AN ABSTRACT OF THE THESIS OF

<u>Ezra Daniel Phipps</u> for the degree of <u>Master of Science</u> in <u>Chemical Engineering</u> presented on <u>May 29, 2013.</u>

Title: <u>Upgrading of a Model Compound of Bio-oil Using Carbon Monoxide in High Temperature Water</u>

Abstract approved:
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Meeting the energy demands of the future is one of the most important challenges facing the engineering community today. An example of this problem is transportation fuels. Most of the current transportation fuels are composed of petroleum hydrocarbons. Finding a viable alternative is important given the potential scarcity of these fuels. Alternatives have been explored including ethanol, biodiesel, hydrogen, and natural gas. It will be difficult for these fuels to replace petroleum fuels due to their inferior performance and, in some cases, the rising price of the feedstocks as they are produced on a larger scale. In addition, some of these fuels are not compatible with current infrastructures, including piping and filling stations, as well as being incompatible with the current fleet of cars.

The ideal scenario for solving the energy problem is to produce a fuel that has the same level of performance as standard petroleum hydrocarbons and originates from a feedstock that is cheap and abundant. For these reasons, a large amount of research in the past couple decades has been dedicated to producing bio-oil from biomass by thermal degradation in the absence of oxygen. Biomass is composed of large oxygenated hydrocarbons containing as many as 60,000 carbons atoms. When

subjected to high temperatures these molecules break apart and oil is produced that more closely resemble liquid fuels.

The primary drawback of bio-oils is that they have high oxygen content. This high oxygen content causes them to have low energy density, low volatility, and a high viscosity. In order to meet the industry standards for transportation fuels, additional processing steps must be completed in order to reduce the oxygen content of the fuels. The most common processing step in use is hydrotreating. During this process bio-oils are heated up to high temperatures in the presence of an excess of hydrogen and a catalyst. The purpose of this is to initiate a hydrodeoxygenation reaction that removes oxygen from the oils in the form of water. This process has been shown to be effective; however the usefulness of the process is limited by the high cost and energy demands of producing hydrogen.

Previous work has also been completed where bio-oils were treated in the absence of hydrogen using high temperature water as a solvent [1]. This process induces a separation of the oil into an aqueous phase and an oil phase which is low in oxygen content. Oxygen is also removed in the form of carbon dioxide due to a decarboxylation reaction. A more detailed review of the material balance for this process demonstrated that the overall amount of oxygen removed was actually quite low and may in fact be statistically insignificant.

The purpose of this research project is to examine the process of treating bio-oils with supercritical water as a solvent in the presence of carbon monoxide. One reason for doing this is that at high temperatures, carbon monoxide reacts with water producing hydrogen and carbon dioxide. In addition, thermodynamic modeling demonstrates that carbon dioxide is one of the more favorable products formed when combining these reactants, which would consume additional oxygen.

Guaiacol, a model compound for bio-oil was treated by heating to supercritical temperatures in the presence of water and varying concentrations of carbon monoxide. The resulting products were analyzed in order to determine the types of

functional groups present, the elemental composition, water content, and in some cases the distribution of products.

The analytical results suggest that catechol, methoxybenzene, and phenol are the primary reaction products with most of the catechol dissolved in the aqueous phase. There is some evidence that there is a relationship between the amount of carbon monoxide in the reactor enclosure and a reduction in oxygen content. Due to the small difference in oxygen content of the primary reaction products and the error inherent to the measurement methods it is not conclusive at this time if that the relationship between carbon monoxide and lower oxygen content is statistically significant.

Future research is required to further validate the results. To supplement the findings of this research it would be helpful to perform a similar experiment under conditions that produce a larger spread in oxygen content. This can be done in several different ways. The reaction residence time could be increased, a different model compound could be used, the conditions could be more severe, and a catalyst could be used as well. By changing these conditions a greater spread of data could be produced and it would be easier to determine statistical significance on that basis.

Upgrading of a Model Compound of Bio-oil Using Carbon Monoxide in High Temperature Water

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Ezra Daniel Phipps, Author

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NOMENCLATURE

G_f	Gibbs free energy	H_f	Heat of formation
WF_O	Water fraction in oil phase	R	Ideal gas constant
WF_M	Water fraction in methanol	$\hat{V}$	Molar volume
MF_D	Methanol fraction for dilution	ω	Acentric factor
K_{eq}	Equilibrium constant for reaction	p	Pressure
N_1	Number of samples in group n	$\overline{Y}_n$	Average of group n
S_n	Standard deviation of group n	Sp	Pooled standard deviation
SE	Standard error for a difference		

Upgrading of a Model Compound of Bio-oil Using Carbon Monoxide in High
Temperature Water

Ezra Daniel Phipps

CHAPTER 1 INTRODUCTION

There have been several decades of research at this point covering the production and treatment of bio-oils from biomass. Bio-oils are created by the pyrolysis of biomass which creates a fuel that is similar to petroleum fuels, except that it is higher in oxygen content. Most of the current research focuses on how to reduce this oxygen content in order to make the fuel useful as a transportation fuel.

The standard method for reducing oxygen content in bio-oils is hydrotreating. Hydrotreating is an effective method of reducing oxygen content that also is the subject of a large body of research. While this process is effective it requires the use of a large amount of hydrogen which is very expensive. The expense of hydrogen during hydrotreatment is one of the main issues making the use of bio-oils cost prohibitive.

Due to the high cost of hydrogen there is a great amount of interest in finding ways to treat bio-oils without using externally produced hydrogen. This research focuses on treating bio-oils by creating hydrogen on site using a water gas shift reaction.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{1.1}$$

For this research guaiacol, a model compound of bio-oil was placed in a reactor with an excess of carbon monoxide and water. The goal of this research is to enhance the treatment of bio-oils by generating hydrogen within the reactor. In addition, oxygen may be removed by a direct reaction between carbon monoxide and the bio-oil, since carbon dioxide is a more thermodynamically favorable product than carbon monoxide.

Using carbon monoxide as a gas instead of hydrogen is desirable due to the fact that carbon monoxide is already produced in many processes that occur in a standard petroleum refinery. In addition carbon monoxide can also be formed from splitting CO_2[2]. At high temperatures thermal splitting of CO_2 requires less energy than

splitting water to form hydrogen. This means given equal performance, using carbon monoxide may be more cost efficient than using hydrogen. If carbon monoxide is found to be effective for facilitating deoxygenation reactions bio oil will be one step closer to being used on a widespread basis as a liquid fuel.

CHAPTER 2
LITERATURE REVIEW

2.1 Biomass Potential for Energy Generation

The ideal scenario for solving the energy problem is to produce a fuel that has the same level of performance as standard petroleum hydrocarbons and originates from a feedstock that is cheap and abundant. For this reason much of the research that has been completed in the last several decades focuses on biomass. Biomass is any material derived from living organisms. One obvious reason that biomass is a desirable feedstock is that it is renewable and abundant. Currently much of the biomass feedstock comes from materials that are currently waste products such as forest debris, corn husks, and other agricultural wastes. This of course means that if the proper technologies can be developed biomass can provide a sustainable source of fuel cheaply. Another reason that biomass is desirable to use is because of the nature of the structure of the compounds it is composed of.

Wood or plant based biomasses are generally composed of three components, Lignin, cellulose, and hemicelluloses. Wood also contains several other chemical groups but they are a minor portion of the total weight. The combination of cellulose and hemicellulose is referred to as holocellulose which accounts for about 65-70% of total weight with the balance composed of lignin. The ratio of these different components can vary depending on the type of wood but are in the same general range. Holocellulose components are polymers composed mainly of the simple sugars such as D-glucose, D-mannose, D-galactose, D-xylose, and L-arabinose. The elemental composition of wood derived biomass is 50% carbon, 6% hydrogen, and 44% oxygen.

The primary difference between cellulose and hemicellulose molecules is their size. Each is comprised of sugars composed of five or six carbons with various oxygen

groups. The number of repeating units that form one cellulose molecule is referred to as the degree of polymerization (DP). The DP of cellulose is in the range of 10,000. Hemicellulose has a DP in the range of a couple hundred. The degree of polymerization corresponds to molecular weights in the tens of thousands. Figure 1 shows the structure of cellobiose which is the repeating unit that cellulose is composed of.
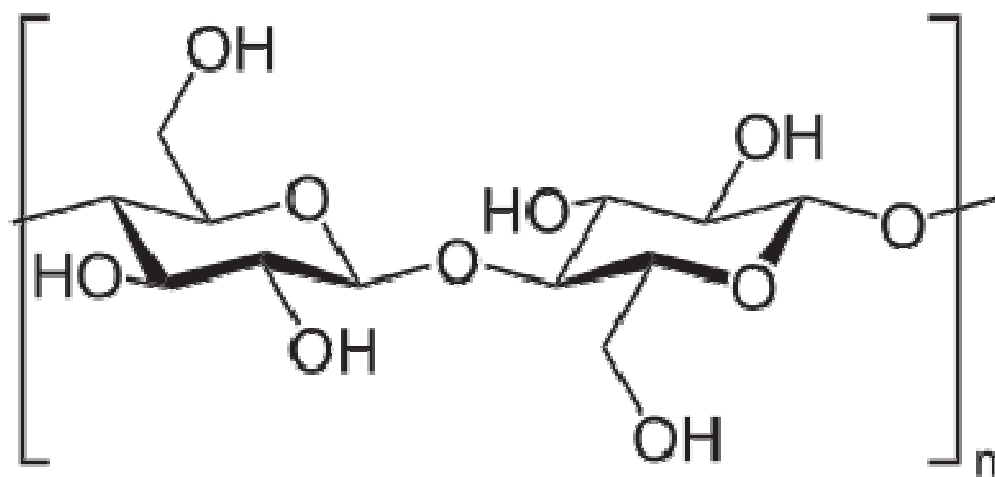
Figure 1: Chemical Structure of cellobiose [3]

Lignins are an aromatic polymer component of biomass. Lignin is like holocellulose in that it has no definite shape and size but the form falls into the same general category. The polymer is mainly composed of guaiacyl, syringl, and p-hydroxyphenyl groups. The size of lignin can vary greatly depending on the particular source with molecular weights ranging from 260 to 50 million [3]. A partial structure of lignin is displayed in figure 2.
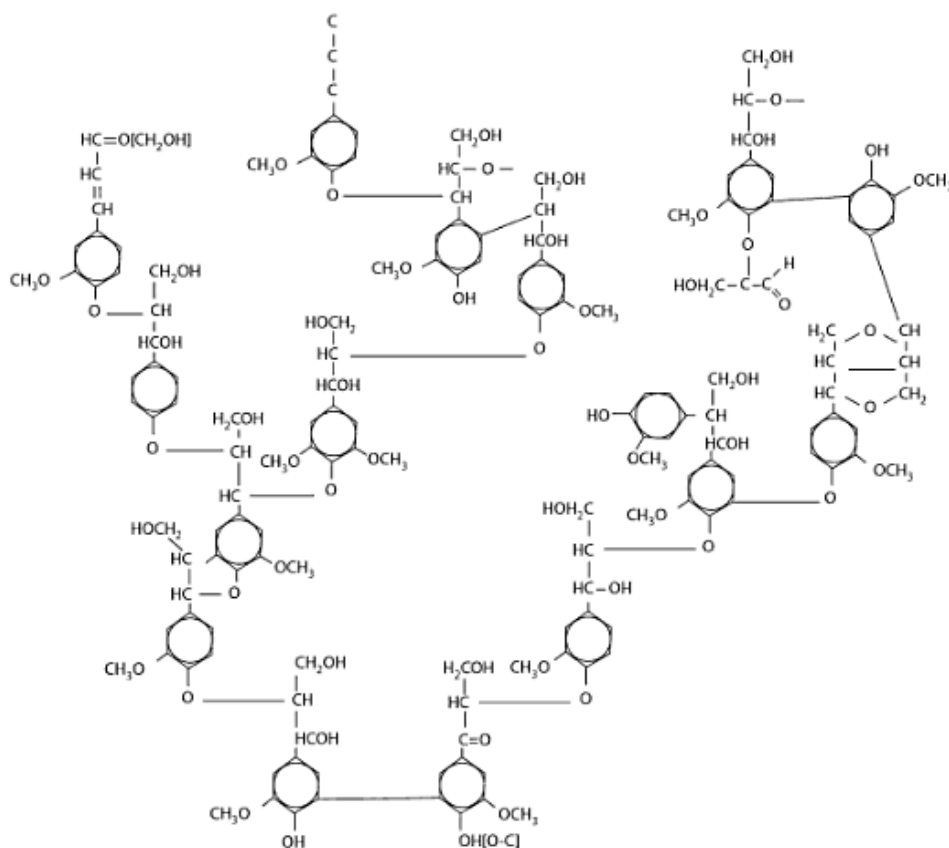
Figure 2: Partial structure of lignin [3]

Given the great energy density of these substances it is easy to see why they would be promising sources of energy. This energy is already utilized a great deal. Human beings obviously consume a lot of biomass in the form of plant based foods. A wood burning fireplace uses this energy by converting it to heat using a combustion reaction. One of the ways that biomass has been used is to generate electricity. This is done by burning biomass and using the heat to generate steam. That steam is then used to turn a turbine. Unfortunately this process has an efficiency of just 35-40% using the most advanced methods. Biomass can also be altered through a fermentation process to produce methane [4].

Another form of fuel that can be produced is hydrogen via gasification of biomass. Gasification is the reaction of biomass with water/steam in the absence of oxygen.

This process can be represented in this case by the reaction between cellulose and water to form hydrogen and CO_2.

$$C_6H_{10}O_5 + 7H_2O \ \rightarrow \ 6CO_2 + 12H_2 \tag{2.1}$$

This reaction is a simplification of the process since many other sugars are used as reactants and light hydrocarbon gases are generally produced as well. This reaction must be completed at high temperatures, generally above 600°C. At lower temperatures biomass simply repolymerizes and forms coke and tar. One of the problems limiting this technology is often the reaction proceeds more quickly than the reactor can be heated which leads to excessive solids formation. This is also a problem with liquefaction which will be discussed later. Much of the research in gasification has focused on catalysis in order to drive the reaction forward at a lower temperature. Some success has been achieved with reactor temperatures as low as 300°C. Some research has also focused on enhancing the heating rate by using smaller diameter reaction units. This approach is problematic due to the formation of coke and bio-oils which will be discussed later. Another way of enhancing heating is to reduce the size of the biomass particles by generating sawdust. A schematic of a typical gasification process is displayed in figure 3.
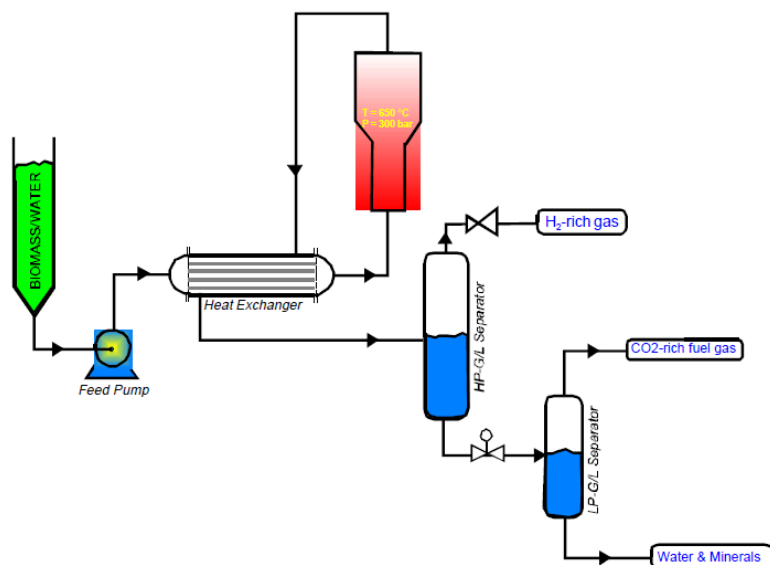
Figure 3: Schematic of gasification process using supercritical water [5]

There are many limitations to using hydrogen as a fuel source. Hydrogen is not compatible with the current energy infrastructure since it is a gas at room temperature. In order for it to be used as a transportation fuel new pipelines and distribution infrastructure would have to be built. In addition, there are safety concerns due to the ease of ignition and the problems inherent with any pressurized gas. For these reasons there has been an enhanced focus on trying to develop a liquid fuel from biomass using pyrolysis.

2.2 Liquefaction Process for Generating Bio-oils

The material in this thesis focuses on treating fuels that are produced by a process referred to as fast pyrolysis or liquefaction. This process is similar to gasification but the reaction times are shorter and no oxygen is present. Often gasification and liquefaction will occur simultaneously to a certain extent. This is actually convenient because the products of gasification can be useful in treating bio-oils. This product is compatible with the current energy infrastructure and given the proper treatment may actually be processed along with standard petroleum hydrocarbons.

The pyrolysis process begins with drying the biomass to below 10% moisture content to minimize the water in the pyrolysis oil product [6]. Feedstocks are then grounded into small particles to increase the surface area and therefore reduce the time for heat transfer during the process. Materials are then heated to temperatures ranging from 400 to 650°C. Heating is done at a very high rate with the peak temperature reached within 30 seconds [7]. The product is then rapidly cooled to quench the reaction. There are several different methods that have been used to heat the reactor. Each of these processes involves the feedstock contacting an inert gas or solid surface such as sand or metal which has been preheated. Descriptions of several different types of processes for producing bio oil are listed in table 1.

Table 1: Types of reactor setups for pyrolysis of biomass

Pyrolysis type	Brief description
Ablative	Mechanical pressure used to push biomass into hot reactor wall
Auger	Biomass is mixed with hot sand with constant mixing
Entrained flow	Essentially a heat exchange with a heated gas stream contacting the biomass
Fluidized bed	Same as Auger but sand fluidized by product gas to enhance heat transfer.

During the pyrolysis process, bonds can break and reform in a wide variety of different ways which are difficult to control. For this reason the distribution of products during pyrolysis is very wide, leading to over 300 different products [8]. The distribution of products includes many compounds that are of ideal size, generally containing 5 to 20 carbons per molecule and are saturated. Smaller hydrocarbons are also formed, some of which are useful as consumer products. Examples are butane which is used in handheld lighters and propane for gas grills. Most of the time, these light products are used internally as process heat or for hydrogen generation. Hydrocarbons also may polymerize and form coke. Under ideal conditions the product distribution is 75% oil, 12% char, and 13% gas [7]. Gas products are generally recycled to be burned as process heat.

Different feed stocks produce oils of differing quality in a couple ways. The lignin portion of biomass tends to produce heavier molecules. This is why the processing time is generally higher for the lignin fraction. It has also been found that feeds with low lignin content produce oils that are low in viscosity and molecular weight [9]. The water content however increases which was determined to be because of the presence of alkali metals. There is generally an inverse relationship between lignin content and the presence of alkali metals [10]. This difference is due to the fact that parts of a plant that transport minerals are generally low in lignin content.

Char formation is a significant issue during the production of bio-oil. Char is not an economically desirable product and it can plug product lines, cause catalyst

deactivation, and reduce reactor surface area. One of the ways of minimizing char formation is the use of a solvent. Solvents create separation between molecules in solution therefore decreasing the odds that they will collide and agglomerate. In the past phenol has been used but is largely phased out due to cost and environmental concerns. Methanol and Ethanol have both been shown to be effective solvents with bio-oil yields greater than when water is used as a solvent. The distribution of products changes as the fraction of solvent increases in the mixture. As the fraction rises above 10% the oil yield decreases slightly but the amount of solid product decreases more dramatically [11].

An ideal solvent will maximize the solubility of biomass derived fuels in order to reduce coke formation, as well as promoting the formation of a low oxygen content product. Research has been performed by Catchlight Energy, a Joint Venture of Chevron and Weyerhaeuser to develop a novel solvent mixture for use in a biomass liquefaction process. The purpose of this solvent was to improve the liquefaction process which accomplishes the goals of producing a higher quality product, while minimizing coke formation, without the use of a catalyst or a hydrogen donor solvent[12].

