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EFFECT OF SUPERCRITICAL WATER TREATMENT ON THE COMPOSITION OF BIO-OIL

By

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EFFECT OF SUPERCRITICAL WATER TREATMENT ON THE COMPOSITION OF BIO-OIL

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The effect of supercritical water treatment on the composition of bio-oil was investigated. Preliminary studies were carried in batch mode using a bio-oil simulant. This bio-oil simulant was designed to mimic crude bio-oil by possessing the same functional groups as are found in crude bio-oil, but with reduced complexity. Experiments of this type allow to be gained of the reaction chemistry involved. These were then followed up by experiments using crude bio-oil. Critical process parameters for all these experiments were reaction time, bio-oil/water ratio, reaction temperature and pressure. One of the objectives of this work was to identify processing conditions that would either suppress formation of, or elimination of the coke precursors. This would then result in a bio-oil with improved storage characteristics and a reduced tendency towards coke formation during catalytic upgrading. The results suggest that supercritical water treatment can effectively eliminate the coke pre-cursors resulting from bio-oil, resulting in a bio-oil with improved properties.

DEDICATION

To my Mother and to her unconditional love and unfailing belief in me

To my Father and to his selflessness which is I admire most

To all my Teachers to whom I owe whatever I know and more

To God for having gifted me with a life I never felt deserving of

To my family and friends who are the essence of my life

To all the people who never say I give up in life

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CHAPTER I

INTRODUCTION

1.1 GLOBAL ENERGY SCENARIO

Continually increasing oil prices combined with increasing energy needs of the developed and developing countries have catalyzed the search for alternate sources of energy. According to a U.S. Department of Energy report, energy consumption in the United States was 97.4 QBTU (quadrillion BTU) during 2002, and was twice that of the second largest energy consumer, China at 43.2 QBTU.[1.1] World energy production and demand has more than doubled during the last three decades. According to the US EIA (Energy Information Administration),[1.2] primary energy production was 215.39 QBTU in 1970, and had increased to 421.73 QBTU in 2003. Another growing concern is the impact on the environment due to increased carbon dioxide emissions resulting from the increased usage of transportation fuels. US EIA 2004 statistics (Figure 1.1) show that the United States leads the tabulation with 5.9 billion metric tons of carbon dioxide emissions annually.

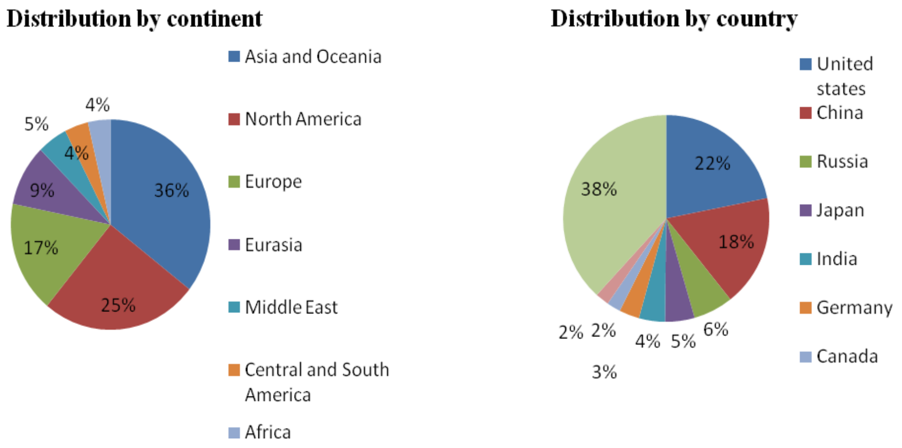


Figure 1.1 Global distribution of CO_2 emissions for 2004. (Data obtained from US EIA statistics[1.2])

The rising levels of greenhouse gas emissions resulted in the Kyoto Protocol in 1997, a set of guidelines designed to curb emissions of greenhouse gases, thereby reducing their impact on climate change in the future. As of November 2007, 174 countries had ratified the protocol.

The widening gap between supply and demand of fossil fuels, as well as the rising environmental concerns regarding high greenhouse gas emissions resulting from their use, has resulted in accelerated research during the last few decades on non-conventional, renewable and cleaner sources of energy. As of 2006,[1.3] renewable energy contributes a mere 7% to the total energy consumption (Figure 1.2). This translates to approximately 6844 trillion BTU annually. Of this 7%, hydroelectric power contributes less than half (approximately 42%) and biomass (including wood, bio-fuels and waste) contributes approximately half (48%).

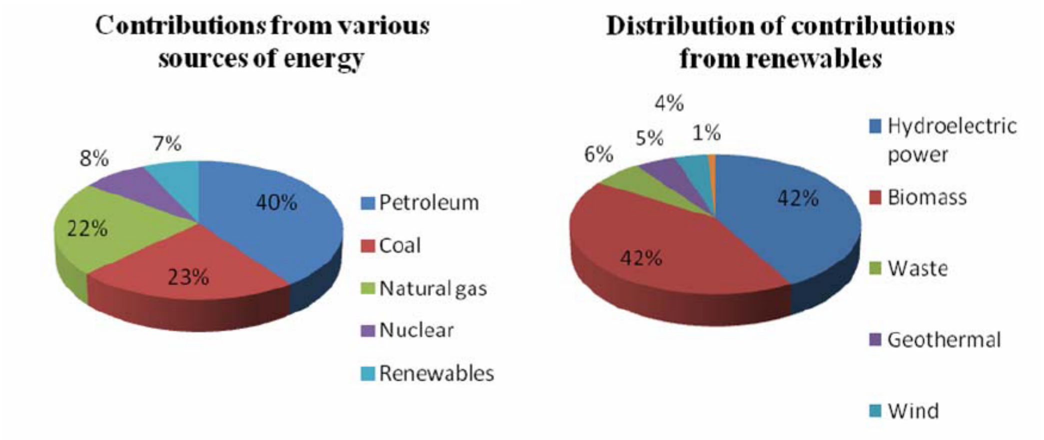


Figure 1.2 Contributions from different forms of energy. (Data obtained from US EIA statistics for the year 2006[1.3])

Trends in the renewable energy market indicate that hydro-electric power showed the highest increase in usage (186 trillion BTU annually, corresponding to a 7% increase)[1.4] as compared to a 28% increase in biofuels and a 45% increase in wind power. Among biofuels, ethanol production increased from 3.9 billion gallons in 2005 to 4.9 billion gallons in 2006,[1.4] aided by Federal tax incentives and the use of ethanol to replace MTBE as the gasoline oxygenate of choice.

Total consumption of biomass in the US for the year 2005 was estimated at 3298 trillion BTU[1.5] with the industrial sector being the largest consumer. With the rest of the world also starting to show an increased interest in biomass as an energy source, the biomass market is staged for unprecedented growth in the next few years. There are many reasons why biomass is such an attractive option as an energy source. Approximately half of the land mass of the continental United States has the potential to grow biomass.[1.6] Since plants consume carbon dioxide, biomass is considered to be greenhouse gas neutral.

The world's estimated energy consumption is projected to reach 702 QBTU by 2030[1.7] (compared to 447 QBTU in 2004). Consumption of liquid fuels is also projected to increase from 83 million barrels in 2004 to 118 million barrels in 2030.[1.7] Energy demand may outpace energy supply unless alternative energy sources are developed to meet the demand. Biomass, already the leading contributor among renewable energy sources in the US, is expected to fuel growing economies in the near future.

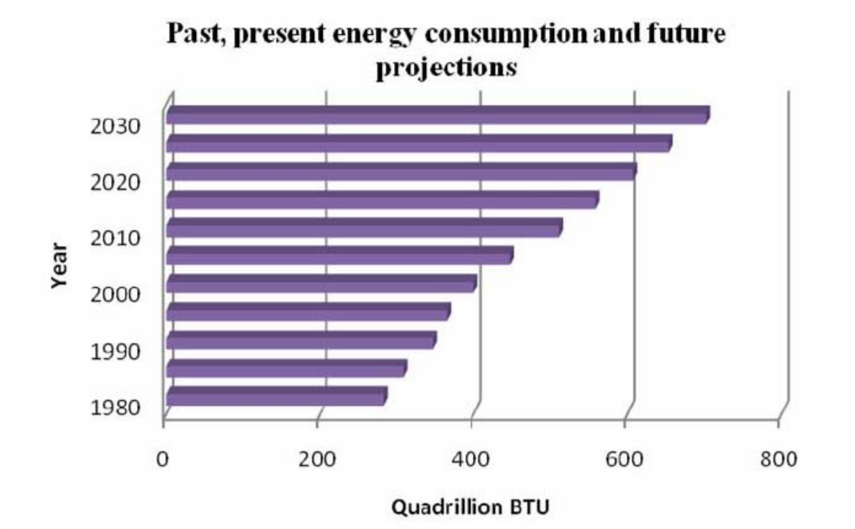


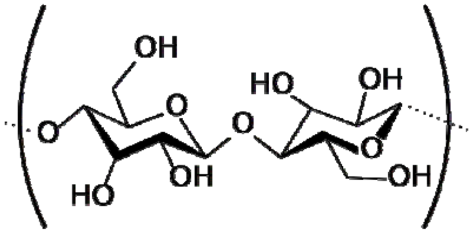
Figure 1.3 Projected trends for energy consumption. (Data obtained from US EIA statistics[1.7])

1.2 BIOMASS

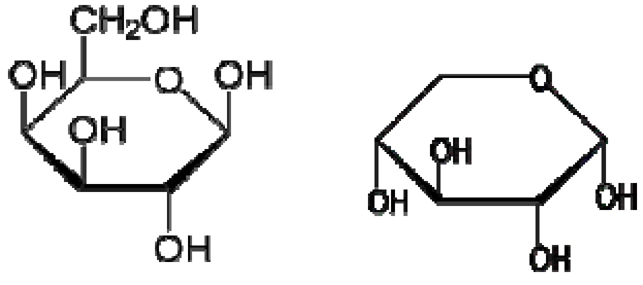
Historically, biomass has always been used for energy. Biomass can be defined as plant and plant-derived material inclusive of residues from agriculture and forestry, as well as industrial and municipal wastes that could be exploited as an energy source.[1.10] Thus, biomass is a broad term referring to a very large class of organic compounds primarily derived from plants. For this same reason, energy from biomass is highly feedstock dependent. The US Department of Energy's Energy Efficiency and Renewable Energy (EERE) program maintains a database that provides information on various properties and composition of a wide range of biomass feedstocks.[1.11]

In general, woody plants are composite materials composed of highly crystalline cellulose and amorphous hemicellulose embedded in a lignin matrix. Studies of the chemical composition of biomass reveal ~ 40-50% cellulose. However, the distribution of hemicellulose and lignin depends on the nature of the feedstock. Hardwoods contain 25-35% hemicellulose, while softwoods contain 28-35% hemicellulose. Softwoods have more lignin (25-30%) than hardwoods (18-22%).

Cellulose is a linear polysaccharide constructed of β-D glucose units linked together by β-1-4 linkages. The average degree of polymerization is about 10000. Hemicelluloses are branched polysaccharides composed primarily of five sugars: glucose, mannose, galactose, xylose and arabinose. The degree of polymerization is about 100-200. Lignin is a highly cross-linked amorphous polymer made up of phenyl propane units. These monomeric phenyl propane units fall into one of the three types depending on the feedstock: p-coumaryl, sinapyl and coniferyl structures. These are more generally referred to as p-hydroxyphenyl, guaiacyl and syringyl units, respectively. Gymnosperm lignins (softwoods like pine etc.) are characterized by the presence of guaiacyl lignins with a small proportion of p-hydroxyphenyl units. In contrast, angiosperm lignins (hardwoods like oak etc.) contain guaiacyl and syringyl units in different proportions. The structures of these various components in biomass are shown in Figure 1.4.

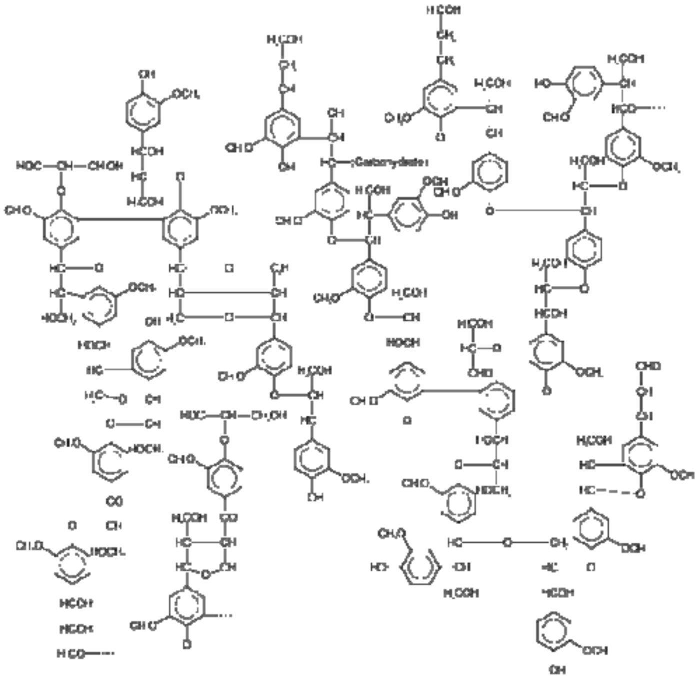


Structure of Cellobiose – monomeric unit of cellulose



β-D-Galactospyranose α-D-Xylofuranose

Galactose (hexose) and xylose (pentose): two of the five sugars which form the building blocks in hemicelluloses



Proposed structure of lignin polymer

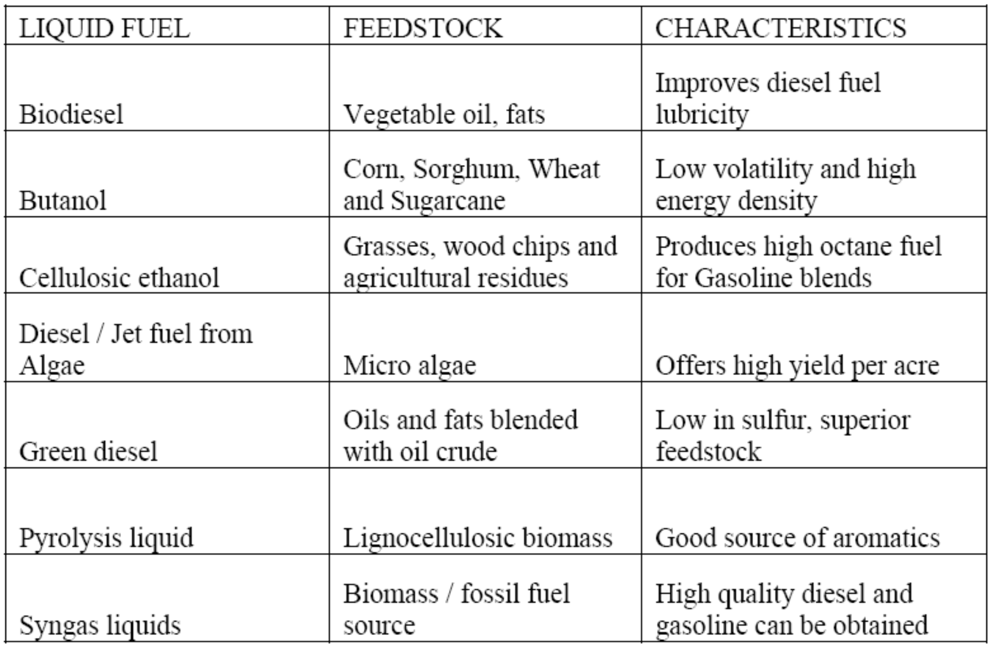
Figure 1.4 Structural components of biomass

1.3 BIOMASS FUELS

Plant crops can be repeatedly grown and harvested making biomass a sustainable resource from which energy can be obtained. As plants consume carbon dioxide during their respiration cycle, they can also help to reduce greenhouse gas levels by acting as a carbon sink. This is considered to be one of the most promising ways to control climate change.[1.8]

Biomass fuels can be classified into three main groups: wood, wastes, and alcohols/biofuels.[1.8] The energy derived from burning wood is mainly used by the industrial and electric utility sectors. The energy in biomass wastes can be harvested in many ways, such as burning of garbage, collection of methane gas from landfills and anaerobic digestion of municipal wastes.[1.8] The alcohols/biofuels category encompasses the broad spectrum of liquid fuels that can be obtained from biomass, including ethanol, biodiesel, butanol, pyrolysis oil or bio-oil, and syngas-derived liquids among others. Table 1.1 is a summary of the various liquid fuels that are currently being produced commercially.

Table 1.1 Liquid fuels and their characteristics. Adapted from NREL release[1.9]



LIQUID FUEL	FEEDSTOCK	CHARACTERISTICS
Biodiesel	Vegetable oil, fats	Improves diesel fuel lubricity
Butanol	Corn, Sorghum, Wheat and Sugarcane	Low volatility and high energy density
Cellulosic ethanol	Grasses, wood chips and agricultural residues	Produces high octane fuel for Gasoline blends
Diesel / Jet fuel from Algae	Micro algae	Offers high yield per acre
Green diesel	Oils and fats blended with oil crude	Low in sulfur, superior feedstock
Pyrolysis liquid	Lignocellulosic biomass	Good source of aromatics
Syngas liquids	Biomass / fossil fuel source	High quality diesel and gasoline can be obtained

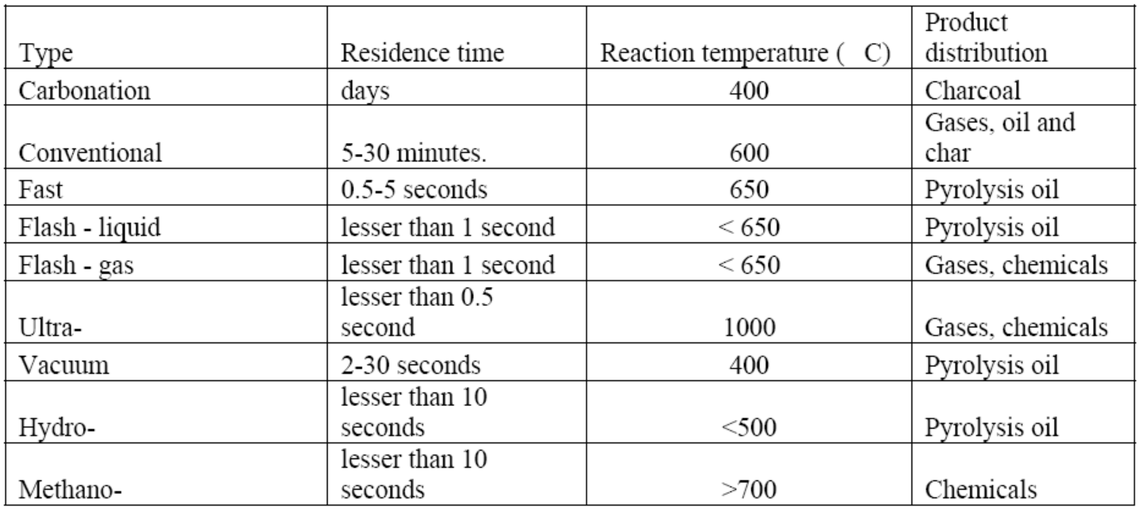
Liquid fuels are the most preferred form of biomass energy. Their wide usage in the industrial sector as heating fuels combined with their versatility as transportation fuels have made them more popular than the other biomass energy forms. Various technologies have been developed to produce usable liquid fuels from plant sources.[1.9] One technology uses enzymes to break down the sugars in cellulosic biomass, which are then subjected to fermentation to produce ethanol. Cornstarch and sugarcane are commonly used feedstocks for this process, although other plant sources are currently being investigated by researchers. Another technology used to produce biodiesel is the catalytic treatment of vegetable oils or fats with methanol or ethanol.

Pyrolysis oil (also known as bio-oil) is produced by the rapid thermal degradation of biomass at high temperature in the absence of oxygen. This technique yields a dark brown liquid known as bio-oil; the process is known as pyrolysis. It has been demonstrated by the US DOE and USDA that 1.3 billion tons of biomass could be produced annually by United States with slight changes in agricultural practices[1.9] and that biomass with the use of existing technology could replace up to 30% of current petroleum usage. Though research on bio-ethanol and biodiesel are both extensive and interesting, they are beyond the scope of this study and further discussion will be restricted to biomass pyrolysis.

1.4 PYROLYSIS

Biomass pyrolysis is the process of thermal decomposition of biomass at elevated temperatures in the absence of oxygen or in the presence of very small amounts of oxygen, much less than required for complete combustion.[1.6] The organic biomass is transformed into gas, liquid, and solid residue; the solid residue containing carbon and ash and the liquid oil being the preferred products. Several types of biomass pyrolysis are in use today (Table 1.2).

Table 1.2 Different versions of pyrolysis (Adapted from Reference 1.12)



Type	Residence time	Reaction temperature (C)	Product distribution
Carbonation	days	400	Charcoal
Conventional	5-30 minutes.	600	Gases, oil and char
Fast	0.5-5 seconds	650	Pyrolysis oil
Flash - liquid	lesser than 1 second	< 650	Pyrolysis oil
Flash - gas	lesser than 1 second	< 650	Gases, chemicals
Ultra-	lesser than 0.5 second	1000	Gases, chemicals
Vacuum	2-30 seconds	400	Pyrolysis oil
Hydro-	lesser than 10 seconds	<500	Pyrolysis oil
Methano-	lesser than 10 seconds	>700	Chemicals

Fast pyrolysis is characterized by moderate thermal treatment at temperatures in the range of 450 to 550 °C with short vapor residence times of ~ 0.5 to 5 seconds in the reactor. The vapors are then condensed to form liquid pyrolysis oil with an attractive yield of around 75%. Ensyn (United States), Dynamotive (Canada) and BTG (Netherlands) are some of the pioneers in this field; each has their own process technology for commercial bio-oil production.

Flash pyrolysis is characterized by much higher temperatures on the order of 650-900 °C with even shorter vapor residence times of less than 1 second.[1.12] Other processes like slow pyrolysis (500-600 °C and longer reaction times of 5-30 min) and hydrothermal liquefaction (using water at high pressures in the presence of alkali) also produce liquid fuels, but are beyond the scope of this discussion.

1.4.1 Fast pyrolysis

Fast pyrolysis decomposes biomass, generating vapors which are then condensed to produce a dark brown liquid known as pyrolysis oil. The bio-oil liquid yield is about 60-75 % with 15-25 % solid char and ~ 10-20 % non-condensable gases.[1.6] Various process technologies have been developed for fast pyrolysis of biomass with variations in process conditions, type of reactor used, and modifications in unit operations involved.

A wide variety of reactor configurations have been used for this process. BTG (Biomass Technology Group) uses a rotating cone reactor, developed by the University of Twente.[1.13] Biomass and sand are introduced near the bottom of the reactor and the rotating motion of the cone carries the solids upward. This configuration also provides excellent thermal contact. This setup does not use any carrier gas, thereby, reducing the capacity of downstream equipment.

Dynamotive Energy Systems Corporation (Vancouver, Canada) was the first company to begin commercial production of bio-oil. They employ a bubbling fluid-bed reactor. The plant located in the vicinity of Toronto has a maximum operating capacity of 66,000 tons of dry biomass per day, with an energy equivalent of 130,000 barrels of oil. The design consists of eight fully assembled modules; this type of modular design of the entire process provides a decentralized system for the production of bio oil.[1.14] The setup generally consists of a FBR (fluidized bed reactor) which uses sand as the fluidizing medium. Pre-treated biomass (after drying and grinding) is fed into the reactor at high temperatures. The heated fluidized sand bed provides excellent thermal contact. The rapid heating generates hot vapors, which then pass through a series of cyclone separators where the char fines entrained in the hot vapors are removed. Vapors, free of char, then pass into a condenser where condensation yields the pyrolysis liquid product.

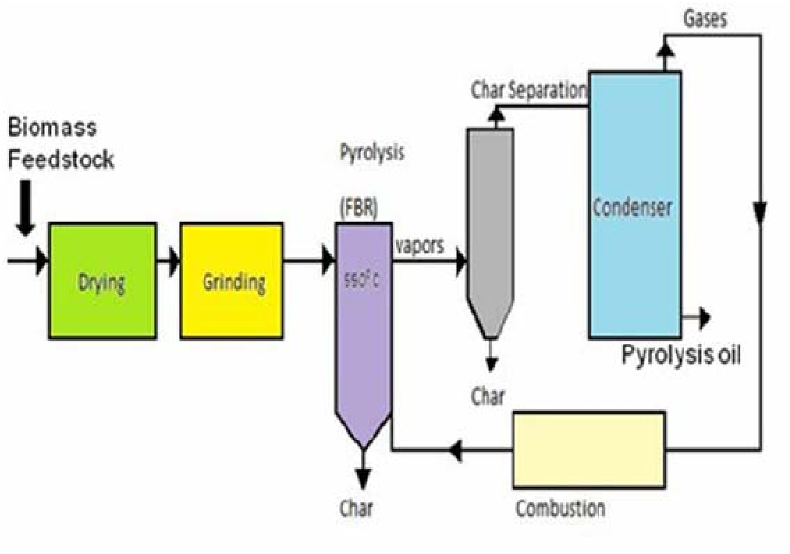


Figure 1.5 Schematic of flash pyrolysis

Mohan (2006)[1.6] provide an excellent review of the various reactor types typically employed in the production of bio-oil via pyrolysis of biomass. These include the CFB reactor (Circulating Fluidized Bed, which primarily uses gas-solid convection as the mode of heat transfer), the ablative reactor (which uses heat transfer through impact and sliding over of biomass over hot reactor surface) and the auger reactor (which uses a cylindrical heated tube).

Some of the drawbacks and challenges in design and operation of fast pyrolysis reactors are:

1. The fact that char catalyzes vapor cracking makes rapid and effective char removal a very important requirement. CFB reactors, characterized by longer char residence times with vapor, result in reduced yield due to loss of volatiles. The quality of bio-oil is further degraded from the presence of char in the condensed product.
2. Scaling to commercial scale poses challenges with the reactor's design. Although a larger ratio of diameter to bed height serves to reduce initial capital costs, it results in poor thermal contact, and hence, ineffective heat transfer.
3. Although CFB reactors have the advantage of very large throughputs, they also suffer from char attrition.
4. Ablative reactors do not require inert gases and can handle larger feed sizes, but have issues with scale up due to larger surface area requirements for heat transfer.

5. Operating at temperatures around 600 °C (as in ablative reactors) causes formation of micro-particulate carbon (soot) due to decomposition of carbon monoxide or other organic vapors.[1.6]
6. CFB reactors require the use of a secondary reactor for combustion of char. This not only adds to the capital cost, but also produces ash, some of which get carried over to the primary pyrolyzer. As char is known to catalyze cracking of organic molecules, it reduces the yield of liquid product.

