern that need to be addressed. One concern is the poor storage stability of biodiesel; the fuel is known to readily autoxidize in the presence of oxygen and form peroxides, which go on to form compounds that degrade the quality of the fuel. Many different studies have shown that this oxidative degradation can cause changes in the acid value (AV), peroxide value (PV), kinematic viscosity ( $\nu$ ), and other properties. The rate and degree of these changes heavily depend on storage conditions, such as temperature, exposure to UV radiation, air space turnover rate, and surface area of liquid/gas interface.

With these known issues of storage stability, it is important to investigate whether or not biodiesel will remain within ASTM specifications throughout reasonable storage periods and conditions. However, as mentioned above biodiesel is not typically sold as a neat fuel, but rather as blends such as B20. This blending helps to reduce the impacts of oxidative products in the biodiesel, but the fuel must still meet ASTM D6751-07b, which is written for B100, before being blended. Also, compounds created during

oxidation may not push the fuel outside of the physical specifications listed by the ASTM, but their presence might create other types of concerns

Carbon deposition and coking are important factors to monitor, because they can cause serious problems with engine performance, degradation, and lifespan. Carbon deposits can cause fuel injector fouling and cylinder scoring within an engine, leading to decreased performance or engine failure. Neat vegetable oils used as fuels have been shown to leave more carbon deposits than diesel fuels, and these deposits are harder and tend to adhere more firmly [2]. The conversion process from vegetable oil to biodiesel greatly reduces the fuel's tendency to create carbon residues, but it is important to test whether the fuel's autoxidation properties will affect the carbon residue over time. Tests such as the Ramsbottom Carbon Residue test or the Micro Method are used to indicate a fuel's tendency for coking, and this study seeks to determine how this tendency changes in biodiesel as oxidation takes place. By developing a profile for carbon coking over time, storage techniques can be adapted to avoid engine fouling by carbon depositions.

# Literature Review

## *Biodiesel History, Sources, and Production*

### **Vegetable and Animal Oils and Biodiesel**

Naturally occurring fats and oils, whether they are from vegetable or animal sources, share the common characteristic of being triglycerides. These are formed of three fatty acids bound to a single glycerol (a tri-alcohol) molecule. It has long been known that many types of engines, diesel engines in particular, can be fueled with vegetable and animal oils, although many issues exist with doing so. Because of the triglyceride configuration, natural oils can have viscosities up to 20 times greater than the viscosity of typical petroleum diesel, making them very difficult to burn in an engine. Many well-documented issues arise, such as poor cold-start characteristics and heavy engine coking, when using untreated vegetable and animal oils.

Research has suggested solutions to the problems associated with using these naturally occurring oils for many years. Early work in 1938 investigated fueling engines with triglycerides and suggested splitting the triglyceride into fatty acids to use as fuel [3]. As research and understanding of triglycerides and fatty acids improved, the current practice of using transesterification to split the triglyceride into fatty acids was found to improve many of the issues surrounding vegetable oil fuels: viscosity is lowered, engine coking is lowered, and most types of air emissions are improved. This practice is now used to create biodiesel fuel on a large scale.

Technically, biodiesel can be considered to be any sort of diesel-quality fuel refined from vegetable or animal fats and oils. There are four main methods of creating biodiesel: transesterification, pyrolysis, microemulsions, and ethanol/diesel fuel blends [4]. Various types and qualities of fuels are created with these differing techniques and source materials; however the term 'biodiesel' in current research is generally limited to esters made only from transesterification of vegetable oils and blends of these esters with petroleum diesel fuels.

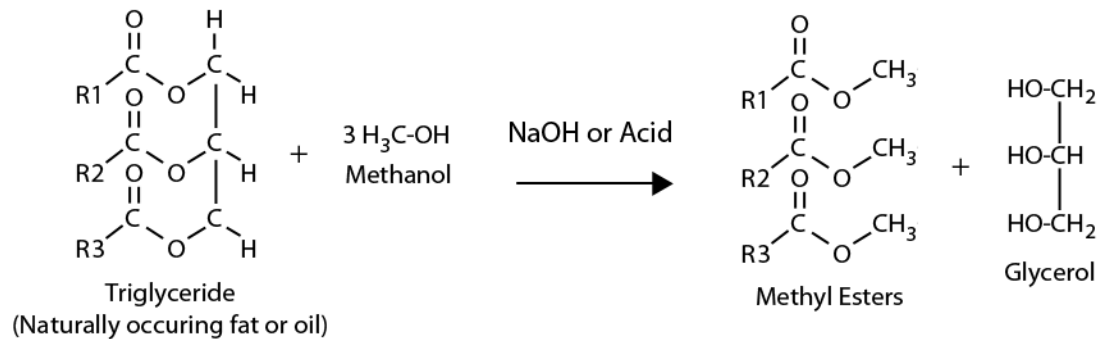
The source plants for the natural oils used in this process vary, and each type of oil creates biodiesel with slightly different properties. Biodiesel is classified depending on source oil, with two common types being soy methyl ester (SME) from soybean oil and canola methyl ester (CME) from rapeseed oil. Biodiesel can also be created from many other types of vegetable oils and animal fats, as well. Although waste oil and animal fats can be used as cheap oil sources, they are more difficult and costly to process and overall quantity of sources is limited. Current research is developing methods of manufacturing using oil from algae crops, which is expected to be a highly efficient source of oil once the technology matures.