Storage conditions can change the nature of bio-oil over time. Bio-oil should be stored at room temperature, or lower. Even if bio-oil is stored at standard room temperature over time the molecular weight will gradually increase and solids will form. Aging can be prevented by refrigeration and it can also be prevented by the addition of a solvent. If bio-oil is stored dissolved in methanol the stability is greatly increased [7].

Pyrolysis products contain about 40-45% oxygen. This key difference between pyrolysis oil and standard petroleum fuels causes the energy density and volatility to be lower and the viscosity to be higher. In addition, the oxygen content can cause the fuel to corrode engine parts, and is not miscible with standard fuels, which makes

refining the fuel difficult. For these reasons bio-oils cannot be used as liquid fuels without additional treatment. In some cases, some of the bio-oil may be so difficult to treat it may be more efficient to burn it for process heat or convert the fuel via gasification to hydrogen [13].

The oxygen percentage of bio-oils can be reduced dramatically by changing the processing conditions of the oil. Bio-oil was produced by heating biomass from room temperature to a variety of different temperatures. There is an inverse correlation between peak pyrolysis temperature and oxygen content. Very high temperatures are not feasible due to the fact that those conditions cause the liquid yield of the products to decrease dramatically [14]. Figure 4 summarizes some of the data collected from an earlier paper examining the relationship between pyrolysis temperature and the bio oil product properties.
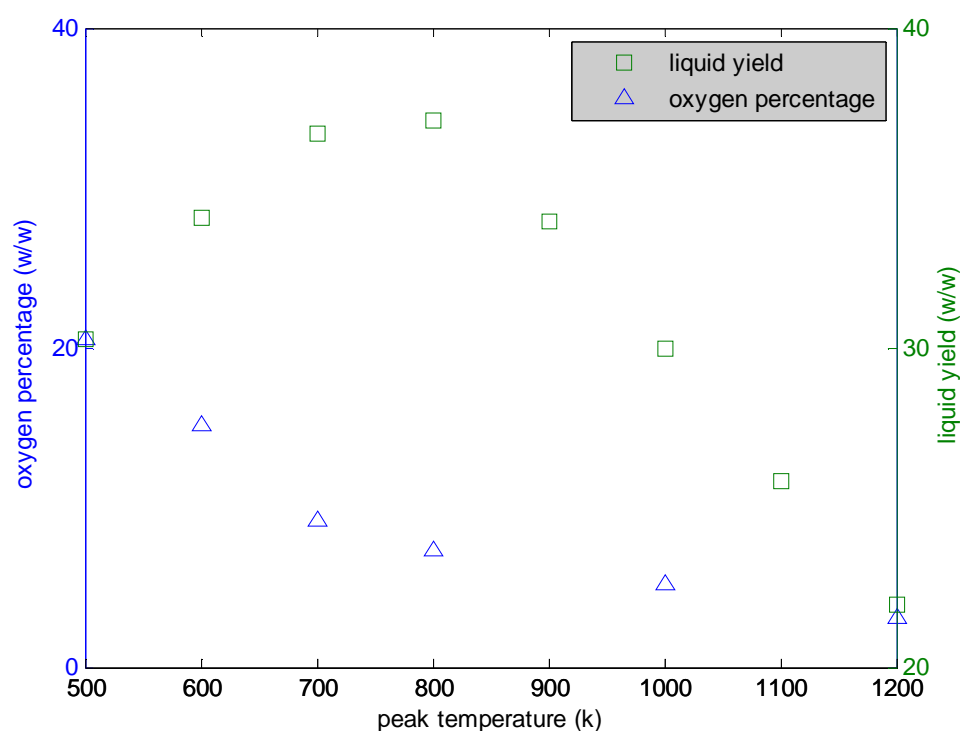
Figure 4: Effect of maximum temperature on yield and oxygen percentage [14]

2.3 Prior Strategies for Bio-Oil Upgrading

Bio-oil can be used as a fuel by itself but the performance will be inferior, which is why an additional processing step is usually added. The most common method for reducing the oxygen of bio-oils and therefore improving the performance is hydroprocessing. Oxygen is removed by adding hydrogen at high partial pressures and high temperatures. At these high temperatures the oxygen bonds break apart and when an excess of hydrogen is available, hydrogen displaces those bonds. The primary reactions that take place during this process are hydrodeoxygenation (HDO) and decarboxylation which are listed as equations 2.2 and 2.3 respectively. For these equations listed below M indicates any type of carbon chain.

$$MCOOH + 3H_2 \rightleftharpoons MCH_3 + 2H_2O \tag{2.2}$$

$$MCOOH \rightleftharpoons MH + CO_2 \tag{2.3}$$

These reactions are the most desirable; however many other reactions occur as well. For example, two of the larger molecules may break apart and reform to produce a molecule that is a very dense solid called coke or char. Small molecules may also break off and instead of reforming, may react with hydrogen to form light gases such as methane and ethane. Process conditions are adjusted in such a way to maximize the desirable products such as gasoline and diesel and minimize the less desirable products. A wide variety of different factors can dramatically impact the distribution of products including temperature, use of a catalyst, processing time, and hydrogen partial pressure. These areas of hydroprocessing have been heavily researched and a detailed summary has been compiled [15].

Hydrotreating was originally developed for treating standard petroleum hydrocarbons. Environmental regulations limited the amount of sulfur and nitrogen that can be present in petroleum hydrocarbons. The reason for this is that during combustion reactions nitrogen and sulfur form nitrogen oxides and sulfur oxides.

These chemical have been determined to pose a risk to the environment and human health. Sulfur and nitrogen are removed from petroleum hydrocarbons through reactions similar to a hydrodeoxygenation reaction.

$$MCN + 3H_2 \rightleftharpoons MCH_3 + NH_3 \tag{2.4}$$

$$MSH + H_2 \rightleftharpoons MH + H_2S \tag{2.5}$$

Due to the very large number compounds present in bio-oils, researchers have often focused on elemental analysis as a way of evaluating the success of hydrotreating and spend less time analyzing specific compounds. Other methods of analysis that are commonly used are gas chromatography and mass spectroscopy (GC/MS), and nuclear magnetic resonance (NMR) spectroscopy [16].

It is difficult to make a judgment about reaction pathways based on GC/MS and NMR data of typical pyrolysis hydrotreating products because the range of products is so wide. In order to simplify the experimental data for hydroprocessing experiments often model compounds are used. Model compounds are compounds that are deoxygenated in a similar way to bio-oils. Typical model compounds include P-Cresol, ethyl phenol, dimethyl phenol, trimethyl phenol, Napthol, and guaiacol [17]. The advantage of using model compounds is that researchers can see the full range of products for a particular reactant and can therefore make judgments about the reaction pathways.

Catalysts are often used to improve the performance of hydrodeoxygenation reactions. Several different studies have demonstrated that the most effective catalyst are NiMo and CoMo formations [15]. Other catalysts such as noble metal catalysts generally have significant issues with fouling. There has been some research that has suggested that noble metal catalysts may be effective for fast pyrolysis under the right reaction conditions [18].

Hydrodeoxygenation is generally considered a more desirable route for deoxygenation than the decarboxylation reaction. The reason for this is the production of carbon dioxide leads to a combination of water gas shift and methanization reactions that lead to increased consumption of hydrogen [19]. Examples of these reactions are as follows:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (2.6)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (2.7)$$

In order for the oil to be generally considered stable enough to be processed, along with fossil-based hydrocarbons, the oxygen percentage must be reduced to below 10%. One of the reasons that this benchmark has been set is that oil with higher oxygen content is not miscible with standard petroleum fuels. The reason that some oxygen content is permissible is that not all forms of oxygen impact the structure of the molecule in the same way. Groups that are detached from the molecule are more reactive and less stable. Once the most reactive oxygen groups have been removed the remaining oxygen is not a significant impediment to the use of the oil as a fuel. While 10% is a good rule of thumb for the amount of oxygen that must be present, indicators like viscosity have to be collected to determine the real impact of the changing structure of the molecule.

Hydrotreating is sometimes completed in stages because oxygen functional groups do not respond the same to varying process conditions. In some cases methoxyphenols, biphenols, and ethers are converted to phenols at lower temperatures. These functional groups are sometimes removed in a separate treatment stage regularly referred to as a stabilization stage. Phenols and furans are the primary functional groups present in bio-oils and are removed more easily [20]. Hydrotreating can also be used to convert triglycerides to diesel fuel. Typically triglycerides have been converted to biodiesel in the presence of methanol or ethanol. Biodiesel but this fuel has a variety of performance problems including a higher

cloud point and lower energy density. The breakdown of hydrodeoxygenation products and their feedstocks are presented in figure 5.
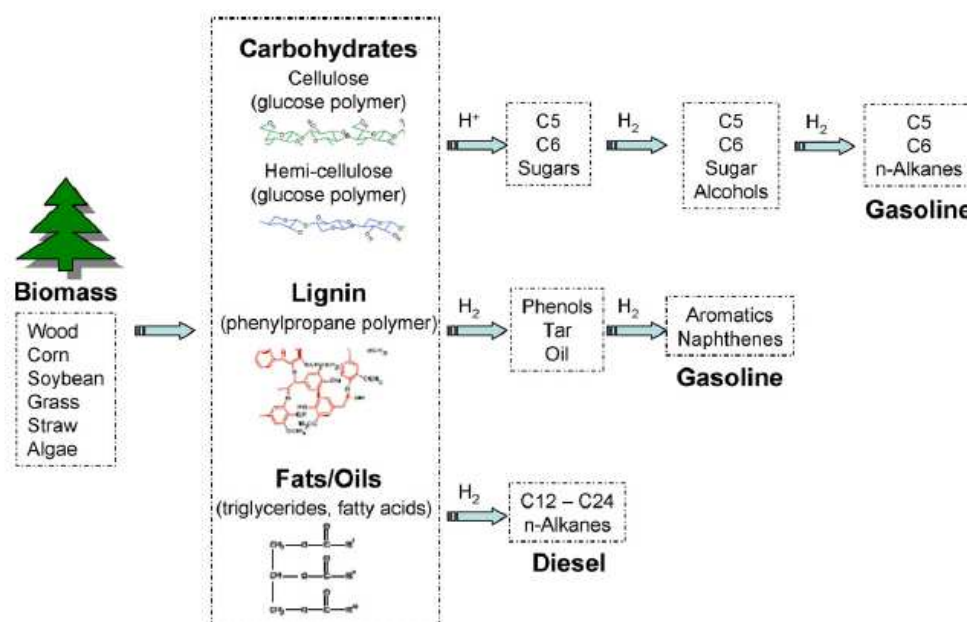
Figure 5: Breakdown of hydrodeoxygenation products [21]

Hydrotreating is generally performed after the formation of bio-oils because the time and processing conditions of the two steps are dramatically different. One strategy that has been tried is to reduce the oxygen percentage during the formation of bio-oils by producing them in the presence of a large amount of hydrogen. In other words, the hydrotreating and fast pyrolysis steps are performed simultaneously. This process is referred to as hydropyrolysis. Hydropyrolysis tests were carried out at pressure up to 10MPa and temperatures between 300°C and 520°C [22]. The oils that were produced had oxygen contents that ranged from 11.5 to 38%. While this is far superior to typical bio-oils additional processing steps would still be required to make the oil refinery compatible.

Hydrotreating is effective at reducing the content of oxygen to levels that are acceptable for refining but the process uses large amounts of hydrogen. A typical figure is 3000 standard cubic feet (SCF) of hydrogen to treat one barrel (BBL) of

bio-oil. Hydrogen is not yet produced cheaply and as a result this process is cost prohibitive. Current research often focuses on ways to deoxygenate oils while reducing the usage of externally produced hydrogen.

One way to reduce the amount of hydrogen that is produced externally is to convert some of the light gas products to hydrogen. Some of the hydrogen for the process can be produced from steam reforming (SR) and partial oxidation (POX) reactions with the light gaseous products of the hydrotreating reactions. As an example, gas phase reactions occurring at 450 - 750°C involving methane are listed below.

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \tag{2.8}$$

$$CH_4 + O_2 \rightleftharpoons CO_2 + 2H_2 \tag{2.9}$$

$$CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \tag{2.10}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{2.11}$$

$$CH_4 + H_2O \rightleftharpoons CO_2 + 4H_2 \tag{2.12}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2.13}$$

POX reactions are exothermic and SR reactions are endothermic. On balance, the process requires an input of energy in the form of heat, but it is much less than would be required to produce hydrogen by some other process, such as water splitting. This process is generally used for hydrogen production in commercial hydrotreating processes but additional hydrogen is usually required to fulfill the hydrogen needs of the process. A flow sheet of the bio-oil process incorporating hydrogen production by steam reforming is presented in figure 6.
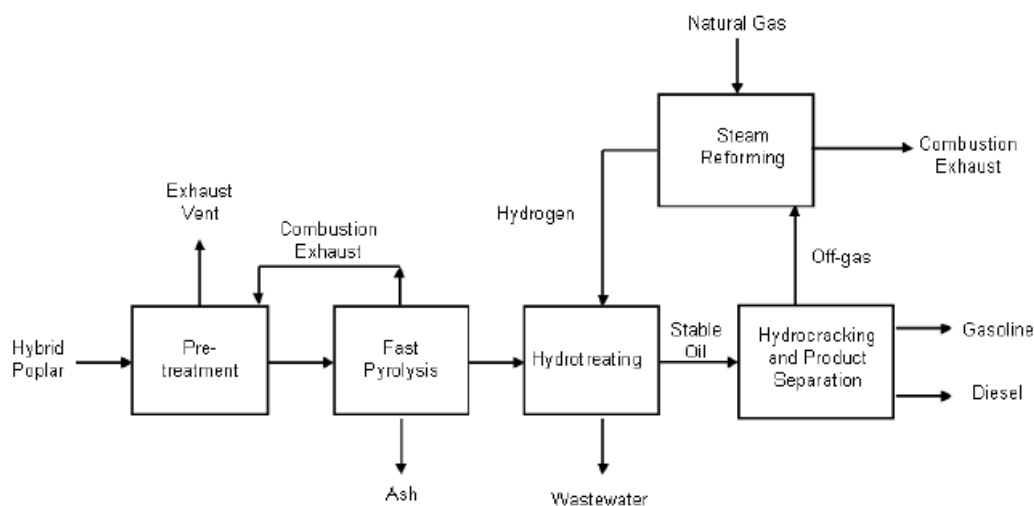
Figure 6: Steam reforming incorporated into bio-oil production [6]

Some work has been completed that focuses on incorporating the steam reforming reaction into the hydrotreating process in order to generate hydrogen internally. The model compound guaiacol was loaded into a reactor with a range of catalysts. The reactor was then heated to a temp of 360°C for a period of 2-4 hours. It was found that a significant amount of oxygen was removed simply by thermal degradation. Water was then added to the reactor to determine if the amount of oxygen removed could be enhanced by producing hydrogen through a steam reforming reaction. It was found that the amount of oxygen percentage dropped from 8% to an average of 2.8% after 4 hours [23].

Some preliminary work has been performed using larger amounts of high temperature water as a solvent for upgrading by high pressure thermal treatment. This process yielded oil that separated into two phases, an oil phase and an aqueous phase. This process produced an oil phase for which the oxygen percentage ranged from 20 to 31.1% and an aqueous phase for which oxygen percentage ranged from 40.5 to 43.4%. As the temperature was increased the oxygen percentage in the oil phase decreased while the composition of the aqueous phase increases [1]. This is due to the fact that the main function of water in this case is to induce a separation and

not to actually remove oxygen in any sort of reaction. A closer look at the material balance for this process shows that the total amount of oxygen removed from the feed is minimal. The difference in the results compared to the work done by Fisk *et al.* (2009) is likely explained by the use of catalysts [1].

Using water as a solvent for reactions of organic compounds is a field that is well developed. High temperature water (over 200 °C) has been shown to support a variety of ionic and free radical reactions. One of the reasons for this is that as water increases in temperature, the dielectric constant is lower. Water molecules become less polar and therefore organic molecules dissolve in water much easier at these high temperatures. This means that polymerization would be less likely to occur and reactions with water would be less limited by mass transfer limitations. The density of water also drops dramatically at high temperatures and approaches that of a standard gas. The hydrogen on water can also act as a hydrogen donor which is especially relevant for upgrading purposes.

Most of the research on hydrotreating that has been performed recently has focused on oxygen removal; however hydrotreating has long been used for the removal of sulfur. In order for crude oil to be processed it must meet minimum standards for sulfur content. In the past there was a plentiful supply of low sulfur or "sweet" crude oil. As those reserves have been gradually depleted it has become necessary to utilized crude oil that contains some sulfur. Sulfur is removed by a process very similar to the process for removing oxygen. Some research has been complete using carbon monoxide as a coreactant for desulfurization. Past research has found that CO and water have mixed results when it comes to yielding similar conversion rates to pure hydrogen. Various aromatic feeds were tested with a sulfur weight percentage of 2.75%. These compounds were then treated with hydrogen and with a mixture of water and carbon monoxide. In both cases the sulfur concentration dropped to below 0.2% by weight [24]. The same method was used by another researcher treat dibenzothiopene, a model compound for sulfur containing crude.

One researcher actually reported higher yields of the desulfurization products for the CO and water mixture than for the typical hydrogen treatment [25].

The research outlined in this thesis focuses on combining the use of high temperature water and carbon monoxide as a stabilization step for a model compound of bio-oil. There is evidence that both of these technologies have been successful on some level and in combination they may remove a substantial amount of oxygen.

CHAPTER 3
MATERIALS AND METHODS

3.1 Preparation of Feed Material for Deoxygenation Experiments

The reactants that were used for the analysis were guaiacol (2-methoxy phenol) and water. The water was deionized water that was produced by reverse osmosis using a system that is made by Ultrapure. The 2-methoxyphenol is produced by Alfa Aesar with a minimum purity of 98%. Both chemicals were loaded into a 125 ml LDPE plastic container. The container was weighed while empty with a standard laboratory scale. The container was then weighed again after addition of guaiacol and water, respectively. The contents were then poured into the autoclave reactor immediately prior to sealing the enclosure. After sealing the contents, the initial pressure and temperature of the enclosure are noted. This is done in order to calculate the total moles of the gas at the beginning of the experiment. This is done to have a basis for comparison to determine how much gas is produced during the reaction.

3.2 Reactor Setup and Experimental Procedure

Experiments were conducted using an Autoclave Engineers autoclave, high temperature bolted enclosure. The reactor is designed to withstand pressure of up to 5000 PSI and temperatures up to 510°C. The enclosure is sealed at the top with 8 bolts, each of which has a head diameter of 1 inch. A metallic seal ring is provided to ensure a tight seal at the top of the unit.

The stirring mechanism is included, capable of speeds up to 3300 rpm. The motor is outside of the bolted enclosure. The motor is attached to a rotating magnet. When the motor is on, this external magnet causes the encapsulated magnet to rotate. This magnetic coupling causes the inner rotor to rotate at the same speed as the motor.

This system is in place to ensure the unit has a minimum number of openings to seal and has insignificant risk of ignition due to moving parts. This magnetic unit is designed for a maximum temperature of 149°C. A cooling water jacket is provided to ensure the temperature does not rise beyond that point.

Several different valves were installed by Autoclave Engineers (AE). There are two valves for the gas inlet and outlet. They are attached at the top of the unit. There is also a liquid sampling valve which drains from a pipe suspended in the middle of the reactor. A flush valve was also installed at the bottom of the reactor for draining liquid. This is a ½ inch valve. This valve seals by inserting the stem into an orifice at the bottom of the reactor. This valve was replaced with a permanent plug when it was determined that it was not feasible to keep the valve free of debris following an experiment due to the large amount of solids formed. The reactor also has a rupture disk at the top which is present in case pressures exceed the maximum amount allowed.