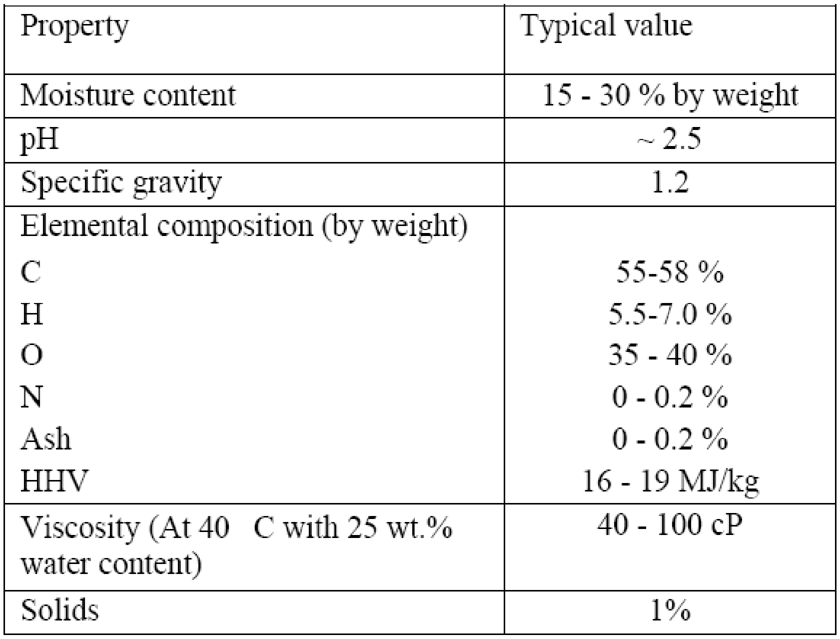
1.4.2 Char removal

As char is a known catalyst for cracking of organic compounds in the vapor phase, its effective removal is critical. A series of cyclone separators is usually employed to separate char from the hot vapor. However, a small amount of char does pass unhindered through these cyclones and is collected along with the liquid product. This char then serves to promote aging reactions in bio-oil. Hot vapor filtration is an effective method of char removal. This technique makes use of a filter to retain the char while allowing the hot vapors to pass through it. A disadvantage of this process is that char retained on the filter surface may initiate cracking of the pyrolysis vapors that pass through the filter, resulting in a reduced yield of liquid product. Pressure filtration also has disadvantages, as char reacts with pyrolytic lignin to form a gel-like surface that may block the filter surface. It is possible to overcome this disadvantage to some degree by using a solvent like methanol or ethanol.[1.15]

1.5 BIO-OIL

The liquid product obtained as a result of fast pyrolysis of biomass is known by different names such as bio-oil, pyrolysis oil, crude bio-oil, pyroligneous acid, liquid smoke, wood oil, liquid wood, etc.[1.15] Bio-oil is a dark brown, free-flowing, highly acidic solution composed of a complex mixture of ~ 400 oxygenated compounds. It is characterized by high water content and an elemental composition that closely resembles biomass. Typical properties of bio-oil are listed in Table 1.3.

Table 1.3 Typical properties of pyrolysis oil (Adapted from Reference 1.15)



Property	Typical value
Moisture content	15 - 30 % by weight
pH	~ 2.5
Specific gravity	1.2
Elemental composition (by weight)	
C	55-58 %
H	5.5-7.0 %
O	35 - 40 %
N	0 - 0.2 %
Ash	0 - 0.2 %
HHV	16 - 19 MJ/kg
Viscosity (At 40 C with 25 wt.% water content)	40 - 100 cP
Solids	1%

As evident in Table 1.3, the heating value of bio-oil at16-19 MJ is significantly less than that of conventional fossil fuels. This is mainly due to the high oxygen content (35-40 %) and water content (typically 15-30%). The density of bio-oil is about 1200 kg/m^3. Due to the presence of significant amounts of organic acids, the pH of bio-oil is very low, generally between 2 and 3. The viscosity of crude bio-oil varies from 40 - 100 cP, and increases with time as a result of aging reactions.

The fact that bio-oil is composed of so many organic compounds, and is closely dependent on the feedstock used, makes exact prediction of the chemical composition of bio-oil very difficult. The compounds in bio-oil can be broadly classified into: hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids and phenols.[1.6]

A list of compounds found in bio-oil produced by pyrolysis was presented by Branca (2003).[1.16] They used GC/MS to identify a number of compounds; those identified and their retention times are listed in Table B.1.[1.16] Only a portion of the compounds (mostly volatiles) are detectable using GC, even with very robust columns. Use of HPLC or GPC (gel permeation chromatography) coupled with MS could be very helpful in identification of polar and non-volatile compounds. Branca et al. also made another interesting comparison by studying the composition of pyrolysis oil produced by different processes (BTG, Dynamotive, etc.).

Bio-oil produced from fast pyrolysis of beech wood was also examined by this group.[1.16] They quantified nearly forty compounds. The most abundant chemicals were acetic acid (4.8-5.5%), hydroxyl propanone (1.1-1.6%), hydroxyl acetaldehyde (0.7-2.3%), levoglucosan (0.2-0.8%), formic acid (0.4-0.6%), syringol (0.3-0.4%) and 2-furaldehyde (0.3-0.35%). The compounds quantified were equal to 62-65 % of the total liquid analyzed. It was observed that syringols, guaiacols and phenols were formed as a result of thermal degradation of lignin. However, while the concentrations of syringols and guaiacols began to drop at higher treatment temperatures (indicative of secondary degradation reactions), the concentration of phenols continued to increase, which indicated that they are formed as a result of secondary degradation reactions. It was also observed that compounds like acetic acid and permanent gases were formed as a result of the secondary degradation reactions.

Another characterization of pyrolysis oil was carried out by Sipila et al.[1.18] They fractionated the oil using water into water-soluble and water-insoluble fractions, each of which was subsequently analyzed.. Three different feedstocks were examined and the results included other physical properties such as flash point and pour point of both fractions as well as the original pyrolysis oil. The flash point of pine oil (76 °C) was higher than that of straw oil (56 °C). This difference was attributed to the lesser amount of water insolubles and higher amount of volatiles in straw oil.

As mentioned before, bio-oil can be produced from a variety of different biomass feedstocks. Hence, there are considerable variations in the composition of various organic compounds found in the resulting bio-oil. For instance, if the feedstock is a hardwood, a significant amount of the phenolics present would have two methoxyl groups attached, due to the presence of syringyl lignin in the raw biomass. Bio-oils made from softwoods do not contain phenols from syringyl lignin. Along similar lines, bio-oil derived from biomass rich in protein content, like alfalfa or bark, is expected to have relatively higher nitrogen content.

The inorganic content of bio-oil is characterized by the presence of ions including carbonates, oxalates, phosphates, silicates, chlorides, and sulfates, of metals such as nickel, copper, iron, and vanadium, of alkali metals such as sodium, potassium, and lithium and of alkaline earth metals such as calcium, magnesium, and barium. Bio-oil has very low sulfur content when compared to many crude oils.

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CHAPTER II

LITERATURE REVIEW

2.1 INTRODUCTION

In recent years, rising oil prices and dependence on fuel imports have stimulated research on alternative energy sources. Biomass, being an abundant and renewable resource, has attracted considerable attention as researchers examine a variety of ways to convert the energy available in biomass into usable fuels. Extensive research during the past two to three decades has resulted in innovative and new treatment and refining processes by which usable fuel can be produced from biomass. Bio-oil is produced from biomass by pyrolysis, which is characterized by the thermal decomposition of biomass at elevated temperatures, in the absence of air. Many different versions of this process have been examined. Two are Fast Pyrolysis and Flash Pyrolysis; they differ in both operating conditions and process duration. Bio-oil is a dark brown liquid with a distinctive odor. This complex mixture of ~ 400 different species contains oxygenated compounds and species with highly reactive functional groups including aldehydes, ketones, esters, ethers, alcohols and carboxylic acids.

Bio-oil, when initially produced, is not in a state of stable thermodynamic equilibrium.[2.1] During storage of the bio-oil, unstable compounds in the mixture tend to undergo further reactions including oligomerization and polymerization, resulting in undesirable changes in composition, viscosity and molecular weight of the produced oil. Bio-oil is also characterized by high oxygen content of ~ 35-40%, resulting in low energy density. These oxygenated compounds are also responsible for problems with thermal and storage stability. The high water content of ~ 15-30% water induces phase separation at elevated temperatures. Hence, upgrading of bio-oil to improve its fuel properties and characteristics has been the focus of extensive research. In this chapter, a literature review on bio-oil properties and bio-oil upgrading is presented.

2.2 PROPERTIES OF BIO-OIL

Bio-oil, or Fast Pyrolysis oil, is a complex assortment of ~ 400 organic compounds, including mainly guaiacols, catechols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid and other carboxylic acids.[2.4] The yield of bio-oil produced from biomass ranges from about 65 - 90 % depending on the feedstock used.[2.2] Bio-oil is characterized by very low sulfur content[2.2] and a high oxygen content of 35 – 40 % when compared to conventional fossil fuels.[2.3] It is very acidic with a pH of 2-3 and is characterized by relatively high moisture content of 15-30 % as compared to 0.1 % of heavy fuel oil obtained from petroleum crude.[2.3] The high water content results in phase separation at elevated temperatures, reducing the energy density/heating value of the fuel. It also contributes to an increase in ignition delay, and in some cases, to a decrease in combustion rate.[2.3] Table 2.1 shows how the physical properties of bio-oil compares with those of heavy fuel oil.

Table 2.1 Physical properties of liquid fuels (Prepared from references 2.3 and 2.37)

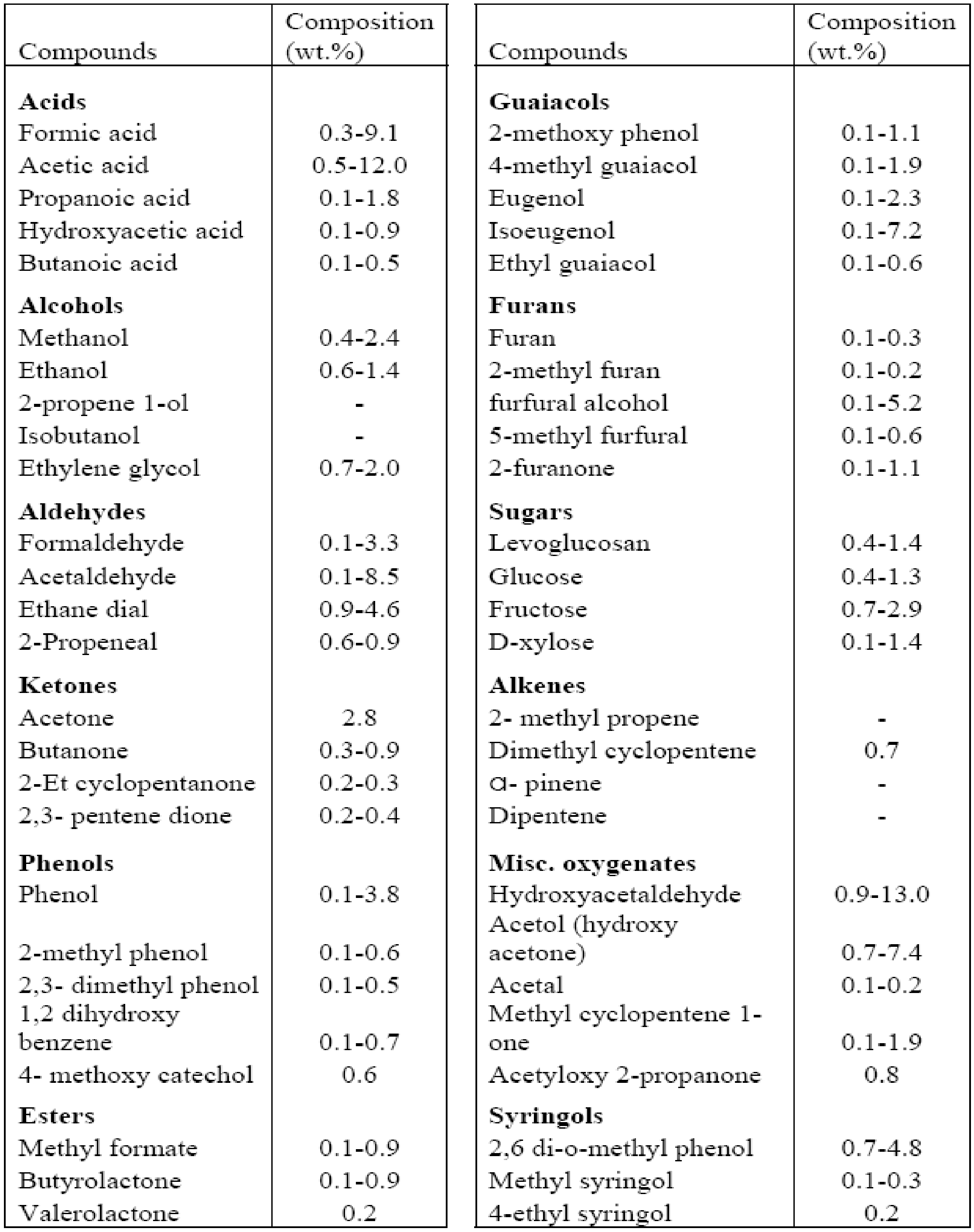
Property	Bio-oil	Heavy fuel oil	Gasoline	No.2 Diesel Fuel	Methanol	Biodiesel
Specific gravity	1.20	0.94	0.72-0.78	0.85	0.80	0.88
Elemental composition						
C	54-58	85	85-88	87	37.5	77
H	5.5-7.0	11	12-15	13	12.6	12
O	35-40	1	0	0	49.9	11
HHV (MJ/kg)	16-19	40	44	43	21	37
Viscosity (cP)	40-100*	180*	-	11-35**	-	35-51**
Auto-ignition temperature (°C)	-	-	257	315	464	-

* measured at 50 °C ** measured at 40 °C

Proximate analysis of bio-oil yields a chemical formula of $C_1H_{1.9}O_{0.7}$, corresponding to ~ 46 wt. % oxygen.[2.4] The high oxygen content results from the many compounds with reactive functional groups including aldehydes, ketones and carboxylic acids. These functional groups are also the major cause of instability associated with bio-oil.

As bio-oil is produced by pyrolysis from biomass, its composition is largely feedstock dependent. Diebold[2.5] provides an excellent review of bio-oil properties. Using feedstocks rich in proteins, like alfalfa, will result in bio-oil having high nitrogen content. Similarly, the phenols, primarily derived from lignin, show varying composition in the bio-oil. In hardwoods, the lignin is primarily composed of syringols (characterized by two methoxy groups) whereas softwood lignin primarily contains guiaiacol (characterized by one methoxy group). Believed to catalyze the polymerization reactions during storage, the inorganic, or mineral content combined with char produced during pyrolysis, has a greater impact on the aging characteristics of the oil. The inorganic content is characterized by the presence of carbonates, oxalates, chlorides, silicates, phosphates and sulfates. Chlorides of calcium, lithium, magnesium, iron, manganese and zinc are known to catalyze acetal formation.[2.5]

Table 2.2 List of prominent compounds in bio-oil (Adapted from reference 2.5)



Compounds	Composition (wt.%)	Compounds	Composition (wt.%)
Acids		**Guaiacols**	
Formic acid	0.3-9.1	2-methoxy phenol	0.1-1.1
Acetic acid	0.5-12.0	4-methyl guaiacol	0.1-1.9
Propanoic acid	0.1-1.8	Eugenol	0.1-2.3
Hydroxyacetic acid	0.1-0.9	Isoeugenol	0.1-7.2
Butanoic acid	0.1-0.5	Ethyl guaiacol	0.1-0.6
Alcohols		**Furans**	
Methanol	0.4-2.4	Furan	0.1-0.3
Ethanol	0.6-1.4	2-methyl furan	0.1-0.2
2-propene 1-ol	-	furfural alcohol	0.1-5.2
Isobutanol	-	5-methyl furfural	0.1-0.6
Ethylene glycol	0.7-2.0	2-furanone	0.1-1.1
Aldehydes		**Sugars**	
Formaldehyde	0.1-3.3	Levoglucosan	0.4-1.4
Acetaldehyde	0.1-8.5	Glucose	0.4-1.3
Ethane dial	0.9-4.6	Fructose	0.7-2.9
2-Propeneal	0.6-0.9	D-xylose	0.1-1.4
Ketones		**Alkenes**	
Acetone	2.8	2- methyl propene	-
Butanone	0.3-0.9	Dimethyl cyclopentene	0.7
2-Et cyclopentanone	0.2-0.3	α- pinene	-
2,3- pentene dione	0.2-0.4	Dipentene	-
Phenols		**Misc. oxygenates**	
Phenol	0.1-3.8	Hydroxyacetaldehyde	0.9-13.0
2-methyl phenol	0.1-0.6	Acetol (hydroxy acetone)	0.7-7.4
2,3- dimethyl phenol	0.1-0.5	Acetal	0.1-0.2
1,2 dihydroxy benzene	0.1-0.7	Methyl cyclopentene 1-one	0.1-1.9
4- methoxy catechol	0.6	Acetyloxy 2-propanone	0.8
Esters		**Syringols**	
Methyl formate	0.1-0.9	2,6 di-o-methyl phenol	0.7-4.8
Butyrolactone	0.1-0.9	Methyl syringol	0.1-0.3
Valerolactone	0.2	4-ethyl syringol	0.2

2.3 UPGRADING OF PYROLYSIS OIL

When bio-oil is produced by fast pyrolysis, there are a number of reactive compounds present in the produced bio-oil that are not in a state of thermodynamic equilibrium. Hence, they will continue to undergo reaction during storage, approaching a stable equilibrium state. As a result of these continuing reactions, the bio-oil viscosity increases over time (process is also sometimes referred to as ‘aging’). The char, formed during pyrolysis, is also known to promote polymerization reactions. These polymerization reactions also contribute to the viscosity increase. High water content results in phase separation, which is a serious concern when bio-oil is used in turbines and internal combustion engines. A significant amount of acids (formic acid, acetic acid, propanoic acid, hydoxyacetic acid, crotonic acid, valeric acid, hexanoic acid, benzoic acid to name a few) are present in bio-oil, making it highly acidic with a pH of 2-3[2.3]. Thus, use of bio-oil in engines or process equipment gives rise to corrosion issues that must be considered. In this section, research on bio-oil upgrading is discussed.

Upgrading of bio-oil over an acid catalyst is a widely accepted method for improving bio-oil properties. The catalytic upgrading alters the composition of bio-oil to make it similar to that of conventional fossil fuels. However, rapid thermal decomposition, due to the high temperatures involved in the process, leads to the formation of thermal coke. This results in catalyst deactivation and plugging, both of which greatly reduce process efficiency.

Valle et al. [2.6] used an integrated thermal treatment and catalytic transformation to upgrade bio-oil. The first step involved thermal treatment of a mixture of 40 wt% bio-oil and 60 wt% methanol at 400 °C in a U-shaped steel tube. This was followed by a catalytic transformation of the bio-oil/ methanol mixture carried out at 450 °C in a fluidized bed reactor with Ni-HZSM-5 zeolite catalyst. The thermal pretreatment step was used to minimize the amount of thermal coke deposition during the catalytic treatment process. This pretreatment significantly reduced the catalyst deactivation. However, catalytic coke formation, which is less compared to thermal coke deposition, was not affected by this pretreatment.

Gayubo et al. [2.7] examined the transformation of bio-oil model compounds, 1-propanol, 2-propanol, 1-butanol, 2-butanol, phenol and 2-methoxyphenol on HZSM-5 zeolite catalyst. Their work demonstrated that the alcohols undergo rapid dehydration and, at temperatures above 350 °C, the olefins formed are further converted to paraffins. This compliments the idea of converting ethanol/ methanol to light olefins or gasoline. In contrast, phenol and 2-methoxyphenol showed low reactivity and gave only low yields of propylene isomers and mixed butenes. Furthermore, experiments with 2-methoxyphenol led to thermal coke deposition. The presence of water in the reaction mixture had an attenuating effect on the catalyst deactivation rate by coke deposition. The researchers hypothesized that this was due to the competition between the water molecules and reaction intermediates for adsorption on the active acid sites.

Efforts examining ways to make other usable fuels from biomass have also been underway for the past decades. Hydrogen has always been of particular interest as an energy source. Hydrogen has several advantages, including being a ‘clean’ fuel and being used in fuel cells. The work of Wang et al.[2.9] at NREL succeeded in producing hydrogen from biomass through a two-step process. The first step was the fast pyrolysis of biomass to produce bio-oil, which was then subjected to catalytic steam reforming to yield hydrogen. This sequential thermal-catalytic process used nickel-based catalysts. The hydrogen yield was as high as 85 % of the stoichiometric value. The researchers indicated that yields could have been much greater, if not for catalyst deactivation and reactor plugging due to coke formation.

Adjaye and Bakshi[2.10] studied the reaction pathways during catalytic conversion of bio-oil model compounds using HZSM-5 catalyst. They also examined the reactivity of the volatile portion of the bio-oil. The volatile portion of the bio-oil for their study was obtained by vacuum distillation of bio-oil at 200 °C and 172 Pa. Compounds with the highest concentration in each chemical group were selected as model compounds. Based on these model compounds, the authors proposed reaction pathways for conversion of acids, esters, alcohols, aldehydes and ketones.

The proposed pathways aid in understanding how coke is formed. One possible reaction pathway for acids and esters suggested is the deooxygenation of the acids or esters to form long chain aldehydes, ketones and water. The alkyl groups attached to the long chain aldehydes and ketones undergo aromatization, followed by alkylation and isomerization to form alkylated benzenes. Some of these aromatic compounds subsequently undergo polymerization. These polyaromatics are thought to then undergo dehydrogenation, resulting in coke formation.

The pathway suggested for alcohols was dehydration to produce water and an alkene. This was then followed by cracking of the alkenes and aromatization to form alkylated benzenes that later undergo polymerization, leading to coke formation.

In the case of aldehydes and ketones, the authors proposed a reaction scheme comprised of dehydration/decarbonylation leading to the formation of water and alkenes (for aldehydes) and hydrocarbon gases and carbon monoxide (for ketones). Both groups undergo oligomerization. The formed oligomers then undergo aromatization, which then polymerize, leading to coke formation.

With ethers, the formation of a phenol and an alkylated ether was suggested as the result of disproportionation. The phenol and alkylated ether then may undergo cracking to form hydrocarbon gases. Some of these gases are then alkylated to form the alkylated phenols.

However, their most innovative contribution was to propose a reaction pathway for the volatile portion of the bio-oil. According to the proposed reaction scheme, deoxygenation and cracking occur first, giving rise to olefins, water and carbon oxides. The olefins then undergo oligomerization, followed by aromatization and alkylation, producing alkylated phenols, which may polymerize to form coke. The authors also proposed two possible reaction pathways for the catalytic conversion of bio-oil using HZSM-5. Both reaction pathway models propose deoxygenation followed by cracking and oligomerization, cyclization, alkylation and isomerization reactions. Some of the produced alkylates may undergo polymerization leading to coke formation.

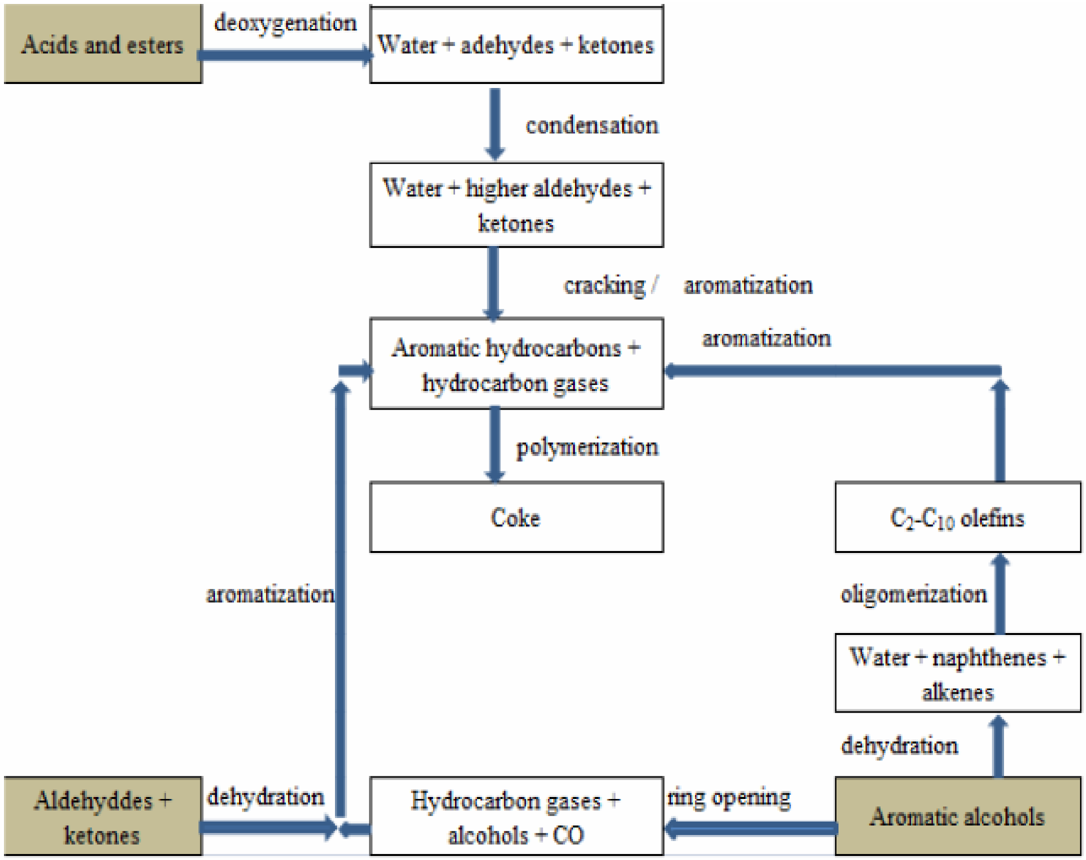


Figure 2.1 Reaction pathways of organic compound conversions (adapted from ref. 2.10)

2.4 AGING STUDIES OF BIO-OIL

Aging of bio-oil has also been studied extensively. The work of Boucher et al. [2.11] on aging and thermal stability of bio-oil produced interesting results. They studied the stability characteristics of bio-oil stored at 40, 50 and 80 °C for up to 168 hr (1 week) and at room temperature for up to one year. The samples were analyzed for phase separation time, viscosity, solid content, water content and average molecular weight. As bio-oil is currently being examined as a potential fuel for gas turbines, the thermal stability characteristics of bio-oil at elevated temperatures are extremely important.