### **Transesterification and Chemical Conversion**

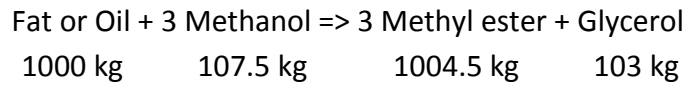
Transesterification is a process that reduces the viscosity of feedstock oils and converts them to a form that is usable in vehicle engines. It splits up the large triglycerides that form plant and animal oils into smaller molecules. The addition of alcohol and caustic catalyst breaks the bonds to the glycerol molecule, leaving glycerol

as a byproduct and the fatty acid methyl esters that are used as biodiesel [5]. The following figure shows a basic representation of this process:

**Figure 1: A Basic Representation of Transesterification of a Triglyceride [5]**



Graboski [6] reports that this process follows the following simplified stoichiometric equation with mass flows calculated for complete conversion of stearic acid triglyceride:



This reaction will take place at slightly above room temperature and convert between 90-97% of the feed oil in an excess of methanol. The unreacted byproducts include glycerol, free fatty acids, and the original oil with various numbers of the three fatty acids separated (mono/di/triglycerides). The free fatty acid forms soap and water as additional byproducts. The fuel is then typically washed to remove the remaining caustic catalyst, which is not recovered in many processes. Although much of the glycerol can be separated through a liquid/liquid separation, some manufacturers use distillation to purify the fuel further.

## ***Fuel Oxidation***

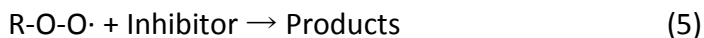
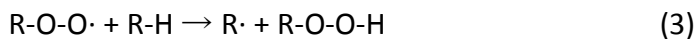
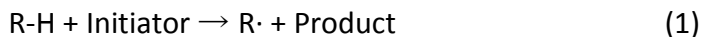
### **Autoxidation and Antioxidant Mechanisms**

Autoxidation occurs when oxygen in the atmosphere reacts with an organic compound and causes degradation into peroxides and hydroperoxides, which are compounds which contain an oxygen-oxygen bond. These reactions tend to initiate between oxygen and a double bond. The hydroperoxides can then decompose and initiate a free-radical chain reaction and cause polymerization into high-weight, cross-linked products. These products can form gums and solids, which can cause serious concerns during combustion.

This type of reaction occurs in many types of organic-based compounds other than fuels, such as rubber, paints, and food. These compounds will degrade at differing rates depending on composition. Autoxidation can take place in the presence of oxygen at room temperature or below, but the rate of reaction is generally increased at increased temperature or in the presence of UV light.

Mechanisms for fuel oxidation have long been known. In 1962, Nixon [7] characterized the mechanism for the autoxidation of gasoline as follows:

#### Autoxidation of Hydrocarbon Reactions



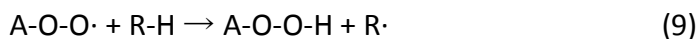
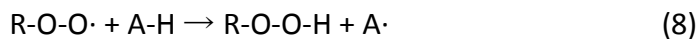
As stated, the resulting hydroperoxides (R-O-O-H) from this reaction can cause an additional free radical chain reaction and polymerize. This polymerization depends on the peroxide free radicals (R-O-O·), which can arise either directly from the intermediate steps of the autoxidation reaction or from the decomposition of hydroperoxide molecules. Sims and Hoffman [8] present the following reactions for this polymerization, which also act as termination steps for the autoxidation reaction above:

#### Hydrocarbon and Peroxide Polymerization Reactions



To prevent these reactions from occurring and degrading a fuel, antioxidants (A-H) are widely used to interrupt these chain reactions and polymerization reactions. Heneghan and Zabarnick [9] present a chain transfer mechanism to describe the function of these antioxidants in quenching the fuel autoxidation:

#### Chain Transfer Reactions



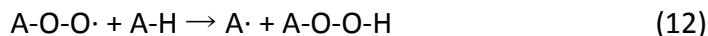
By using an antioxidant that will speed and slow the appropriate reactions, the rate of fuel oxidation can be controlled. Specifically, Reaction (8) must proceed readily in order to neutralize the peroxide radical. Reaction (9) must then proceed very slowly so that additional hydrocarbon free radicals are not created. This combination of effects should work to quench Reactions (2) and (3) in the original hydrocarbon autoxidation.

Heneghan and Zabarnick [9] also present reactions describing the autoxidation of the antioxidant itself, which they describe as having an additional role in solids creation



as the fuel ages. The mechanism for autoxidation is below. It is analogous to the fuel oxidation reactions, but with an antioxidant molecule rather than a hydrocarbon:

#### Autoxidation of Antioxidants Reactions



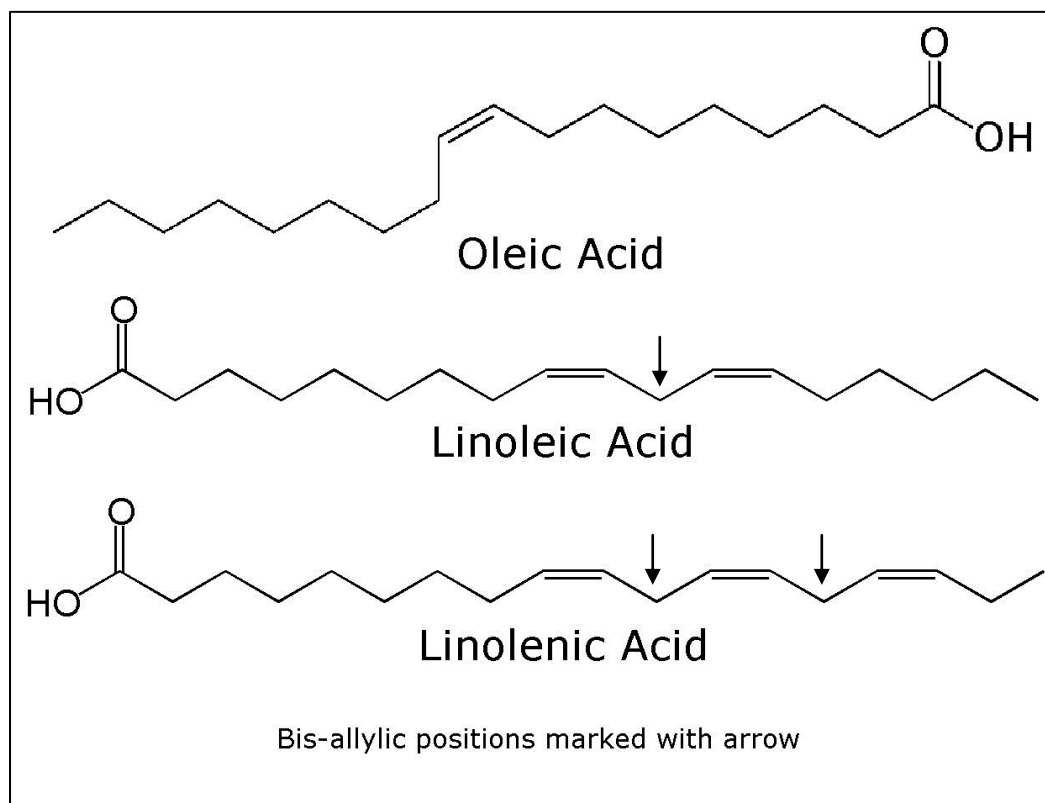
Heneghan and Zabarnick [9] propose that Reaction (14) is the main pathway of solids production, with the inhibitor being an additional A-O-O· radical.

### **Oxidative Stability of Biodiesel**

Biodiesel is widely known to readily experience autoxidation. In a detailed literature review, Knothe [10] states that the main concern for autoxidation of biodiesel is the number and position of double bonds in the fuel. Unsaturated fuels experience a higher degree of autoxidation, with positions allylic to double bonds being very likely to oxidize. Linoleic acid and linolenic acid have one and two *bis*-allylic positions respectively—carbon atoms with single bonds to both neighboring carbon atoms, which in turn each have double bonds to the next carbon atoms on the chain (essentially a single-bonded carbon sandwiched between two carbons with double bonds). As a result of these *bis*-allylic orientations, linoleates and linolenates have rates of oxidation 41 and 98 times greater, respectively, than that of oleates, which only have one carbon-carbon double bond and no carbons in the *bis*-allylic position. Biodiesels contain esters of all

three of these compounds. These three components (oleates, linoleates, and linolenates) all increase biodiesel's tendency to oxidize and break down.

**Figure 2: Chemical Structures of Oleates, Linoleates, and Linolenates**



The ASTM standards for biodiesel list an oxidation stability test (EN 14112), while the ULSD standards do not. The oxidation stability is measured as the Rancimat induction time (RIT), and B100 is required to have a minimum RIT of 3 hours. This can be problematic to meet using biodiesel oxidized during storage. Bondioli [11] reported the initial RIT of fresh CME was slightly less than 10 hours, but this dropped to about 2 hours after 32 days of storage in a glass container. After storage in an iron container, the RIT dropped below 3 hours in just 17 days and more or less stabilized at less than 0.5 hours after 32 days.

## Effects of Oxidation on Biodiesel

Extensive research has been done to determine the effects of oxidation and extended storage on biodiesel fuels. Studies by du Plessis *et al.* [12], Mittlebach *et al.* [13], Thompson *et al.* [14], Dunn [15], Monyem *et al.* [16], and McGuire [17] showed changes in almost all properties of biodiesel after oxidation. In these studies, changes were shown in acid value (AV), peroxide value (PV), cetane number (CN), kinematic viscosity, brake-specific fuel consumption (BSFC), heating value, and specific gravity (SG), as well as in the emissions of total unburned hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM). Depending on factors such as fuel type, storage conditions, and oxidation method and duration, these changes occurred to various degrees throughout literature.

Regardless of testing method, these studies have all shown oxidized biodiesel to experience an increase in AV and CN, and typically also show an increase in PV and viscosity. PV is not seen as a good indicator of oxidation because some research shows that PV value will reach a maximum value and then begin to decrease [12]. This occurs when the concentration of the highly reactive peroxides reaches a level where they are reacting quickly enough to be destroyed as fast as or faster than they can be created.

Dunn [15] suggests the increases in AV and viscosity are the best indicators of oxidation due to their more linear increases and ease of measurement; however other research, such as that of McGuire [17], has shown significant oxidation with little increase in viscosity of the fuel. McGuire suggests that this is due to his experimental design, in which the biodiesel was oxidized in a sealed container. Under these

conditions, the lighter, volatile compounds were unable to be released to the atmosphere. In studies using open air containers, marked increases in viscosity were seen due to these volatile compounds escaping and leaving behind the heavier, more viscous carbon compounds.

McGuire [17] also investigated oxidized biodiesel using Gas Chromatography Mass Spectrometry (GCMS) to determine what new compounds arise in biodiesel as it ages. GCMS analysis creates a data curve with peaks indicating organic compounds of various weights and degrees of saturation. As expected, analysis of fresh biodiesel showed the presence of oleaic, linoleic, and linolenic acid methyl esters, as well as palmitic and stearic acid methyl esters. However, the GCMS curves of oxidized biodiesel show similar peaks, so the newly created compounds could not be determined. McGuire suggests this is due to new, oxidized compounds having similar molecular weights to the original compounds, thus the new peaks are obscured by the original peaks. This research was unable to specifically identify compounds arising from oxidation; however it determined the increased oxygen content of oxidized fuels has an effect on the combustion characteristics.

## ***Carbon Residue and Coking***

### **Concerns Arising from Carbon Residue**

Carbon residue, regardless of arising from biodiesel or ULSD, can cause engine damage and degradation. It can cause fuel injector fouling and cylinder scoring within an engine, leading to decreased performance or engine failure. Although biodiesel is known

to leave fewer deposits than ULSD, they are a widely recognized problem when burning any carbon-based fuel in an internal combustion engine.