The reactor has two thermocouples attached. One of the thermocouples are placed inside a thermowell that is suspended in the reactor. The other thermocouple is placed alongside the heating mechanism which surrounds the main reactor body. The reason for the use of two thermocouples is that the reactor has a cascade temperature control system. This means that there are two different control loops and they are dependent on each other. This of course means the changes in one temperature has a cascading effect. The reactor also has a pressure gauge attached which is only a function of temperature and molar volume.

In addition to the elements of the system that were factory installed by AE, additional parts were installed. External piping was installed to transport nitrogen and carbon monoxide to the reactor from pressurized cylinders. Ball valves and needle valves were installed at every opening in the reactor. The piping also led to a ventilation system at the ceiling of the room. A snorkel is also suspended in order to

reduce the harm of volatile toxic components during the filling of the reactor. A cooling water line was also installed to run water though the cooling jacket surrounding the mixture motor. The cooling water demands were 0.3 gallons per minute (GPM). A schematic of the reactor setup is displayed in figure 7.
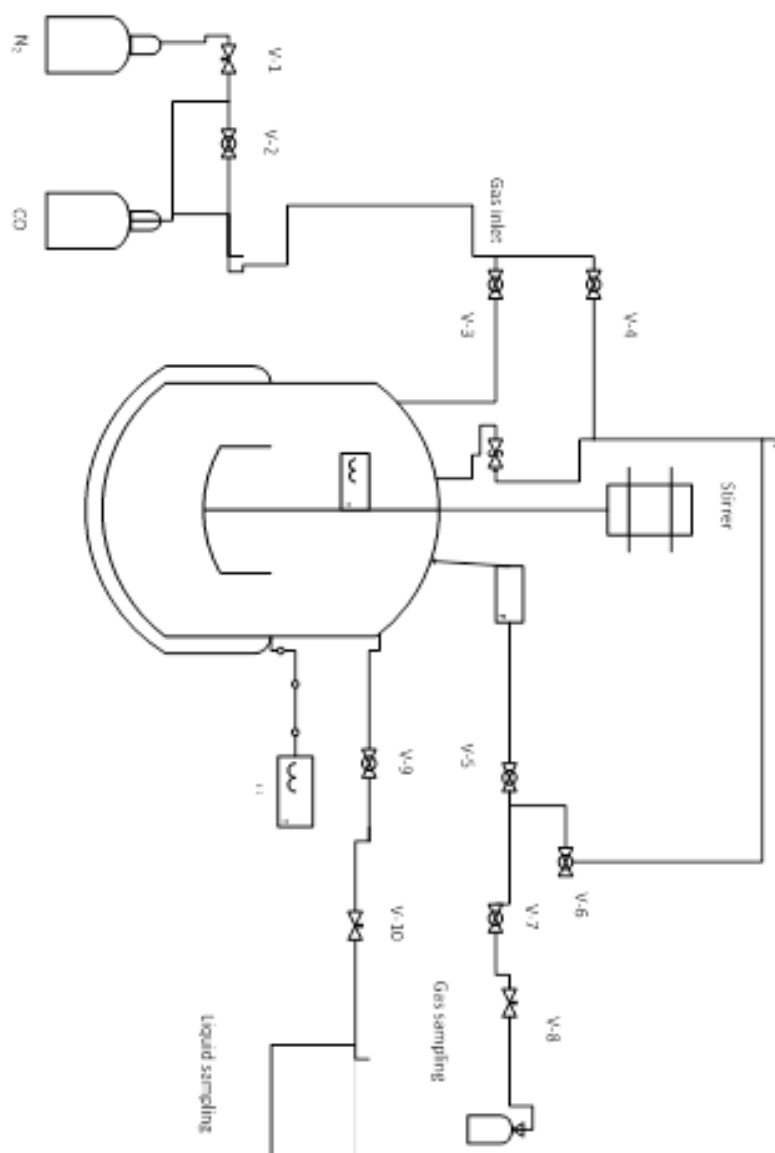

Figure 7: Schematic of autoclave reactor and surrounding equipment

The two thermocouples, the stirring mechanism, the reactor heater, and the pressure gauge are all attached to a Sentinel Series Controller. This control box is attached to a computer via a USB connection. The controller then communicates with computer software via PLC interaction software known as DirectSOFT32. This software drives a user interface know as Watchtower® which provides real-time info about the pressure of the reactor, the temperature of the two thermocouples, stirring speed, and the current set point. The user can adjust the stirring speed temperature set point, and the ramp rate for temperature increased.

Each time an experiment was run a procedure was carefully followed in order to ensure the safety of the experiment and the results. The first part of the standard operating procedure is the preparation of the reactor body for the experiment. First the liquid contents were poured into the reactor. A snorkel was suspended right over the contents during this time to minimize inhalation of toxic compounds. Anti-seize compound was then applied to the bolts in order to prevent galling at high temperatures. The reactor body was then raised and sealed by tightening all of the bolts. The bolts were then tightened to a final torque of 110 ft-lbs. Bolts are incrementally tightened in a staggered opposite sequence in order to minimize shear stress on the bolts, seal, and flanges. Heat resistant padding was then strapped to the reactor. The Sentinel Controller was turned on and given five minutes to boot up. The software was opened followed by another five minutes. Watchtower® is used to display the reactor conditions.

After the reactor has been set up the reactor must be vented in order to reduce the concentration of oxygen to one part per million. All of the valves were checked to ensure that all of the valves that control the flow of gases are closed. The regulator of the nitrogen cylinder is then opened. The pressure must be checked to ensure it is high enough to supply the necessary gas. The regulator can then be adjusted to a pressure of about 250 PSI. The inlet valves to the cylinder must then be opened to allow the gases to flow into the reactor. Once the reactor has reached a maximum

pressure the incoming valves can then be closed. The drain valves can then be opened to reduce the pressure in the reactor to atmospheric. The pressure is reduced slowly at a rate of 10-15 PSI per minute so that liquid and solid components do not bubble up through the product lines. This process reduces the oxygen percentage in the reactor by dilution. These steps can then be repeated 5 times to ensure the oxygen percentage is reduced to the necessary level.

The reactor is now ready for operation. The stirring mechanism is turned on. Once the stirring mechanism is turned on the heater can then be turned on. The set point and ramp rate should be checked to ensure proper operation. The cooling water needs to be turned on so the stirring motor does not burn out. The pressure needs to be monitored closely so it does not exceed the maximum pressure for the reactor. The pressure goes up quickly once the temperature approaches supercritical so the user must be careful to turn down the heater well below where the maximum pressure is reached.

Once the desired residence time has been reached the heater should be turned off. The stirring mechanism is left on to increase the rate of cooling. Once the temperature is reduced to below 100°C the product can then be removed. First the bolts need to be loosened using the breaker bar. They can then be unscrewed using a ratchet wrench.

3.3 Collection of Reaction Products

Following the completion of the experiment, measures were taken to account for all of the reaction products to the maximum extent possible. The products that were produced were in the form of liquid, vapor, and solid products. Prior to unsealing the reactor the pressure of the reactor was noted. A sample of the gas is then collected to determine the distribution of gaseous products using gas chromatography. The reactor is then unsealed and the liquid contents are poured into a graduate cylinder, which is used due to the fact that it has a wide mouth and is

easier to pour into using the reactor. Acetone is then used to rinse out the remnants of liquid product from the reactor and the cylinder. The liquid products and the acetone wash are placed into separate LDPE plastic containers. During the reaction a solid layer will be formed. It is necessary to remove as much of this solid product as possible. Initially most of the solid is scraped from the walls of the reactor. Acetone can then be used to dissolve as much of the remaining solids as possible. The liquid products were then poured into a separatory funnel. The contents were then left overnight to separate. The water and oil were then collected in separate containers. In some cases efforts were made to remove the remaining oil dissolved in the aqueous phase. This was done by adding 2-3 ml of dichloromethane to the water phase and allowing the oil phase to separate. This extraction was performed 2-3 times. The dichloromethane was then removed using rotary evaporation. Each of the products that were produced during the extraction process is displayed in figure 8.

Figure 8: Oil phase product, Extracted aqueous phase, Initial aqueous phase, and Initial oil phase

3.4 Analytical Equipment

In order to evaluate the success of the experiments performed, a variety of analytical techniques must be used to determine the chemical composition of the components

of both the reactants and the products. Karl Fischer titration was used to determine the weight fraction of water contained in each sample. The elemental composition of the samples was determined using an organic elemental analyzer. Fourier transform infrared spectroscopy (FTIR) was used to determine the presence of particular functional groups. Individual components that are produced during the reaction are identified using nuclear magnetic resonance (NMR) spectroscopy and gas chromatography mass spectroscopy GC-MS.

FTIR spectroscopy is used to determine what functional groups are present in the sample. This is done by exposing the sample to IR radiation and measuring the amount of radiation both absorbed and reflected. A broadband light source provides the full spectrum of wavelengths to be analyzed. An interferometer is then used to allow certain wavelengths of radiation to pass through the sample. The interferometer is a mirror than moves back and forth at a specified distance from the source beam. As the different wavelengths of light pass through the sample the amount reflected and absorbed changes based on the vibrations of the bonds in the molecules of the sample. The frequency of the vibration depends on the size of the molecules and the ionic strength of the bond between them. Tables have been compiled that indicate the frequencies of particular types of chemical bonds. During FTIR analysis a plot is produced of absorbance versus wavenumber.

CHNS/O Analyzer analysis is also a useful tool for doing preliminary analysis of oils. CHNS/O Analyzer analysis is a form of gas chromatography. Liquid or solid samples are vaporized through either combustion or pyrolysis. The vapors are then picked up by a carrier gas. Undesirable gases are either converted or filtered out. The remaining gases then pass through the chromatography column. Different gases are used as indicators for particular elements in the compound. The peak areas for each of the compounds are then compared to peak areas of a known standard. The weight of a particular element can then be deduced from that relationship. The

weight of that sample is then used to determine a percent composition for particular elements.

CHNS/O Analyzer analysis gives the elemental composition of a particular sample. In many cases, oil samples are not pure. Many oils, especially those with high oxygen content are not completely immiscible in water. This means that in order to determine the composition of these oils, Karl Fischer titration must be performed in order for the results of the elemental analysis to be useful. Karl Fischer titration works by adding iodine to a solution in the presence of water. This iodine then undergoes a reaction to consume the water.

$$I_2 + 2H_2O + SO_2 \rightarrow 2HI + H_2SO_4 \tag{3.1}$$

Initially a pretitration is performed in order to ensure that no water is present in solution initially. A platinum electrode is used to determine if any water is present. The sample is then added to the solution. Iodine is then added until the electrode indicates that water is no longer present. Once that occurs iodine is no longer added and the amount of water is calculated based on the amount of iodine added.

The samples that were analyzed were a mixture of oil and water. Once the water content was found using titration the elemental breakdown could be found using a mass balance combined with the results from the elemental analysis. As expected the nitrogen content of the compounds is nearly insignificant. Any nitrogen present could in fact be simply due to small amounts of air making it into the system.

Some of the samples were analyzed using gas chromatography and mass spectroscopy. When using this equipment, a sample is injected into a column that has helium flowing through it. The components of the sample are then separated based on the different rates of evaporation for each component. The separate components can then be fed into a mass spectrometer. The mass spectrometer can then be used to determine the chemical structure of the sample. The downside of this

technique is that some oils can degrade because of the high temperatures used for gas chromatography. Some initial work was performed to use liquid chromatography to separate bio-oils for analysis by mass spectroscopy. Liquid chromatography differs from gas chromatography in the sense that separation of components is based on differences in affinity for the solvent flowing through the column as opposed to difference in evaporation rates. The gas products were analyzed using gas chromatography. The gas product peaks were compared to standard peaks for nitrogen and carbon dioxide.

NMR spectroscopy is used for identifying and analyzing organic compounds. The identification method is based on the magnetic spin of ^1H, ^{13}C, ^{15}N, ^{19}F and ^{31}P atoms. Only atoms that have an odd number of protons can be detected using NMR since those atoms have a dipole moment and angular momentum. NMR spectroscopy is based on the magnetic properties of the nucleus of an atom, which is positively charged. During analysis a constant magnetic field is applied. A radio frequency pulse is then applied. The magnetic field is disturbed at certain frequencies dependent on the nuclei being observed. The disturbance of the magnetic field depends on the atom being detected and the neighboring atoms as well.

Scanning Electron Microscopy (SEM) analysis was performed on the coke products in order to provide surface images and elemental composition for the samples. SEM uses a high energy beam to determine several properties of a sample. During this process x-rays, auger electrons primary backscatter electrons, and secondary electrons are rejected. The x-rays give information about the elemental composition of the sample and the ejected electrons give a picture of the surface structure of the sample.

Not all of these tools will be used in every case. Some of these different methods produce data that can be produced quickly at low cost without much effort to

interpret. These methods include FTIR, elemental analysis, and KF titration. Other methods of analysis including NMR, mass spectroscopy, and SEM are only used in some unique cases in order to get a more detailed analytical result. All of the analytical tools along with their manufacturer and model are listed in table 2.

Table 2: List of analysis equipment used

Instrument	Manufacturer	Model
Elemental Analyzer	ThermoFisher Scientific	Flash 2000
Karl Fischer titrator	Mettler-Toledo	V30 Volumetric Titrator
FTIR	Bruker	Vertex 70
Gas Chromatogram	Hewlett Packard	SRI 8610C
Gas Chromatogram	Agilent Technologies	8890N
Mass Spectrometer	Jeol	JMS-600H
SEM	FEI	Quanta 600F
NMR	Bruker	Ultrashield 400 plus

3.5 Experimental Procedure for Elemental Analysis

The most important piece of analysis that must be collected for each sample is the elemental composition because it shows exactly how much oxygen has been removed from the oil products. Every time a sample is collected four samples must be run. The feed oil should be analyzed in case there is degradation over time. The oil phase must be analyzed as well. Finally the char should also be analyzed. Two duplicates are taken for each sample to ensure statistical significance of the data. The CHNS/O Analyzer consists of an auto sampler, two furnaces, two gas sources, and a thermal conductivity detector. Each of the furnaces is packed with material designed to filter out the appropriate products in order to analyze for either carbon and nitrogen, or oxygen. Two gas streams pass through each of the two columns. One of the gas streams is a reference stream which consists of inert gas, in this case helium. The other column contains the product of the combustion/pyrolysis reaction.

The flows of each of the gases for CHN analysis are displayed in figure 9.
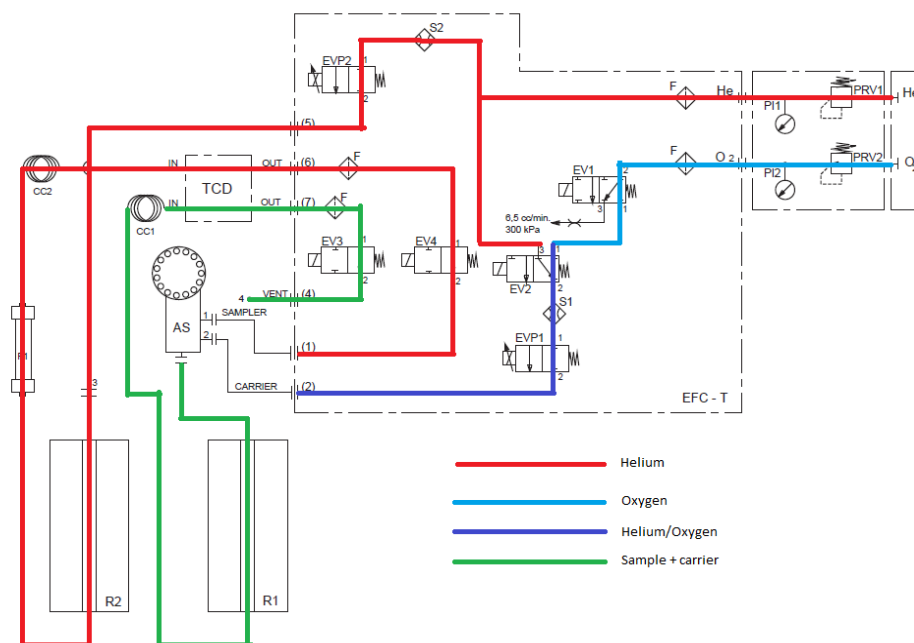
Figure 9: Pneumatic diagram of elemental analyzer setup configured for CHN analysis

Samples are placed in tin cups and weighed on a balance. These tin cups are placed into the auto sampler. The auto sampler then drops the samples into the appropriate column where they are burned. When performing CHN analysis the columns undergo a standard combustion reaction producing carbon dioxide and water as well as some nitrogen oxides. These nitrogen oxides are then reduced to elemental nitrogen. The production of these gases leads to a change in thermal conductivity picked up by the detector. A chromatogram is then produced for each of the three gases mentioned which translates to an elemental weight for carbon, hydrogen, and nitrogen, respectively. Oxygen analysis is similar but the sample undergoes pyrolysis in the absence of oxygen producing nitrogen, carbon monoxide, and hydrogen. Elemental oxygen is then calculated based on the size of the peak for carbon monoxide. The conditions of these processes for CHN and O analysis are displayed in table 3.

Table 3: Operating conditions for elemental analysis (flow rate ml/min)

Analysis	Temp (°C)	Carrier	Reference	Oxygen
CHN	950	140	100	250
O	1060	100	100	N/A

After combustion, a chromatogram is produced based on the signal of the TCD. The area of the peaks is then compared to the peak areas of a standard. There is generally a linear relationship between the peak area of the signal gases and the weight of the element being analyzed for. Using the weight of the sample and the signal from the chromatogram the weight composition of the sample is calculated.

3.6 Experimental Procedure for Karl Fischer titration

Karl Fischer titration is used to determine the water content of each sample. The reason for this is that in order to make a valid comparison of the oil phases of the product and reactant a comparison must be made on a water free basis. If this is not done the elemental analysis data will be misleading.

The titration unit consists of a pump, syringe, three reservoirs, a reaction unit, an electrode, and a stirring mechanism. First, a pretitration is performed in order to ensure that no water is present at the beginning of the experiment. The sample is then injected and a reagent is supplied that reacts with water. The amount of water is then calculated based on the amount of reagent added.

The maximum amount of water that the instrument can detect is approximately 53ml. As soon as this value is reached the titration device stops recording data. This creates a problem because if a sample is smaller than 100ml it is difficult to get consistent data because the smaller the sample the larger the error in the volume measurement. This problem was solved by diluting the samples with methanol. The sample was then tested for water percentage. The amount of water was then calculated based on the measurement of the diluted sample. This calculation is outlined below.

$$WF_O = \frac{WF_S - WF_M(MF_D)}{(1 - MF_D)} \qquad (3.3)$$

After water percentage has been determined it can be used to determine the composition of the oil phase on a water free basis. In order to ensure the small water content of the methanol does not interfere with the measurement a desiccant is used to reduce the water content to the smallest amount possible. Sample blanks are then collected using pure methanol. The reading of the sample blanks is combined with the reading of the diluted sample to calculate the water content of the oil.

3.7 Thermodynamic Modeling of the Impact of CO using HYSYS®

To provide further justification for using carbon monoxide to treat bio-oils in the presence of high temperature water, thermodynamic modeling was completed using HYSYS®. Due to the complexity of pyrolysis oil modeling the entire process would be extremely difficult. In this case, benzoic acid has been used as a model compound to represent pyrolysis oil. The following are a couple of reactions that are expected to take place involving benzoic acid and carbon monoxide.

$$C_6H_5COOH + 3H_2 \rightleftharpoons C_7H_8 + 2H_2O \qquad (3.4)$$

$$C_6H_5COOH \rightleftharpoons C_6H_6 + CO_2 \qquad (3.5)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3.6)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (3.7)$$
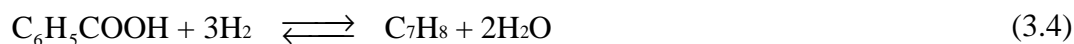
Gibbs free energy of reaction can be used to determine the relative favorability of each reaction. The Gibbs free energy can be related to the equilibrium of the reaction according to the following relationship.

$$K_{eq} = e^{-\frac{\Delta G_r}{RT}}$$
(3.8)

The thermodynamic properties of each reactant and the resulting reactions are summarized in tables 4 and 5.