The weighed samples were kept in an oven maintained at the desired temperature for the required length of time (1, 6, 24 and 168 hr). They were then removed from the oven, and stored in an ice bath to stop the aging reactions. The samples were weighed before and after to ensure that no volatiles were lost during the experiment. When bio-oil was heated for 168 hr at 80 °C, the viscosity, when measured at 30 °C, was increased by a factor of 3.6. The temperature at which the viscosity is measured is also important. Aging effects were more significant when viscosity was measured at lower temperatures. It was also found that the molecular weight increase after heating bio-oil for one week at 80 °C was equivalent to that attained after keeping it at room temperature for a year. Also, aging during the one year experiment at room temperature, was more dramatic during the first 65 days. After this first 65 days, a plateau in the viscosity was reached.

Boucher's group also studied the effect of methanol addition on the aging of bio-oil. They concluded that addition of methanol at levels of up to 5 % (by weight) did not affect the phase separation rate, whereas addition of 15 % methanol substantially delayed the phase separation. The rate at which viscosity increased was also less with methanol addition. However, this trend was reversed during the longer storage period. After 195 days of storage, the aging rates were faster with methanol addition when compared to that of raw bio-oil. The authors hypothesized that this was possibly due to the reaction of methanol with reactive compounds in the bio-oil, leading to esterification reactions, which contribute to aging due to the formation of heavier compounds. To simulate the real-time environment in a gas turbine system, thermal shock experiments were performed by rapidly heating the sample to 80 °C. They concluded that methanol addition stabilized the bio–oil, stabilization being inferred by a lesser increase in the viscosity of methanol-diluted bio-oil as compared to that of raw bio-oil.

The research contributions of Czernik and Diebold in bio-oil upgrading have been quite significant. Their work at NREL has been widely published and acknowledged by the research community over the years. Diebold and Czernik[2.12] investigated the effect of additives on the stability and storage characteristics of bio-oil. They found that the aging reactions could be slowed down by molecular dilution of the reactive components or through formation of stable products with the reactive functional groups. For example, they showed that if the aldehyde groups were converted to acetals by reaction with alcohols, the availability of aldehyde groups for polymerization reactions was reduced. This could significantly reduce the aging in bio-oils.

Methanol and water were both investigated as additives in the studies of Czernik and Diebold. The additives were chosen based on their cost and on their relative role in desirable reactions that stabilize the bio-oil. Ethanol, acetone, methyl isobutyl ketone and soybean oil methyl ester were also examined as potential additives. The samples were aged in vials sealed with fluorinated plastic seals. Care was taken to ensure that no volatiles were lost during the experiment by weighing the samples before and after the experiment. The viscosities were measured using a Brookfield viscometer. From their data, an empirical aging correlation was obtained by linear regression and is given by:

$$\log_{10}(A) = 13.365 - \frac{4194}{T} \tag{2.1}$$

where A is the aging rate in cP/day, and T is in K.

Based on overall additive effectiveness, Czernik and Diebold concluded that the best results were obtained with methanol, acetone or a mixture of acetone and methanol. Water did not give rise to the best results based on overall additive effectiveness. The decrease in heating value associated with water addition combined with its impact on the tendency of bio-oil to phase separate more than offset its significantly lower cost. Even though methanol is more costly than water, it is economical to use since it does not lower the oil's heating value. They also concluded that the effect of methanol was more pronounced when added before the aging reactions began, compared to its addition to aged oil. GPC analysis of molecular weights showed that methanol addition did not significantly alter the molecular weight distribution of the aromatics (GPC does not detect the molecular weights of non-aromatic compounds). However, the time taken to attain the terminal molecular weight increased due to methanol addition. The authors also suggested that reduction of aging through use of methanol is accomplished in two ways: first, methanol acting as a molecular diluent; and second, methanol reacting with reactive components to form stable compounds.

Another approach that has been examined to improve bio-oil properties is reduction of water content. The presence of water reduces the heating value of the bio-oil and induces phase separation. Light volatiles are believed to contribute largely to ageing and lowering of flash point. Oasmaa and his group[2.13] developed a process called the concentration method of upgrading bio-oil. Their objective was to obtain a homogeneous bio-oil with low solids content and higher flash point.

Oasmaa and coworkers produced bio-oil from forestry residue and pine sawdust by pyrolysis at 520 °C for 1-2 s using a transport-bed reactor. The condensed liquid product from the process was concentrated by evaporation in a Buchi Rotavapor equipped with a vacuum controller. The operating temperature was maintained at 40 °C to prevent the cracking of sugars. The pressure was gradually decreased from atmospheric pressure to 20 Torr. This was to remove water and other volatile compounds that boil below 120 °C. This concentration method was followed by methanol addition.

Bio-oil with a water content of 3.8 % was achieved. The loss of volatile compounds, mostly acids, aldehydes and ketones, was 7.5 %. These compounds contain the reactive functional groups that act as precursors to coke formation. Thus, the concentration method of Oasmaa (2005)[2.13] also results in a stabilized bio-oil. For the produced bio-oil, the HMM increase was less during an accelerated stability test (High molecular mass lignin material – includes dichloromethane insolubles and char).

Another desirable outcome from this concentration method is that the unpleasant odor of the pyrolysis oil was completely eliminated. Oasmaa et al identified that the unpleasant odor was largely due to 2-butenal, which was the main component in the lightest fraction. Low molecular weight aldehydes, ketones and aromatic hydrocarbons also contributed to the unpleasant odor. Although methanol addition improved the stability of the oil as well as lowering the viscosity, it reduced the flash point from 62 – 95 °C to 52 – 54 °C.

Fisk (2006)[2.14] examined the effectiveness of catalytic deoxygenation of bio-oil over base catalysts. They based their studies on a model bio-oil, composed of ten compounds. The choice on the compounds chosen to formulate the synthetic bio-oil was based on the most reactive functional groups present in bio-oil. The base catalysts used in this upgrading were commercial ZnO and in-situ LDH (Mg-Al and Zn-Al layered double hydroxide) catalysts.

The synthetic bio-oil was composed of 5% (by weight) methanol, 12% acetaldehyde, 14% acetic acid, 4% glyoxal, 8% acetol, 8% glucose, 17% guaiacol, 4% furfural, 8% vanillin and 20% water. The catalysts used were analyzed for surface area by BET and it was found that the mixed oxides of Mg-Al and Zn-Al had a very high surface area of 242 and 121 m^2g^{-1}, respectively, when compared to a mere 15 m^2g^{-1} for ZnO. The experiments were carried out in a micro-reactor system with the sample loading adjusted to yield a WHSV (weighted hourly space velocity) of 5 hr^{-1} at 400 °C. The treated and untreated samples were analyzed using GC-MS.

Elemental analyses of the oil, aqueous and solid phase were performed and showed that, although the oxygen content in the aqueous phase increased as a result of the catalytic treatment, the oxygen content in the oil phase dropped from 45 % to 30 % by weight. The solids contained between 2-12 % oxygen, with higher oxygen content observed for catalytic treatment and lower oxygen content for non-catalytic thermal treatment. Thus, these studies confirmed that deoxygenation reactions occur as a result of catalytic treatment with higher reactivity using Mg-Al catalyst and lower reactivity with ZnO and Zn-Al catalysts.

2.5 SUPERCRITICAL WATER

Water near or above its critical point (374 °C , 218 atm) is attracting increased attention as a reaction medium in organic chemistry.[2.15] Beyond the critical point, water becomes a dense fluid, often termed as 'dense gas' due to its gas-like diffusivity and liquid-like density. In this region beyond the critical point, the distinction between phases disappears. At these conditions, water possesses properties very different that water at ambient conditions. In the supercritical fluid state, properties like density, viscosity, and dielectric constant among others, exhibit large variations when small changes in temperature and pressure occur. The dielectric constant, which is about 78 at ambient conditions (25 °C), reduces drastically to 2 – 6 at supercritical conditions, comparable to that of non-polar solvents. This makes it possible to solubilize organic compounds in supercritical water that are not soluble in water at ambient conditions. The number and persistence of hydrogen bonds are also diminished.[2.15] Savage (1999)[2.15] provides an excellent review of the various chemical reactions accomplished with supercritical water (SCW) as the reaction medium. According to Savage, the ion product, or dissociation constant (K_W)[*]of water as it approaches the critical point is about three orders of magnitude higher than at ambient conditions. K_W decreases as the critical point is passed. The increase in the ion product as the critical point is approached corresponds to higher concentrations of both H_3O^+ and OH^- ions, thereby making supercritical water an effective medium for acid- and base-catalyzed reactions. The H_3O^+ ion concentration is also sufficiently large that some acid-catalyzed reactions may proceed without any catalyst addition.

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[*] The self ionization of water is a reaction in which two molecules of water react to form a hydroxonium ion and a hydroxide ion. The reaction is as follows:

$$2H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

This reaction is also known as Autodissociation of water for which the equilibrium constant is given by $K_{eq} = ([H_3O^+][OH^-])/[H_2O]$ and $K_{eq}\,[H_2O]^2 = K_W = 1.0 * 10^{-14}$ mol^2 dm^{-6} at room temperature. (where K_W is defined as the ion product or dissociation constant of water)

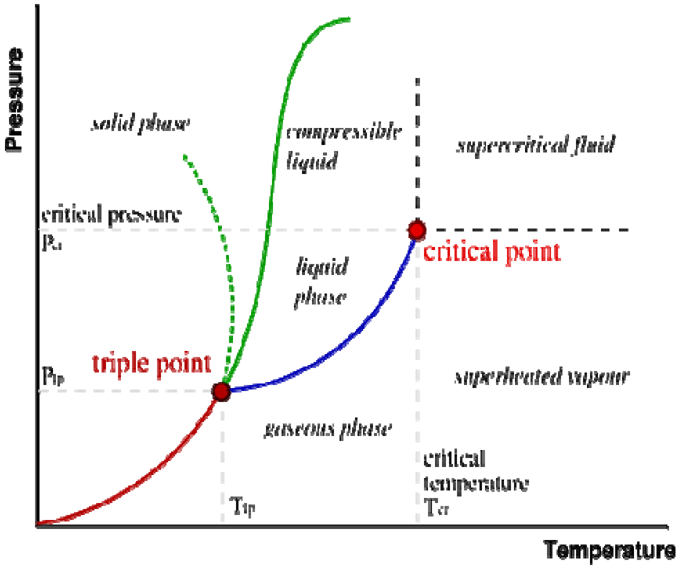

Figure 2.2 Phase diagram describing the supercritical region among various other phases

Adschiri et al.[2.16] used a NiMo/Al_2O_3 catalyst for hydrogenation and removal of sulfur from dibenzothiophene (model compound for light or heavy oil desulfurization) using supercritical water as the reaction medium. They concluded from their studies that carbon monoxide-SCW (SCW- Supercritical water) and formic acid-SCW gave higher conversions than H_2-SCW showing that hydrodesulfurization could be achieved in a supercritical water reaction medium without the use of expensive hydrogen gas.

Taylor et al.[.17] conducted experiments to investigate reforming of organic compounds in supercritical water at 550-700 °C and 27.6 MPa. Experiments examined the impact of methanol concentration and operating temperature on the reforming reaction. Also examined were ethanol and ethylene glycol. The results of Taylor et al. demonstrated that methanol could be converted to hydrogen, yielding a gas with low methane content, and a CO/CO_2 ratio close to the equilibrium ratio. Conversions obtained when ethanol or ethylene glycol were employed were not impressive.

The work of Carlsson et al.[2.18] on citric acid conversion to methacrylic acid was driven by the need for improved and cost-effective ways of converting citric acid. Citric acid is produced by fermentation of molasses and other sugars using the microorganism *Aspergillus niger*. Decarboxylation and dehydration mechanisms were consistent at near and supercritical conditions leading to conversion of citric acid to itaconic acid to methacrylic and hydroxyisobutyric acids.

It has been reported by numerous research teams that several compounds hydrolyze in supercritical water. Esters are known to undergo autocatalytic hydrolysis to form carboxylic acids and alcohols. Hydrolysis in water at near-critical conditions has been known to effectively depolymerize synthetic polymers. Polyethylene terphthalate and polyurethane foams have been hydrolyzed to diacids and glycols and to diamines and glycols, respectively.

Katritzky et al.[2.19] and Kuhlmann et al.[2.20] have demonstrated that the supercritical water medium is capable of $^1H/^2H$ exchange. Both the Kuhlmann group and the Kartritzky group examined several organic compounds with D_2O/supercritical water as the reaction medium. They found that simple alcohols did not participate in the $^1H/^2H$ exchange reactions. However, in the α position of ketone carbonyl groups, a rapid and nearly complete exchange was accomplished.

Sasaki (1998)[2.21] investigated the hydrolysis of cellulose in subcritical and in supercritical water. Primary products were glucose, fructose and oligomers. At subcritical conditions, a lower yield of hydrolysis products was obtained as the products that formed underwent rapid decomposition. However, near the critical point, the hydrolysis rate became more than an order of magnitude greater than the decomposition rate. As a result, a very high yield of hydrolysis products was obtained. The work of Kabyemela[2.22] was more extensive and examined supercritical conditions as well as milder conditions where the reactions were slower and only partial conversion achieved. Hence, it was possible for this group to examine the kinetics and reaction mechanisms. They observed that glucose undergoes interconversion with fructose or decomposes to products like erythrose and glyceraldehyde. A high yield of erythrose was obtained at supercritical conditions.

Subcritical and supercritical water gasification of cellulose, starch, glucose and biomass waste was carried out by Williams.[2.23] This extensive work examined the effect of temperature in the subcritical and supercritical regimes on the yields of gases, oil, char and water. The biomass waste used in this study was cassava waste, which is the skin part of the cassava tropical root tuber cultivated in Africa and South America. The experiments were carried out by taking known weights of the model compounds in the reactor with a calculated volume of water and hydrogen peroxide. Although cellulose and starch are based on the same monomer (glucose), they have different chemical structures and physical properties. This difference is also apparent in the products that each forms with supercritical water. Yields of char, CO and C_1-C_4 hydrocarbons were higher with cellulose than with starch. With glucose, a significantly higher production of hydrogen gas was observed. With cassava waste, the product distribution was similar to that obtained with cellulose. The composition of oil produced from these very different feedstocks was studied using Fourier Transform Infrared Spectrometry and was found to be similar and not strongly influenced by the feedstock.

Ehara and Saka[2.24] proposed a combined supercritical and subcritical water treatment for cellulose hydrolysis. They were motivated to do this because it was known that cellulose was more prone to fragmentation at supercritical conditions and more prone to dehydration at subcritical conditions. Hence, a combined process of supercritical water treatment for short reaction times, followed by subcritical water treatment, was proposed. This combined process proved to effectively control fragmentation, resulting in an increased yield of hydrolysis products.

Antal et al.[2.25] investigated biomass gasification in supercritical water using corn- and potato- starch gels and wood sawdust. At severe treatment conditions of over 650 °C and 22 MPa, the organic content in the feedstock was vaporized. Very impressive yields of greater than 2L of gas/g of feedstock with hydrogen content as high as 57 mol % were observed. Elemental analysis of gas samples was accomplished with Proton-induced X-ray Emission (PIXE), a non-destructive method that can quantify up to 72 elements. One undesirable outcome of these experiments was that the extreme conditions resulted in extensive corrosion of the reactor walls, which were Ni and Hastelloy.

Another group from Japan, Matsumura et al.[2.26] extensively reviewed the potential of biomass gasification in near- and super-critical water. In their review, they presented a list of reactors that could be used, operating conditions and design aspects. They concluded that SCWG was an attractive option as a technology for biomass gasification. Biomass gasification in supercritical water has attracted a great deal of attention worldwide.

A group from Germany, Schmieder et al.[2.27] reported that biomass and organic waste can be effectively gasified at supercritical conditions into a hydrogen-rich gas. Their studies with biomass and glycine (as a model compound of proteins) at 600 °C and 250 bar showed that both could be completely gasified by addition of KOH or K_2CO_3. Alkali metal salts present in the reaction mixture are believed to act as acid-base catalysts that increase the rate of the water-gas shift reaction, thereby, helping to maintain a low CO concentration. One big advantage of this process is the ability to process wet biomass, which improves process economics as costly de-watering or drying pretreatment steps are not necessary. It is interesting to note that the authors reported no damage to the reactor walls caused by corrosion at extreme conditions as was reported by other researchers. The reactors used in this study were made of Inconel 625.

These promising results with supercritical water prompted researchers to explore reactions of oxygen-containing compounds in a supercritical water reaction medium. Yu and Savage[2.28] examined the decomposition of formic acid under hydrothermal conditions. Their studies concluded that decarboxylation and dehydration were the two parallel paths with hydrogen and carbon dioxide being the major products. They concluded that water acted as a catalyst to accelerate the decarboxylation reactions, while dehydration reactions are favored in the gas phase. Various other organic compounds were studied in SCW by Katritzky et al.[2.29] Of these various compounds, cyclohexyl phenyl ether was completely converted. The major products formed were phenol and methyl cyclopentene, which are believed to be the result of acid-catalyzed cleavage of the C-O bond. The authors suggested that the H^+ ions from water at supercritical conditions catalyzed this reaction.

Reactions of phenols in a SCW environment are also another relevant topic. Martino et al.[2.30] conducted studies on the oxidation of CHO- and CH_3- substituted phenols in supercritical water at 250 atm and 460 °C. With these experiments, they investigated the effects of residence time, phenol concentration, and oxygen concentration on the reaction rate. To model the kinetics, they used the rate expression:

$$rate = Ae^{\frac{-Ea}{RT}}[organic]^a[O_2]^b[H_2O]^c \tag{2.2}$$

The oxygen concentration was set such that it was in excess and remained almost constant over the course of the experiment. Simplifying the rate law to reflect this, rate law parameters were evaluated by fitting of the experimental data to the non-linear rate law. This evaluation of parameters in the rate law was executed using SimuSolv (software package), which uses the method of maximum likelihood for parameter determination. Martino and co-workers concluded that the CHO- substituted phenols were more reactive than CH_3- substituted phenols. The oxidation of cresols showed that the order of reactivity was ortho > para > meta. It was also concluded from the studies that oxidation of cresols proceeds along three parallel paths: demethylation to form phenol; oxidation of the methyl group to form hydroxybenzaldehyde; and ring opening. Ring opening is characterized by formation of carboxylic acid intermediates, which subsequently undergo decarboxylation to produce CO_2.

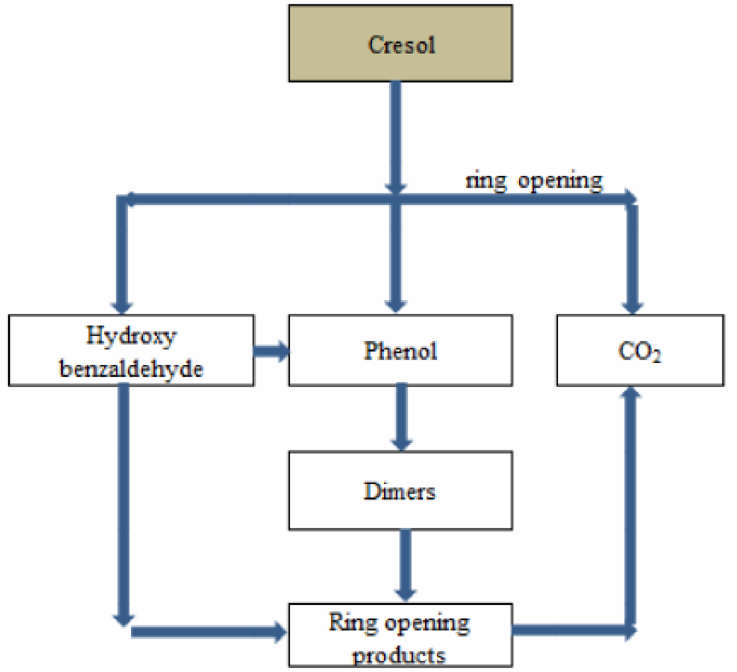

Figure 2.3 Reaction pathways of supercritical water oxidation of cresol (adapted from ref. 2.30)

Broll et al.[2.31] carried out extensive research on the chemistry of many model compounds in supercritical water. Their effort focused on developing an explanation of the reaction kinetics. Also provided were supporting measurements of density, extent of corrosion and phase boundary lines in subcritical and supercritical states of water. The phase boundary lines were studied by metering defined quantities of water and the model compound into a cold viewing cell. The pressure was then increased in the system as a result of increased vapor pressure due to heating. The phase transitions were identified visually. By varying pressure and recording several phase transitions, the phase boundary line was drawn. To measure density, water and a second compound were metered into a heated viewing cell maintained at a constant temperature. As the volume of the cell was fixed, by metering more of the liquids, the densities corresponding to different pressures could be recorded. Corrosion studies were carried out at temperatures of 330 - 410 °C and pressures of 25 – 35 MPa. The test materials, in the form of metal plates, were placed in aqueous solution. The metal ion concentration in the solution before and after treatment was measured by atomic absorption spectroscopy. The samples were also analyzed using gravimetry, optical microscopy, scanning electron microscopy, energy-dispersive X-ray analysis and X-ray diffraction.

Broll and coworkers reported that conversion of 1,4- butanediol diacetate in the subcritical region increased from 39 % (at 250 °C) to 100 % (at 350 °C). 1,4-butanediol and tetrahydrofuran were obtained as the hydrolysis products. One example of a dehydration reaction was that of ethanol, which formed ethylene only under supercritical conditions. For cyclohexane, partial oxidation was observed with cyclohexene, cyclohexanol, cyclohexanone as well as carboxylic acids, CO and CO_2 identified as the products. Reactions with formaldehyde above the critical point led to formation of methanol, formic acid, CO and CO_2. Acetic acid remained stable up to 400 °C. However, in the temperature range of 475 – 600 °C and at 24.6 MPa, it reacted to form CO_2 and CH_4.

Sato et al.[2.32] examined the use of a micro-reaction system for supercritical water-aided reactions to reduce the reaction time required to achieve the desired conversions by rapid heating and quenching. A very interesting result was obtained with conversion of cyclohexanone oxime to ε-Caprolactum wherein ε-Caprolactum was synthesized only in the narrow temperature of 573-673 K. The maximum yield was obtained at 643 K above which the yield decreased with a temperature increase. This was an isolated case of strong thermal preference of a reaction in a supercritical system. It was equally interesting to observe that the same operating conditions yielded only 1.9 % of ε-Caprolactum when a slower heating rate of 6 K s^{-1} was used.

Sato et al.[2.33] also investigated the effect of water density on the gasification of lignin with Ni-supported on MgO catalyst at sub- and super-critical water conditions from 523 – 673 K. There is a great deal of literature that emphasizes the importance of water density at supercritical conditions for controlling reaction kinetics. It was found that the main gas products were hydrogen, methane and carbon dioxide, and that the amount of gases increased with an increase of Ni loading on MgO. The highest yield of total gases on a carbon basis was 78 % and was achieved at 673 K with water density at 0.3 g/cc.

Biomass conversion using supercritical water has been investigated by numerous research groups. Decomposition of lignin in supercritical water – phenol mixtures was examined by Saisu et al.[2.34] The addition of phenol is known to suppress the condensation of reactive intermediates from the lignin decomposition products. For coal extraction, phenol-SCW mixtures have been shown to be an effective solvent.[2.34] The addition of phenol with alcohols and aldehydes in a supercritical water medium forms alkylates. Thus, phenol is believed to act as a capping agent, which can effectively prevent char formation in supercritical water. The experiments were carried out with and without phenol, at 673 K and with water densities between 0-0.5 g/cc. During runs without phenol, the TIS (Tetrahydrofuran insoluble) yield decreased. The TS (Tetrahydrofuran soluble) became lighter in weight as water density was increased while TIS became heavier. Some of the reactive sites in compounds derived from lignin as a result of supercritical water reactions react with phenol to form heavier fragments. An increase in phenol/lignin ratio reduced the polymerization of TIS products with the phenol acting as a capping agent.

An in-depth investigation of the mechanisms involved in reaction of acetaldehyde in supercritical water was studied by Nagai et al.[2.35] The non-catalytic reaction pathways were studied at 400 °C and water densities of 0.1-0.6 g/cc. It was observed that five different types of reactions were possible: (i) decarbonylation to carbon monoxide and methane; (ii) self-disproportionation (two molecules of the same aldehyde) to form ethanol and acetic acid; (iii) cross-disproportionation (with two different aldehydes) to form ethanol and carbonic acid; (iv) condensation reaction to form crotonaldehyde with release of water (formed as a short-lived intermediate in supercritical conditions which further undergoes decarbonylation and polymerization reactions): and. (v) polymerization of crotonaldehyde and propylene, formed by decarbonylation of crotonaldehyde to yield polypropylene.

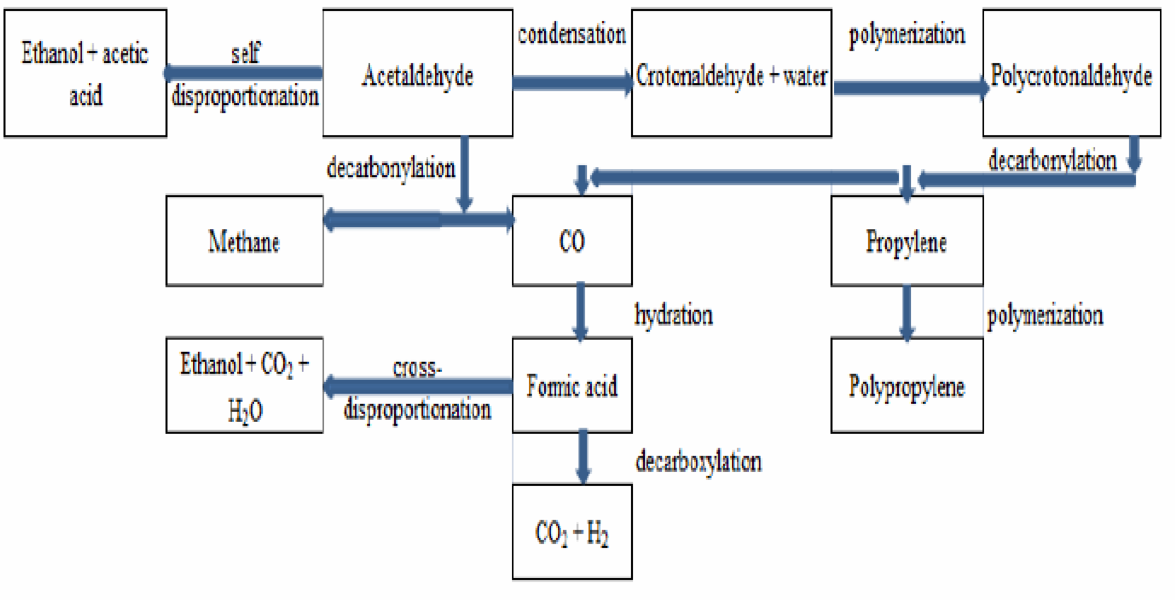

Figure 2.4 Non-catalytic reaction pathways of Acetaldehyde in SCW (adapted from ref. 2.35)

Sinag et al.[2.36] investigated the hydropyrolysis of cellulose in supercritical water in the presence of K_2CO_3 by using glucose as a model compound at temperatures of 400 °C and 500 °C and pressures of 30 and 50 MPa. The addition of alkali salts is known to increase the yield of hydrogen and carbon dioxide by accelerating the water-gas shift reaction. The potassium content of real biomass was replicated by using 0.5 wt% K_2CO_3 in the study. The key compounds identified as products were furfural, phenol, substituted phenols and acids.