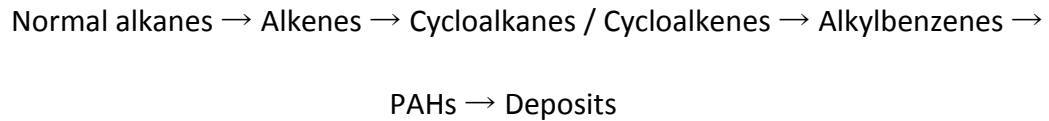
### **Mechanisms of Carbon Deposition in Jet Fuel**

There are many different mechanisms proposed describing carbon deposition and carbon residue formation. Although these mechanisms have not been studied in great detail for biodiesel fuels in particular, many studies exist for petroleum fuels and jet fuel in particular. These studies can be seen as analogous and indicators as to the deposition mechanism that occurs in biodiesel, even though it is likely that the actual process differs.

Li [18] outlines these different carbon deposition mechanisms in jet fuels under a wide variety of operating conditions. Two main types of deposition mechanisms are recognized: decomposition of hydrocarbons to elemental carbon and hydrogen and polymerization of hydrocarbon species into polynuclear aromatic hydrocarbons (PAHs) that grow into carbonaceous deposits. One major factor determining whether the hydrocarbons are decomposed or polymerize is the presence or absence of a metal catalyst. If a metal catalyst is present, hydrocarbons are typically decomposed into carbon residue, but in the absence of a catalyst (or thermal deposition) polymerization into carbon residue is the dominating mechanism.

Before the fuel can proceed to form carbon deposits, the reaction must first be initiated to break down the hydrocarbons. Li [18] describes two main regions in the thermal stability of jet fuels: the liquid phase thermal autoxidation at low temperatures (<350°C) and gas phase pyrolysis at high temperature (>450°C). Autoxidation causes a

stage of hydroperoxides formation, and the resulting deposits tend to have large amounts of oxygen and settle out as spheres since they are insoluble with the bulk fuel. Pyrolysis mechanics are less understood, but are believed to form aromatic deposits through the following steps:



The details of these pyrolysis reactions are described with the Rice-Kossiakoff mechanism and the Fabuss, Smith, and Satterfield mechanism, depending on reaction temperature and pressure.

Presence of a metal catalyst is shown to interact with the hydrocarbon degradation in various ways and cause several different types of carbon deposit formation, such as filamentous carbon, laminar graphite carbon, and amorphous carbon. While these demonstrate real-world effects that would be expected in a metal-walled engine cylinder, it should not play a role in testing biodiesel fuels in a glass Ramsbottom vial.

Non-catalytic carbon deposits are described by Li as falling into two main categories: gas-born carbon formation that arises from interactions of gaseous, low molecular weight hydrocarbons to form large planer molecules, and surface nucleated carbon formation that creates laminated graphite structures built up on a substrate. Gas-born carbon formation is better understood than surface formation and is believed to most likely arise from PAH precursors. Surface formation is believed to arise at any

point in a longer series of precursor reactions that range from small species such as hydrocarbon radicals to larger molecules, aromatics, or radicals.

In summary, the carbon deposit formations from jet fuel described by Li [18] are outline below:

- Liquid phase autoxidation (lower temperature jet fuel degradation)
  - Insoluble, oxygen-rich deposits
- Pyrolysis (higher temperature jet fuel degradation)
  - Hydrocarbon decomposition
    - Catalytic reactions (metal present)
      - Filamentous carbon formation
      - Laminar carbon graphite formation
      - Amorphous carbon formation
  - Polymerization
    - Non-catalytic reactions (thermal degradation)
      - Gas-based deposit formation
      - Surface nucleated carbon formation

It is important to note again that the mechanisms briefly described above were all developed to explain the characteristics of jet fuel, and many of them involve polymerization of aromatic compounds into PAHs and larger molecules. Therefore, it would be expected that a higher concentration of aromatics in the fuel would lead to increases in the carbon residue formation and the relative importance of the polymerization mechanisms which rely on these aromatic compounds.

However, biodiesel has very different characteristics than both ULSD and jet fuel in this respect. While Bernabei, *et al.* [19] reported finding more than 60 types of

aromatic compounds in aviation jet fuel and Monyem, *et al.*[16] reports that 31.0% of the hydrocarbons in number 2 diesel are aromatics, Monyem, *et al.* and other authors have reported that biodiesel has no aromatic compounds. This is due to the absence of aromatics in the triglyceride molecules that comprise the source oils. Because of the lack of aromatics in biodiesel, dedicated studies need to be made to determine exactly what mechanisms are employed to form carbon residue in biodiesel combustion.

### **Importance of Saturation in Carbon Residue Formation**

Research into using neat vegetable oil as a fuel without transesterification into biodiesel has shown a link between the degree of saturation and the amount of carbon deposits formed. Korus *et al.* [2] showed that a more unsaturated fuel, that is one with more carbon-carbon double bonds, will form more carbon deposits than a saturated fuel. As with the relationship between biodiesel and autoxidation, their study linked the amount of carbon residue formed to the amounts of oleic, linoleic, and linolenic fatty acids in the fuel. Of the three vegetable oils tested, linoleic safflower oil gave the greatest amount of injector coking even though it had the lowest viscosity. This shows that the degree of saturation is the overriding factor of carbon formation and more important than the viscosity of the fuel.