Table 4: Summary of Thermodynamic Properties of Reactants

Component	Formula	G_f(kj/mole)	H_f(kj/mole)
Water	H_2O	-228.61	-241.8
Carbon Monoxide	CO	-137.16	-110.6
Carbon Dioxide	CO_2	-394.37	-393.51
Hydrogen	H_2	0	0
Methane	CH_4	-50.49	-74.52
Benzoic Acid	C_6H_5COOH	-214.2	-294.1
Benzene	C_7H_8	129.6	-50.17
Toluene	C_6H_6	122.2	82.88

Table 5: Summary of Thermodynamic Properties of Reactions

Reaction	ΔG_r(KJ/mole)	ΔH_r(KJ/mole)
3.4	-120.8	-186.5
3.5	-50.5	-229.4
3.6	-28.6	41.1
3.7	-141.9	-205.7

The thermodynamic properties of these reactions demonstrate that all of these reactions are very favorable and will continue to be favorable even as temperatures rise. What this indicates is that the reactions were allowed to proceed to equilibrium the reactions would nearly arrive at completion. This is not likely to happen due to the limits based on kinetics. Further analysis of the potential products based purely on thermodynamics was done using HYSYS®.

The reactor that was selected in HYSYS® is the Gibbs reactor. This reactor produces products based on the minimization of Gibbs free energy. This means that reactions may take place outside of the simplified model presented earlier. This reaction also assumes that every reaction proceeds to equilibrium. The reason that this type of reactor was chosen is that other types of reactors in HYSYS® require kinetic data

that is not available. While this reactor will provide some insight into the possible product distributions it is important to note that the actual system will have a much wider distribution of products and the production of those products will have differing reaction kinetics.

The HYSYS® flow sheet has two initial feed streams. One of those streams contains a mixture of benzoic acid and water. The other stream contains either hydrogen or carbon monoxide. These streams enter a mixer and are then fed to the reactor. The reactor contains two product streams. One of these streams contains products in the liquid phase and the other contains products in the vapor phase. In most cases all of the products are in the vapor phase. The HYSYS® flow sheet is displayed in figure 10
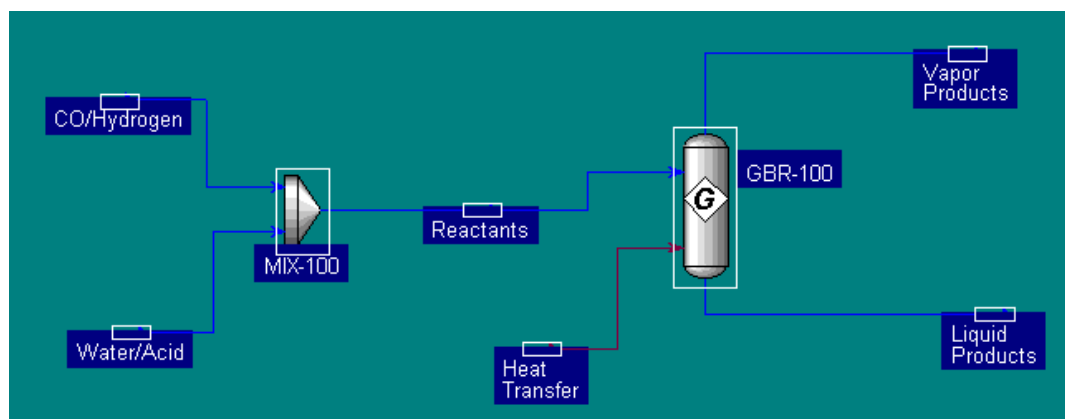

Figure 10 : HYSYS® flowsheet for benzoic acid deoxygenation reaction

In order to make a reasonable comparison of the different reaction settings it is necessary to make sure the reactor is running at the same temperature and pressure for all of the different flow rates. In order to make the conditions equal a heat transfer term must be added to account for the differing heats of reaction. If the reactor conditions are adiabatic, the temperature of the reactor increases with gas flow. This increase in temperature is due to the fact that exothermic side reactions occur. The heat transfer term is reduced with increasing gas flow rate in order to keep the temperature constant.

The model contains the independent variables heat transfer, and gas flow rate. These variables are compared to the dependent variables including the yield of each product, and the product temperature. A case study was used to analyze the response of all of the dependent variables to changes in the independent variables. A case study runs the HYSYS® simulation once for each different permutation of a range of values for each independent variable. A visual of the case study generated using HYSYS® is displayed in figure 11.
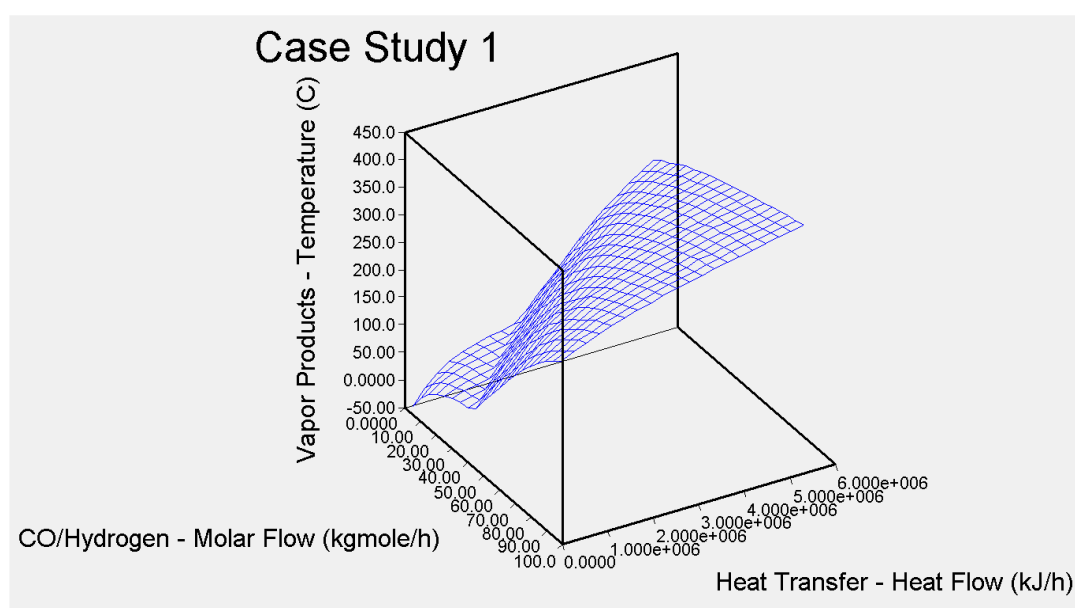

Figure 11: Case study for the impact of heat duty and gas flow on temperature

For each flow rate there is data for a range of different temperatures. In order to isolate a data series where the gas flow rate is increasing with minimal temperature changes a MATLAB program was created to pick out data points across the isothermal region of the graph. This data was then plotted to show how changing the gas flow rate impacts the product distribution at consistent reaction conditions.

Since the production of benzene occurs primarily through the decarboxylation route it is expected that the addition of gas will have no impact on the production of benzene. This is almost exactly what is observed. The exception to this rule is that at high flow rates of hydrogen the production of benzene goes down. This is because

the production of carbon dioxide drives the reaction backward. The yield of toluene is impacted much more greatly due to the change in gas flow. This change could not simply be due to the hydrodeoxygenation reaction which indicates that carbon monoxide reacts with benzoic acid directly. These results are documented in figure 12.

The yield of desired products goes down with increasing flow rate for hydrogen due to the production of undesirable gaseous products, specifically methane, and carbon dioxide. This is due to the fact that the methanization reactions are extremely favorable, so excess hydrogen is immediately consumed. The distribution of these gas products is displayed in figure 13. Reaction temperature was stabilized by adding heat to the reactor. As gas flow increased, more gaseous products were formed. The heat of reaction for the gas forming reactions is highly exothermic, therefore reducing the need for external heating. The amount of heat added and the impact on the temperature for each setup is shown in figures 14 and 15.
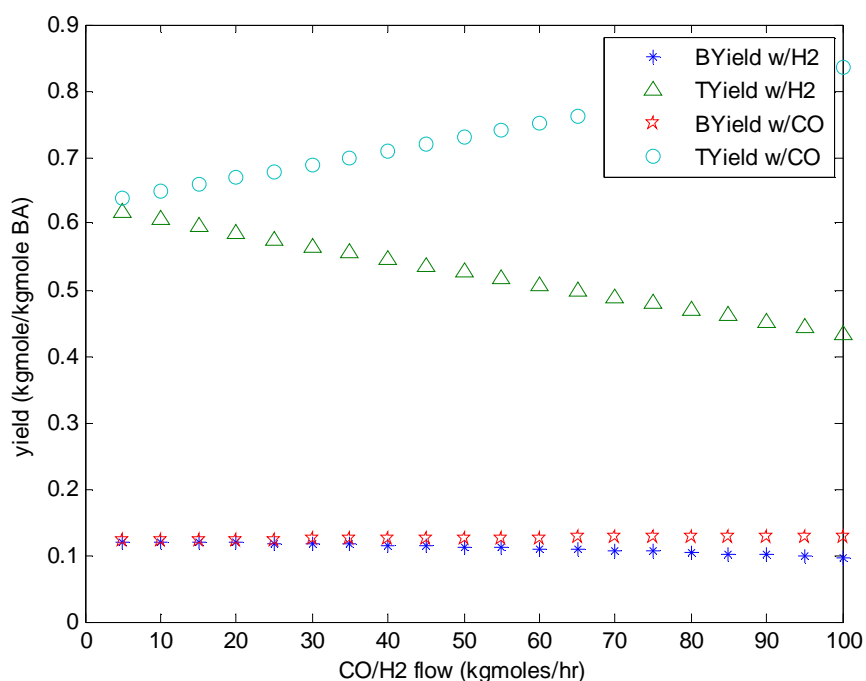

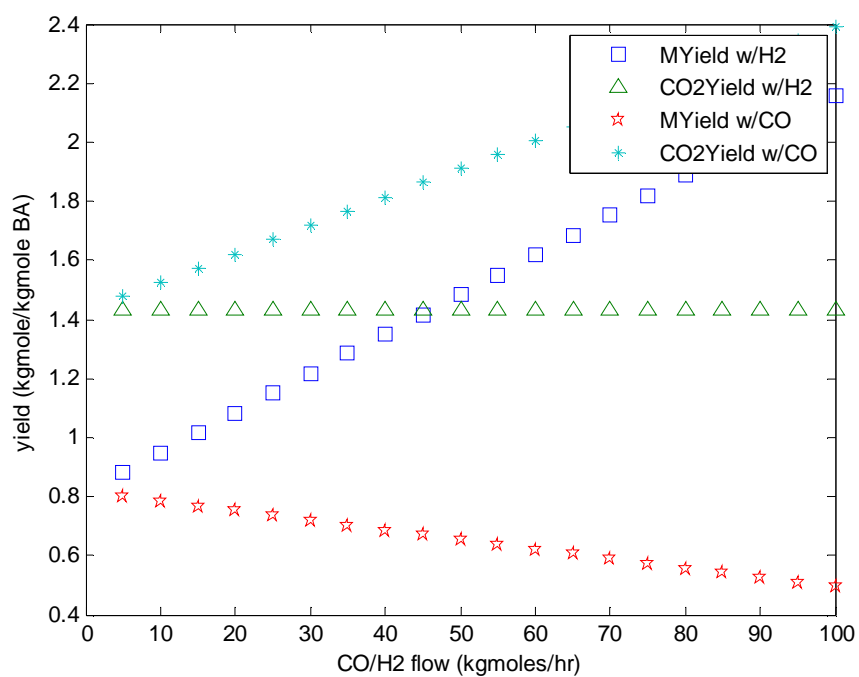Figure 12: Distribution of liquid products compared to benzoic acid feed

Figure 13: Yield of gas products compared to benzoic acid feed
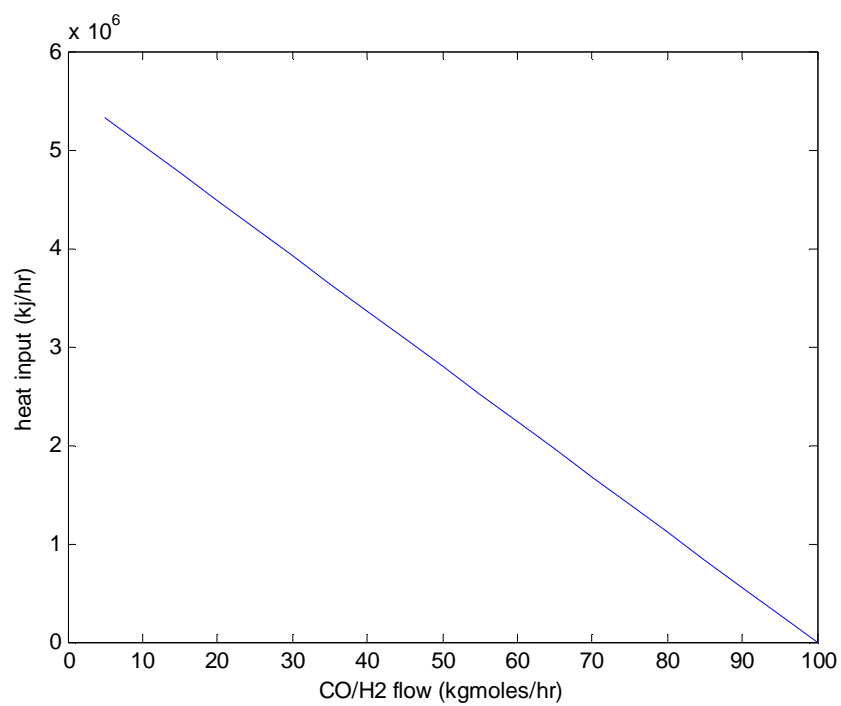
Figure 14: Process heat added compared to gas flow
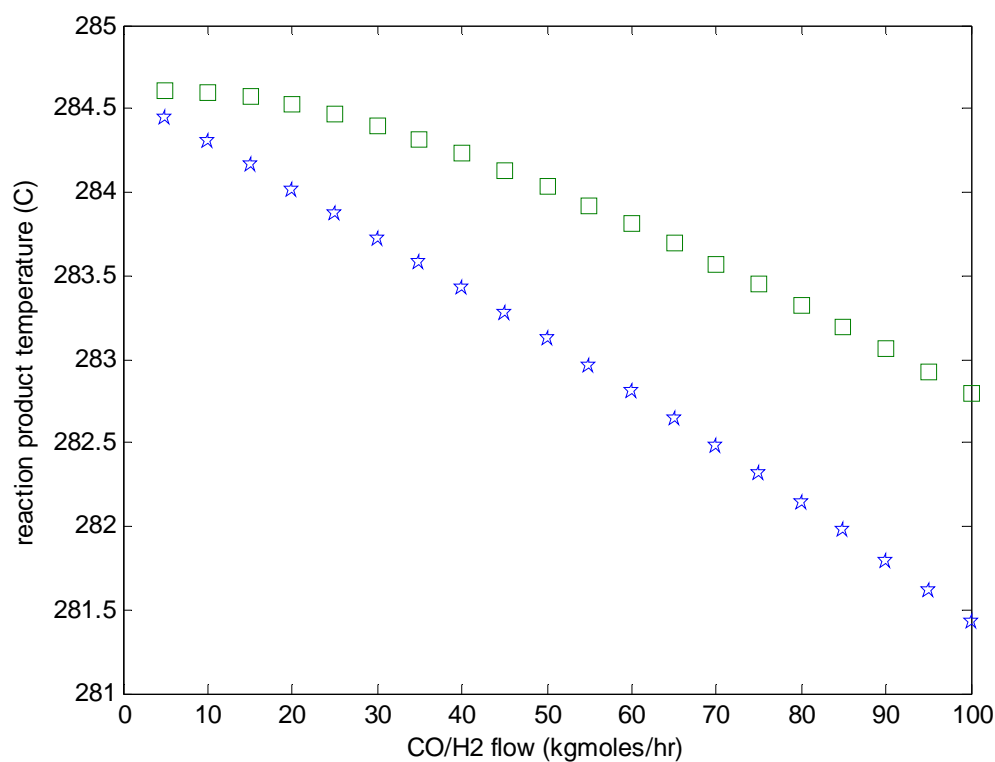
Figure 15: Stability of reaction temperature due to heat addition

The details provided concern the simulated reaction of benzoic acid; however, a similar simulation was created using both vanillin and guaiacol. In all cases the total yield of the desired reaction products was higher in the presence of carbon monoxide than it is with hydrogen. This data indicates that, if kinetics were not relevant, carbon monoxide would almost certainly be effective at facilitating deoxygenation reactions. Experimental data must then be collected to determine if the necessary reaction do in fact proceed in the appropriate time frame.

CHAPTER 4
EXPERIMENTAL RESULTS

4.1 Motivation for Research

As outlined in the literature review section, past research has demonstrated that carbon monoxide in the presence of water has been used in order to facilitate reactions that typically require the use of hydrogen. One such reaction that requires hydrogen is the deoxygenation reaction that is utilized in order to treat bio-oil.

The goal of this research is to demonstrate that carbon monoxide, in the presence of high temperature water can also be used to facilitate deoxygenation reactions that are used to treat bio-oil. Thermodynamic modeling and the body of research surrounding the water gas shift reaction suggests that this approach may be effective. Guaiacol is used as a model compound in this case to test whether carbon monoxide can be effective for this purpose.

This chapter will document experiments that were performed using guaiacol with the goal of removing oxygen from the compound that exists in the form of an alcohol group and an ether group. Initially guaiacol was heated without carbon monoxide present in order to replicate the results of previous experiments performed with bio-oil in the presence of high temperature water. Analysis techniques were then applied to this oil in order to confirm the idea that high temperature water has some limited effectiveness for reducing oxygen.

Guaiacol was then treated in the presence of carbon monoxide in order to determine if there is a significant difference in oxygen reduction due to the presence of carbon monoxide. The assumption of this work is that the properties of guaiacol are similar enough to bio-oil that the results of this work can then be generalized to bio-oil as a whole.

In addition to determining the amount of oxygen removed it was also a goal of this project to perform a material balance on all of the products formed as a second way of confirming the validity of the results. Data was collected on the solid coke product and the gaseous products to determine the rough elemental composition. The goal of collecting this data was too determine the amount of carbon in the original oil phase that was recovered in the oil phase.

4.2 Determination of proper molar volume

When water and bio-oil is heated up to supercritical conditions the molar volume drops dramatically. Since the reactor that is being used is a fixed volume, this means that as the temperature gets closer to super critical, the pressure will increase dramatically. In order to determine the maximum volume that can be used at the reactor conditions the Soave-Redlich-Kwong (SRK) equation of state was used as a model. The SRK model was selected because it is sensitive to departures from ideal behavior. The SRK equation of state is as follows.

$$\frac{RT}{\widehat{V}-b} - \frac{\alpha a}{\widehat{V}\left(\widehat{V}+b\right)} = P \tag{4.1}$$

$$a = 0.42747\frac{(RT_c)^2}{P_c} \tag{4.2}$$

$$b = 0.08664\frac{RT_C}{P_C} \tag{4.3}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2 \tag{4.4}$$

$$T_r = \frac{T}{T_c} \tag{4.5}$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 \tag{4.6}$$

Prior to running the reactor the SRK equation of state was used to determine the maximum molar volume that can be present in the reactor at a given pressure and temperature. The properties of bio-oil are not known so water was used in order to

approximate the molar volume. The volume of the reactor is known so the number of moles of liquid can then be calculated based on the molar volume. From that value the initial volume of liquid that should be added to the reactor can be calculated. A plot was created showing the volume of liquid that would have to be added to yield a range of pressures and is displayed in figure 16. This calculation was completed at a couple of different temperatures within the operating range. In order to simplify the calculations it was assumed that the contribution of nitrogen was negligible.