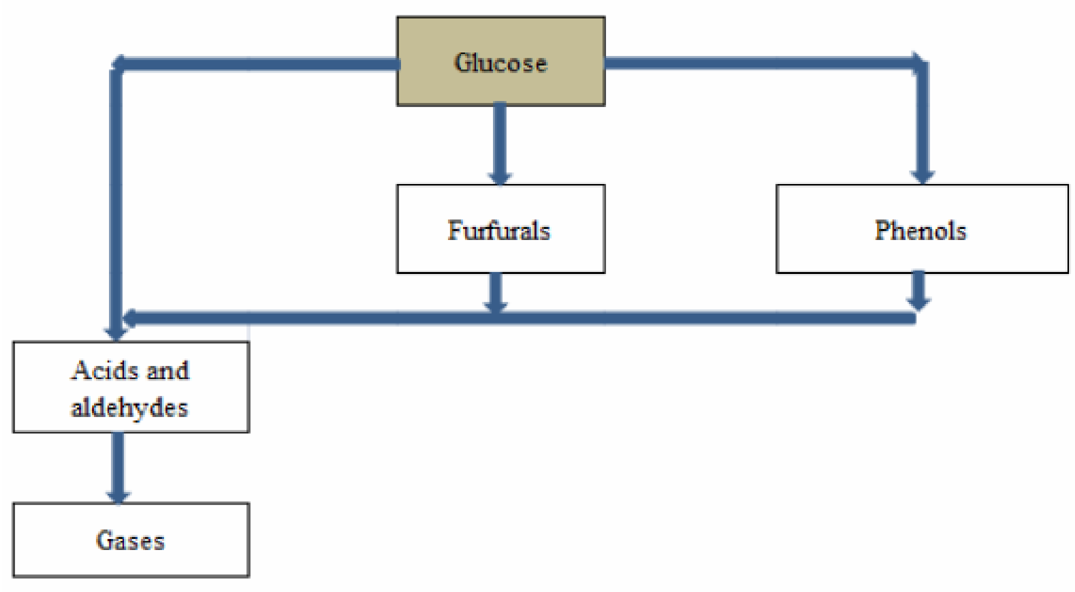

Figure 2.5 Simplified reaction pathways for glucose conversion

Supercritical water has also been effectively used to depolymerize highly cross-linked polmers such as styrene-butadiene (SBR) rubber. At temperatures between 300 – 450 °C and pressures between 135 – 170 bar with the presence of 0-5 wt% hydrogen peroxide (oxidant), SBR was depolymerized to give benzene, toluene, ethylbenzene, styrene, phenol, acetophenone, benzaldehyde and benzoic acid. At the 1% significance level, ANOVA (Analysis of Variance) proved that temperature and oxidant concentration were the influential factors of the deploymerization process. It was proposed that the depolymerization of SBR in SCW follows a free-radical mechanism, initiated by the dissociation of hydrogen peroxide aided by heat, propagation and termination.

The simulation of a supercritical water system was carried out by Cummings et al.[2.38] to investigate on the equilibrium structure and properties of supercritical water. This was carried out by taking two different approaches. The first employed a simple point charge (SPC) model, wherein they assume the water molecule to be a Lennard-

Jones sphere. This was motivated by work done by de Pablo et al.[2.39] which gave excellent prediction of critical point values obtained by using SPC model and Gibbs ensemble simulation. The second approach used Gear's fourth order predictor corrector method to solve Newton's laws of motion. The dielectric constant was determined using reaction field technique for different density states of supercritical water and showed reasonably good agreement.

2.6 OBJECTIVES OF THE PROPOSED WORK

Catalytic treatment using acid catalysts like HZSM-5 has been one of the well accepted methods for upgrading of bio-oil. However, the efficiency of this process is greatly reduced due to coke formation which tends to cause catalyst deactivation and plugging. If this coke formation could be suppressed before the bio-oil is subjected to catalytic treatment, it will not only help to improve catalyst life and efficiency, but also help to realize the greater goal of improved bio-oil.

Coke is formed as a result of thermal decomposition of certain reactive compounds in bio-oil like acids, esters, ketones and aldehydes (for instance furfural, vanillin). These compounds undergo series of reactions that result in formation of polyaromatics that could possibly undergo dehydrogenation to form coke.[2.10] Thus, one of the possible ways to suppress coke formation is to eliminate these coke-forming precursors from the bio-oil.

Supercritical water as a reaction medium for organic reactions has attracted a lot of attention over the years. Acid-catalyzed reactions are known to proceed to completion in supercritical water medium without the presence of acid catalyst.[2.15] Hence it is proposed to examine the effect of supercritical water treatment on the composition of bio-oil; in particular, to investigate the possibility of elimination of the coke precursors from bio-oil. Process parameters examined by these experiments will be reaction time, bio-oil/water ratio, temperature and pressure.

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CHAPTER III

METHOD AND MATERIALS

3.1 EXPERIMENTS WITH BIO-OIL SIMULANT

3.1.1 Motivation of bio-oil simulant studies

The complexity associated with the presence of hundreds of compounds in bio-oil makes a study of the chemistry and the interactions between different compounds in a supercritical water medium extremely difficult. Many investigators choose to selectively study model compounds, either alone or in well-defined simple mixtures, in an effort to more fully examine the chemistry involved in the numerous reactions that take place. Due to the large number of compounds in bio-oil, a systematic study taking single compounds, or even binary or ternary mixtures, would be very tedious and time consuming. Examination of these very simple chemical systems also does not simulate the actual chemical environment in bio-oil, where molecules of different chemical species interact, collide and may participate in reactions. An intermediate approach, which reduces the complexity of the chemical system, yet at the same time also resembles the original bio-oil system may provide increased understanding of the bio-oil treatment process.

Fisk et al.[2.14] used such an approach in their work focused on the effectiveness of select base catalysts for bio-oil deooxygenation. In their studies, they employed a simulant, a model bio-oil, which was composed of ten compounds. The selection of these compounds was based on the most reactive functional groups present in bio -oil. This provides a simple system in which select model compounds could be studied. The simulant recipe developed by Fisk et al. (2006) was employed in a portion of the experimental studies conducted for this thesis. Figure 3.1 shows the chemicals employed in the simulant recipe, as well as their respective weight % in the simulant.

3.1.2 Bio-oil simulant composition

Vanillin (>98% pure), methanol (99.8% pure), glyoxal (40% sol. in water), acetol (90%), acetaldehyde (>99.5% pure), α-D-glucose (96% anhydrous), guaiacol and acetic acid (glacial, 99% pure) were purchased from Aldrich Chemical Company. Furfural (99% pure) was purchased from Acros Organics. Distilled water obtained from the Hand Chemical Laboratories (Mississippi State University) was used in all the experiments. All chemicals were used without any further purification.

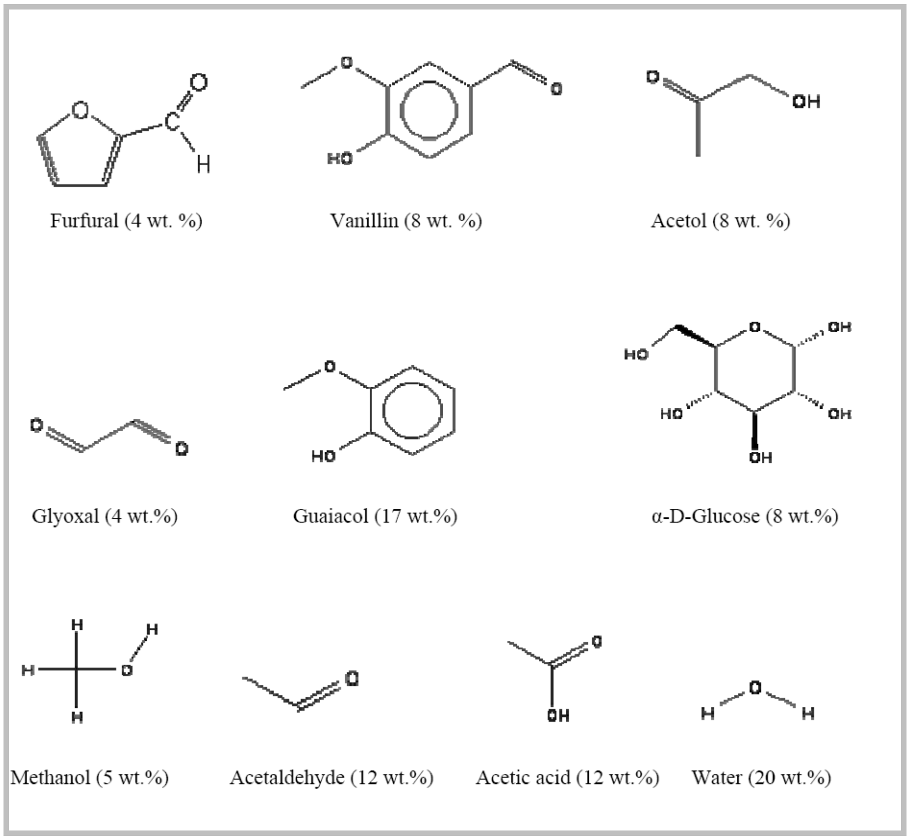


Figure 3.1 Compounds used in the preparation of bio-oil simulant

3.1.3 Preparation of bio-oil simulant

Bio-oil simulant was prepared based on the model bio-oil developed by Fisk et al.[3.1] Acetol (8 wt.%) was weighed and placed in a 1 liter conical flask mounted on a stirring plate. Methanol (5 wt.%), glyoxal (4 wt.%), guaiacol (17 wt.%), acetic acid (12 wt.%) and furfural (4 wt.%) were weighed and added to the conical flask sequentially in the order specified. Vanillin (8 wt.%) and glucose (8 wt.%) in the required amounts were added in small measures to the mixture at five minute intervals to facilitate dissolution. Undissolved glucose was dissolved in water (20 wt.%) and the mixture added to the conical flask. The contents were stirred for 30 minutes. Then acetaldehyde (12 wt.%) was added to the solution. After five minutes of further mixing, the contents in the conical flask were transferred into a container, sealed and stored in the refrigerator until use.

Figure 3.2 Bio-oil simulant used in the study

3.1.4 Experimental methodology

A Parr reactor (Model 4570, 500 mL capacity), made of Hastelloy C276 with a maximum pressure rating of 5000 psi and a maximum temperature rating of 500 °C was employed for all experiments. The system is also equipped with a Model 4857 controller. Operation of the reactor could be auto-programmed or manually controlled at the computer interface using the CALogix software available from CAL Controls.

Figure 3.3 Parr reactor setup used in the batch studies

The empty reactor vessel was sealed and a torque wrench was used to apply 40 lb_f of torque to all the reactor bolts in equal increments of 10 lb_f each time. Graphite gaskets were used to seal the reactor vessel. The reactor was subjected to leak testing by pressurizing the reactor to 2000 psig using either nitrogen or helium gas. Pressure in the sealed vessel was observed for one hour to ensure the integrity of the gasket seal. After a successful leak test, the reactor was evacuated using a Edwards 2-stage high vacuum pump until fine vacuum was achieved. The calculated mass of bio-oil simulant required for the particular experiment was then metered into the reactor through the liquid sampling valve using a capillary tube aided by vacuum. This was followed by addition of the predetermined mass of distilled water using the same procedure. Evacuation of the reactor before charging the reactants serves the dual purposes of removing any oxygen (air) that could be present in the reactor when it is sealed, and of providing a convenient means of charging the reactants into the vessel.

The total charge to the reactor was limited to 130 g (± 5g) to achieve the desired supercritical conditions. The determination of total charge was based on simulation of the reactor system using ChemCAD (Version 5.6); the results of these calculations are included in section 3.3.1. After charging the reactants to the reactor, the heating cycle commenced. The set point temperature was increased in steps of 50 or 75 °C temperature set point increment until the desired operating temperature was attained. Temperature was held at the set point for the desired reaction time after which cooling was initiated. The heating cycle generally required ~ 150 minutes to attain the desired operating temperature; cooling of the reactor and its contents required ~2 hours to reach ambient temperature.

3.1.5 Product analysis

After completion of the experiment, gaseous and liquid products were collected, weighed and stored. The solid coke obtained was oven-dried at 105 °C for one day; it was then weighed. The reaction vessel was filled with hot water and allowed to sit for some time for cleaning purposes. Acetone and dichloromethane were then used as solvents to ensure complete cleaning of the reactor prior to its next use.

Gas and liquid products were both analyzed using an Agilent GC/MS equipped with both TCD (thermal conductivity) and FID (flame ionization) detectors. While gas products were analyzed only qualitatively, liquid products were analyzed both quantitatively as well as qualitatively. Analytical support was provided by the Department of Forest Products at Mississippi State University.

3.2 EXPERIMENTS WITH CRUDE BIO-OIL

3.2.1 Crude bio-oil and its properties

Bio-oil used in the experiments performed in this research was provided by the Department of Forest Products at Mississippi State University. This bio-oil was produced by the fast pyrolysis of biomass at 450 °C with pine wood feedstock. Properties of the untreated bio-oil are provided in Table B.1.

Quantitative analysis was performed on the untreated bio-oil to provide a means for establishing the effectiveness of treatments examined in this research. The quantitative analysis results are furnished in Table B.2.

3.2.2 Experimental methodology

The Parr reactor was used for all experiments. For experiments with crude bio-oil, the calculated mass of water was added to the reactor directly followed by addition of calculated mass of bio oil. The reactor was then sealed and torque wrench was used to apply 40 lb_f of torque to all the reactor bolts in equal increments of 10 lb_f each time. A graphite gasket was used to seal the reactor vessel. Vacuum was applied through opening of the gas sampling valve to the vacuum pump until fine vacuum was achieved. This helps to remove any oxygen (in air) that could possibly have been present in the system. The total charge into the reactor was varied between 100 to 130 g to achieve the desired supercritical conditions.

3.2.3 Product analysis

The procedures detailed in Section 3.1.5 were followed for product analysis of crude bio-oil as well as bio-oil that had undergone treatment.

3.3 INITIAL REACTANT CHARGE CALCULATIONS

In batch studies involving supercritical water as a reaction medium, it is important to calculate the mass of water that should be initially charged in order to achieve the desired supercritical conditions (both temperature and pressure). This becomes a more complex endeavor with the presence of other chemicals in the system. However, it became quite evident during preliminary experiments for the oil-water binary system at varying oil/water ratios that the temperature versus pressure profiles did not show any significant deviations from that of pure water. Figure 3.4 shows a comparison of the temperature/pressure profile for various oil/water ratios. Hence, the impact of oil/water ratio was ignored in the calculations.

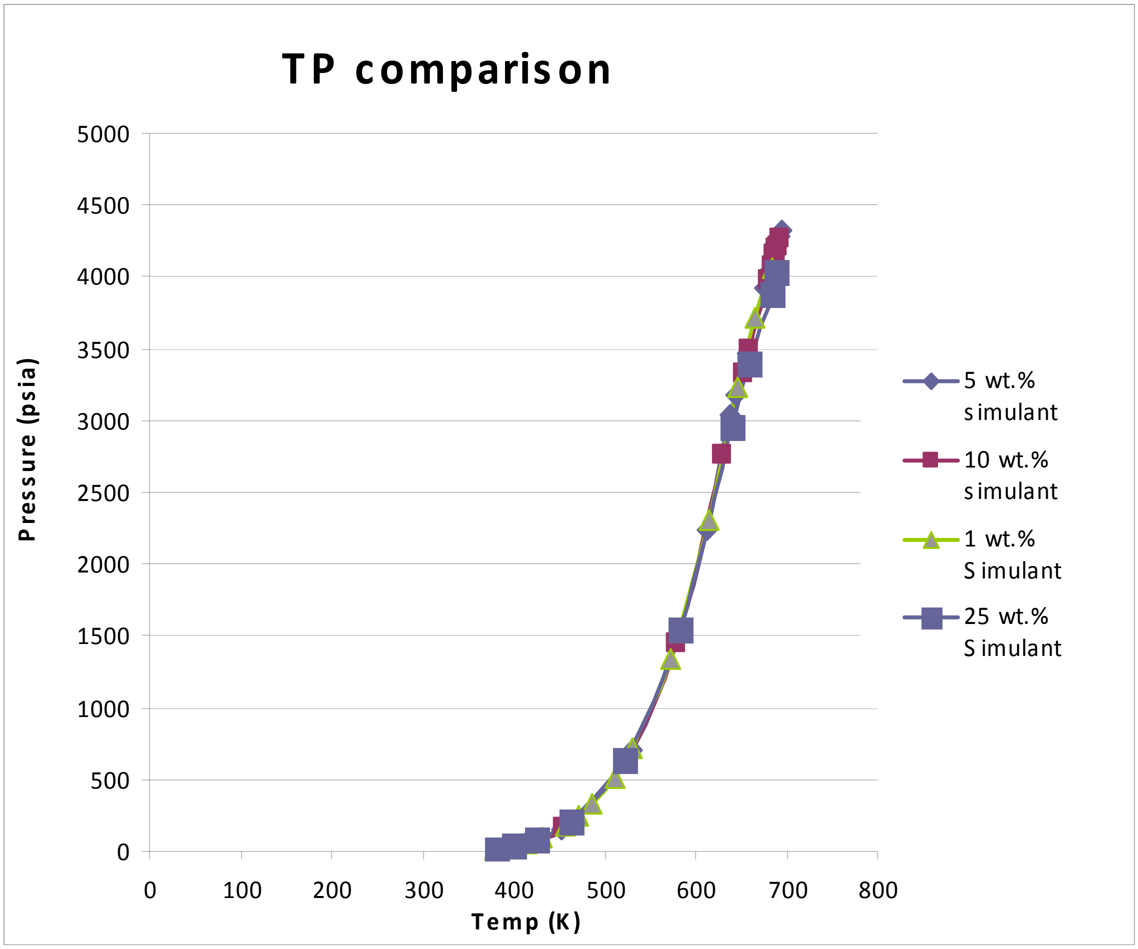


Figure 3.4 Temperature vs. pressure profile for various oil-water ratios

3.3.1 Construction of phase envelopes using ChemCAD

Before the charge of water (mass) can be computed for various operating conditions, the vapor pressure at each temperature must be known in order to evaluate the molar volume. From this molar volume, the charge of water (mass) can be determined. ChemCAD was used to construct the necessary phase envelopes.

In ChemCAD, a single input stream to the reactor was entered in the flowsheet mode. The input stream parameters were then specified. The thermodynamic property package in ChemCAD provides a variety of options for evaluation of K-values, enthalpy, entropy and density. These options include use of equations of state such as the Peng-Robinson, Soave-Redlich-Kwong, and SAFT, or activity coefficient models such as NRTL and UNIQUAC. Using one of these models, a phase envelope was constructed for vapor fractions of 0.1, 0.25, 0.5 and 0.75 and at the bubble point. Along with the temperature and pressure, compressibilities in the liquid and vapor states are also computed, and these can be used along with the known reactor volume to determine the appropriate change of water to be used for a particular combination of temperature and pressure.

Calculation of thermodynamic properties was completed using 5 different thermodynamic models: Peng-Robinson, Soave-Redlich-Kwong, SAFT, NRTL and UNIQUAC. Comparison of predictions with experimental data (i.e., steam tables) indicated that the Peng-Robinson equation of state gave the best predictions over the full range of temperature/pressure considered, even in the critical region.

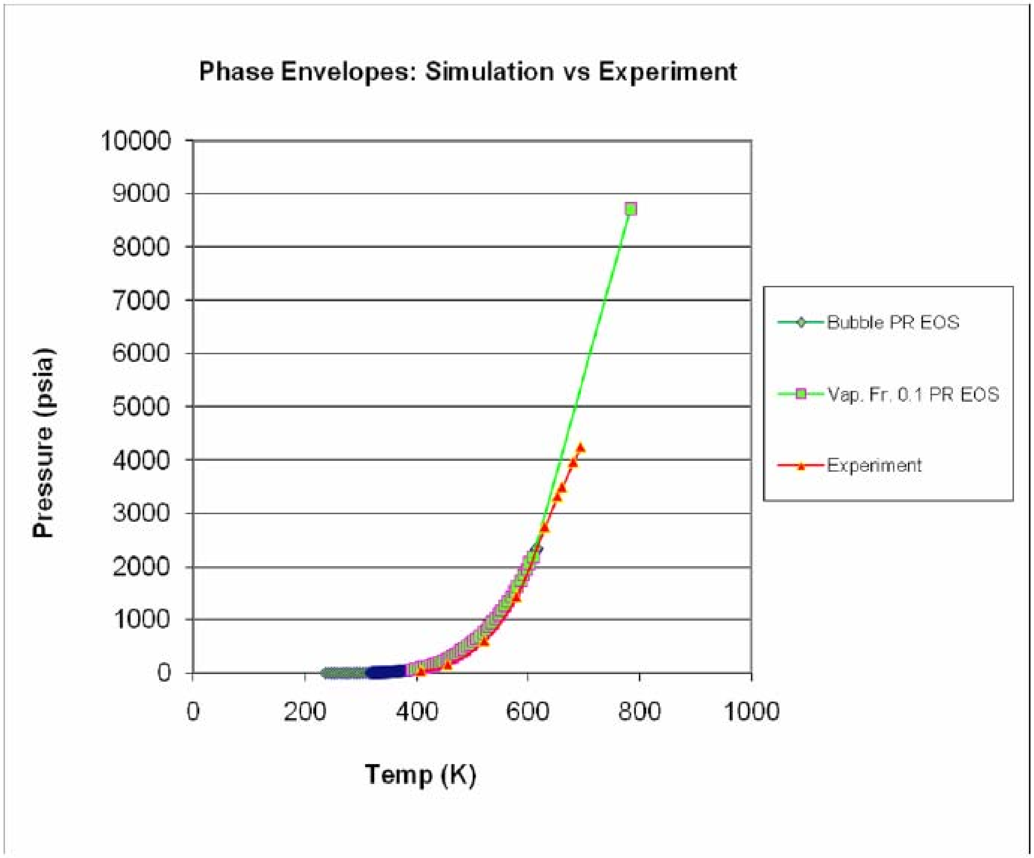


Figure 3.5 Temperature vs. pressure profile from experiment and ChemCAD simulation

3.3.2 Molar volume calculations using Peng-Robinson equation of state

From the preliminary examination of temperature/pressure profiles, the Peng-Robinson equation of state was identified as the method best able to predict available data. Thus, the Peng-Robinson equation of state was employed for molar volume calculations. In 1976, Ding-Yu Peng and Donald B. Robinson[3.1] developed a two-parameter cubic equation of state (henceforth referred to as the PR equation of state) which is of the form:

$$P = \frac{RT}{\upsilon - b} - \frac{a}{\upsilon(\upsilon + b) + b(\upsilon - b)} \tag{3.1}$$

The parameters a and b are related to critical constants for the material, to the acentric factor, and to the reduced temperature of interest.

$$a = a_c * \alpha \tag{3.2}$$

$$a_c = \frac{0.45724R^2T_c^2}{P_c} \tag{3.3}$$

$$\alpha^{0.5} = 1 + m_i(1 - T_r^{0.5}) \tag{3.4}$$

where m_i is related to acentric factor:

$$m_i = 0.37646 + 1.54226\omega_i - 0.26992\omega_i^2 \tag{3.5}$$

Parameter b is given by:

$$b = \frac{0.07780RT_c}{P_c} \tag{3.6}$$

Given two of the three intensive properties (T, P, v), the third is determined by solving the resulting cubic equation of state. General solution of the cubic equation gives rise to three roots. For the supercritical region, there should exist only 1 real root for the molar volume, given temperature and pressure, with the remaining two roots being complex conjugates. This molar volume is then used with the available reactor volume of 423 cc to determine the charge of water required. These calculations were performed for each pressure and temperature combination to be employed during experiments to determine the mass of water required to achieve supercritical conditions.

3.3.3 Thermodynamic calculations to evaluate pressure using PR equation of state:

The vapor pressure corresponding to each operating temperature must be known for molar volume calculations to determine the water mass to be charged for each experiment. ChemCAD may be used to generate phase envelopes containing this information, vapor pressure as a function of temperature. An alternative method is to employ equivalence of fugacities in the saturated liquid and saturated vapor states to identify the vapor pressure at a given temperature. For the PR equation of state, the fugacity of a pure component is:

$$\ln\frac{f}{P}=(z-1)-\ln(z-B)-\frac{A}{2\sqrt{2}B}\ln\left[\frac{z+2.414B}{z-0.414B}\right] \tag{3.7}$$

Where z the compressibility factor, and A and B are defined as:

$$z=\frac{P\upsilon}{RT}\quad , \; A=\frac{aP}{R^2T^2}\quad \text{and}\quad B=\frac{bP}{RT}$$

On substitution of z, A and B, equation 3.9 becomes:

$$\ln\frac{f}{P}=\left[\frac{P\upsilon}{RT}-1\right]-\ln\left[\frac{P\upsilon}{RT}-\frac{bP}{RT}\right]-\left(\frac{\frac{aP}{R^2T^2}}{2\sqrt{2}\,\frac{bP}{RT}}\right)\ln\left[\frac{\frac{P\upsilon}{RT}+2.414\frac{bP}{RT}}{\frac{P\upsilon}{RT}-0.414\frac{bP}{RT}}\right] \tag{3.8}$$

On cancellation of terms in the numerator and denominator and with subsequent rearrangement, equation (3.10) becomes:

$$\ln\frac{f}{P}=\left[\frac{P\upsilon}{RT}-1\right]-\ln\left[\frac{P(\upsilon-b)}{RT}\right]-\left(\frac{a}{b}\right)\left(\frac{1}{2\sqrt{2}RT}\right)\ln\left[\frac{\frac{P}{RT}(\upsilon+2.414b)}{\frac{P}{RT}(\upsilon-0.414b)}\right] \tag{3.9}$$

Further simplification reduces the above equation to:

$$\ln\frac{f}{P}=\left[\frac{P\upsilon}{RT}-1\right]-\ln\left[\frac{P(\upsilon-b)}{RT}\right]-\left(\frac{a}{b}\right)\left(\frac{1}{2\sqrt{2}RT}\right)\ln\left[\frac{\upsilon+2.414b}{\upsilon-0.414b}\right] \tag{3.10}$$

The fugacity coefficient is (ϕ) = f/P. Thus:

$$\ln \Phi = \left[\frac{P\upsilon}{RT} - 1\right] - \ln\left[\frac{P(\upsilon - b)}{RT}\right] - \left(\frac{a}{b}\right)\left(\frac{1}{2\sqrt{2}RT}\right)\ln\left[\frac{\upsilon + 2.414b}{\upsilon - 0.414b}\right] \tag{3.11}$$

The fugacity coefficient for each phase, liquid and vapor, respectively, are:

$$\begin{aligned} \ln \Phi_v &= \left[\frac{P\upsilon_v}{RT} - 1\right] - \ln\left[\frac{P(\upsilon_v - b)}{RT}\right] - \left(\frac{a}{b}\right)\left(\frac{1}{2\sqrt{2}RT}\right)\ln\left[\frac{\upsilon_v + 2.414b}{\upsilon_v - 0.414b}\right] \\ \ln \Phi_l &= \left[\frac{P\upsilon_l}{RT} - 1\right] - \ln\left[\frac{P(\upsilon_l - b)}{RT}\right] - \left(\frac{a}{b}\right)\left(\frac{1}{2\sqrt{2}RT}\right)\ln\left[\frac{\upsilon_l + 2.414b}{\upsilon_l - 0.414b}\right] \end{aligned} \tag{3.12}$$

Identification of vapor pressure is accomplished iteratively. For a given operating temperature, a value is assumed for the pressure. Molar volumes of saturated liquid and saturated vapor are evaluated from the cubic equation of state. These volumes are used along with the operating temperature and assumed pressure to evaluate the fugacity coefficient of each phase, ϕ_v and ϕ_l. For the saturated state, these fugacity coefficients should be equal. Pressure is adjusted until the equivalence of fugacity is established.