### **Fuel Testing and Specifications for Carbon Residue**

Carbon residue can be tested using several different methods; three common methods are the Ramsbottom test (ASTM D 524 – 04), the Micro Method (ASTM D 4530 – 07), and the Conradson test (ASTM D 189) [21, 22]. These tests determine the amount of carbon residue formed by a fuel after evaporation and pyrolysis take place. The



testing methods do not combust the fuel or use a test engine, but rather heat the fuel to high temperatures in specialized containers to cause rapid evaporation. Thus, the results give an indication as to the amount of residue that will be left behind in an engine and not an actual measurement of residue in a combustion cylinder. A correlation curve for converting between Ramsbottom carbon residue and Conradson carbon residue is provided in the ASTM standards for Ramsbottom testing. Since the test results are equivalent between the Micro Method and the Conradson test, results can be easily converted between any test methods.

B100 and ULSD have different requirements for carbon residue, and carbon residue is testing using different methods for each fuel. The ASTM specifications for B100 require a maximum of 0.05% carbon residue by mass using the Micro Method [23]. This is equivalent to a 0.1% Ramsbottom carbon residue by mass. The specifications for ULSD have a maximum of 0.35% Ramsbottom carbon residue by mass, meaning ULSD can leave more carbon residue than B100 [24]. The Ramsbottom test was used for all experimentation in this thesis.

## ***Overview and Expected Results***

Overall, carbon deposition from biodiesel is much lower than that of ULSD, potentially due to the lack of aromatics in biodiesel making formation of large aromatic residue structures difficult. The standards for ULSD allow for 3.5 times more Ramsbottom carbon residue than that created by B100. Although B100 may be pushed out of specifications if oxidation is shown to increase carbon residue, it will likely have

less of an overall impact than comparable ULSD. The Ramsbottom carbon residue of B100 would have to show large increases to leave as much carbon residue as ULSD.

As a fuel ages and oxidizes, some of the fuel will polymerize into heavier, more viscous compounds and some will split into lighter, volatile molecules that may, depending on storage conditions, escape the bulk fluid. This can leave a more viscous fuel, and more viscous fuels typically leave more Ramsbottom carbon residue. However if the fuel is oxidized in a sealed container, these lighter compounds may not be able to escape and the overall viscosity of the fuel mixture will remain largely unchanged, as shown by McGuire [17]. In this case, viscosity changes should have less of an effect on carbon residue, and the changes in the fuel's chemistry should be the overriding factor for controlling carbon deposition.

Another main effect that oxidation could have on carbon residue is the breakdown of double bonds in the fuel for the creation of hydroperoxides. Research has shown that oxidation often initiates at double bonds in fuel structure. If these double bonds are eliminated in the reaction, a fuel could become more saturated. As Korus, *et al.* [2] has shown, the degree of a fuel's saturation is more important in carbon residue formation than the viscosity of the fuel. If these findings, demonstrated using neat vegetable oils, hold true for biodiesel, then the carbon residue can be linked to saturation. If the degree of saturation in the fuel increases during oxidation, then carbon residue can be expected to decrease as the fuel oxidizes. Any increase in viscosity will likely be overshadowed by an increase in saturation. However, the literature has not

conclusively shown what changes take place in the saturation of biodiesel as it ages and whether the saturation increases or decreases.

## Experimental Setup

### *Ramsbottom Testing*

The standard test method for Ramsbottom Carbon Residue of Petroleum Products, ASTM D 524, was followed for all carbon residue and coking tests [21]. In this procedure, an empty glass coking bulb is first heated in a 550°C oven for 20 minutes to remove water and decompose any organic matter that may be on the bulb. After heating, the bulb is then placed into a desiccator to cool. Once cool, the empty bulb is accurately weighed to a tenth of a milligram. The bulb is then carefully loaded with fuel using a syringe and reweighed. To minimize fuel splattering, all tests were carried out using a fuel sample size of approximately 1 g. The bulb and fuel are then placed back into a 550°C oven for 20 minutes to allow rapid evaporation of volatile compounds, then cracking and coking reactions on the heavier residues remaining in the bulb. After heating, the bulb is placed back in the desiccator to cool before being accurately weighed one final time. The carbon residue is calculated as a percentage of the total fuel sample using the following equation:

$$\text{Carbon Residue} = \frac{\text{Mass of Carbon Residue}}{\text{Mass of Sample}} \times 100$$

The Ramsbottom test method is the required test method for the ASTM specifications of petroleum-based diesel fuels. However, the ASTM specification for biodiesel fuels requires an equivalent test known as the Micro Method, ASTM D 4530. Because of this, the Ramsbottom results were related to Micro Method values using

correlation data provided by ASTM. Ramsbottom carbon residue can be converted into Conradson carbon residue (ASTM D 189) using a provided curve. Conradson carbon residue is statistically equivalent to Micro Method residue, so they are equivalent on a one-to-one basis. Using these relationships, the Ramsbottom data found through experimentation could be compared to the ASTM specifications for biodiesel.

The ASTM Ramsbottom test standards include curves for calculating expected repeatability and reproducibility of the test, where repeatability is the difference from trial to trial run by the same operator using the same materials and equipment and reproducibility is the difference from trial to trial run by a different operator using the same fuel but different, equivalent laboratory equipment. These curves give an expected error based on the average carbon residue results obtained during testing, and were used to calculate error for these tests. A further discussion of error is below.

### ***Coking Change in Biodiesel after Natural Oxidation during Storage***

The first phase of experimentation carried out was to test the coking properties of various fuel types before and after a storage period. This experiment was to determine if any differences would arise from between fuel types and to determine whether oxidation would increase or decrease the amount of carbon residue left in the Ramsbottom test.