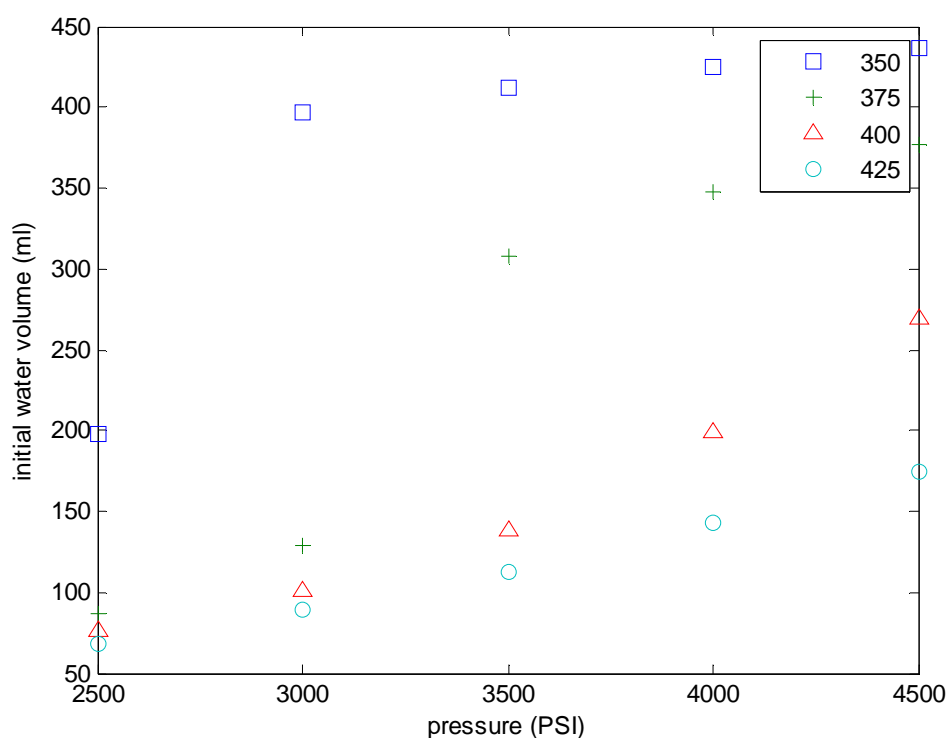Figure 16: Maximum initial water volume for expected operating temperatures and pressures.

As this plot shows, according to the SRK equation of state as the temperature gets higher the maximum allowable number of moles in the reactor drop dramatically. This is an important constraint to keep in mind. A safety factor was added because the properties of guaiacol are not known and water is a rough approximation.

4.3 Analysis of Degradation Products of Guaiacol in High Temperature Water

In order to obtain significant amount of oxygen removal it has generally been necessary for hydrogen to be present in the reaction media. Past research has shown some oxygen removal can be initiated simply by thermal degradation in the presence of high temperature water. In order to confirm the validity of these results, data was collected comparing thermal degradation products of guaiacol at maximum temperatures of 350°C and 400°C respectively, in the presence of water. The degradation products were analyzed using elemental analysis, FTIR, gas chromatography and NMR spectroscopy.

The oil phase for each of the reactor runs was analyzed using FTIR in order to determine the change in functional groups. The purpose of this analysis is to determine if there is a decrease in the vibrational frequencies associated with functional groups that include oxygen. The plot of the data at 350°C displayed in figure 17, shows that the changes in all functional groups are barely perceptible at those conditions. This suggests that the operating temperature is not high enough to significantly impact the structure of the molecule. At 400°C the change in the vibrational frequencies of the functional groups was much more apparent as displayed in figure 18. The specific change that was most clear was the difference in the peak at wavenumbers between 1000 and 1400 cm^{-1}. This peak corresponds to a change in the methoxy functional groups present both in the original compound methoxyphenol, and one of the degradation products methoxybenzene. This suggests that a significant amount of the functional group was removed. It is difficult to determine how much of the alcohol group was removed due to the presence of water. This is because the hydrogen bonds in the water produce the same signal as the alcohol group. This means any reduction in OH bonds as part of the aromatic compound are drowned out by the signal produced by the water. For this reason FTIR analysis is not an effective tool for determining if a product like methoxybenzene was produced.
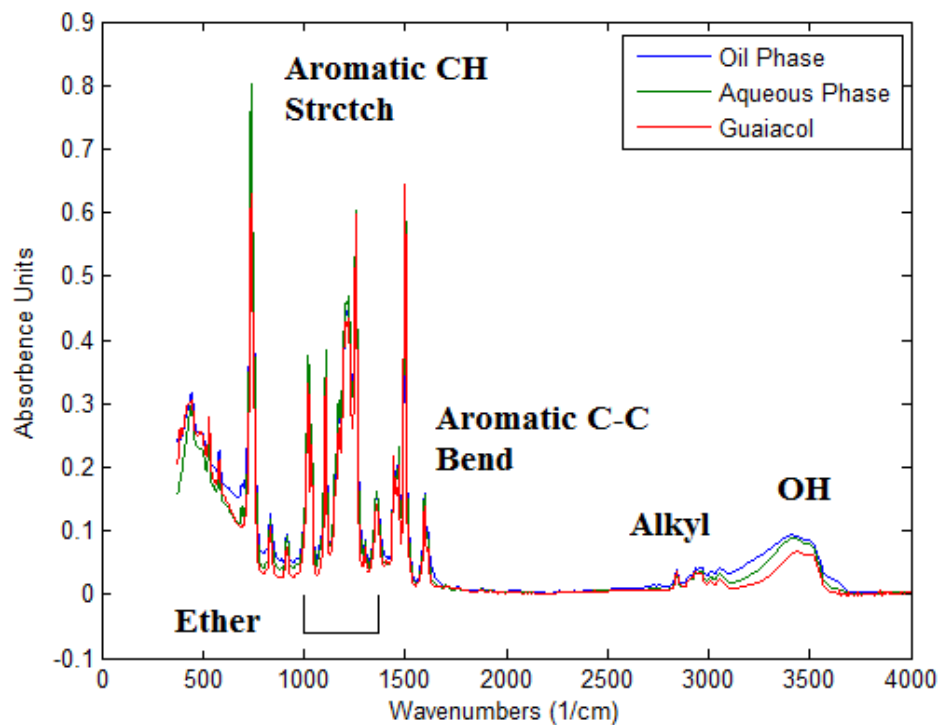
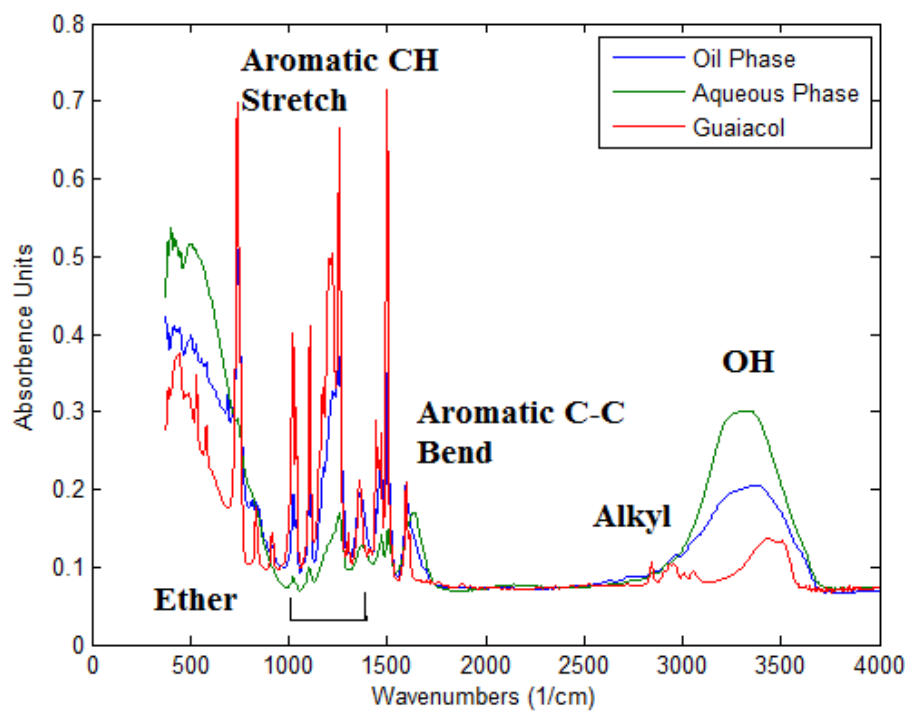Figure 17: FTIR data for guaiacol and deoxygenation products at 350°C

Figure 18: FTIR data for guaiacol and deoxygenation products at 400°C

While FTIR is used to determine changes in functional groups elemental analysis is used to determine overall elemental composition. The general function of this measurement is to obtain a general estimate of oxygen content in order to determine if the oxygen content of the oil has decreased. For each run a maximum of six different samples were collected. These samples represented the oil phase products formed, aqueous phase product formed, starting material, coke formed in the reactor, extracted oil product, and the aqueous phase following the extraction. These samples were analyzed using elemental analysis, and the results of these experiments are displayed in table 6.

Table 6: Elemental analysis data for degradation products of guaiacol

Sample	Carbon %	Hydrogen %	Max Temp (°C)
Oil Phase	58.2	6.23	400
Aqueous Phase	13.3	8.22	400
Guaiacol	66.8	6.01	400
Coke	76.5	4.06	400
Extracted Oil	67.1	6.18	400
Extracted Aqueous	8.08	7.79	400
Oil Phase	65.4	6.16	350
Aqueous Phase	4.43	8.58	350
Coke	74.8	4.06	350
Extracted Oil	49.3[x]	4.85	350
Extracted Aqueous	3.19	8.65	350
[x]Indicates that NMR data show dichloromethane may still be present			

This data shows that in all cases the carbon percentage for the oil phases is lower than it is for the starting material. This is misleading because each of these samples contains a significant amount of water. In order to determine the carbon content of the oil the composition of the oils must be determined on a water free basis. In order to do this Karl Fischer titration was performed on the oil phase for each of the samples. After determining the water percentage in each of the samples the carbon and hydrogen composition was determined algebraically for each of the samples. The oxygen is then calculated based on the assumption that no other elements are

present in the sample in any significant amounts. The results of these calculations for each of the oil phases are displayed in table 7.

Table 7: Oil composition determined using KF titration data

Sample	Water %	Carbon %	Hydrogen	Oxygen %	Max
Oil Phase	17.7	70.7	5.21	24.1	400
Extracted	12.5	76.7	5.47	17.8	400
Oil Phase	6.66	70.0	5.81	24.1	350

This data would indicate that a very small amount of oxygen was removed and the composition of the oil is similar in both cases. This is obviously in conflict with the FTIR data which would indicate there should be more oxygen removal at a maximum temperature of 400°C. This discrepancy is likely due to errors in measurement which will be discussed in greater detail later on. In order to develop a robust form of analysis it was necessary to obtain more information about the reaction products under these conditions.

Prior to performing a more detailed analysis of the reaction products it is helpful to look at the past research using guaiacol as a model compound. During degradation, both the methoxy and alcohol groups may be removed, but the methoxy removal is generally more favorable[26]. Since there is an excess of water in the reactor in some cases a hydrogen molecule may be donated to remove the methoxy group which is then displaced by the remaining OH group. A flow sheet showing the breakdown of the potential degradation products of guaiacol is shown in figure 19.
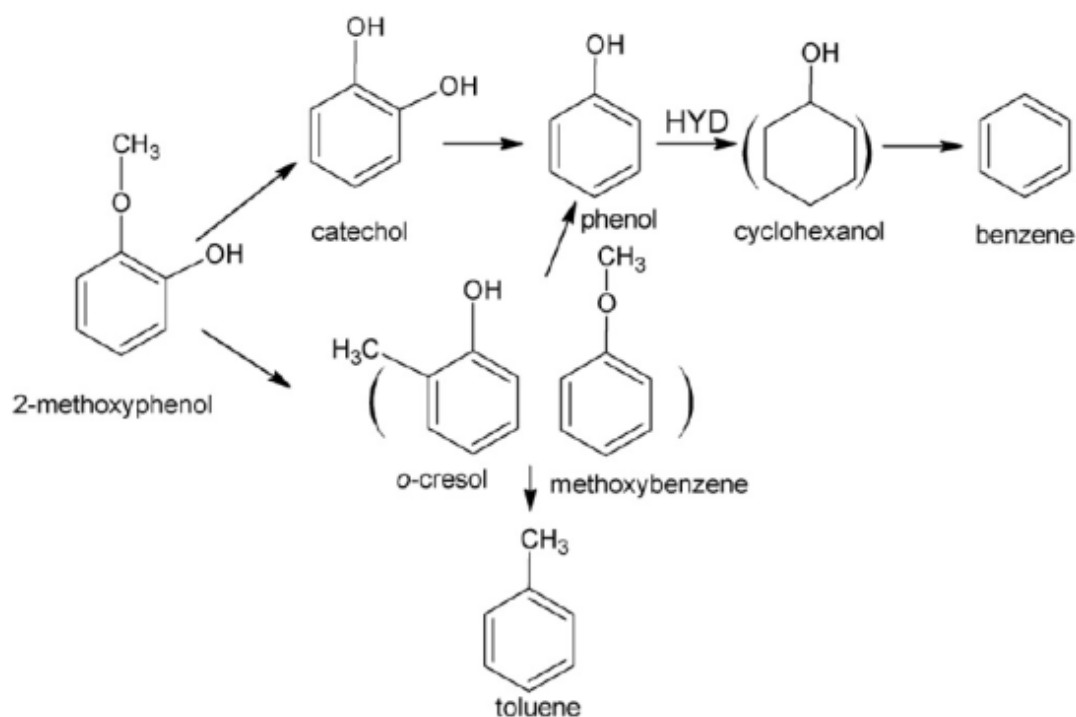
Figure 19: Reaction network for HDO of guaiacol (Zhao *et al.,* 2011)

Since the reaction is completed using relatively modest conditions without the use of a catalyst it should be expected that the primary reaction products including catechol, phenol, o-cresol, and methoxybenzene would make up the bulk of the samples.

In order to obtain a better understanding of the validity of the FTIR and elemental analysis data, additional analysis was performed as a basis for comparison. The first form of analysis of the reaction products is NMR spectroscopy. The samples analyzed were the starting material guaiacol, the extracted oil product produced at 350°C, and the oil phase produced at a temperature of 400°C. The extracted oil product was analyzed in order to determine degree of difference of products formed in the extracted phase and oil phase. The oil phase was analyzed at 400°C to determine if the elemental composition estimate is accurate.

Analyzing hydrogen spectra is simpler than analyzing carbon spectra since hydrogen atoms that are part of the same functional group will generally appear at the same

area in the spectrum. This is easily observed by looking at the spectrum of the starting material. The spectrum has three peaks which correspond with aromatic, alcohol, and ester functional groups. The numbers at the bottom correspond to the integration areas for each of the peaks. The relative areas of the peaks correspond to the number of atoms represented. In this case the guaiacol molecule has a total of eight hydrogen atoms. Four of the atoms are present in the aromatic ring, three are present in the methoxy group and one is attached to the alcohol group. The integration of these peaks matches the expected ratios almost exactly as displayed in figure 21. The expectation is that the reaction products will have lower ratios of hydrogen atoms from the alcohol group and ether groups in comparison to the aromatic group. The spectrum for the oil produced at 350°C figure 22 shows additional peaks created at a shift of about 2.2 ppm but for the most part the peaks are very similar to the original compound. The spectrum of the oil created at 400°C figure 23 shows a dramatic change in the ratio of aromatic hydrogen to methoxy hydrogen atoms. This suggests that a significant ratio of the guaiacol molecules had the methoxy group removed. These results are of course consistent with the results found using FTIR analysis and not consistent with the elemental analysis data.

After gaining a basic understanding of what has occurred using the ^{1}H spectra the ^{13}C spectrum can be used to get a better understanding of exactly what has was formed during the reaction. The reason for this is that each carbon atom produces a peak at a different place on the NMR scale. Shift patterns were calculated for each of the expected products using reference materials for typical NMR spectroscopy [27]. These calculated shift patterns are displayed in table 8. These results were then compared to the NMR spectra that were produced. In order to explain the ^{13}C spectra an identifier must be applied to each unique carbon group in order to explain how they affect the spectrum that is produced. These unique identifiers are labeled in figure 20.
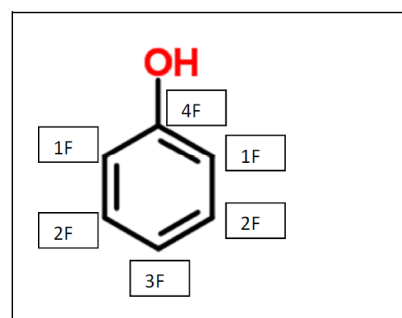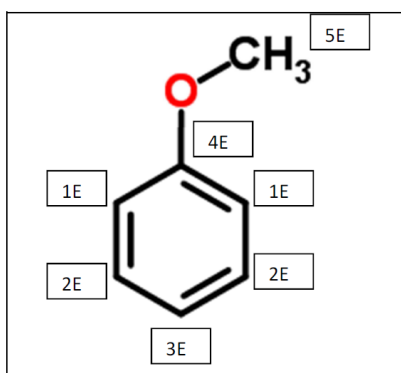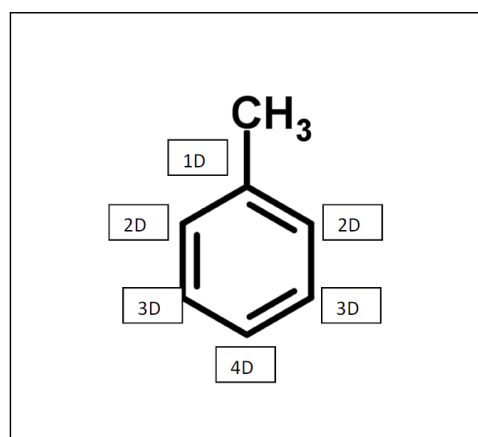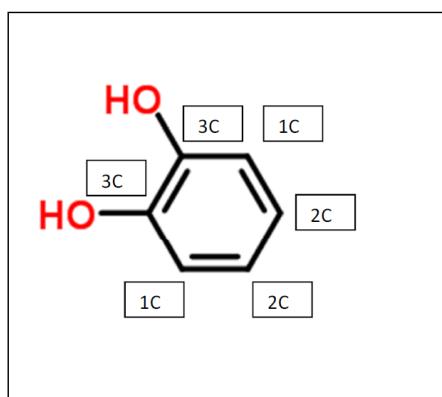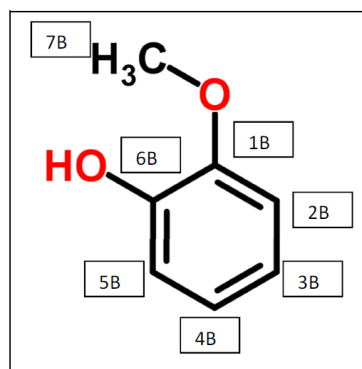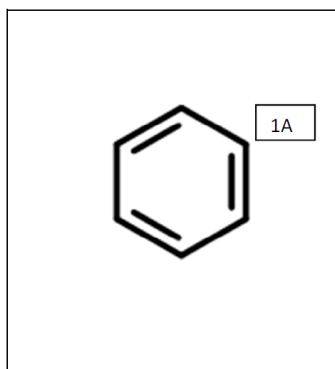
Figure 20: Chemical structures of potential molecules present for NMR sampling with identifiers for all of the unique carbon groups