REFERENCES

3.1 Peng D., Robinson D.B., A New Two-Constant Equation of State, *Ind. Eng. Chem., Fundam.*, **1976**, 15(1), 59-64.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 EXPERIMENTS WITH BIO-OIL SIMULANT

Bio-oil simulant was prepared according to the specifications in Chapter III. For each experiment, both qualitative and quantitative analysis of the samples, pre- and post-treatment, was performed using GC-MS as described in Chapter III. Experiments were carried out with the bio-oil simulant to study the product distribution after treatment with water at near and supercritical conditions. This approach was taken to more readily identify the reaction pathways for each of the model compounds. The experiments were designed to examine the effect of operating temperature, bio-oil/water ratio and reaction time on the product distribution. The control variables were fixed:

- Peak operating temperature : 300, 380 and 420 °C
- Percent bio-oil by weight in oil-water mixture : 1, 5, 10, 25 wt.%
- Reaction time : 1, 5 hr

4.1.1 Untreated bio-oil simulant composition

A quantitative analysis of the untreated bio-oil simulant was performed using GC-MS; the results of this analysis are given in Table B.1. Thirty three target compounds were quantified.

Figure 4.1 Bio-oil simulant used in the studies

4.1.2 Effect of temperature

Batch studies to examine the effect of temperature on the product distribution were carried out by fixing the bio-oil/water ratio at a constant value and varying the operating temperature from sub-critical to near-critical and to supercritical conditions. The reaction time was set at either one or five hours.

- Manipulated variable:

Operating temperature	: 300, 380 and 420 °C

- Fixed variables:

Percent bio-oil in bio-oil-water mixture	: 25 wt. %
Reaction time	: 1, 5 h

It has been found in the literature that furfural is a large contributor to catalyst coking. Experimental results indicated that using the proposed treatment, furfural was effectively converted to products along with formation of coke. An average conversion of 81.56% was achieved at 300 °C. While the conversion at 420 °C was similar at 79.18%, the conversion at 380 °C was slightly better at 83.33%.

Guaiacol is also known to contribute to catalyst coking. One of the possible reaction pathways for coke formation is the generation of phenol and of alkylated ether, resulting from disproportionation. The phenol and alkylated ether may then undergo cracking to form hydrocarbon gases. Some of these gases are then alkylated to form alkylated phenols, which subsequently undergo polymerization leading to coke formation.[2.10] In this work, it was evident that more guaiacol was formed during the first hour of reaction. Reaction for a longer period resulted in a portion undergoing further reaction and being eliminated. The formation of guaiacol is very likely due to the disproportionation of vanillin. Phenol is one of the likely products from guaiacol as evidenced by the comparable rate of phenol formation and rate of guaiacols conversion during the extended reaction period of 5 hr. (Figures 4.2 and 4.3).

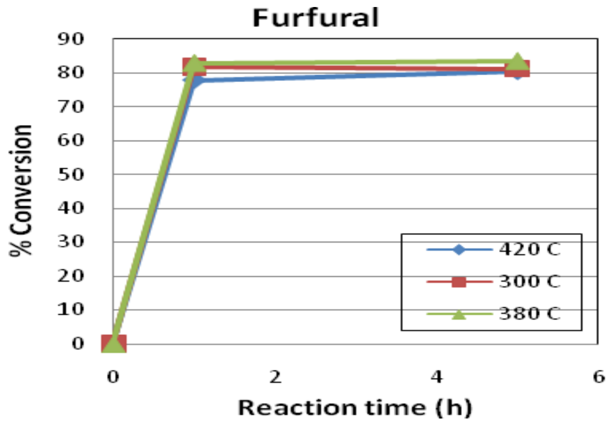


Figure 4.2 Conversion of furfural

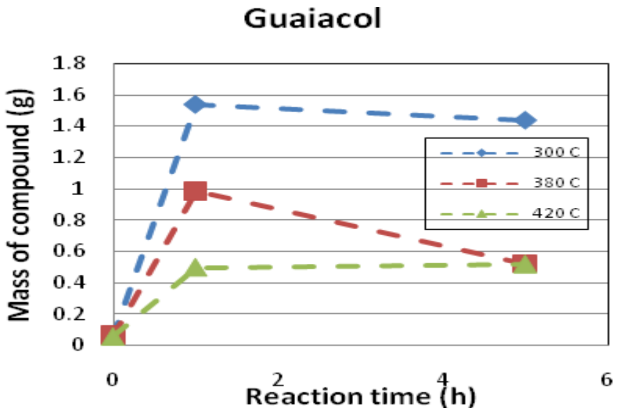


Figure 4.3 Formation of guaiacol

The formation of guaiacol was significantly greater at 300 °C, while conversion of guaiacol was considerably faster at 380 °C during the longer reaction period. This also compares well with a faster rate of phenol formation at 380 °C, which supports the fact that phenol is formed from guaiacol. The formation of phenol during the first hour of reaction suggests that conversion of vanillin to form guaiacol and conversion of already available guaiacol to phenol are reactions that proceed in parallel.

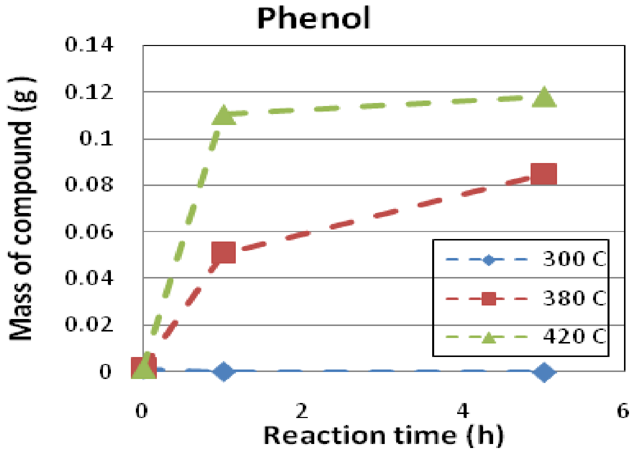


Figure 4.4 Formation of phenol

Phenol formation was significantly higher at 420 °C while negligible formation of phenol was observed at 300 °C. One interpretation of this result is that while conversion of vanillin to guaiacol is highly favored, the subsequent conversion of guaiacol to phenol is not favored at 300 °C. This preference was not observed with treatment at near and supercritical conditions; at the higher temperatures, both reactions were observed to occur.

Catechol (1,2-benzene-diol) was one of the prominent compounds in the product phase. The formation of catechol was significantly higher at 420 °C, reasonably high at 380 °C and notably lower at 300 °C. One explanation is the formation of this compound and of other substituted phenols from phenol. The low yield of catechol at 300 °C can be explained by the low phenol yield at the same operating temperature.

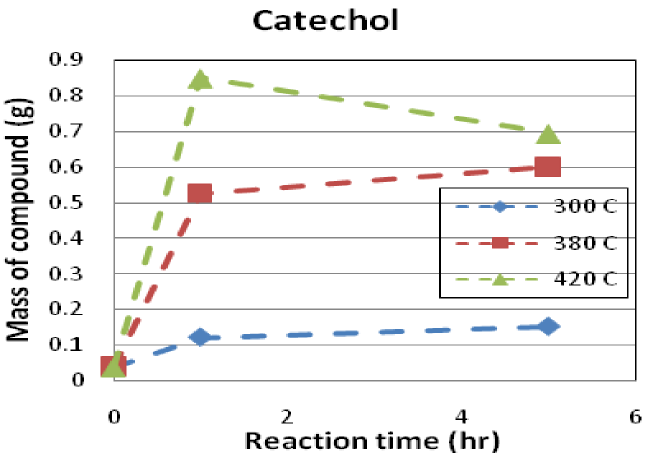


Figure 4.5 Formation of catechol

Since vanillin is a major contributor to coke formation, identification of conditions that result in elimination of vanillin is important. From the experimental results, the conversion of vanillin was essentially complete at all operating conditions examined, with an average conversion of 99.88%. The operating temperature did not significantly impact the achieved conversion; complete conversion was achieved independent of the operating temperature. Thus, it is concluded that although guaiacol may be one of the likely products from conversion of vanillin, other products such as 4-ethyl 2-methoxy phenol and 4-methyl 2-methoxy phenol must also be formed from vanillin.

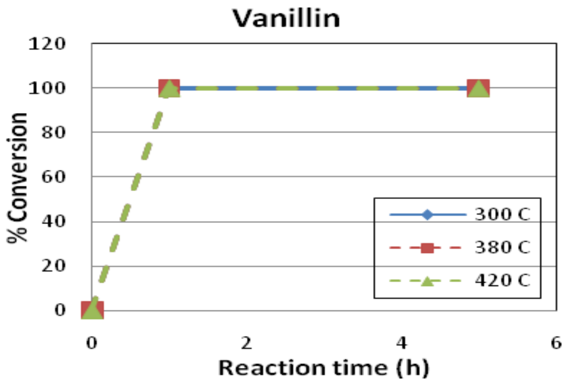


Figure 4.6 Conversion of vanillin

Levoglucosan, formed from the thermal decomposition of glucose, has been reported in the literature to be one of the precursors in bio-oil leading to coke formation. While levoglucosan conversion at 300 °C during one hour reaction time was only ~ 15.70%, almost complete conversion of levoglucosan was achieved at the higher operating temperatures. During the longer reaction time, the conversion at 300 °C also reached 100%. Glucose is known to form levoglucosan, which in turn undergoes thermal decomposition to form furans.

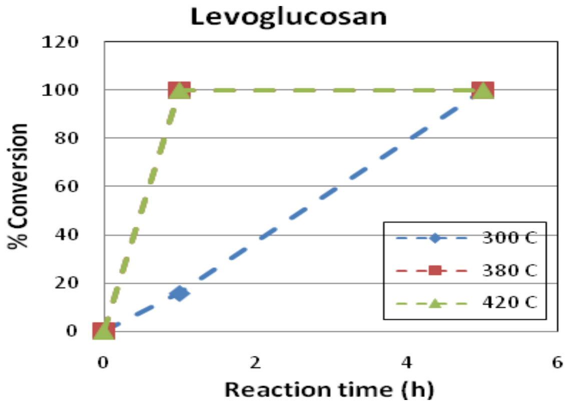


Figure 4.7 Conversion of levoglucosan

The bio-oil simulant contains 12 % by weight of acids in the form of acetic acid. One possible reaction pathway for acids as suggested by Adjaye and Bakshi [2.10] is the deooxygenation of acids to form long-chain aldehydes, ketones and water. The alkyl groups attached to the long-chain aldehydes and ketones undergo aromatization, followed by alkylation and isomerization to form alkylated benzenes. Some of these aromatic compounds undergo subsequent polymerization. These polyaromatic hydrocarbons are thought to then undergo dehydrogenation, resulting in coke formation.

Oleic acid, one of the prominent compounds present in the untreated sample, was almost completely converted in all experiments, regardless of operating temperature. Complete elimination of oleic acid in the treated sample is a positive finding, as the presence of these acids may promote coking.

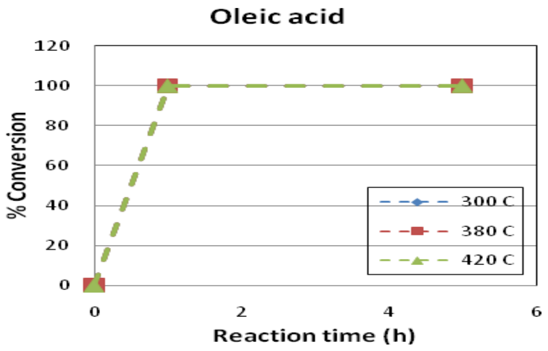


Figure 4.8 Conversion of oleic acid

While essentially complete conversion of oleic acid was achieved, acetic acid was identified in the treated sample. Acetic acid formation was significantly greater at 380 and at 420 °C, compared to 300 °C for the one hour reaction time. With a five hour reaction time, acetic acid formation was less compared to the one hour reaction time at 380 and 420 °C, indicating that acetic acid was consumed during reactions at these temperatures during the longer treatment time.

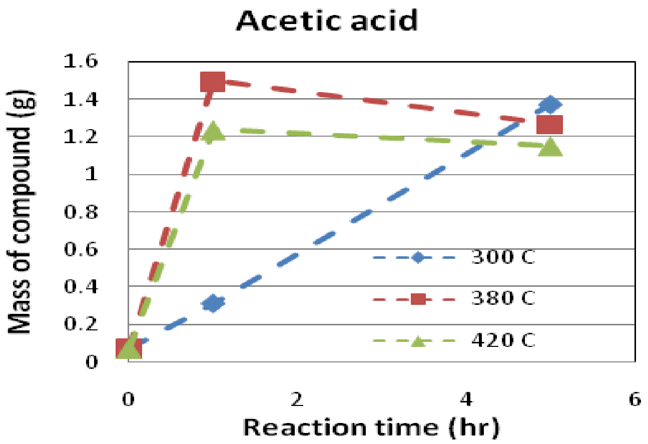


Figure 4.9 Formation of acetic acid

Acetol, one of the compounds present in the bio-oil simulant was only partially converted during the treatment at subcritical conditions (300 °C). In contrast, during the treatments at near and supercritical conditions, complete conversion was achieved. Low MW hydrocarbon gases, carbon monoxide and carbon dioxide are the likely products resulting from conversion of acetol.

4.1.3 Effect of bio-oil/water mass ratio

Batch studies to understand the effect of initial bio-oil/water mass ratio on the product distribution were carried out by fixing the reaction time and operating temperature and changing the bio-oil/water mass ratio initially charged. The operating conditions were:

- Manipulated variable:

  Percent bio-oil by weight in bio-oil/water charge : 1, 5, 10 and 25 wt.%

- Controlled variables:

  Operating temperature : 300, 380 and 420 °C

  Reaction time : 1, 5 hr

It was observed that with treatment at 300 °C, the effect of composition on furfural conversion was much less pronounced. Complete conversion of furfural was achieved with 1, 5 and 10 wt.% while approximately 80 % conversion was achieved with 25 wt.% oil in the initial sample. With 10 wt.% at near supercritical conditions (380 °C), the effect of composition was not as clear. This is evident from the fact that though a complete conversion of furfural was possible at 300 °C, only about 30 % conversion was achieved at 380 °C; however, the conversion at 420 °C was much higher (~ 80%). However with 25 wt.% oil in the feed, this anomaly was not observed as about 80 % conversion was achieved regardless of the treatment temperature.

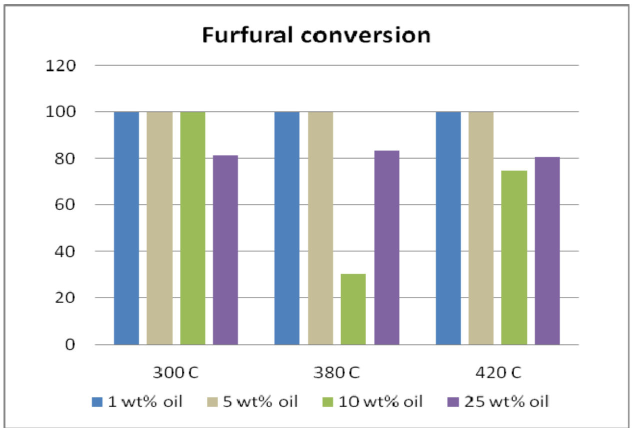


Figure 4.10 Conversion of furfural for various oil compositions

In case of vanillin, one of the other compounds of interest, the effect of composition on conversion was almost non-existent. Essentially complete conversion of vanillin was achieved regardless of the oil composition or the treatment conditions.

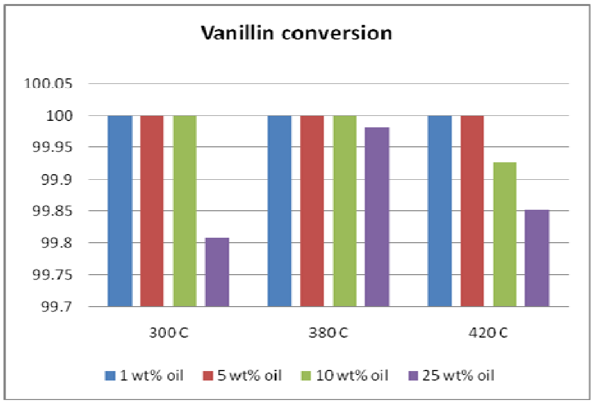


Figure 4.11 Conversion of vanillin for various oil compositions

In general, the intensity and diversity of reactions increased with an increase in bio-oil/water ratio. This is not unexpected as this ratio is increased. Unreacted acetic acid, guaiacol and acetol along with 3-methyl phenol were the most prominent products in the liquid phase with 1 wt.% bio-oil. In contrast, with 5 and 10 wt%, a broad spectrum of products including phenol, methyl and ethyl phenols, catechol and propenoic acid were present in the liquid phase and acetaldehyde, lower alkanes, alkenes, cycloalkanes and carbon oxides were present in the gas phase. The range of products was even greater with 25 wt% bio-oil. This is expected as there are a number of reactions that occur simultaneously or can occur sequentially as formed intermediate products undergo reaction with unreacted components to produce other species. With the lower oil composition in the experiments, due to the lesser availability or non-availability of unreacted components, these side reactions are less likely to occur. Hence the lower bio-oil/water ratio results in less diverse range of products. Also of interest is the increased rate of gas products formation with higher oil composition in the feed. This is indicative of the fact that cracking reactions are aided by the availability of more of the unreacted oil components.

4.1.4 Effect of reaction time

A temporal study of the process can lead to a better understanding of the kinetics of the reactions. These studies were carried out by observing 1 and 5 hour reaction time and by varying the oil composition and operating temperature in each case. The results indicate that most of the reactions proceed very quickly and are essentially complete within the first one hour of reaction time. This is supported by the results for the conversions achieved at 1 hour reaction time that are almost equal or comparable to those at 5 hours reaction time.

Another interesting observation was that the products were more diversified during the longer reaction period. This was most likely due to the reaction of intermediates formed during the shorter reaction time with each other or with the unreacted components. It was also evident that, regardless of oil composition and operating temperature, there was significantly lower formation of gas products during the first hour of reaction time. However, gas products begin to form during the extended treatment period, which supports cracking reactions occurring to a greater degree during the longer reaction time.

For some compounds, reaction time was found to play a greater role. At supercritical conditions, acetic acid was formed during the first hour of reaction time. At five hours reaction time, acetic acid conversion was lower than achieved in one hour reaction time. This is most likely due to participation of acetic acid in the cracking reactions.

The amount of coke formed during the shorter reaction time was very comparable to that formed during the longer reaction time. This indicates that reactions which lead to coke formation occur within the first hour of treatment.

4.2 EXPERIMENTS WITH CRUDE BIO-OIL

Bio-oil produced by fast pyrolysis of pine wood at 450 °C was obtained from the Forest Products Department at Mississippi State University. Batch studies were carried out with crude bio-oil to examine the effect of treatment with water at near and supercritical conditions on the composition, and hence, the storage and stability characteristics of bio-oil. The experiments were designed to examine the effect of operating temperature, bio-oil/water ratio and reaction time on the product distribution. The control variables were fixed as follows:

- Peak operating temperature : 300, 380 and 420 °C
- Percent oil composition in oil-water mixture : 25 and 50 wt.%
- Reaction time : 0.5, 1, 5 hr

4.2.1 Untreated crude bio-oil composition

Physical property and quantitative analysis data of the untreated crude bio-oil are given in Table 4.1 and 4.2 respectively. Though the report quantifies 33 target compounds, discussion here will be restricted to a subset of compounds within these 33 that are believed to play a greater role in aging and coke formation in bio-oil.

Figure 4.12 Crude bio-oil used in the studies

Table 4.1 Properties of untreated bio-oil

Some physical properties of pine wood derived bio-oil that was used in this study are listed below:

S.No.	Property	Units	Value
1	Moisture	Wt. %	16.06
2	Acid value		80.56
3	pH	N/A	3.14
4	Density	g/cc	1.19
5	Viscosity (at 50 degree Celsius)	cSt	29.95

GPC Analysis of sulfuric acid treated pine wood bio-oil was performed, the details of which are furnished below.

Instrument configuration:

Waters 600E System Controller, Waters 410 Differential Refractometer, Viscotek TriSEC GPC software version 2.61, Column Plgel 3 um 100A300x7.5mm, Mobile phase: tetrahydrofuran, flow rate: 1 mL/min, Injection volume 20 µL, Calibration: 6 point Polystyrene (162-5120 g/mol)

Sample Description	Sample Conc.(mg/mL)	Mw	Mp	Mn
Pine wood Bio-oil	6.030	410	240	330

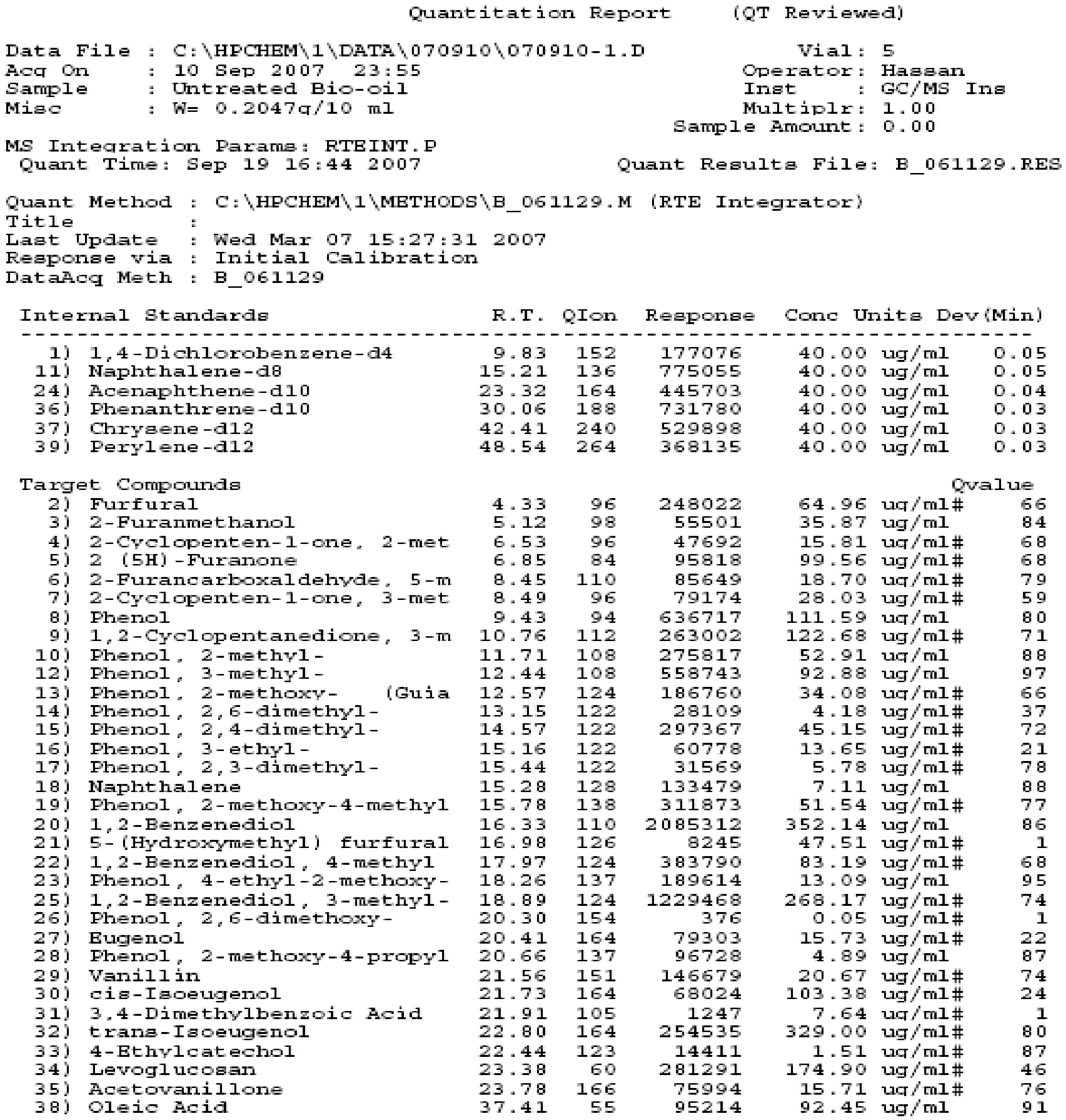
M_W: molecular weight

M_P: peak molecular weight

M_N: number-average molecular weight

Table 4.2 Quantitative report of untreated bio-oil

Bio oil obtained from pyrolysis of pine wood at 450 °C was used in the experiments.