### **Fuel Selection and Characterization**

A total of six different biodiesel fuels and one standard ULSD fuel as a control were chosen for this research. All of the biodiesels were used as a neat fuel; no blended

fuels were tested. Sampled fuels were taken from a variety of source materials and current conditions. These fuels are described below:

**Table 1: Fuels Tested in Natural Oxidation Experiment**

Fuel Type	Description
TR Soy	Twin Rivers SME biodiesel
B100	High-quality Peter Cremer biodiesel distilled to remove impurities then treated with a chemical antioxidant
PC B99	Fresh Peter Cremer B-99 fuel
Waste Oil based Biodiesel	Biodiesel created through transesterification of a waste oil source
Waste Oil based Biodiesel oxidized for 24 hours	The same fuel as Sample 4, but oxidized under similar conditions to the reactor used in the second half of this experimentation for 24 hours before testing began.
ULSD – Petroleum Based Diesel	Standard ULSD fuel

### **Oxidation Conditions**

Each fuel was placed into a 20 mL glass sample vial for storage throughout testing. The Ramsbottom test was first carried out on all seven fuels before storage. Each test was carried out multiple times to find an average carbon residue value. Some of the repetitions were deemed as invalid due to factors such as chipped Ramsbottom vials or foreign material adhered to the exterior of the Ramsbottom vial during testing, creating faulty weights.

After conducting the initial tests, the vials were sealed with air space above the fuel. The fuels were then allowed to oxidize naturally under identical conditions. The sample vials were placed upright in a dark container and stored undisturbed at room temperature for five months to allow time for natural oxidation reactions to occur in

each fuel. After this storage period, each fuel was retested using the Ramsbottom test to determine coking properties after the oxidation period.

### ***Coking Change in Biodiesel after Artificial Oxidation over 24 Hours***

The second phase of experimentation was to determine how the coking properties of a single type of biodiesel fuel change over time. This experiment artificially oxidized a single fuel type in a heated, closed reactor with a constant stream of oxygen for 24 hours, with samples being pulled every 12 hours for Ramsbottom testing. SME treated with an antioxidant additive package was used for this experiment. This fuel was chosen as it represents a high-quality biodiesel fuel with chemical additives, much like what would be expected from professionally-made biodiesels.

### **Oxidation Reactor Conditions**

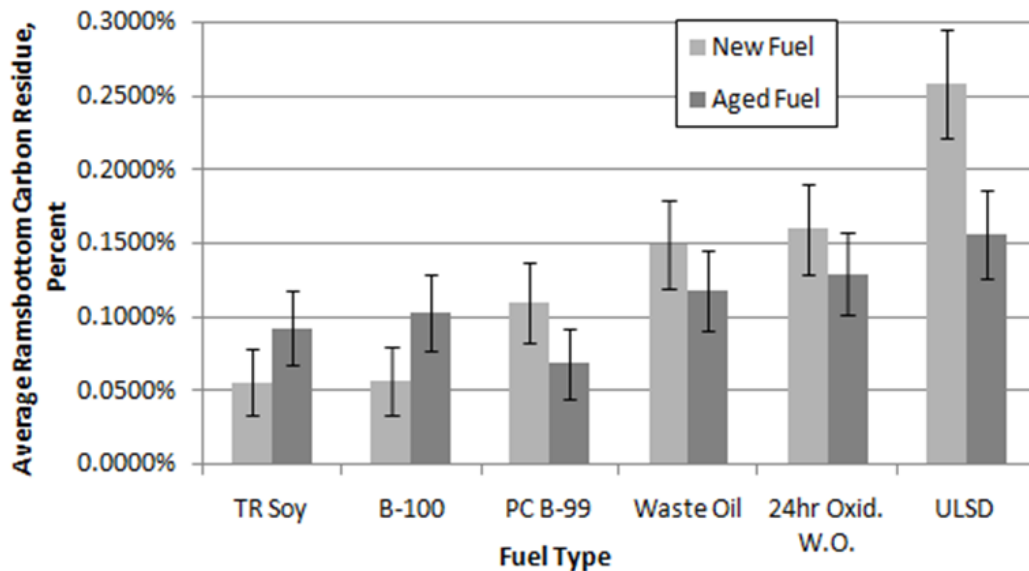
The reactor used in this experiment was set up following an identical procedure to that used by McGuire [17]. A closed reactor was fitted with a magnetic stirrer, a sparge rod, and band heaters and then filled with fresh SME. The fuel was continuously stirred while being heated to 60°C and bubbled with pure oxygen at 7kPa gauge pressure. The oxygen was heated and then bubbled through the mixture at 1 standard liter per minute (slpm). Under these conditions, the fuel was oxidized in 6 hour increments with samples being pulled every 12 hours until the fuel had been oxidized in the reactor for 24 hours. In between the 6 hour increments, the reactor was allowed to cool and remained off for a day so that the reactor would not be run unsupervised.

## Results

### *Coking Change in Biodiesel after Natural Oxidation during Storage*

Results from the natural oxidation experiment were varied. Four of the 6 biodiesel fuels tested showed decreases in carbon residue as the fuel aged. The other two fuels showed increases. However, most of the variations were not exceedingly large; many of the differences are within expected ranges of error. The ULSD tested showed a marked decrease in carbon residue. The graph below shows these changes and the table shows the sample data for each test.