Table 8: Predicted pattern of potential components for ^{13}C NMR spectrum

Name	(unique carbon identifier-, chemical shift expected)
Benzene	(1A,128.15)
Guaiacol	(1B,147.1),(2B,115.7),(3B,122.4),(4B,122.3),(5B,116.7),(6B,140.7)
Catechol	(1C,117.3),(2C,123),(3C,142.3)
Toluene	(1D,148.7),(2D,128.3),(3D,128.4),(4D,125.9)
Methoxybenzene	(1E,114.1),(2E,129.5),(3E,120.7),(4E,160)
Phenol	(1F,115.7),(2F,130.1),(3F,121.4),(4F,155.1)

These predicted values can then be compared to actual peaks that were produced. The spectrum for the water soluble component produced at 350°C (figure 24) indicates that the original compound is still the dominant species present but there is some evidence that catechol was formed. There was also a peak that could be associated with benzene. A spectrum was also produced for a sample that ran at about 400°C (figure 25), which contained all of the same peaks as the 350°C sample, and additional product peaks were found which were consistent with methoxybenzene and phenol. There also is some evidence that toluene was formed but those peaks are very small and it is difficult to obtain much information from them. The peaks associated with the compounds mentioned are marked on the ^{13}C spectra below.
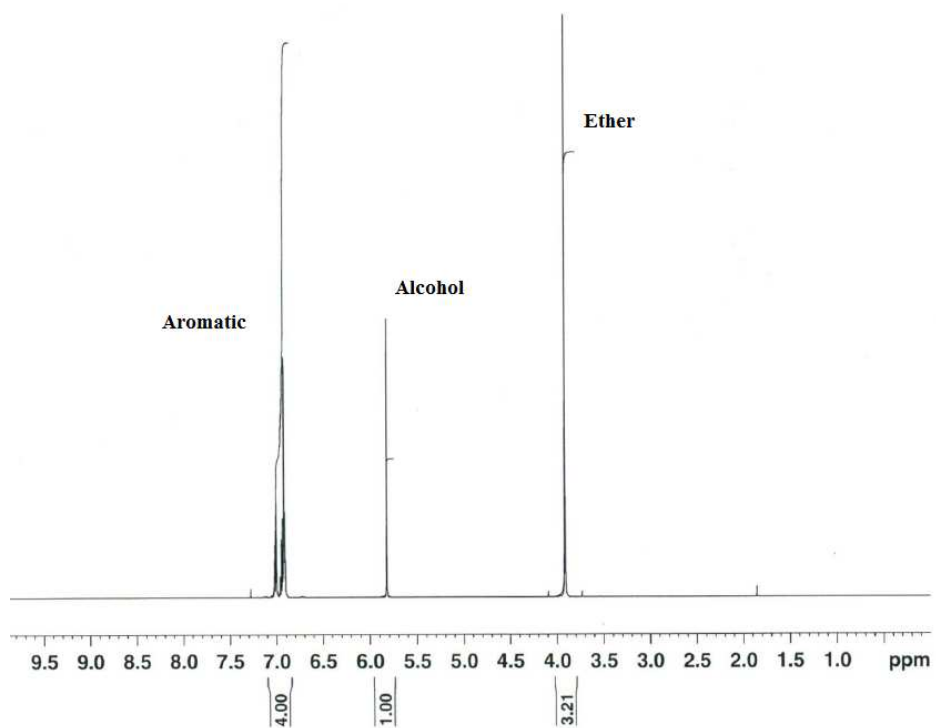
Figure 21: ^{1}H NMR spectrum of guaiacol
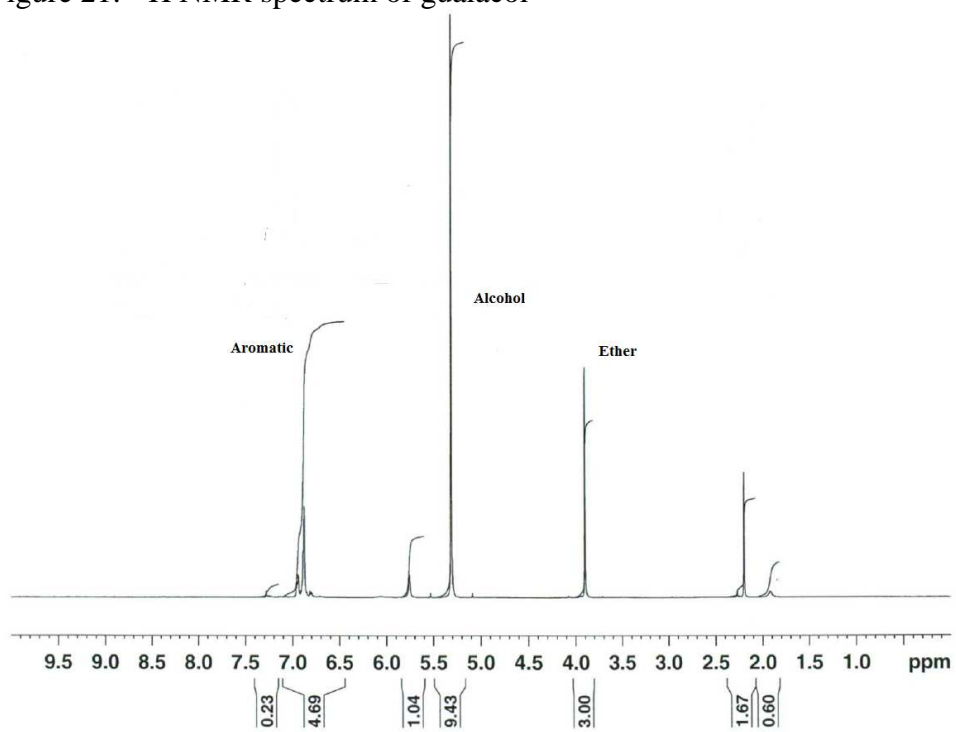
Figure 22: ^{1}H NMR spectra of extracted oil product produced at 350°C
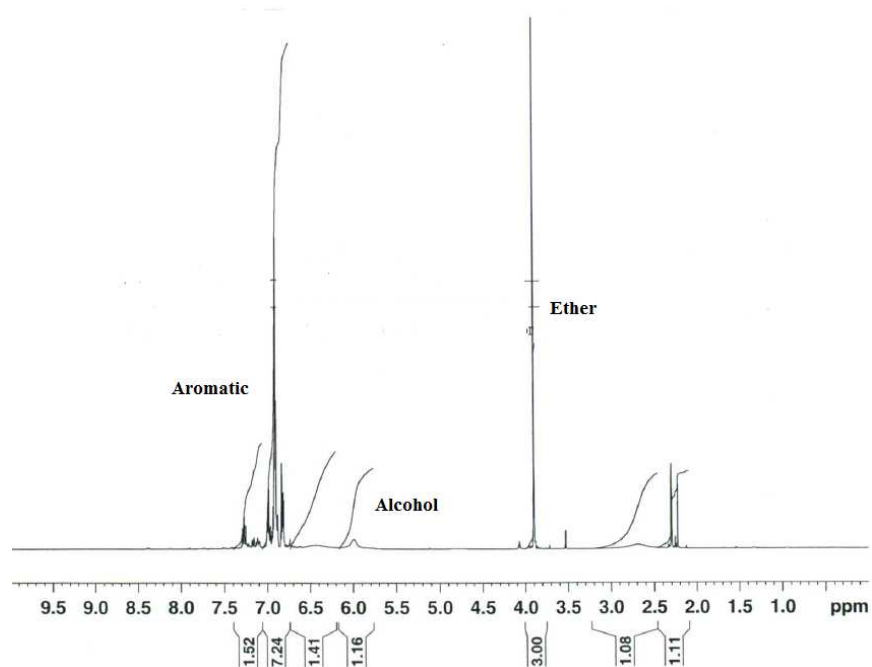
Figure 23: ^{1}H NMR spectra of oil product produced at 400°C
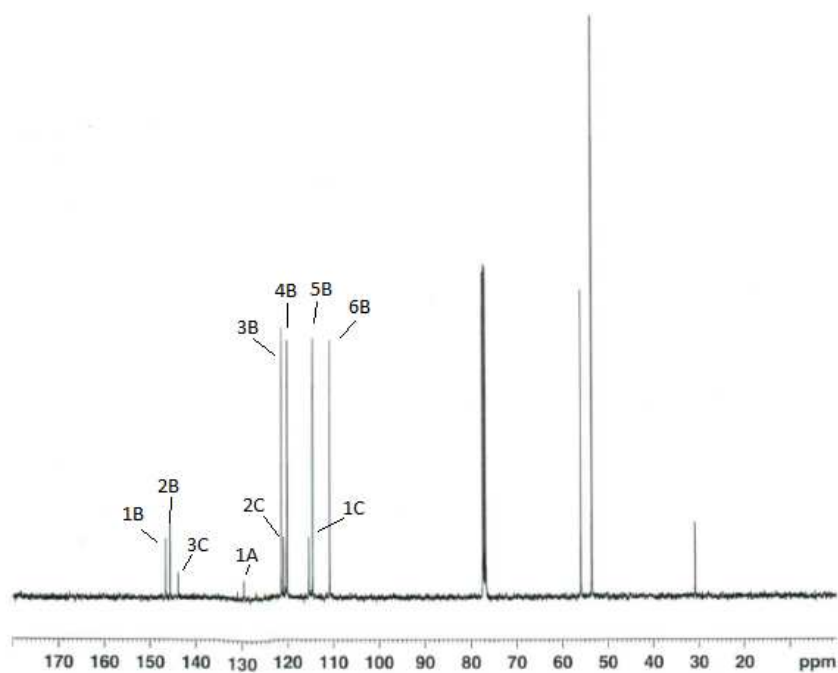
Figure 24: ^{13}C NMR spectrum of guaiacol degradation products in aqueous phase at 350°C
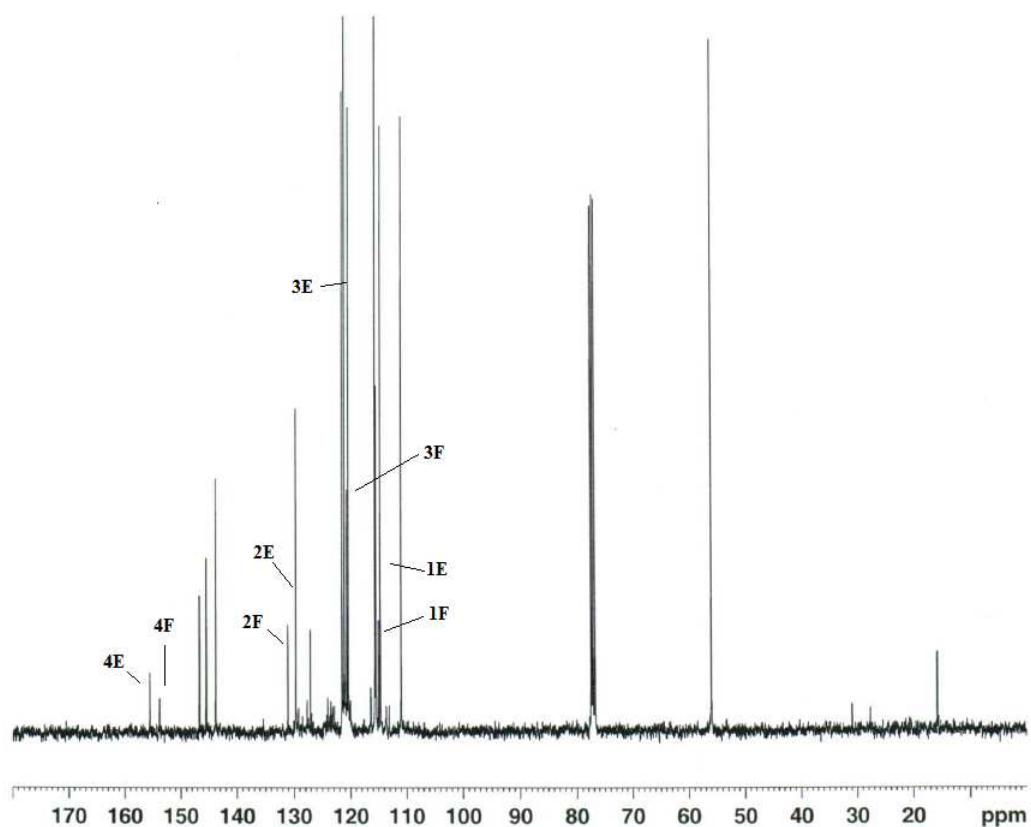
Figure 25: ^{13}C NMR spectrum of guaiacol degradation products in oil phase at 400°C

In order to confirm the results of the NMR analysis the sample collected for a reaction temperature of 400 °C was analyzed by GC-MS. The results of the GC-MS analysis are presented in table 9.

Table 9: Results from GC-MS of sample produced at 400°C with no CO

M/z ratio	Likely compound
124	Guaiacol
109	Catechol
108	Methoxybenzene
94	Phenol

In addition to these three peaks a peak was detected with an m/z ratio of 109. This is close to the molar mass of catechol (110) and therefore likely corresponds an ion of that compound. The area of the peak was much smaller than the other three peaks. In many ways the GC-MS analysis is consistent with the NMR analysis. Both forms

of analysis indicate that phenol and methoxybenzene are the primary reaction products. The GC-MS however does not clearly detect catechol which suggests that may be a limitation of that analysis method. It is possible that the GC column was not effective at separating catechol and therefore it was difficult to differentiate between catechol and the other components.

4.4 Guaiacol Degradation in the Presence of Carbon Dioxide

Earlier it was confirmed that oxygen can be removed from guaiacol by thermal degradation in the presence of high temperature water. Experiments were then performed to determine if the amount of deoxygenation can be improved by including carbon monoxide. Several tests were run with guaiacol and water in the presence of carbon monoxide. Each test was run at a temperature of 400°C, since that temperature yielded a reaction product in the absence of carbon monoxide. The amount of carbon monoxide in the enclosure was varied in order to determine the impact of gas. In each case the initial total gas pressure in the enclosure was approximately 300 PSI. The reactor was filled with CO to obtain approximate partial pressure of 0, 100, 200, and 300 PSI with the balance N_2.

The first test that was used to determine if carbon monoxide had a significant impact was FTIR. Based on previous results FTIR can be effective in determining whether or not the methoxy group has been removed. FTIR analysis is presented in figure 26 for oil product produced with no CO and several different partial pressures.
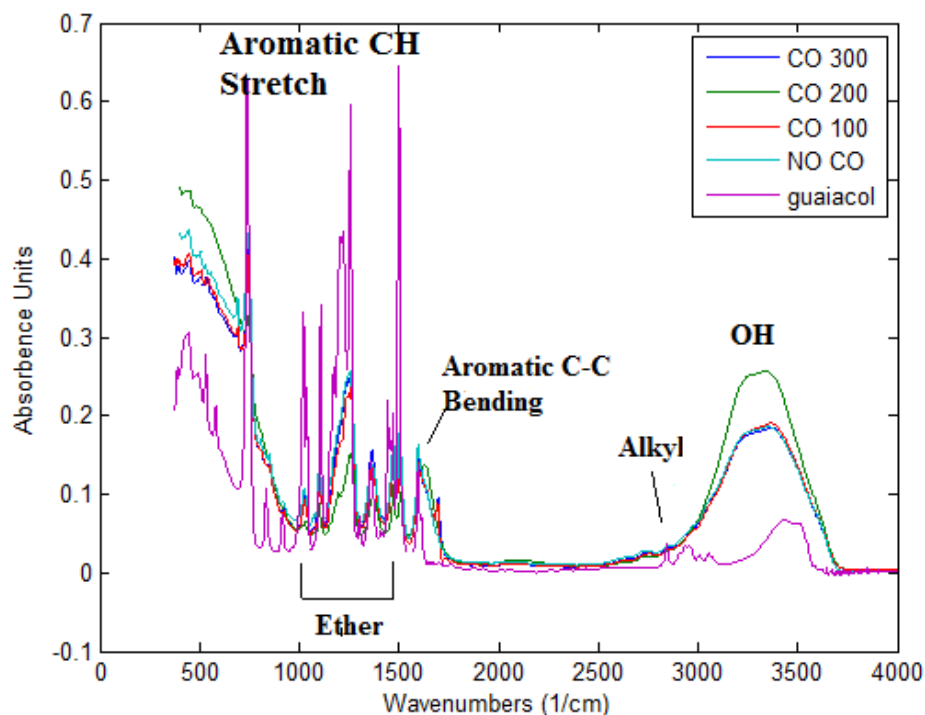
Figure 26: FTIR data for guaiacol and degradation products at various partial pressures of carbon monoxide at a temperature of 400°C

Figure 26 shows that there are not large differences in the presence of the methoxy group for the different samples of bio-oil. There may be some smaller differences in functional groups but they would have to be detected with more exact forms of measurement. In all cases the methoxy group was most definitely removed to a significant extent which is expected given the temperature of the reaction.

Elemental analysis was then used to determine the amount of oxygen that had been removed during the reactions. Elemental analysis data is displayed in table 10.

There are a couple key differences between the elemental analysis data using carbon monoxide and previous data collected. First the carbon percentage in the oil phase is lower and the carbon percentage in the aqueous phase is higher. This suggests that some of the products are more soluble in water than the reactant. In addition, for the samples produced with carbon monoxide partial pressures of 0 and 200 PSI the

product produced consisted of one phase. Care was taken to ensure that the reactor conditions were as similar as possible for all trials with the exception of the amount of carbon monoxide so the precise reason for this difference is unknown. Reasons for this discrepancy are analyzed in the discussion section.

Table 10: Elemental analysis data for reaction products using carbon monoxide

Sample	Carbon %	Hydrogen	CO Partial Pressure (PSI)
Oil Phase	48.5	7.54	300
Aqueous Phase	18.2	7.96	300
Coke	21.6	3.68	300
Oil (Extracted)	50.5	7.23	200
Aqueous	36.7	8.33	200
Coke	21.1	3.92	200
Oil Phase	42.2	7.35	100
Aqueous Phase	21.2	6.18	100
Coke	30.4	4.65	100
Oil (Extracted)	50.9	7.01	0

The low percentage of carbon in the oil phase can be explained by the high water content of the oil. KF titration analysis demonstrates that the water content is dramatically higher for these trials than for the previous trials. Since the higher water content is consistent for all trials this higher water content is likely due to the higher extent of reaction based the more extreme conditions due to the higher number of total moles in the reactor enclosure. The elemental composition of each oil sample, calculated using KF analysis data is presented in table 11.

Table 11: KF analysis for oil produced and estimated oil composition

Sample	Water %	Carbon %	Hydrogen %	Oxygen %	CO Partial Pressure (PSIG)
Oil Phase	41.6	83.0	4.99	12.0	300
Oil (Extracted)	35.2	77.9	5.18	16.9	200
Oil Phase	44.0	75.5	4.39	20.1	100
Oil (Extracted	28.2	70.9	5.39	23.7	0

This data provides some limited evidence that higher carbon monoxide partial pressures do in fact cause the oxygen percentage in the oil phase to decline. The issue of the margin of error of this data however is significant and will be discussed in the discussion section.

Much like the previous samples the elemental analysis data does not provide much information about the exact reaction products formed. GC-MS was performed on the oil that formed with an initial partial pressure of 200 PSI for carbon monoxide. The main purpose of this analysis is to determine if the presence of carbon monoxide leads to a greater spread of reaction products. The compounds detected using GC-MS are displayed in table 12.