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                              Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\070910\070910-1.D              Vial: 5
Acq On    : 10 Sep 2007  23:55                          Operator: Hassan
Sample    : Untreated Bio-oil                           Inst    : GC/MS Ins
Misc      : W= 0.2047g/10 ml                            Multiplr: 1.00
                                                   Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Sep 19 16:44 2007                 Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                   R.T. QIon  Response  Conc Units Dev(Min)
 ------------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4          9.83  152    177076    40.00 ug/ml    0.05
  11) Naphthalene-d8                 15.21  136    775055    40.00 ug/ml    0.05
  24) Acenaphthene-d10               23.32  164    445703    40.00 ug/ml    0.04
  36) Phenanthrene-d10               30.06  188    731780    40.00 ug/ml    0.03
  37) Chrysene-d12                   42.41  240    529898    40.00 ug/ml    0.03
  39) Perylene-d12                   48.54  264    368135    40.00 ug/ml    0.03

 Target Compounds                                                       Qvalue
   2) Furfural                        4.33   96    248022    64.96 ug/ml#     66
   3) 2-Furanmethanol                 5.12   98     55501    35.87 ug/ml      84
   4) 2-Cyclopenten-1-one, 2-met      6.53   96     47692    15.81 ug/ml#     68
   5) 2 (5H)-Furanone                 6.85   84     95818    99.56 ug/ml#     68
   6) 2-Furancarboxaldehyde, 5-m      8.45  110     85649    18.70 ug/ml#     79
   7) 2-Cyclopenten-1-one, 3-met      8.49   96     79174    28.03 ug/ml#     59
   8) Phenol                          9.43   94    636717   111.59 ug/ml      80
   9) 1,2-Cyclopentanedione, 3-m     10.76  112    263002   122.68 ug/ml#     71
  10) Phenol, 2-methyl-              11.71  108    275817    52.91 ug/ml      88
  12) Phenol, 3-methyl-              12.44  108    558743    92.88 ug/ml      97
  13) Phenol, 2-methoxy-   (Guia     12.57  124    186760    34.08 ug/ml#     66
  14) Phenol, 2,6-dimethyl-          13.15  122     28109     4.18 ug/ml#     37
  15) Phenol, 2,4-dimethyl-          14.57  122    297367    45.15 ug/ml#     72
  16) Phenol, 3-ethyl-               15.16  122     60778    13.65 ug/ml#     21
  17) Phenol, 2,3-dimethyl-          15.44  122     31569     5.78 ug/ml#     78
  18) Naphthalene                    15.28  128    133479     7.11 ug/ml      88
  19) Phenol, 2-methoxy-4-methyl     15.78  138    311873    51.54 ug/ml#     77
  20) 1,2-Benzenediol                16.33  110   2085312   352.14 ug/ml      86
  21) 5-(Hydroxymethyl) furfural     16.98  126      8245    47.51 ug/ml#      1
  22) 1,2-Benzenediol, 4-methyl      17.97  124    383790    83.19 ug/ml#     68
  23) Phenol, 4-ethyl-2-methoxy-     18.26  137    189614    13.09 ug/ml      95
  25) 1,2-Benzenediol, 3-methyl-     18.89  124   1229468   268.17 ug/ml#     74
  26) Phenol, 2,6-dimethoxy-         20.30  154       376     0.05 ug/ml#      1
  27) Eugenol                        20.41  164     79303    15.73 ug/ml#     22
  28) Phenol, 2-methoxy-4-propyl     20.66  137     96728     4.89 ug/ml      87
  29) Vanillin                       21.56  151    146679    20.67 ug/ml#     74
  30) cis-Isoeugenol                 21.73  164     68024   103.38 ug/ml#     24
  31) 3,4-Dimethylbenzoic Acid       21.91  105      1247     7.64 ug/ml#      1
  32) trans-Isoeugenol               22.80  164    254535   329.00 ug/ml#     80
  33) 4-Ethylcatechol                22.44  123     14411     1.51 ug/ml#     87
  34) Levoglucosan                   23.38   60    281291   174.90 ug/ml#     46
  35) Acetovanillone                 23.78  166     75994    15.71 ug/ml#     76
  38) Oleic Acid                     37.41   55     95214    92.45 ug/ml      91
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4.2.2 Effect of temperature

Batch studies to examine the effect of temperature on the product distribution were carried out by fixing the bio-oil/water ratio at a constant value and varying the operating temperature between subcritical, near-critical and supercritical conditions. The reaction time was either one hour or five hours. Experimental operating conditions were:

- Manipulated variable:

Peak operating temperature	: 300, 380 and 420 °C

- Controlled variable:

Percent oil composition in bio-oil/water mixture	: 25, 50 wt. %
Reaction time	: 1, 5 h

Furfural is known to be one of the greatest contributors to catalyst coking in bio-oil. Hence, removal of furfural and/or other coke precursors may be one approach to produce bio-oil that can be further processed using hydrotreating or hydrodeoxygenation catalysts to produce bio-oil with improved storage and stability characteristics.

The results (Figure 4.13) show that furfural was very effectively converted during the treatment. An average conversion of 93.78% was observed with treatment at subcritical conditions (300 °C). The conversion at near-critical conditions (380 °C) was slightly less at 90.28% while treatment at 420 °C gave an average furfural conversion of 92.38%. This is interesting as the conversions achieved using the crude bio-oil were greater than achieved with the bio-oil simulant.

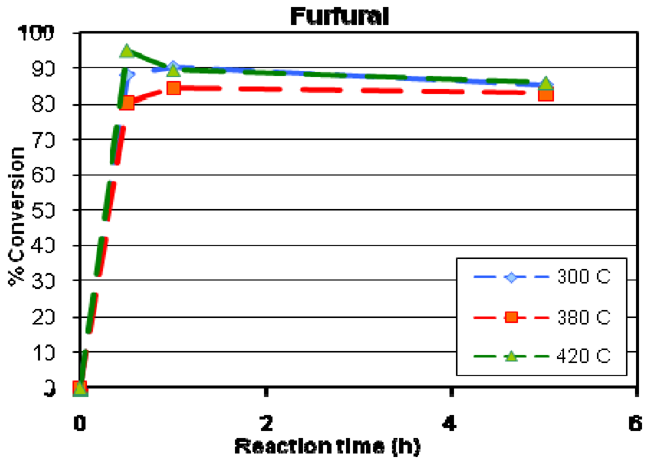

Figure 4.13 Conversion of furfural (with 25 wt% oil)

Guaiacol may undergo disproportionation leading to the formation of phenol and alkylated ether, which may then undergo cracking to form hydrocarbon gases. Some of these gases may then get alkylated to form alkylated phenols, which subsequently undergo polymerization leading to coke formation.[2.10] The results from experiments using 50 wt.% bio-oil showed that the guaiacol conversion was almost complete at 420 °C with an average conversion of 99.33% while that at near supercritical conditions (380 °C) was found to be less at 89.57%. Subcritical treatment was not very effective in converting guaiacol with an average conversion of only 69.92%. Thus, a strong temperature preference for reactions was observed with crude bio-oil (Figure 4.14).

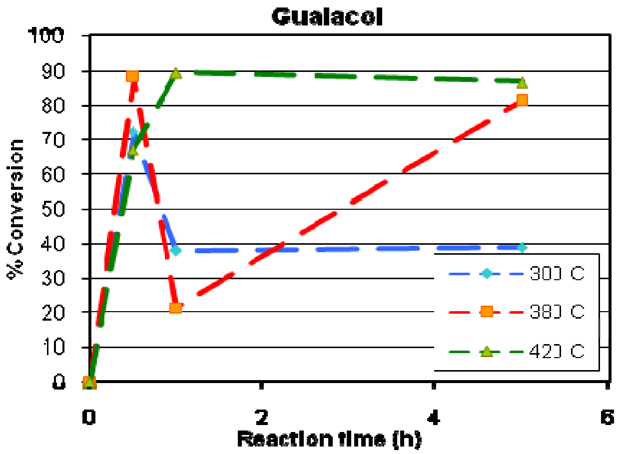

Figure 4.14 Conversion of guaiacol (with 50 wt% oil)

With phenol, the conversion was influenced to a lesser degree by operating temperature. Phenol conversions were greater at subcritical conditions (300 °C) compared to those achieved at higher temperatures. This distinction, however, disappeared during the longer reaction time. For the longer reaction time, conversions achieved at all three treatment conditions were comparable.

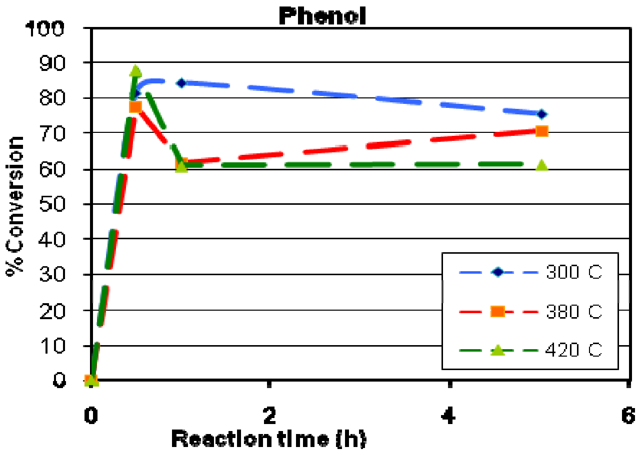

Figure 4.15 Conversion of phenol (with 25 wt% bio-oil)

The conversion of catechol was not significantly impacted by the reaction temperature (Figure 4.16). Catechol and other substituted phenols are most likely formed from phenol. This may explain the finding of lower catechols conversions achieved during the longer reaction time due to the lower phenol conversions during the longer reaction time.

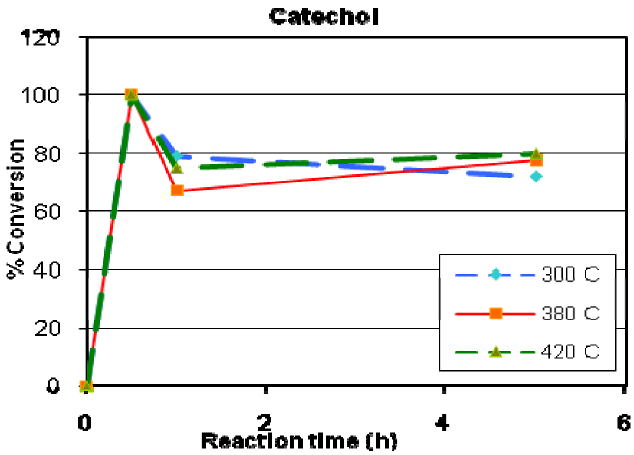

Figure 4.16 Conversion of catechol

As mentioned previously, vanillin is known to be a contributor to coke formation. In this work, essentially complete conversion of vanillin was achieved regardless of operating conditions (Figure 4-17). Guaiacol, a product resulting from disproportionation of vanillin; as well as compounds including 4-ethyl 2-methoxy phenol and 4-methyl 2-methoxy phenol were also likely formed from vanillin, although very low yields were obtained.

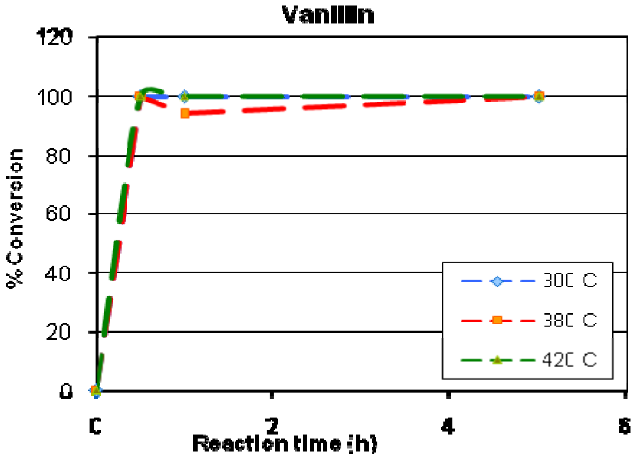

Figure 4.17 Conversion of vanillin

Levoglucosan, formed from the thermal decomposition of glucose,is one of the precursors in bio-oil that lead to coke formation. With the exception of one set of experimental conditions (at 380 °C and 1 hour reaction time), essentially complete conversion of levoglucosan was achieved, regardless of operating conditions (Figure 4.18). Glucose is known to form levoglucosan as a result of thermal decomposition which in turn undergoes further decomposition to form furans. This is evidenced by the presence of furans in the product vapor phase.

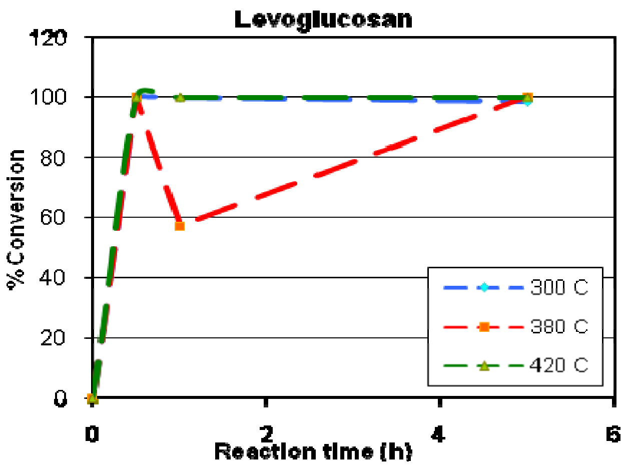

Figure 4.18 Conversion of levoglucosan

One possible reaction pathway for acids, suggested by Adjaye and Bakshi,[2.10] is the deoxygenation of the acid to form a long chain aldehyde, a ketone and water. The alkyl groups attached to the long chain aldehydes and ketones undergo aromatization, followed by alkylation and isomerization to form alkylated benzenes. Some of these aromatic compounds subsequently undergo polymerization. These polyaromatics are thought to then undergo dehydrogenation, resulting in coke formation.

Experimental results indicated that acetic acid formation followed a very similar trend to that obtained with bio-oil simulant (Figure 4.19). During the first hour of treatment, acetic acid formation was observed at all three operating temperatures. The longer reaction time (5 hours) showed a reversal of trends at near and supercritical conditions (380 and 420 °C), wherein acetic acid was consumed during treatment. At subcritical conditions, acetic acid formation continued throughout the five hour reaction period.

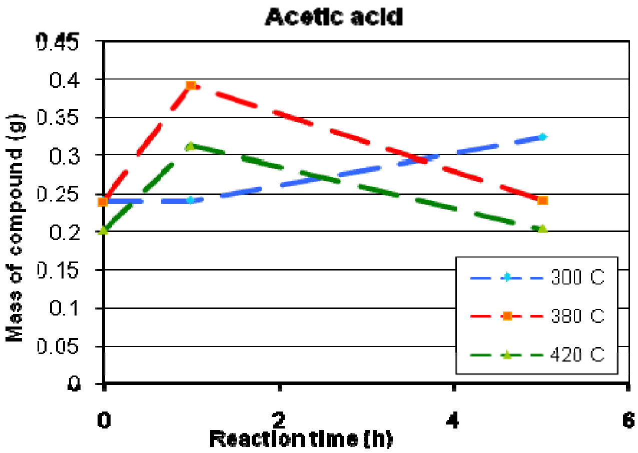

Figure 4.19 Formation of acetic acid

Another acid that was prominent in the untreated bio-oil was oleic acid. Experiment results (Figure 4.20) demonstrated essentially complete (100%) conversion of oleic acid at all operating temperatures. The presence of these acids (acetic and oleic) promotes coking. Hence, complete elimination of oleic acid in the treated bio-oil sample is a very encouraging result.

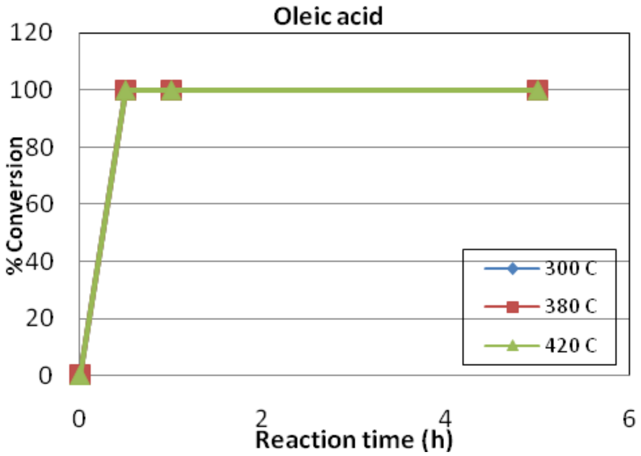

Figure 4.20 Conversion of oleic acid

4.2.3 Effect of bio-oil/water mass ratio

Batch studies to understand the effect of bio-oil/water mass ratio on the product distribution were conducted. Reaction time and operating temperature were controlled. The operating conditions were:

- Manipulated variable:

  Percent oil composition in oil-water mixture : 25 and 50 wt.%

- Controlled variable:

  Peak operating temperature : 300, 380 and 420 °C

  Reaction time : 0.5, 1, 5 hr

With furfural, the reaction did show a preference towards greater bio-oil/water mass ratio. As evident in Figure 4.21, almost 100% conversion was achieved with 50 wt% bio-oil while the conversion with 25 wt% was only about 90%. This could possibly due to the fact that a higher oil concentration facilitates more active and effective collisions that aid the occurrence of the desirable reactions.

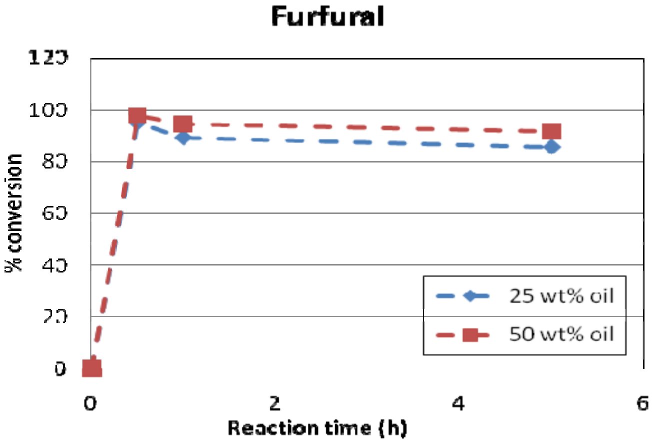

Figure 4.21 Effect of bio-oil/water mass ratio on the conversion of furfural

For guaiacol, similar results were achieved (Figure 4.22), with better conversions at higher bio-oil/water weight ratios. The difference between the conversions achieved with the two bio-oil/water weight ratios was more pronounced at the lower operating temperature (300 °C).

One of the likely products formed from guaiacol is phenol. A significantly higher rate of formation of phenol was observed with treatment using the higher bio-oil/water ratio of 50 % compared to that observed with 25 % (Figure 4.23). This also complements the fact that phenol is formed from guaiacols; high conversion of guaiacol resulted in a higher yield of phenol as observed in these experiments.

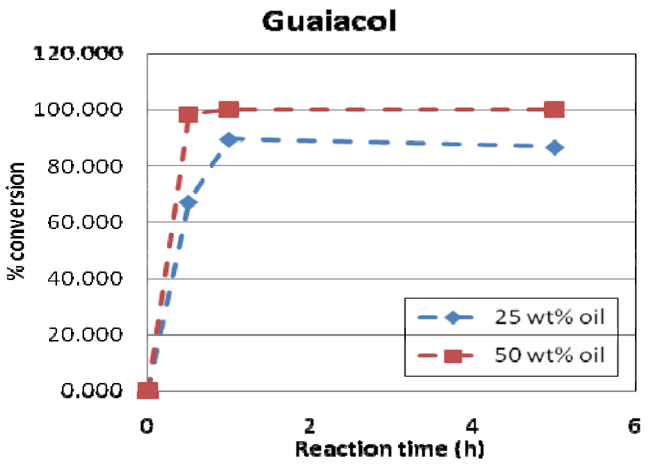

Figure 4.22 Effect of bio-oil/water mass ratio on the conversion of guaiacol

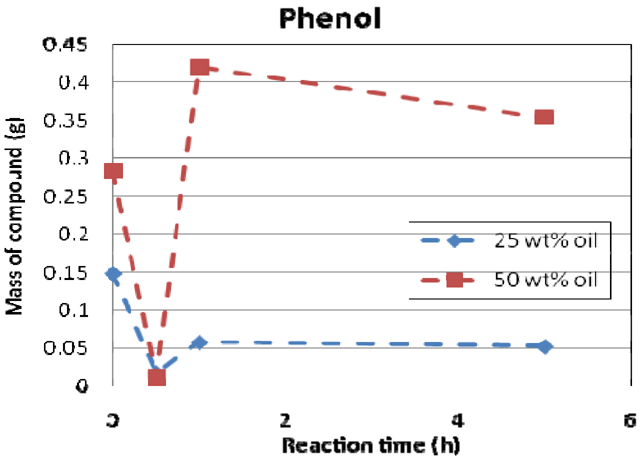

Figure 4.23 Effect of bio-oil/water mass ratio on the yield of phenol

With catechol, bio-oil/water mass ratio was less significant. However, the difference in catechol conversion was more pronounced during the longer reaction period (Figure 4.24). Considering the very high phenol yields, it is possible that a portion of the catechol is decomposing to form phenol. This trend is opposite to that observed with the bio-oil simulant (formation of catechol observed for simulant).

In case of vanillin, neither bio-oil/water mass ratio nor operating temperature had any significant impact on conversion. Almost complete conversion was achieved regardless of the operating conditions and bio-oil/water mass ratio (Figure 4.25).

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*All graphs shown in this discussion are at 420 °C. Graphs for other treatment conditions can be found in Appendix C.

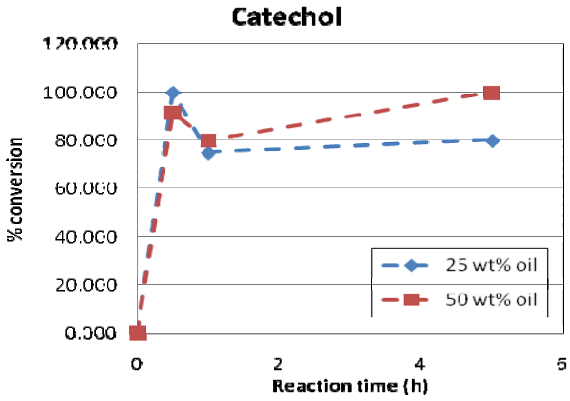


Figure 4.24 Effect of bio-oil/water mass ratio on the conversion of catechol

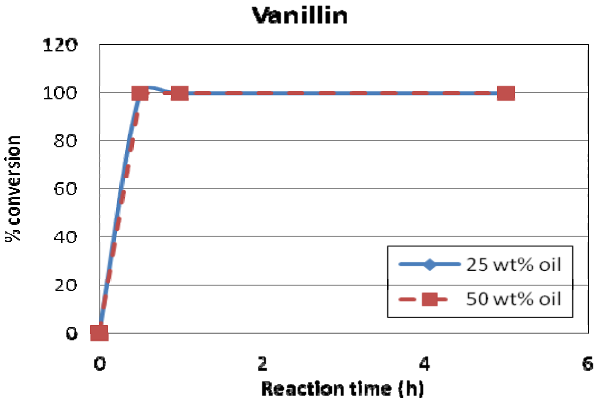


Figure 4.25 Effect of bio-oil/water mass ratio on the conversion of vanillin

Levoglucosan (Figure 4.26) was also completely converted regardless of the operating temperature or bio-oil/water ratio in the reactor charge. Levoglucosan undergoes thermal decomposition, possibly forming furans.

Acids are known to lead to coke formation. Thus, elimination of acids from the bio-oil is a very effective processing step prior to catalytic upgrading of bio-oil. Experimental results indicated that oleic acid was essentially completely converted during treatment regardless of the operating temperature or bio-oil/water ratio.

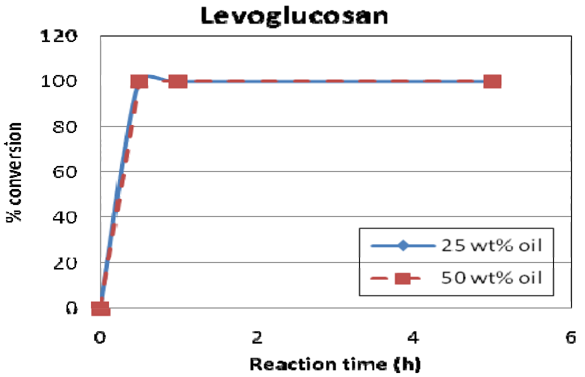


Figure 4.26 Effect of bio-oil/water mass ratio on the conversion of levoglucosan

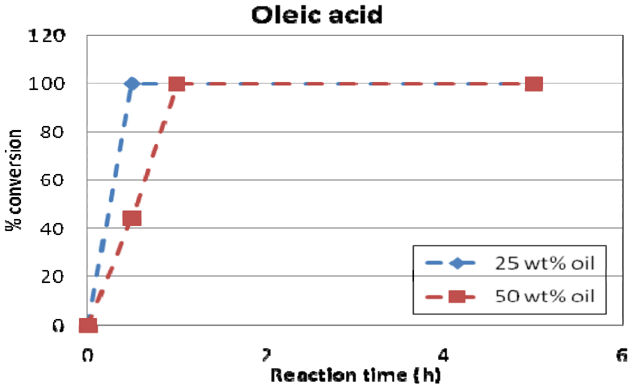


Figure 4.27 Effect of bio-oil/water mass ratio on the conversion of oleic acid

In the case of acetic acid (Figure 4.28), a significantly higher rate of formation of acetic acid was observed with the higher bio-oil/water ratio (50%). The rate of formation of acetic acid with 25 % bio-oil/water ratio was almost negligible. During the longer reaction time with 50 wt% bio-oil/water ratio, the acetic acid that is formed undergoes further reaction.

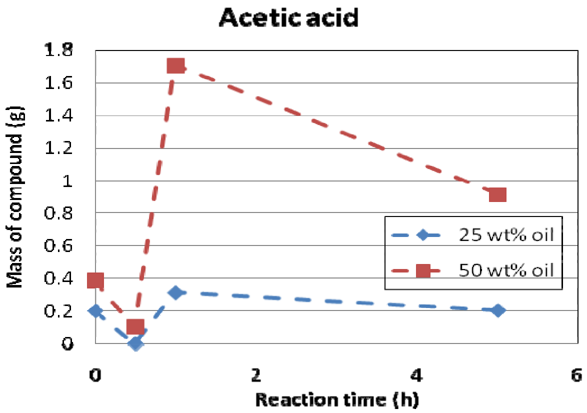


Figure 4.28 Effect of bio-oil/water mass ratio on the formation of acetic acid

4.2.4 Effect of reaction time

An examination of temporal behavior in the reaction system can lead to better understanding of the kinetics of the reactions. These temporal studies were carried out by keeping reaction time constant and varying the oil composition and operating temperature. The findings are similar to those obtained with the bio-oil simulant. The majorities of reactions occur rapidly and have essentially gone to completion within the first hour of reaction time. The conversions achieved at 5 hours reaction time are essentially equivalent to those achieved at 1 hour reaction time. This may also be interpreted that the reaction mixture has achieved a quasi-equilibrium state as most of the components present to not undergo further reactions or conversion during the extended reaction time.