**Figure 3: Change in Ramsbottom Carbon Residue of New vs. Aged Fuels for Various Fuel Types**





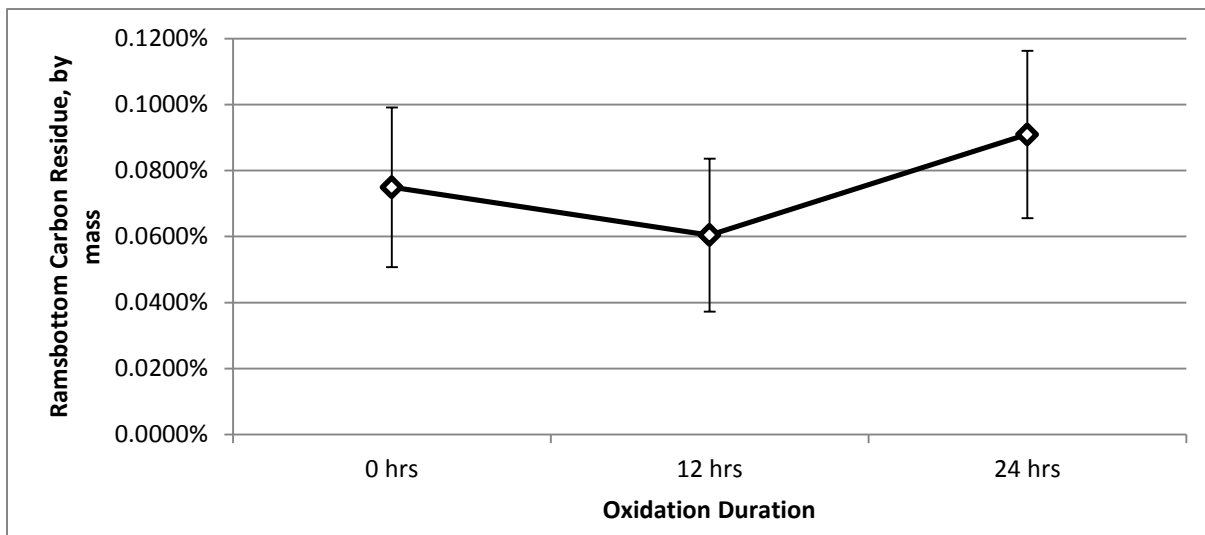
**Table 2: Results for Ramsbottom Testing on Naturally Oxidized Fuel Samples**

Fuel	Sample	Ramsbottom Carbon Residue, %	Average Carbon Residue, %
TR Soy	Fresh	1	0.0555
		2	0.0839
		3	0.0282
	Aged	1	0.0887
		2	0.0967
B-100	Fresh	1	0.0811
		2	0.0482
		3	0.0401
	Aged	1	0.1004
		2	0.1059
PC B-99	Fresh	1	0.1349
		2	0.0945
		3	0.1004
	Aged	1	0.0773
		2	0.0655
		3	0.0631
Waste Oil	Fresh	1	0.1491
		2	0.1496
		3	0.1503
	Aged	1	0.1103
		2	0.1160
		3	0.1279
24hr W.O.	Fresh	1	0.1736
		2	0.1459
	Aged	1	0.1279
		2	0.1222
		3	0.1386
ULSD	Fresh	1	0.1911
		2	0.3268
		3	0.2407
		4	0.2747
	Aged	1	0.1664
		2	0.1723
		3	0.1292

## ***Coking Change in Biodiesel after Artificial Oxidation Over 24 Hours***

Results of Ramsbottom testing on the fuel samples oxidized over 24 hours showed little change over the oxidation period. As shown in the figure below, the average residue measured from two tests on each sample decreased at 12 hours but increased at 24 hours. However, these changes are all within the error specified by the repeatability of the Ramsbottom test, so no statistically relevant change was detected. Also, it is important to note that all measurements were below the ASTM standard of 0.1% Ramsbottom carbon residue (0.05% carbon residue from the Micro Method).

**Figure 4: Average Ramsbottom Carbon Residue of Artificially Oxidized Biodiesel**



**Table 3: Results for Ramsbottom Testing on Artificially Oxidized Fuel Samples**

Oxidation Duration	Sample	Ramsbottom Carbon Residue, %	Average Carbon Residue, %	Average Repeatability, +/- %
0 hrs	1	0.0736	0.0749	0.0242
	2	0.0763		
12 hrs	1	0.0595	0.0604	0.0232
	2	0.0613		
24 hrs	1	0.0963	0.0909	0.0253
	2	0.0856		

## Discussion

### *Summary of Findings*

Results from the tests carried out did not conclusively show that carbon residue increases or decreases as the fuel ages.

During the first phase of testing, the amount of carbon residue increased for some fuels and decreased for others. However the changes were typically within the expected standard of error calculated using the repeatability curves supplied by the ASTM Ramsbottom guidelines. The only fuel that showed a statistically significant change was the large decrease carbon residue that arose from aged ULSD. Carbon residue from the ULSD decreased by 39.6% after the fuel was aged. The results for the biodiesel samples chosen showed all combinations of results: slight variations likely within the expected error for testing, carbon residue increases in Twin Rivers SME and Peter Cremer B100, and carbon residue decreases in Peter Cremer B99. In a comparison of before and after photographs of the fuels, no visual changes were seen in any of the fuels.

The second phase of testing showed the overall effectiveness of the commercial antioxidant package. After 24 hours, the oxidized fuel was visually indistinguishable from the fresh fuel. McGuire reported seeing significant color change in both SME and CME fuels without chemical additives after oxidation. Carbon residue was not significantly changed from the fresh sample to the two oxidized samples. Also, all results showed a Ramsbottom carbon residue of less than 0.1%, which is equivalent to the

ASTM standards of 0.05% carbon residue from the Micro Method. Therefore, this testing shows that carbon residue was not a concern when using a high-quality fuel with an oxidation package.

It should be noted that none of the biodiesel samples tested at any point during this experimentation would have been above the standards for ULSD carbon residue. While some fuels were above the B100 standards, the total residue is still less than that created by the ULSD already widely in use today. The use of biodiesel, even fairly low-quality biodiesel, can then be expected to cause less cylinder damage, fewer engine failures, and an overall reduction in problems arising from engine coking. While using low-quality biodiesel may cause concerns, the Ramsbottom test results seem to show that engine coking is not one of them.