Table 12: GC-MS analysis of sample formed at 400°C with a CO partial pressure of 200 PSI

M/z ratio	Likely compound
197	6H-Benzo(C) Chromene –6-ol
181	Xanthene
124	Guaiacol
108	Methoxybenzene
94	Phenol

Three replicates of the sample were run with GC-MS and those three samples each produced five peaks in common. Three of those peaks represented molecules that were produced in the previous experiment. Those peaks corresponded to guaiacol, methoxybenzene, and phenol. Two other peaks were detected that correspond to large molecules which are have not been identified in previous research but have been identified as xanthene and 6H – benzo(C) chromene-6-ol which are displayed in figure 27. Those peaks may account for the reduction in oxygen content that is observed with the elemental analysis data. They also may explain the peaks in the NMR spectrum that were originally associated with toluene and benzene. A sample was also run for GC-MS that was collected at a pressure of 300 PSI with no carbon monoxide. This sample produced three peaks which matched up with the three primary products.

Xanthene · 6H-Benzo(C)Chromene-6-ol
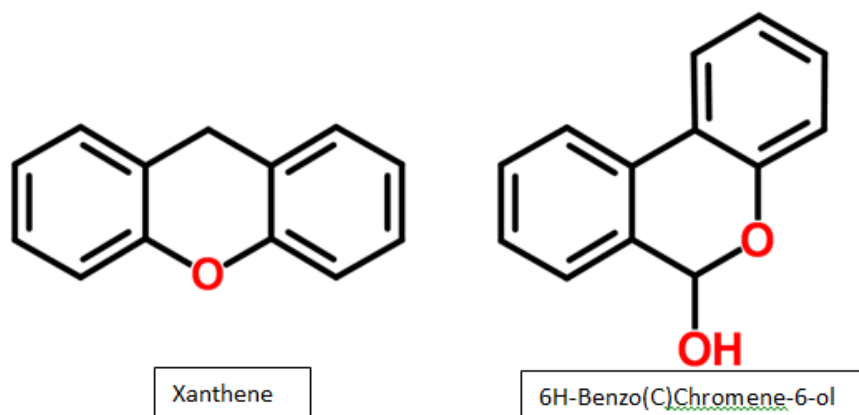
Figure 27: Structure of additional molecules detected with GC-MS analysis

GC-MS analysis is effective at finding the distribution of products however it is not a very good quantitative method. The differences between the amounts of product formed can more easily be seen by comparing samples produced at conditions that have the most striking difference. The products that were compared were the extracted oil product formed with no carbon monoxide present and the oil product formed when the enclosure contained a maximum partial pressure of 300 PSI CO_2. These products were compared due to the fact that they are likely to have the largest difference in the distribution of reaction products. The 13C NMR spectra of both of these samples are presented in figure 28 and 29 along with peak identification.

Figure 28: ^{13}C spectra of sample formed with a CO partial pressure of 300 PSI

Figure 29: ^{13}C spectra of sample formed in the absence of CO

These samples demonstrate that for both samples the primary reaction products are methoxybenzene, phenol, and catechol. There are also some peaks that suggest that benzene, and toluene is formed on a minor level as well. There is a difference in peak height which may be an indication of the different amounts of products formed.
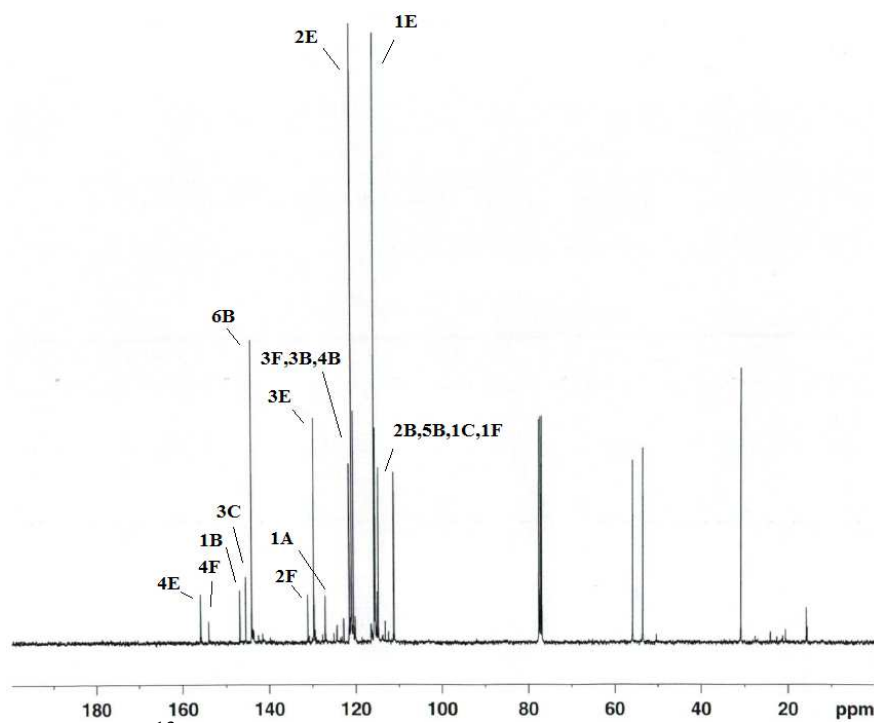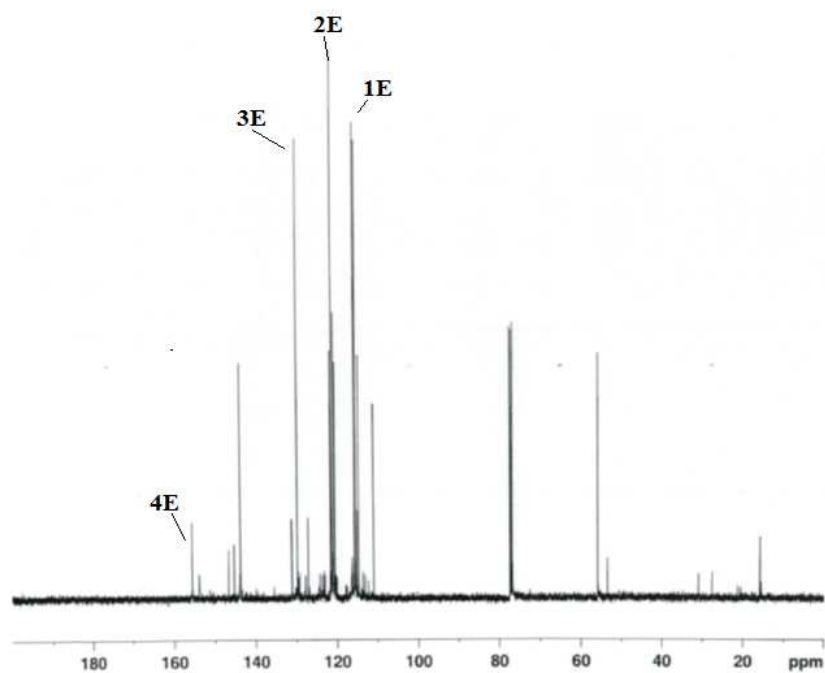
Hydrogen NMR data can also be used to confirm the distribution of products. This can be presented most effectively by simply presenting the peak areas for all of the hydrogen groups and comparing the ratios. This demonstrates the reductions or increases in different functional groups. This data is presented below in Table 13.

Table 13: ^{1}H NMR analysis of samples

Sample	OH-Aromatic	Methoxy-Aromatic
Guaiacol	.25	.803
350°C-Ambient	.211	.610
400°C-Ambient	.114	.294
400°C-Blank	.06	.15
400°C-300PSI	.04	.16

This data clearly represents that the overall extent of reaction rises dramatically as the temperature and pressure rises. It is not as clear that carbon monoxide has a significant impact on the overall extent of reaction.

4.5 Analysis of Coke Product Formed in the Presence of Carbon Monoxide

Data was collected concerning the composition of the coke product in an attempt to complete the material balance with the hope of determining how much carbon was recovered during the reaction. The elemental analysis data for the coke product was analyzed further due to the fact that the carbon content of the coke was much smaller based on the trials in which carbon monoxide was used than it was for the trials with no carbon monoxide. It should also be noted that the amount of coke produced was also significantly higher for the carbon monoxide trials. The coke product further analyzed by dissolving it in acetone and pouring the products through filter paper.

The acetone was then removed from the wash product using a rotary evaporator. The elemental analysis results are presented in table 14.

Table 14: Elemental analysis data for washed coke product

Sample	Carbon %	Hydrogen %	CO Pressure
Washed Coke	22.6	3.90	300
Washed Coke	21.1	3.92	200
Washed Coke	21.9	3.97	100

These results indicate that the oil product was bonded to the coke which caused the carbon content of the samples to be artificially inflated. FTIR analysis of the oil wash product indicates that it is similar in structure to the oil in the oil phase. When the coke is rinsed the elemental analysis data is remarkable consistent for each of the three trials with carbon monoxide. The results are not a likely reflection of what the coke actually looks like since coke is generally composed of mostly carbon. The more likely explanation for the low values of carbon and hydrogen content is the fact that the coke product is not as volatile as the coke product formed in earlier trial and therefore the elemental analysis is not yielding 100% combustion. The elemental analysis data does have the benefit of providing a reasonable estimate of the ratio of carbon to hydrogen content in the coke.

In order to obtain a more detailed assessment of the composition of the coke product SEM analysis was performed on the coke product formed with a CO partial pressure of 200 PSI. It was determined that only one sample needed to be analyzed due to the similarity of all of the samples both in terms of elemental analysis and appearance. SEM EDS analysis gives elemental composition of a solid. SEM results do not detect small compounds like hydrogen but can detect a variety of other atoms. The atoms detected included carbon, oxygen, neon, magnesium, silicon, and iron. Most likely the atoms that were detected other than carbon and oxygen are not part of the compound but are shavings that were swept up along with the coke. The SEM data for carbon and oxygen is presented in table 15 for the six SEM measurements. An image displaying the surface morphology of the coke is displayed in figure 30.

Table 15: EDS elemental analysis data for washed coke product

Carbon %	Oxygen %	C/O Ratio
55.60	19.07	2.92
79.84	15.95	5.01
87.81	12.19	7.20
80.33	15.74	5.10
83.76	15.89	5.27
84.86	15.02	5.65

It is appropriate to disregard the results of the first sample since there seems to be a significant amount of material present that is not composed of coke. This data provides a reasonable estimate of what the ratio C/O ratio is for the coke product. This estimate for the C/O ratio comes to 5.65. This is obviously much more reasonable than the estimate that comes purely from elemental analysis since this suggests that the sample is mainly composed of carbon which is more typical of a coke product.
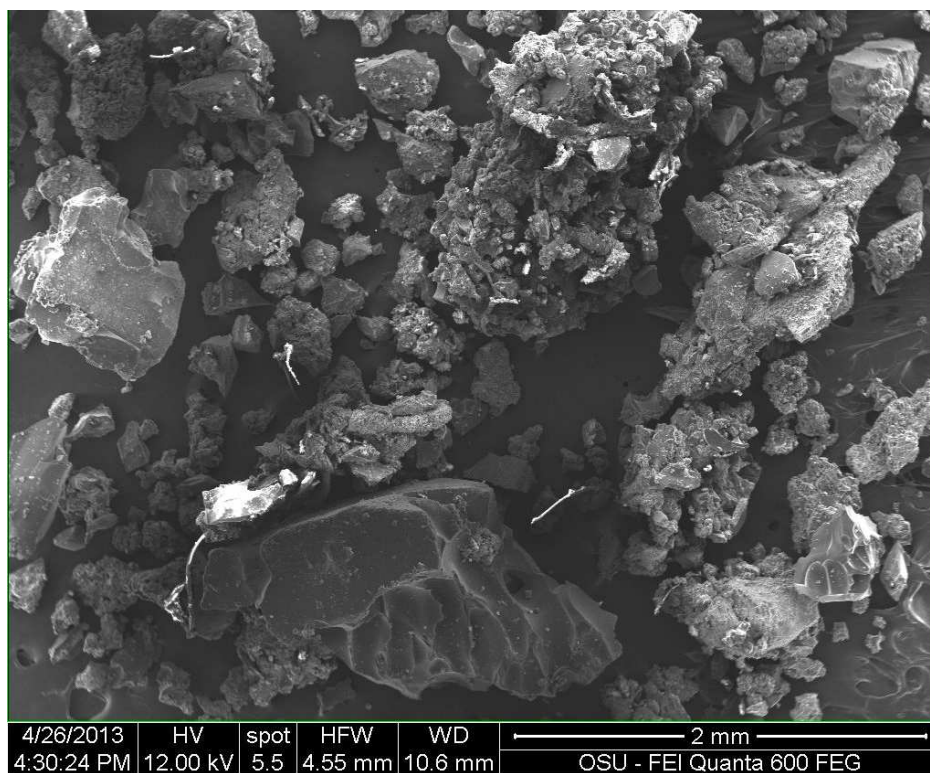
Figure 30: SEM image of coke formed from guaiacol reaction with a partial pressure of 200 PSI

Another important piece of data that must be collected to close the material balance is the makeup of the gases formed during the reaction process. During each trial the enclosure was filled with a combination of carbon monoxide and nitrogen. Temperature and pressure data was collected each time one the gases was added, the ideal gas law was then used to estimate the exact distribution of gases at the beginning of each trial. At the end of each trial a sample of the remaining gas was collected and was analyzed using gas chromatography. The results for each of the trials are displayed in figures 31 through 34.

Figure 31: Distribution of gas products formed with no carbon monoxide present
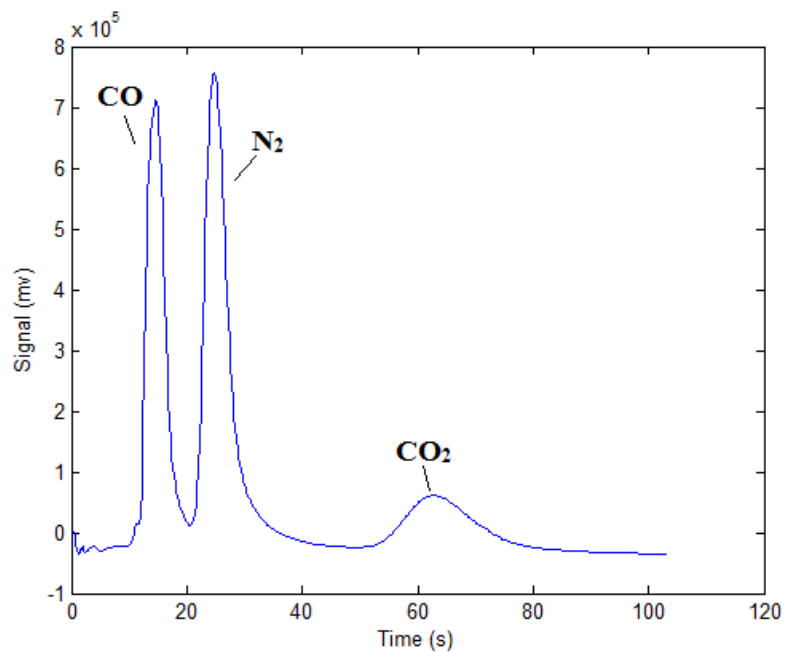
Figure 32: Distribution of gas products formed with a carbon monoxide partial pressure of 100 PSI
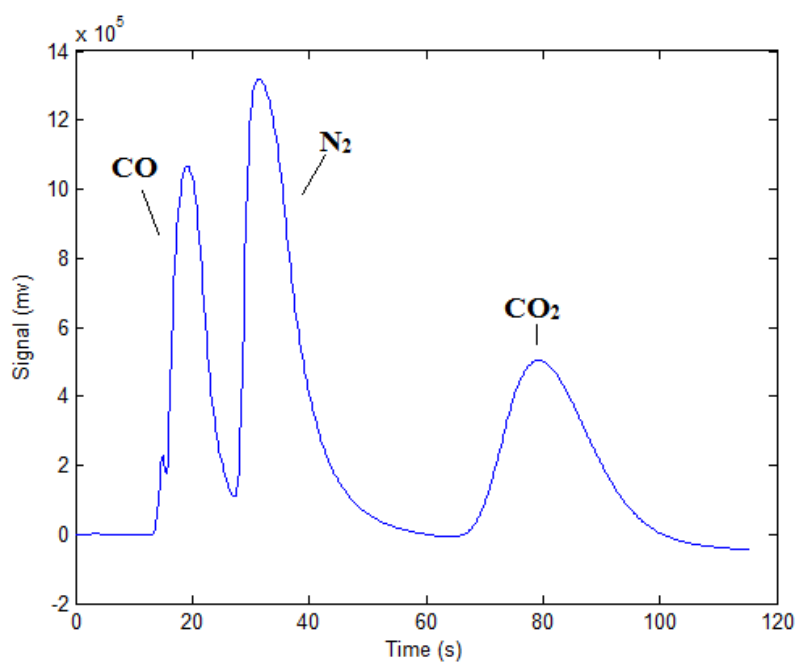
Figure 33: Distribution of gas products formed with a carbon monoxide partial pressure of 200 PSI

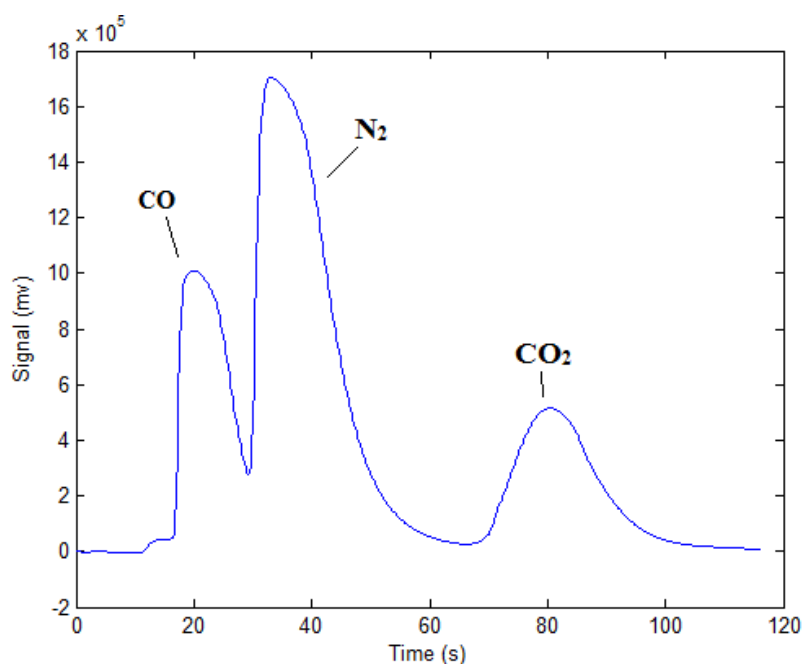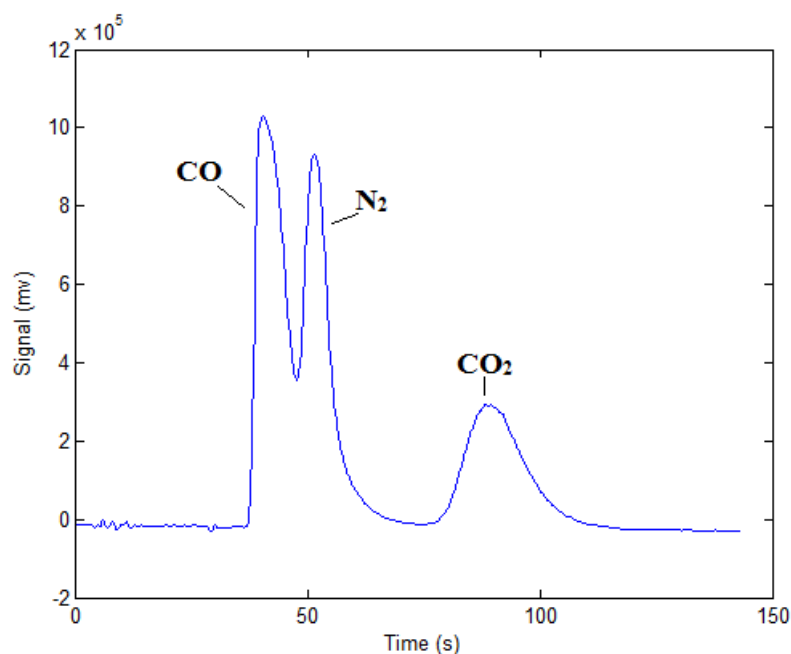Figure 34: Distribution of gas products formed with a carbon monoxide partial pressure of 300 PSI

For each trial the final distribution of gases was determined by determining the area of each of the peaks using the Riemann sum method. This method is difficult to use since the peaks are not well separated in some cases there appear to be split peaks. The area of each peak was then compared to the total peak area to determine the composition. These compositions were then compared to the initial compositions determined during the ideal gas law. The breakdowns of the final and initial compositions are displayed in table 16.