The operating conditions employed for the temporal studies were:

- Manipulated variable:

Reaction time	: 0.5, 1 and 5 hr

- Controlled variables:

Peak operating temperature	: 300, 380 and 420 °C
Bio-oil/water mass ratio	: 25, 50 wt. %

Almost complete conversion of furfural was achieved during the first hour of reaction time. A longer reaction time did not change the furfural content of the treated bio-oil.

Guaiacol was effectively converted during the one hour reaction time regardless of operating conditions. However, during the extended reaction time (5 hours), at 300 and 420 °C, no appreciable conversion of guaiacols was found, but significant guaiacol conversion was observed at 380 °C. Phenol showed similar trends during the longer reaction time. At 300 and 420 °C, phenol conversion did not show an increase whereas at 380 °C, a slight increase in conversion was noted. These results are indicative that at near supercritical conditions, reactions may be enhanced.

Experimental results indicated that catechol conversion reached a maximum during the first 30 minutes of reaction time, followed by a drop in conversion during longer reaction times. It is hypothesized that this drop in conversion is due to the possible formation of catechol from phenol and other reaction intermediates. At extended reaction times, a plateau in the conversion is evident (Figure 4.14). With vanillin, oleic acid and levoglucosan, essentially complete conversion was achieved within the first hour of reaction time.

The conversion of acetic acid in the crude bio-oil was very similar to that observed for acetic acid in the bio-oil simulant. During the first hour of reaction time, acetic acid was formed regardless of the operating conditions. During the longer reaction time, acetic acid was consumed at near and supercritical conditions (380 and 420 °C) and acetic acid was formed during treatment at 300 °C.

4.3 PRODUCT PHASE DISTRIBUTION

A comprehensive compilation of data from crude bio-oil experiments was performed to study the phase distribution of products after treatment. It is desirable to maximize the fraction of material that is retained in the liquid phase, while minimizing the fraction of material that is found in the solid product (char).

Experiments using bio-oil simulant (Figure 4.29) revealed that the solid product formation was slightly higher at the higher operating conditions (7 wt.% for treatment at 380 and 420 °C) than at subcritical conditions (5 wt.% at 300 °C).

For experiments using 25 wt% bio-oil in the initial charge, a comparison with reaction temperature as the basis showed that the average amount of solid product was slightly higher at 300 °C (16.32 wt.%) when compared to that with the higher operating temperatures (13.52 and 16.63 wt.% at 380 °C and 420 °C, respectively.) The amount of liquid product did not show any significant difference over the range of operating temperatures examined, averaging a liquid product of 85.14 wt.%. On average, about 0.35 percent of the initial charge was converted to gas phase products (Figure 4.30).

In contrast, experiments using 50 wt.% bio-oil in the initial charge did not exhibit clear trends in phase production as a function of operating temperature (Figure 4.31). The average amount of solid products was 21.62, 18.98 and 22.65 wt% for 300, 380 and 420 °C, respectively. The increase in the amount of solid products generated during treatment is attributed to the increased amount of bio-oil in the initial charge. However, it is interesting to note here that although the mass of oil was doubled (compared to the 25 wt% bio-oil experiment), the amount of solid phase in the product increased by a factor of 1.45. This does indicate that the formation of solid products is slightly lower when the bio-oil/water ratio in the initial charge is increased. The fraction of material in the gas phase at the end of treatment was increased by a factor of 2.79 when the higher bio-oil/water ratio was used. This result is interpreted that a higher bio-oil/water ratio in the initial charge results in more extensive cracking during treatment. This is supported by recognizing that the increased bio-oil/water ratio in the initial charge effectively increases the number of collisions between potential reactants in the cracking reactions, due to their increased number density during treatment. The overall fraction of initial charge found in the liquid product was generally lower when the higher bio-oil/water ratio was employed (77.90 wt. % on an average.)

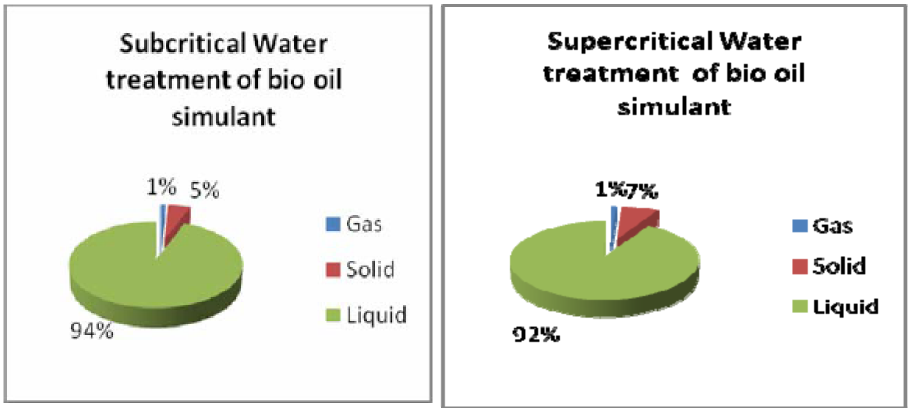


Figure 4.29(a) Figure 4.29(b)

Figure 4.29 Product phase distribution of treatment of bio-oil simulant

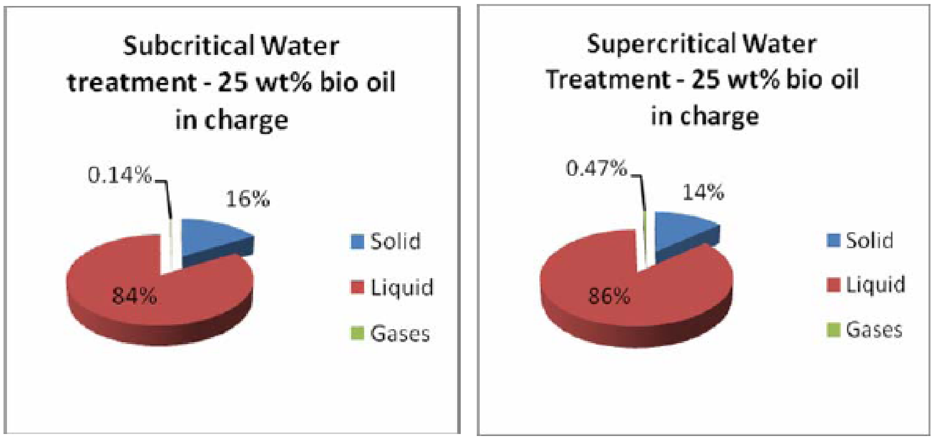


Figure 4.30(a) Figure 4.30(b)

Figure 4.30 Product phase distribution with treatment at (a) 300 °C for 25 wt. % oil charge. (b) 380 °C and 420 °C for 25 wt. % oil charge

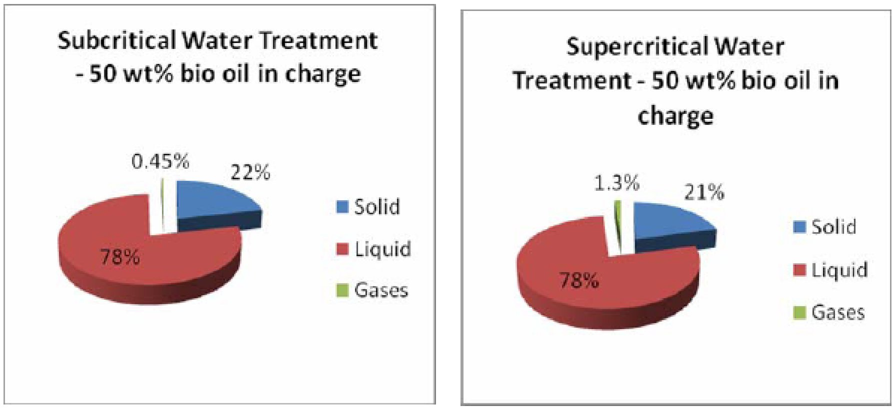


Figure 4.31(a) Figure 4.31(b)

Figure 4.31 Product phase distribution with treatment at (a) 300 °C for 50 wt. % oil charge. (b) 380 °C and 420 °C for 50 wt. % oil charge.

4.4 EXPERIMENTS WITH METHANOL AS COSOLVENT

Methanol is known to improve the storage and stability characteristics of bio-oil. Diebold and Czernik [2.12] showed that the addition of alcohols such as methanol can slow down the aging reactions that occur in bio-oil by serving as a molecular diluent and also by reacting to form more stable compounds that do not participate to bio-oil aging. Hence, experiments were designed to study the influence of methanol as a co-solvent with water on the final product distribution and storage characteristics of the treated bio-oil.

The operating conditions were:

- Manipulated variable:

  Percent methanol by weight in initial charge : 0, 5 wt.%

- Controlled variables:

Peak operating temperature : 300, 380 and 420 °C

Bio-oil/water mass ratio : 25 wt.%

Reaction time : 1 hr

Furfural is well known as a serious contributor to coke formation during catalytic upgrading of bio-oil. Hence, removal of furfural can be an effective treatment step prior to catalytic upgrading of bio-oil. Experimental results indicate that at 300 and 420 °C, methanol addition lowered the conversion of furfural (Figure 4.32). However, at near supercritical conditions (380 °C), the conversion of furfural was significantly higher with the addition of methanol compared to that achieved without methanol addition.

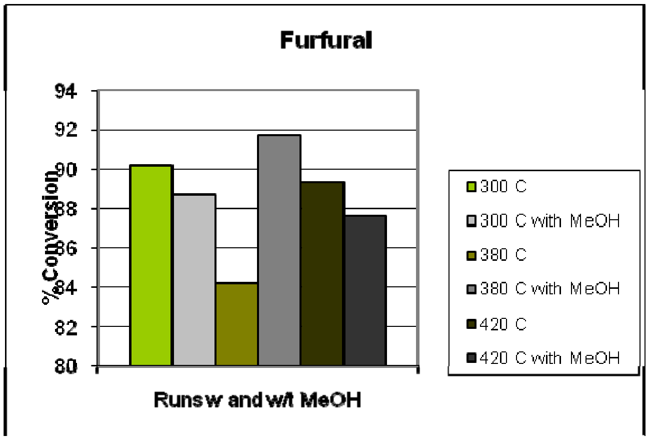


Figure 4.32 Influence of methanol addition on the conversion of furfural

Similar results were observed for guaiacol (Figure 4.33).. The conversions at 300 and 420 °C were not significantly influenced by methanol addition. However, at near supercritical conditions (380 °C), guaiacol conversion increased by a factor of 1.77 due to methanol addition. Phenol conversion did not show any marked improvement at 300 °C.

However, it was quite evident that methanol addition improved the phenol conversion by approximately 6% and 12% at 380 and 420 °C, respectively (Figure 4.34). For catechols (Figure 4.35), however, methanol addition did not result in an increase in conversion at any of the operating conditions.

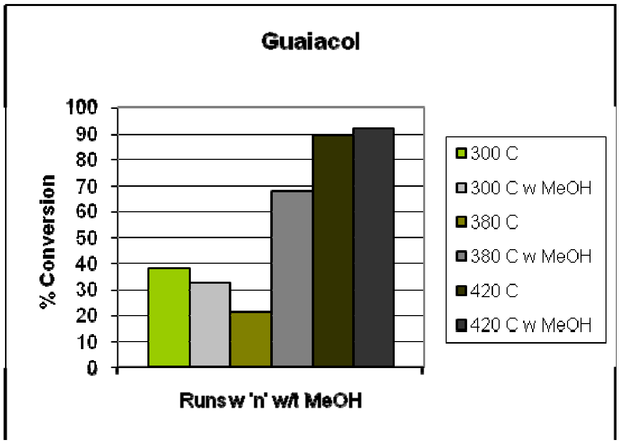


Figure 4.33 Influence of methanol addition on the conversion of guaiacol

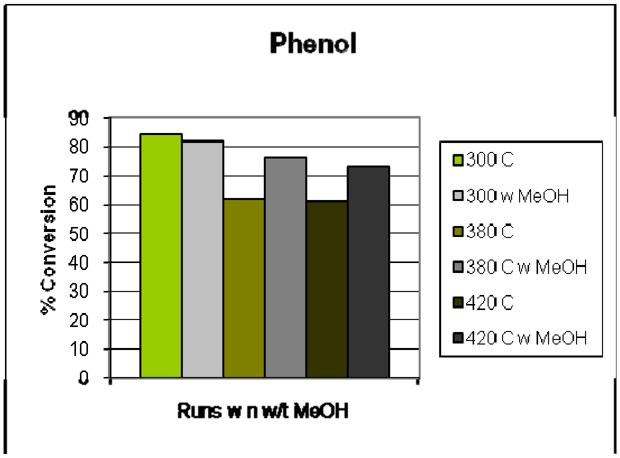


Figure 4.34 Influence of methanol addition on the conversion of phenol

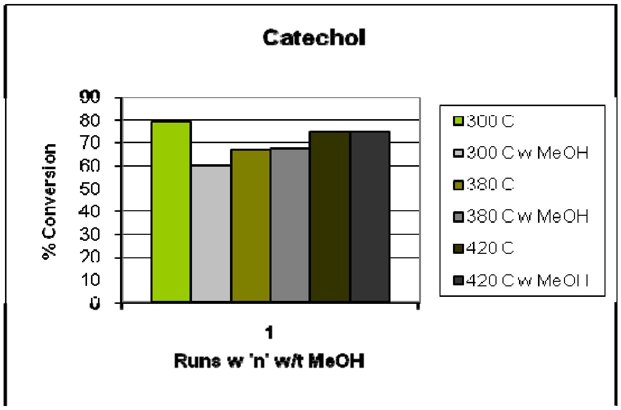


Figure 4.35 Influence of methanol addition on the conversion of catechol

In the case of vanillin, the influence of methanol addition on conversion showed mixed trends (Figure 4.36). At 300 °C, vanillin conversion was decreased by 2.5% while at 380 °C, it was increased by ~5%. At 420 °C, there was no significant change in the conversion as a result of methanol addition.

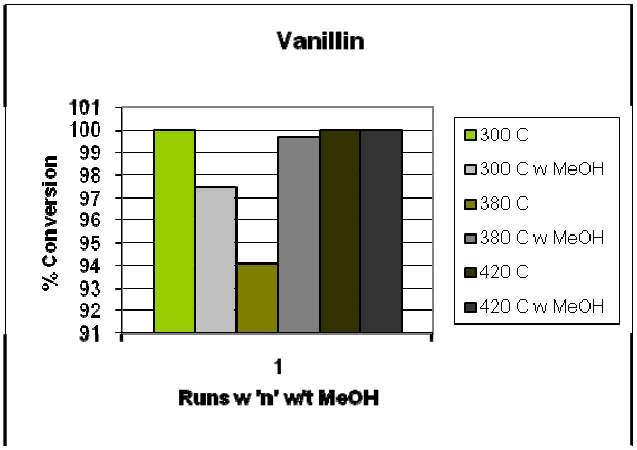


Figure 4.36 Influence of methanol addition on the conversion of vanillin

Methanol addition resulted in significant improvement in conversion of levoglucosan (by a factor of 1.67) at 380 °C (Figure 4.37). At other treatment temperatures, however, methanol addition did not result in any significant change in conversion.

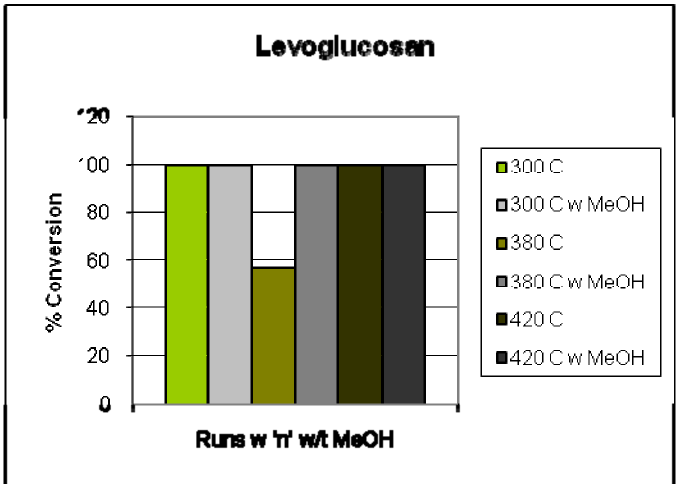


Figure 4.37 Influence of methanol addition on the conversion of levoglucosan

Since acids are known to contribute to coke formation, elimination of acids through reaction is desirable. When methanol was added to the initial charge to the reactor, the conversion of acids decreased (Figure 4.38). The addition of methanol promoted the formation of acids during treatment. Methanol addition increased the acetic acid yield at 300 and 380 °C (Figure 4.38) and resulted in a slight reduction in its formation at 420 °C.

It is also evident from Figure 4.34 that oleic acid was almost completely converted during the treatments without methanol addition. When methanol was included in the initial reactor change, oleic acid was produced rather than consumer during treatment (Figure 4.39).

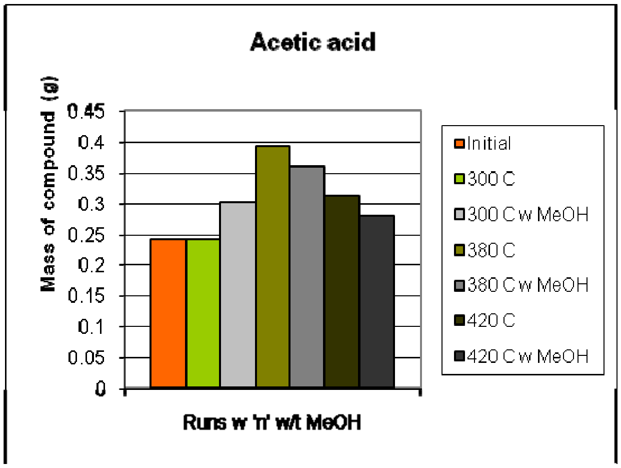


Figure 4.38 Influence of methanol addition on acetic acid formation

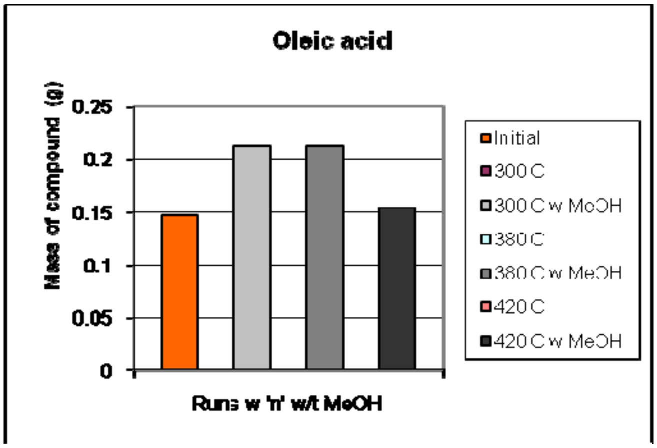


Figure 4.39 Influence of methanol addition on the conversion of oleic acid

4.5 CHEMICAL PRODUCT DISTRIBUTION AFTER TREATMENT

From the experimental results, it was evident that treatment with near critical and supercritical water significantly altered the bio-oil composition. Some compounds were effectively removed by the treatment, and as they disappeared, other compounds were formed. Examination of the product distribution provides a means to evaluate the treatment process. GC/MS results obtained by the Forest Products Laboratory on submitted samples indicated which of the target compounds were present in the treated bio-oil. As no effort was undertaken to separate the treated bio-oil from the water used in the treatment process, the samples submitted for analysis were diluted and thus, concentrations reported by the Forest Products Laboratory in these samples were much lower than in the crude bio-oil sample. These lower concentrations are due in part to the water present in the sample; as the amount of water used for treatment was determined by the bio-oil/water mass ratio, direct comparison of concentrations between runs is not possible, nor is comparison of concentrations in crude bio-oil and treated sample. However, it is possible to determine actual mass of a given component present initially and present after treatment for those components which are among the 33 target compounds for which quantitative information is available.

In addition to the quantitative analysis on the 33 target compounds, qualitative analysis of the liquid phase also allows identification of other compounds present in some amount in the sample. Possible formation pathways for these compounds are examined as each qualitatively identified compound is discussed. Qualitative analysis of the captured gas samples from the reactor was also performed. These results, too may be examined to identify possible formation pathways for the identified gas-phase compounds.

Tables 4.3 and 4.4 at the end of this section have a list of target compounds and tentatively identified compounds and how their composition is altered as a result of this treatment for various treatment conditions. Table 4.5 has a list of prominent compounds that were present in liquid product identified through qualitative analysis performed using GC-MS. Table 4.6 has a complete list of all the products that were present in gas phase, identified through qualitative analysis performed using GC-MS.

It was interesting to observe that while formation of certain compounds showed strong dependence on reaction conditions, certain other compounds were formed for almost all the combination for reaction conditions tried. Among products in the liquid phase, while guaiacol formation was more pronounced at the lower treatment temperature substituted phenols were more prominent with treatment at higher temperatures. This could also be due to the fact that conversion of guaiacol to phenols is more favored at the higher temperatures.

Acetic acid and propanoic acid were formed at all treatment conditions. However during the longer treatment time (5 hours), acetic acid was partially getting converted with treatment at 380 and 420 °C. Another distinct pattern observed from the treatment was that aliphatic compounds were generally formed only at higher operating temperatures, preferably at 420 °C.

For products in the gas phase, a wider spectrum of products were formed during the longer treatment time evidently as a result of cracking reactions which were observed to be more prominent during that time.

4.5.1 Possible reaction pathways for formation of new compounds

Some of the possible reaction pathways that could offer an explanation on how these new compounds identified in liquid product could have likely been formed follow:

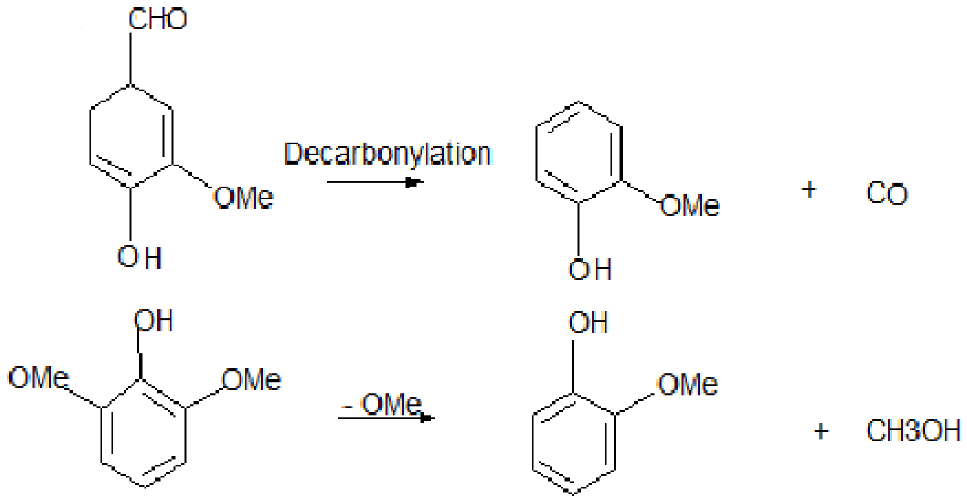
1. Benzene

Possible formation could be through hydrogenolysis of any of the following compounds: Phenol, guaiacol and catechol

2. Guaiacol

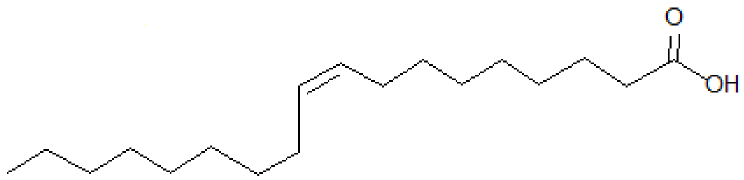
It may be formed as a result of methylation of available catechol or due to cracking of vanillin or syringol. Decarbonylation of vanillin has a higher possibility as disproportionation and decarbonylation reactions like that of benzaldehyde to benzene have been reported to occur in supercritical water environment.

The likely reactions follow:



3. Acetic acid

As we see disappearance of oleic acid, acetic acid could be a likely product due to the cracking of oleic acid. The concentration of acetic acid formed is lesser than the initial concentration of oleic acid. Hence cracking of oleic acid may also result in other lower acids. It could also be formed from formic acid through methylation.



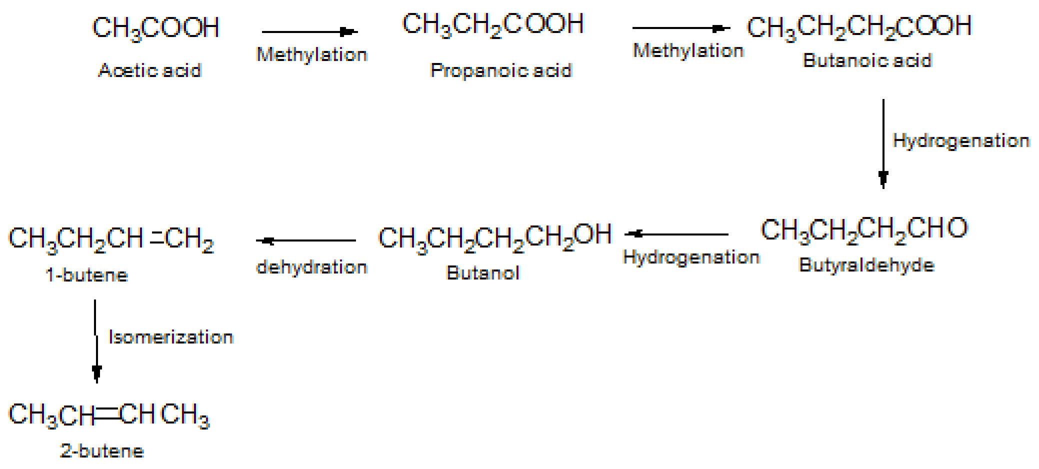
Oleic acid

4. Propanoic acid

It could be formed as a result of chain extension reaction of acetic acid (methylation). It could also be a likely product formed as a result of cracking of oleic acid ($C_{17}H_{33}COOH$).

5. 2-butene

This must also be a product formed due to the cracking reactions, one of the possible reaction pathways from acetic acid is explained below:



8. Ethyl catechol

It may be formed as a result of ethylation of catechol.

9. Propene

Propene can also be formed from the methylation of acetic acid and successive hydrogenation of propanoic acid and propenal to yield propanol which can undergo dehydroxylation to form propene.

10. Butane diol

Butane which is formed as a result of cracking reactions may undergo hydroxylation to form butane diol.

11.	Cyclohexane

It may be formed as a result of hydrogenation of benzene or from phenol through dehydroxylation and subsequent hydrogenation.