### ***Sources of Error in Testing***

During experimentation, care was taken to ensure the testing procedure was identical from sample to sample. The same balance, accurate to a tenth of a milligram, was used for all masses, and the same heating oven was used for all tests. Testing vials were handled with metal tongs at all times to prevent any foreign material or oils from contaminating the surface of the bulbs due to skin contact.

However, the Ramsbottom test still produced variations when analyzing a single type of fuel; experimental error was preventing identical results from trial to trial. The sources for this error were myriad; small amounts of fuel blocking the neck of the sample bulb could impede some rapid evaporation, small differences in the amount of

fuel loaded into the bulb or fuel droplets being sprayed onto the sides of the bulb could cause different evaporation characteristics, contamination could adhere to the sample bulb either in the oven, during weighing, or during storage in the desiccator, or tiny pieces of the bulb could fragment off the delicate edge of the neck during transport to and from the oven.

Another major factor for error in this experiment is how many tests had been carried out before a sample was tested. Since the Ramsbottom test requires a certain amount of manual dexterity to perform correctly, results improved as more tests were done. Handling the bulbs into and out of the oven as well as to and from the balance requires manipulation of tongs in an unwieldy manner. Filling the bulbs with the syringe required precise and careful movements to use the proper amount of fuel and cause as little blockage of the neck as possible. The first few samples run show wide variations from test to test as these motions were practiced. By the end of testing, the procedure was much easier and the results have significantly less variation.

To account for these errors, some samples that showed unreasonable results were thrown out, such as vials that had visible chips. Also, the ASTM standards for the Ramsbottom test include data curves for predicting the sample difference based on the average carbon residue percent for a given fuel. Using these curves, the expected difference from sample to sample can be found for test repeatability by the same operator and apparatus and test reproducibility based on different operators in different laboratories. Since all experimentation was carried out using approximately 1.0 g of fuel rather than 4.0 g, it is possible that expected sample differences from these

curves are not applicable to the results of the experimentation. Furthermore, each fuel was sampled only 2 or 3 times, making establishing true residue averages difficult.

## Conclusions

From these results, it cannot be said with certainty how fuel oxidation during storage affects carbon residue characteristics of biodiesel. Testing of the ULSD indicates that a 40% decrease occurred when the fuel was aged. However, the testing of artificially oxidized fuel strongly indicates that use of a high-quality biodiesel with an additives package to prevent oxidation will inhibit any major changes in carbon residue formation over time. Therefore, changes in carbon residue and engine coking are not likely to be a concern when using such a fuel.

## *Suggestions for Future Work*

Several additional experiments could be done to expand upon this work further. The first would be to repeat the artificially oxidation experimentation with several different types of fuels, including fuels without additives packages. This would show a comparison between the high-quality, professionally-made fuel used in this lab and a lower-quality fuel that might be more similar to something made by a small scale or backyard producer of biodiesel.

Another area that would be interesting to explore would be the actual in-engine coking properties of oxidized biodiesels. This thesis only used the Ramsbottom test to determine carbon residue. The Ramsbottom test is an indicator of how much residue a fuel will create in an engine; obviously, this may differ in real-world conditions. Experimentation using test engines would better mimic actual conditions.

One major area of interest is the difference between the deposition mechanisms described for jet fuel by Li and those for biodiesel. In particular, what is the chemical reasoning for the large difference in carbon residue between ULSD and biodiesel? Does it arise from the difference in degree of saturation, amount of aromatics, or some other property? While such understanding would take significant work to achieve, it would likely enhance knowledge and methods of thought for not only biodiesel, but petroleum based fuels and other types of biofuels as well.

Outside concerns with biodiesel, the accuracy of this experiment could be better reported if the ASTM standards included correction factors for their correlation and error curves when using a 1.0 g sample as opposed to a 4.0 g sample. The guidelines say that under certain conditions, a 1.0 g sample can be used, but they do not state expected differences in the results when using a lighter sample. Had this information been available, the results of this work could be stated more confidently.



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# Academic Vita

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### EDUCATION

The Pennsylvania State University, State College, PA  
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Minor in International Studies

Universidad de Ciencias Empresariales y Sociales, Buenos Aires, Argentina  
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**Advanced Spanish Program, IES Study Abroad**

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Universidad Iberoamericana, Puebla, Mexico

**Mexican Culture and History Study Abroad Program**

**Summer 2006**

### AWARDS

Two time recipient - Raja V. and Geetha V. Ramani Honors Scholarship  
2008 & January 2008 – January 2009

January 2007 – January

Matthew J. Wilson Honors Scholarship  
2009

January 2008 – January

Two time recipient - Chevron Corporation ENVSE Scholarship  
2008 & January 2008 – January 2009

January 2007 – January

### EXPERIENCE

Chevron Corporation, Gulf of Mexico Business Unit

**Health, Environment, and Safety Intern**

**Summer 2009**

- Drafted a substantial report on the relevance and business impacts of upcoming greenhouse gas legislation for the business unit with quantized prospective areas for emissions reductions
- Streamlined issues with training and paperwork of naturally occurring radioactive materials handling
- Standardized and streamlined implementation of Stormwater Pollution Prevention Plans

Anheuser-Busch, Newark, NJ Brewery

**Environment, Health, Safety, and Security Intern**

**Summer 2008**

- Created flowcharts integrating Title V Air Permit requirements with photographs and maps of on-site equipment to facilitate easy understanding of legal requirements
- Performed weekly chemical leak and spill prevention inspections of all potential sources on-site
- Wrote application for and received New Jersey STAR recycling award for the brewery

Horizon Wood Products

**Various Positions and Responsibilities**

**2001 – Present**

- Handle variety of tasks from general labor to international sales meetings
- Assist with building and equipment layout and design during construction and renovation
- Attend trade shows, sales meetings, etc. as a company representative

**LANGUAGES**

English – Native Language

Spanish – Speak, read, and write with competency