Table 16: Approximate distribution of gas products at the beginning and end of each trial

Order of Completion	Initial Composition		Final Composition		
	CO	N_2	CO	N_2	CO_2
4	0	100	23.3	56.0	20.7
2	31.2	68.8	36.1	49.7	14.2
3	67.2	32.8	25.3	46.2	28.6
1	89.2	10.7	43.1	33.6	23.3

The primary area of interest is the percentage of CO_2 produced. There does not appear to be any relationship between the amount of CO_2 produced and the amount of carbon monoxide in the reactor enclosure at the beginning. This is likely due to a change in reactor conditions. There was a small leak in the reactor enclosure which was not noticed until later. There also was a difference in the ambient temperature and there is some variation in the control system. Unfortunately this data is almost certainly not accurate enough in order to be used in any material balance. This conclusion is based on the fact that the nitrogen gas should be inert during the reaction process but the percentage of nitrogen as a portion of the total is very different for the starting and finishing conditions for all of the reaction runs. This indicates that the data should only be considered a rough approximation. This is likely due to the fact that some ambient air mixed with the sample itself leading to results which are closer to the composition of air then the sample itself.

CHAPTER 5

DISCUSSION

5.1 Distribution of Products

The combination of the GC-MS data and the NMR data indicate that the distribution of reaction products consists almost entirely of guaiacol, catechol, methoxybenzene, and phenol. The elemental composition of each of those products is displayed in table 17.

Table 17: Elemental composition of products

Compound	Carbon %	Hydrogen%	Oxygen %
Guaiacol	67.7	6.50	25.8
Catechol	65.5	5.49	29.1
Methoxybenzene	77.7	7.46	14.8
Phenol	76.6	6.43	17.0
6H-Benzo(C)	78.8	5.09	16.1
Xanthene	85.7	5.53	8.8

Given the similarities in the elemental composition of the primary components one of the problems with trying to evaluate the impact of the treatment of the bio-oils is determining the statistical significance of the results that are obtained. The oxygen content of the primary reaction products has a relatively small spread. This is a problem since there is a significant margin of error with our method of measuring oxygen content. Figure 35 illustrates the fact that changing the product distribution dramatically with regards to the primary reaction products does not have a large impact on the overall oxygen percentage.
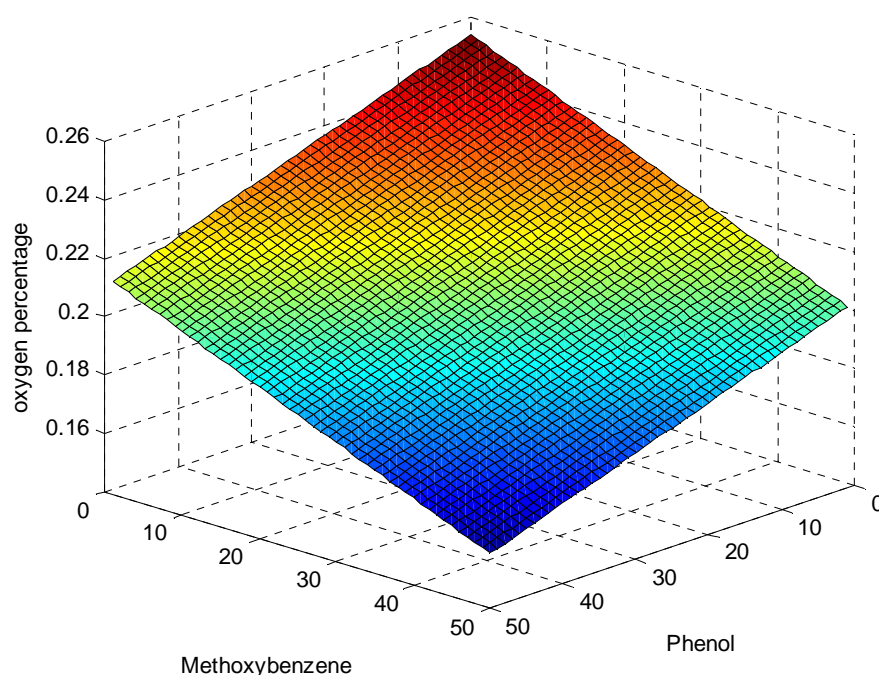
Figure 35: Impact of the distribution of products on the oxygen percentage in the oil phase

Table 18: Standard deviations for Karl Fischer and CHNS/O Analyzer analysis data for various compositions of carbon monoxide

CO % Composition	% SD	%SD
0	4.70	3.77
31.2	5.13	6.28
67.2	5.58	9.19
89.2	1.00	1.08

Oxygen content was calculated for each oil phase sample that was produced with varying partial pressures of carbon monoxide. Oxygen content in the oil phase can then be compared to starting carbon monoxide composition. This data suggests that there is a correlation between carbon monoxide content and oxygen removal. In order to determine the validity of the data margins of error must be added to any presentation of the data. Since the oxygen content is determined based on Karl Fischer titration and CHNS/O Analyzer analysis the standard deviation for each

measurement is presented in table 18. These standard deviations are then incorporated in to plot of oxygen composition versus oxygen content which is displayed in figure 36.
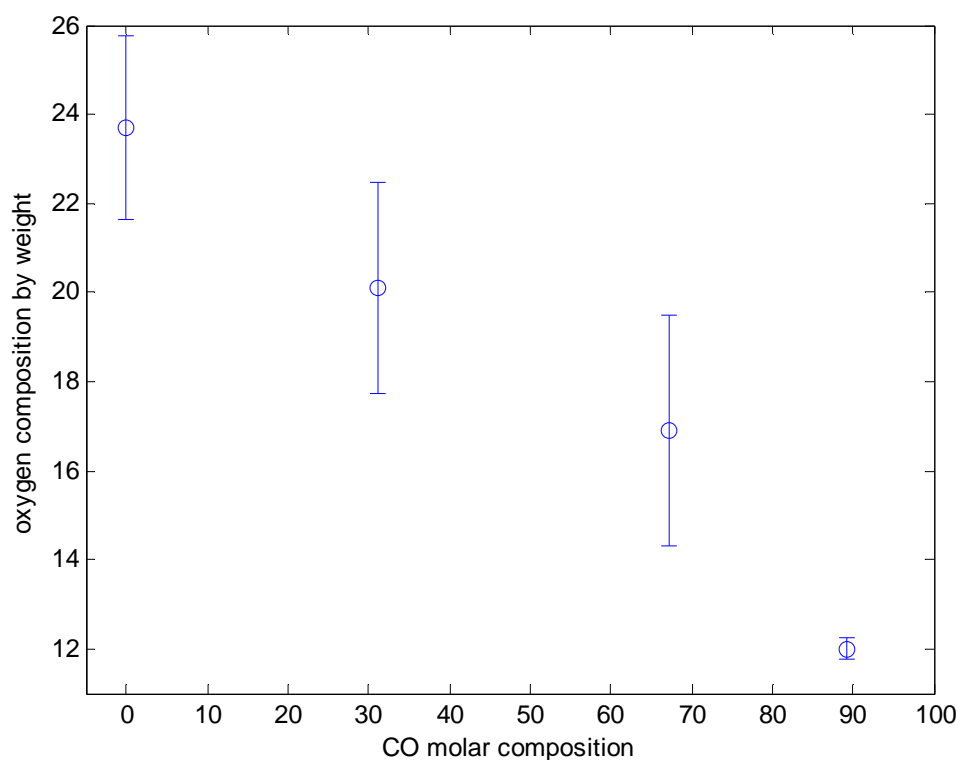
Figure 36: Plot of oxygen composition and CO molar composition with error bars

This data suggest that carbon monoxide has an effect on oxygen content. One aspect of the data that could be questioned is the fact that the oxygen content of the sample produced with the highest composition of carbon monoxide has lower oxygen content than Phenol. This may be due to the fact that larger amounts of xanthene and benzo chromene were formed under those conditions. It may also be due to the fact that some benzene and toluene were formed as well. The results when the CO molar composition is zero can be viewed skeptically, as well, due to the fact that the oxygen content is similar to that of the starting material. This is likely due to the fact

that a significant amount of catechol is formed which balances out the amount of lower oxygen content products that are formed.

The second question that has to be asked is if the differences in the results are statistically significant. This can be done by performing a paired t-test comparing the samples collected with no carbon monoxide at 300 PSI and the samples collected with a partial pressure of 300 PSI CO. In this case the null hypothesis is that there is not statistically significant difference between the two groups of samples. The t-test is performed using the relationships listed below and the parameters listed in table 19.

$$Sp = \sqrt{\frac{(n_1 - 1) s_1{}^2 + (n_2 - 1) s_2{}^2}{(n_1 + n_2 - 2)}}$$ (5.1)

$$SE(\overline{Y_2} - \overline{Y_1}) = s_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}$$ (5.2)

$$t - statistic = \frac{(\overline{Y_2} - \overline{Y_1}) - null}{SE(\overline{Y_2} - \overline{Y_1})}$$ (5.3)

Table 19: Parameters for Statistical Comparison of Samples with and Without Carbon Monoxide

$\overline{Y_1}$	$\overline{Y_2}$	n_1	n_2	s_1	s_2
12.0	23.7	3	4	.81	2.21

Calculations using these ratios correspond to a t-ratio of 8.49. This t-ratio means that there is a greater than 99.9% confidence that the null hypothesis can be rejected. This means that there is very clearly a statistically significant difference between the two groups of samples. While this shows that there is a statistically significant difference between the two samples it does not demonstrate a statistically significant difference between the reactor conditions. This is due to the fact that the reactor was only run once for each particular set of reactor conditions. It was not possible to conduct the number of replicates necessary to obtain triplicate samples for each set of reactor conditions. This means that statistical analysis cannot be applied to the reactor

conditions themselves. The consistency of the relationship between carbon monoxide and oxygen content does however, suggest a significant trend.

5.2 Water Content of Oil Phase

During the reaction two oil phases are formed. During the carbon monoxide trials the carbon percentage in the aqueous phase varied from 18-37%. This means that a significant amount of oil was dissolved in the aqueous phase. Analysis focused on the oil phase due the fact that catechol has by far the highest solubility in water of all of the obvious reaction products. The solubility of each of the reaction products from Perry's chemical handbook is displayed in Table 20.

Table 20: Water solubility of guaiacol degradation products of guaiacol

Compound	Solubility (g/100ml)
Guaiacol	1.7
Methoxybenzene	0.16
Phenol	8.7
Catechol	43
O-Cresol	3.1
Benzene	0.18
Toluene	0.047

Phenol and catechol are common reaction products so it should be expected that the amount of oil dissolved in the water phase would increase as the conversion goes up. This explains why catechol is not easily detected in the GC-MS results which focus on the oil product.

One key inconsistency in the data that must be addressed is the fact that the runs completed at a CO partial pressure of 100 and 300 PSI produced a product that naturally settled into two phases and the runs completed with partial pressures of 0 and 200 PSI produced a product that was one phase. The oil product was then separated by extraction using methylene chloride. It is unclear why this difference exists. It is likely due to the fact that there is some variation in the temperature

profile of the run due to variations in the control system. Figure 37 focuses on the temperature range above 350°C due to the fact that thermal reactions do not occur to a significant extent at temperatures lower than that.
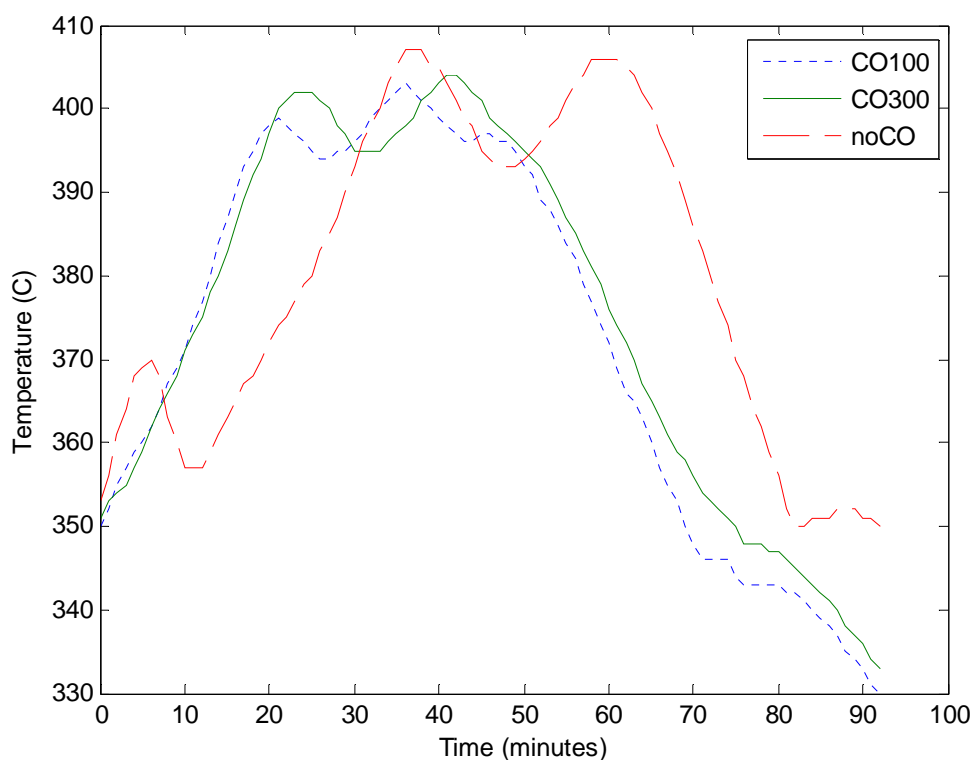
Figure 37: Distribution of temperatures for several reaction runs

In each case the set point for the final temperature was 400°C and the ramp rate was set to 9°C per minute. The temperature was held in the general range of 400°C for a period of 30 minutes and then the heater was shut off and the reactor enclosure was allowed to cool. Since there is no active cooling control for the system there will necessarily be some variation in cooling that occurs due to ambient conditions. It should also be noted that there appears to be a positive association between the products that form one phase and the amount of CO_2 formed. This likely means that the methoxy groups are coming off in the form of CO_2 and is displaced by the OH groups left over to form catechol.

5.3 Analysis of Solid Coke Product

An additional piece of the analytical results which should be analyzed is the coke product. Coke is generally composed of carbon and hydrogen but the SEM analysis of the coke clearly indicates that oxygen is present. Even though the coke product was only partially combusted it still provides a reliable estimate of the ratio of carbon to hydrogen in the coke products. When this is combined with the carbon to oxygen ratio stemming from the SEM analysis a system of equations can be developed to estimate the overall composition of the product.

$$C + H + O = 100, \frac{C}{H} = 5.56, \frac{C}{O} = 5.65 \qquad (5.4)$$

Solving for this system of equations leads to an elemental composition of 73.7% C, 13.3% H, and 13.0% O. Given the large amounts of coke formed during each reaction these results indicate that large amount of carbon are lost due to solids formation. This problem could likely be alleviated by decreasing the residence time of the reaction. This could be done by heating up the oil faster and introducing a cooling mechanism.

CHAPTER 6
CONCLUSIONS

6.1 Temperature Dependence

The first goal of the research is to confirm previous results published by Mercader *et al*. (2010) that indicated high temperature water without any external gases produces a two phase product with slightly reduced oxygen content. It is clear in the absence of carbon monoxide there is at least some reaction product formed by treating guaiacol in high temperature water. The FTIR results indicate that this is the case, as demonstrated by the fact that vibrations consistent with the methoxy group decrease in intensity when the reactor is heated up to a temperature close to supercritical. There is also a larger amount of carbon dissolved in the aqueous phase which indicates compounds are forming which are more soluble in water than the feed material. The GC-MS and NMR analysis also indicates that typical reaction products are formed from guaiacol.

6.2 Impact of Carbon Monoxide

After it was determined that high temperature water could be effective in and of itself for facilitating deoxygenation reactions a further goal was to demonstrate that carbon monoxide would enhance the deoxygenation results by generating hydrogen eternally and driving the production of CO_2. This was done by producing four different samples using the same conditions for each run while varying the partial pressure of carbon monoxide.

The first method that was used to determine the difference between the samples was FTIR. This method produced a spectrum that was nearly identical for each sample produced. CHNS/O Analyzer analysis data was then combined with Karl Fischer titration in order to determine the approximate oxygen content of the product. These

results indicated that there is a negative correlation between carbon monoxide partial pressure and oxygen content. Unfortunately the error of this data is significantly large in comparison with the range of data so it is unclear how large the impact of carbon monoxide is. The GC-MS analysis indicates that the distribution of products is larger with a larger amount of carbon monoxide compared to a similar sample produced with no carbon monoxide. It is difficult to discern the impact that carbon monoxide has on reaction products using NMR analysis due to the similarity of the signal produced by all of the potential reaction products. The information that is available does display some evidence that methoxybenzene is produced to a greater extent in the presence of carbon monoxide.

The totality of evidence that was gathered suggests that carbon monoxide has some impact on the amount of oxygen content of the bio-oil model compound but the results of the CHNS/O Analyzer analysis and Karl Fischer titration data likely overstates the impact on the process.

6.3 Material Balance

One of the original goals of this project was to close the material balance. For this reason data was collected in order to determine the composition of the gaseous products and the solid (coke) products. The purpose of collecting this data is to determine how much carbon from the feed material was recovered in the oil products. This approach turned out to be problematic due to the uncertainty of the validity of the results of the composition of the solid and gas products. Gas samples that were collected were likely unreliable due to the fact that the sample mixed with ambient air which skewed the results. The composition of the coke could be used to determine the amount of carbon lost during the reaction however it is difficult to determine the exact amount of coke formed and it is unknown how much of the carbon content can be attributed to the feed oil and how much can be attributed to the carbon monoxide gas due to the lack of reliable data regarding gas phase

composition. One of the goals for further research in this area is to collect more reliable data on the gas phase so that a more complete material balance can be completed.

6.4 Future Research

The primary goal of this research is to determine if bio-oil in the presence of high temperature water will have higher rate of oxygen removal in the presence of carbon monoxide than it will with an inert gas. The thermodynamics of the reaction determine that carbon monoxide should have an impact and past research indicates that it should as well. The data collected suggest there is a likely correlation between higher carbon monoxide content and lower oxygen content for oils that are treated in the presence of high temperature water. This correlation is very weak however and it would be helpful to produce a range of data that provides a greater range of oxygen content. There are a couple key reasons why carbon monoxide may have not a very large impact for these particular experiments. One is the fact that the kinetics of the reaction is limiting its effectiveness. Due to the formation of coke the residence time of the reaction is somewhat limited. If the gas phase shift reactions are too slow the rate may be increased by incorporating a catalyst. A second reason could be that the range of partial pressures for carbon monoxide was too low. For this particular project safety limitations prevented any setup that would lead to a partial pressure of CO higher than the 300 PSI. This means that on a molar basis there was not a large excess of CO. The same experiment could be setup with a much larger excess of CO which is typical for hydrotreating reactions.

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