12.	Ethyl acetate

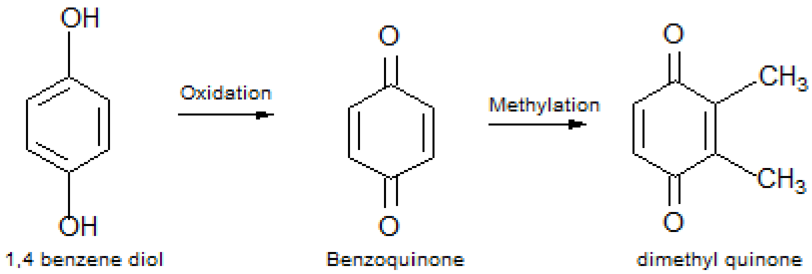
It is most likely formed as a result of esterification of acetic acid and ethanol.

13.	Cyclopentenes

It is one of the likely products from the hexose sugars. Can also be formed as a result of cyclization and subsequent cracking of oleic acid.

14.	Dimethyl quinone

It is likely a product formed as a result of oxidation and subsequent methylation of 1,4 benzene diol. The possible reaction pathway is explained below:



15.	Octadiyne

This is could be formed as a result of addition of straight chain alkenes or alkynes that get formed as a result of cracking reactions.

16.	Formic acid methyl ester / formic acid ethyl ester

This is likely formed as a result of esterification reactions involving methanol and ethanol respectively with formic acid.

17. Furan

This is one of the likely products formed from furfural and from the pentose sugars.

18. 2, 5 dihydro furan

It is likely formed due to the hydrogenation of furan.

19. Carbon dioxide

This is the most prominent compound found in the gas phase. Although multiple reaction pathways could be suggested, one possible pathway is through the decarboxylation of organic acids in bio-oil.

Table 4.3 Quantitative analysis results (25 wt.% bio-oil / 75 wt.% water in charge)

		Crude bio-oil	Liquid product from treatment								
	All concentrations are in µg/mL		Reaction temperature (° C)								
			300 °C			380 °C			420 °C		
			Reaction time (h)			Reaction time (h)			Reaction time (h)		
S. no.	Compound		0.5	1	5	0.5	1	5	0.5	1	5
1	Furfural	64.96	1.12	2.73	3.27	2.72	3.43	4.06	4.34	2.48	3.35
2	2-Furanmethanol	35.87	N.D.	N.D.	N.D.	N.D.	0.22	0.60	N.D.	0.31	0.67
3	2-methyl 2-cyclopenten-1-one	15.81	2.50	3.84	3.40	2.28	3.51	2.33	2.13	2.23	1.54
4	2-furanone	99.56	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
5	5-methyl 2-furancarboxaldehyde	18.70	N.D.	N.D.	0.04	N.D.	0.06	0.14	0.12	0.06	0.03
6	3-methyl 2-cyclopenten-1-one	28.03	0.70	1.15	1.61	1.07	1.46	1.39	1.28	0.99	0.11
7	Phenol	111.59	4.78	7.45	9.26	8.96	14.28	12.00	10.75	15.67	15.56
8	3-methyl 1,2- Cyclopetanedione	122.68	0.97	0.15	0.19	N.D.	0.28	N.D.	N.D.	N.D.	0.07
9	2-methyl phenol	52.91	1.54	2.34	4.20	3.67	7.35	6.69	4.98	7.02	8.88
10	3-methyl phenol	92.88	2.37	3.11	4.23	5.22	7.09	7.76	7.28	7.37	10.54
11	2-methoxy phenol	34.08	4.01	9.06	7.09	4.06	8.99	2.32	1.72	1.27	1.61
12	2,6 dimethyl phenol	4.18	N.D.	N.D.	0.16	0.08	0.29	0.46	0.19	0.42	0.65
13	2,4 dimethyl phenol	45.15	0.03	0.84	1.47	1.43	2.19	2.55	0.13	2.35	3.84
14	3-ethyl phenol	13.65	0.06	0.15	0.60	0.15	0.67	1.23	0.09	0.71	2.62
15	2,3 dimethyl phenol	5.78	0.09	0.16	0.16	0.11	0.11	0.65	0.93	0.36	0.99
16	naphthalene	7.11	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	0.02
17	2-methoxy 4-methyl phenol	51.54	1.71	2.08	2.89	1.79	1.27	1.41	1.49	0.69	1.37
18	1,2 benzene diol	352.14	N.D.	31.40	33.32	N.D.	38.60	28.56	N.D.	31.56	25.37
19	5-hydroxymethyl furfural	47.51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
20	4-methyl 1,2 benzene diol	93.19	N.D.	14.55	15.86	13.90	17.71	18.20	N.D.	17.48	16.64
21	4-ethyl 2-methoxy phenol	13.09	0.29	0.37	0.50	0.31	0.20	0.19	0.24	0.02	0.20
22	3-methyl 1,2 benzene diol	268.17	N.D.	25.41	30.86	20.04	37.75	29.06	20.08	29.68	20.25
23	2,6 dimethoxy phenol	0.05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
24	eugenol	15.73	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03
25	2-methoxy 4-propyl phenol	4.89	0.05	0.09	0.19	0.04	0.08	0.08	0.01	0.33	0.08
26	vanillin	20.67	N.D.	N.D.	N.D.	N.D.	0.41	N.D.	N.D.	N.D.	N.D.
27	cis-isoeugenol	103.38	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
28	3,4 dimethyl benzoic acid	7.64	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
29	trans eugenol	329.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
30	4-ethyl catechol	1.51	N.D.	0.61	0.12	0.09	0.12	0.34	0.13	0.40	0.03
31	levoglucosan	174.90	N.D.	0.18	0.96	N.D.	25.16	N.D.	N.D.	N.D.	N.D.
32	acetovanillone	15.71	0.04	0.44	0.20	N.D.	0.05	N.D.	N.D.	N.D.	N.D.
33	oleic acid	92.45	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
34*	propanoic acid	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	9.6	5.0	N.D.	6.9
35*	butanoic acid	N.D.	N.D.	N.D.	N.D.	N.D.	4.8	4.7	N.D.	4.3	N.D.
36*	acetic acid	151.3	N.D.	64.9	69.1	N.D.	82.9	64.6	N.D.	84.1	60.1
37*	1,2-propane diol	N.D.	N.D.	N.D.	N.D.	N.D.	6.6	N.D.	N.D.	N.D.	N.D.
38*	1-hydroxy 2-propanone	113.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
39*	1,3 butane diol	22.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
40*	1-methyl acetic acid	41.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
41*	2 hydroxy Imidazol 2-one	49.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
42*	4-methyl 5H furan	23.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
43*	trimethyl urea	10.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
44*	2-allyl phenol	10.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
45*	2-methoxy 4-vinyl phenol	28.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
46*	benzeneacetic acid	55.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
47*	hexa decanoic acid	17.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

* - Tentatively Identified Non-target Compounds N.D. - Not Detected

Table 4.4 Quantitative analysis results (50 wt. % Bio-oil / 50 wt. % water in charge)

All concentrations are in µg/mL		Crude bio-oil	Liquid product from treatment								
			Reaction temperature (° C) 300 °C			380 °C			420 °C		
			Reaction time (h)			Reaction time (h)			Reaction time (h)		
S. no.	Compound		0.5	1	5	0.5	1	5	0.5	1	5
1	Furfural	64.96	N.D.	N.D.	N.D.	0.51	2.49	N.D.	0.66	2.65	2.96
2	2-Furanmethanol	35.87	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
3	2-methyl 2-cyclopenten-1-one	15.81	5.45	6.61	N.D.	0.92	N.D.	N.D.	0.50	N.D.	N.D.
4	2-furanone	99.56	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
5	5-methyl 2-furancarboxaldehyde	18.70	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
6	3-methyl 2-cyclopenten-1-one	28.03	0.12	3.79	N.D.	0.71	N.D.	N.D.	N.D.	N.D.	N.D.
7	Phenol	111.59	6.99	49.13	46.70	2.22	119.40	122.30	N.D.	124.78	73.30
8	3-methyl 1,2- Cyclopetanedione	122.68	N.D.	N.D.	N.D.	1.46	N.D.	N.D.	N.D.	N.D.	N.D.
9	2-methyl phenol	52.91	1.93	5.34	15.23	0.33	31.91	29.31	N.D.	36.90	23.94
10	3-methyl phenol	92.88	2.27	14.26	9.48	0.60	29.29	15.08	N.D.	12.02	20.39
11	2-methoxy phenol	34.08	6.97	10.11	9.00	2.26	3.14	N.D.	N.D.	N.D.	N.D.
12	2,6 dimethyl phenol	4.18	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
13	2,4 dimethyl phenol	45.15	0.68	N.D.	N.D.	N.D.	1.04	1.27	N.D.	1.56	1.21
14	3-ethyl phenol	13.65	N.D.	N.D.	N.D.	N.D.	1.92	N.D.	N.D.	N.D.	N.D.
15	2,3 dimethyl phenol	5.78	N.D.	N.D.	N.D.	N.D.	1.49	N.D.	N.D.	N.D.	N.D.
16	naphthalene	7.11	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
17	2-methoxy 4-methyl phenol	51.54	2.56	4.99	1.26	0.32	N.D.	N.D.	N.D.	N.D.	N.D.
18	1,2 benzene diol	352.14	N.D.	47.73	37.69	N.D.	52.35	27.40	N.D.	52.69	N.D.
19	5-hydroxymethyl furfural	47.51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
20	4-methyl 1,2 benzene diol	93.19	N.D.	N.D.	N.D.	N.D.	15.44	N.D.	N.D.	16.99	N.D.
21	4-ethyl 2-methoxy phenol	13.09	0.33	N.D.	N.D.	0.03	N.D.	N.D.	N.D.	N.D.	N.D.
22	3-methyl 1,2 benzene diol	268.17	N.D.	N.D.	23.01	N.D.	56.72	34.90	N.D.	43.96	N.D.
23	2,6 dimethoxy phenol	0.05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
24	eugenol	15.73	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
25	2-methoxy 4-propyl phenol	4.89	0.03	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
26	naphthalene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
27	naphthalene	103.38	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
28	3,4 dimethyl benzoic acid	7.64	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
29	trans eugenol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
30	4-ethyl catechol	1.51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
31	levoglucosan	174.90	N.D.	7.03	293.70	N.D.	7.13	N.D.	N.D.	7.13	N.D.
32	acetovanillone	15.71	0.49	N.D.	N.D.	0.54	N.D.	N.D.	N.D.	N.D.	N.D.
33	oleic acid	92.45	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
34*	propanoic acid	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D.
35*	butanoic acid	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D.
36*	acetic acid	151.3	138.9	350.9	483.4	N.D.	517.1	N.D.	N.D.	506.6	188.5
37*	1,2-propane diol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	402.4	N.D.	N.D	N.D
38*	1-hydroxy 2-propanone	113.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
39*	1,3 butane diol	22.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
40*	1-methyl acetic acid	41.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
41*	2 hydroxy Imidazol 2-one	49.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
42*	4-methyl 5H furan	23.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
43*	trimethyl urea	10.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
44*	2-allyl phenol	10.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
45*	2-methoxy 4-vinyl phenol	28.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
46*	benzeneacetic acid	55.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D
47*	hexa decanoic acid	17.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	N.D

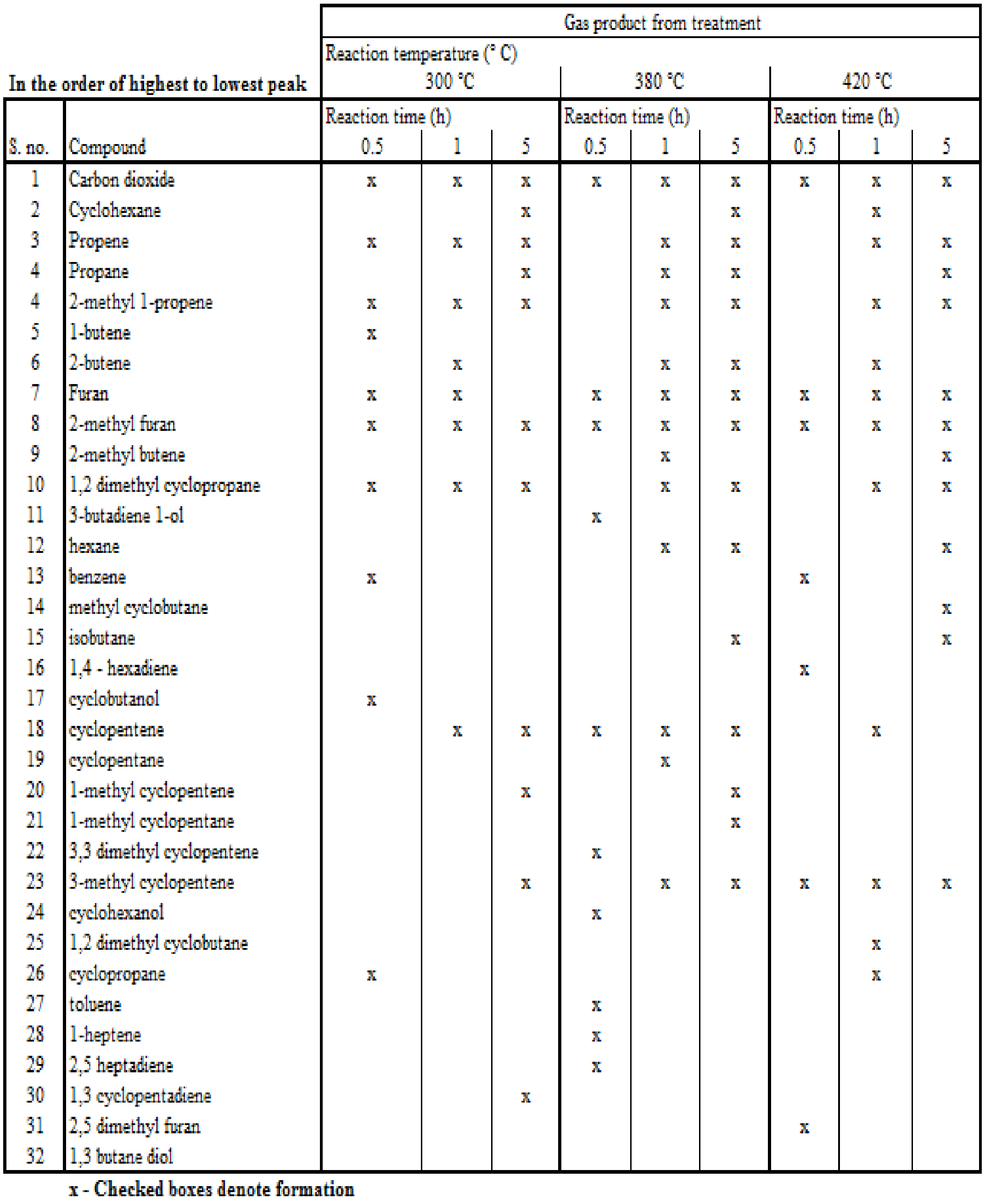
* - Tentatively Identified Non-target Compounds

Table 4.5 List of new compounds formed – identified through qualitative analysis (Liquid phase products)

			Liquid product from treatment								
			Reaction temperature (° C)								
			300 °C			380 °C			420 °C		
		Retention	Reaction time (h)			Reaction time (h)			Reaction time (h)		
S. no.	Compound	time (min)	0.5	1	5	0.5	1	5	0.5	1	5
I	**AROMATICS**										
1	**Benzene**	19.72		x			x				x
2	**Phenols**										
2-a	Guaiacol	2.52	x	x	x		x				
2-b	2-methyl phenol	11.66				x	x	x	x		x
2-c	3-methyl phenol	12.33					x		x		x
2-d	4-methyl catechol	19.72			x		x	x		x	
2-e	4-ethyl catechol	21.21			x		x				
2-f	4,5 dimethyl 1,3 benzene diol	20.36					x	x			
3	**Acids**										
3-a	Acetic acid	1.70	x	x	x		x	x	x	x	x
3-b	Propanoic acid	2.29		x	x		x	x	x	x	x
3-c	Butanoic acid	3.63						x		x	
4	**Esters**										
4-a	Formic acid methyl ester	2.88									
4-b	Formic acid ethyl ester	2.23		x			x				
4-d	Formic acid 1-methyl propyl ester	2.16				x					
5	**Ethers**										
5-a	2-vinyloxy ethanol	2.14			x	x					
5-b	2-ethoxy propane	2.26			x	x			x		
5-c	5-methoxy 1-pentanol	2.16									
5-d	1-methoxy 2-propane	2.19	x								
6	**Misc. oxygenates**										
6-a	1-methyl hydroperoxide	2.25									
6-b	dimethyl hydroquinone	20.42								x	
6-c	2,5 dihydro furan	12.07		x							
6-d	cyclohexen -1 yl 1-ethanone	12.49				x					
6-e	α- hydroxy benzeneacetic acid	27.59									
II	**ALIPHATICS**										
7-a	3-penten 1-yne	9.31		x			x	x			x
	1,5 hexadiyne	12.35									x
7-b	2,4 hexadiyne / 1,5 hexadiyne	9.75					x				
7-d	2-hexanol	2.27								x	
7-e	1,7 octadiyne	19.19								x	
7-f	3-methyl 2-butanol	2.15									x

x - Checked boxes denote formation

Table 4.6 List of new compounds formed – identified through qualitative analysis (Gas phase products)



In the order of highest to lowest peak

		Gas product from treatment								
		Reaction temperature (° C) 300 °C			380 °C			420 °C		
		Reaction time (h)			Reaction time (h)			Reaction time (h)		
S. no.	Compound	0.5	1	5	0.5	1	5	0.5	1	5
1	Carbon dioxide	x	x	x	x	x	x	x	x	x
2	Cyclohexane			x			x		x	
3	Propene	x	x	x		x	x		x	x
4	Propane			x		x	x			x
4	2-methyl 1-propene	x	x	x		x	x		x	x
5	1-butene	x								
6	2-butene		x			x	x		x	
7	Furan	x	x		x	x	x	x	x	x
8	2-methyl furan	x	x	x	x	x	x	x	x	x
9	2-methyl butene					x				x
10	1,2 dimethyl cyclopropane	x	x	x		x	x		x	x
11	3-butadiene 1-ol				x					
12	hexane					x	x			x
13	benzene	x						x		
14	methyl cyclobutane									x
15	isobutane						x			x
16	1,4 - hexadiene							x		
17	cyclobutanol	x								
18	cyclopentene		x	x	x	x	x		x	
19	cyclopentane					x				
20	1-methyl cyclopentene			x			x			
21	1-methyl cyclopentane						x			
22	3,3 dimethyl cyclopentene				x					
23	3-methyl cyclopentene			x		x	x	x	x	x
24	cyclohexanol				x					
25	1,2 dimethyl cyclobutane								x	
26	cyclopropane	x							x	
27	toluene				x					
28	1-heptene				x					
29	2,5 heptadiene				x					
30	1,3 cyclopentadiene			x						
31	2,5 dimethyl furan							x		
32	1,3 butane diol									

x - Checked boxes denote formation

4.6 ANALYSIS OF PHYSICAL PROPERTIES

Another perspective to look at is to examine physical properties like water content, acidity and elemental composition of liquid product the results of which are discussed in this section.

4.6.1 Water content analysis

The result from water content analysis are given in table E.1 in appendix E. Bio-oil used in this study contains 16.08 % by weight moisture. Depending on the charge the composition of water in the initial charge varied between 50 and 75 % by weight for experiments using 50 and 25 % by weight of bio-oil respectively. Using these data the total amount of water present in the initial charge can be calculated. Water content in the treated liquid samples were analyzed at Department of Forest Products using Karl Fischer apparatus. These results reveal that mixed trends were observed. Although most of the experiments led to a reduction in water content, some of the experiments did increase the water content as a result of the treatment. Reduction in water content was higher at shorter reaction times (0.5, 1 hour) when compared to the 5 hour treatment. The presence of methanol did reduce the efficiency of reduction in water content at 300 °C. However at the higher operating conditions, it did not show to have any significant influence on reduction of water content. However using higher bio-oil (50 wt.%) in the charge did have a negative influence on the reduction in water content, as witnessed by the formation of water as a result of the treatment. However, using lesser bio-oil in the charge gave good results with a maximum reduction in water content of 31.87% and a minimum of 5.87%.

4.6.2 Acid value analysis

Results of acid value analysis performed on the treated liquid samples are given in table E.2 in appendix E. Acid value of untreated bio-oil was 80.56. The results reveal that the acid value of samples of experiments using 50 wt. % bio-oil in charge were higher than that using 25 wt. % bio-oil as expected due to the increase in acidity contributed by increase in bio-oil composition. Reaction temperature showed to have a strong influence on acidity of the treated liquid samples. Treatment at higher temperatures showed better results with respect to reduction of acid value. The average acid values of samples treated at 300, 380 and 420 °C were 30.14, 21.90 and 18.74 respectively. Likewise, reaction time also had a reasonable influence on the acid value of the treated samples. Longer the reaction time, lesser was the acid value. For experiments using 25 wt.% bio-oil in charge, the acid value of treated samples were 20.10, 17.34 and 16.46 for 0.5, 1 and 5 hour reaction times respectively. Similar trends were observed with experiments using 50 wt. % bio-oil, wherein the acid value of treated liquid samples were 35.95, 32.24, 29.65 for 0.5, 1 and 5 hour reaction times respectively.

4.6.3 Elemental composition analysis

The results of elemental analysis are given in table E.3 in appendix E. Elemental analysis of untreated bio-oil and treated liquid samples were carried out by Department of Forest Products analytical laboratory. These results reveal that the carbon, hydrogen, nitrogen and oxygen composition was 38.84, 6.44, 0.39 and 54.33 % by weight respectively. By knowing the mass of bio-oil and water charged for each experiment, the mass balance of carbon, hydrogen, nitrogen and oxygen in the feed was determined (Refer table E.3). Similarly, with the knowledge of mass of liquid product obtained from each experiment, a mass balance of carbon, hydrogen, nitrogen and oxygen in the treated liquid sample was made. This revealed that there is a significant reduction in carbon and oxygen content as a result of the treatment. Bio-oil composition in charge did show significant influence on the efficiency of reduction in oxygen content. Average reduction in oxygen content was found to be 18.44 and 22.92 % when using 50 wt.% and 25 wt.% bio-oil respectively. Reaction time was also found to have a reasonable influence on reduction in oxygen content. Shorter reaction time resulted in a greater reduction in oxygen content. On an average, reduction in oxygen content was 21.17, 23.67 and 16.83 % for 0.5, 1 and 5 hour reaction times respectively. Reaction temperature also showed to have a reasonable influence over reduction in oxygen content. On an average, reduction in oxygen content was 23.43, 21.29 and 18.29 % for treatment at 300, 380 and 420 °C respectively. Hence a lower reaction temperature is favored. However hydrogen composition was not altered much as a result of the treatment.

4.7 PHASE SEPARATION STUDY WITH BIO-OIL SIMULANT

The main objective of this component was to evaluate the threshold water content that the bio-oil simulant could hold without undergoing phase separation. Experiments were carried out by placing 10 g of bio-oil simulant in a 100 mL beaker. The beaker was then mounted on a stirring plate and stirred with the help of a magnetic stirrer at 300 rpm.

Distilled water was filled into a burette positioned just over the beaker. Aliquots of 0.5 cc of water were metered into the beaker. After addition of each aliquot, the beaker contents were stirred for ~ 5 minutes, then halted. Visual inspection of the beaker contents for phase separation was carried out. This procedure was repeated until phase separation occurred. Phase separation was observed after addition of 4.5 cc of water addition. This corresponded to 44.83 % by volume of water in the system (including water that was already present in the bio-oil simulant). Complete results for the phase separation studies are contained in Appendix C.

4.8 MISCIBILITY STUDIES WITH DIESEL

4.8.1 Treated and untreated bio-oil simulant with diesel

Miscibility of the treated and untreated bio-oil simulant with diesel was studied by taking different proportions of bio-oil simulant to diesel (50 wt.% bio-oil simulant in the mixture to 5 wt% bio-oil stimulant; decrements of 5wt.%). The pseudo-binary mixture was then placed in a 100 mL beaker, mounted on a stirring plate and stirred with a magnetic stirrer at 300 rpm for about 5 minutes. Visual inspection of the sample allowed assessment of miscibility. For all mixtures examined, immiscibility was observed, with the formation of two liquid phases.

4.8.2 Treated bio-oil with diesel

Miscibility of the treated bio-oil with diesel was studied by taking different proportions of bio-oil to diesel from as high as 50 wt% bio oil sample in the mixture to as low as 5 wt% bio oil sample in decrements of 5wt% each time. Organic phase of the bio-oil samples were also used in the study (The aqueous and organic phase of the bio-oil samples were obtained by using dichloromethane as the organic solvent).

Figure 4.40 Separation of aqueous and organic phases using dichloromethane

The multi-component system was then taken in a 100 mL beaker, mounted on a stirring plate and stirred with the help of a magnetic stirrer at 300 rpm for about 5 minutes. After this, visual inspection of the sample was carried out. The experiments revealed that for all the combinations tried (including that of the organic phase of the treated bio-oil with diesel) two liquid phases were present.

Figure 4.41 Miscibility studies with diesel

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 SUMMARY OF THE WORK

This work investigated the effect of supercritical water treatment on the composition of bio-oil. One of the primary objectives of the proposed work was to change bio-oil composition, especially through elimination of undesirable components that contribute to coke formation. Preliminary studies were carried out in a 500 mL Parr reactor using supercritical water treatment on a model bio-oil which were aimed at gaining a better understanding of the bio-oil treatment process and the chemistry involved. This model bio-oil which was prepared using ten compounds[2.14] had the reduced complexity, yet had the same reactive functional groups as in the original bio-oil. This was later followed up with studies using supercritical water treatment on crude bio-oil. The critical process parameters were reaction temperature, reaction time and oil/water mass ratio. The operating temperatures chosen were 300 , 380 and 420 °C while the oil composition chosen were 25 and 50 wt.%. The time length of treatment was varied between 30 minutes, 1 hour and 5 hours. The studies revealed that some of the undesirable components that were known to contribute significantly towards coke formation were effectively converted or eliminated as a result of the treatment.

5.2 CONCLUSIONS

Studies to examine the product distribution of supercritical water treatment of bio oil revealed that some coumpounds that has been known to contribute seriously to coke formation have been effectively converted or eliminated. Furfural is known to be one of bigger contributors to coking of catalysts. It was found that as a result of the treatment, an average conversion of 93.78, 90.28 and 92.38% were achieved with treatment at 300, 380 and 420 °C respectively. Though it did not show any preference for operating temperature, the conversion using 50 wt.% bio-oil in initial charge was superior to that using 25 wt.% bio-oil in initial charge. This was also confirmed from statistical analysis using ANOVA performed using SAS software at 90% significance level (results are included in Appendix D). In contrast, Guaiacol conversion showed a clear preference for operating conditions. While conversion at 420 °C was very impressive at 99.33%, the same at subcritical conditions (300 °C) was 69.92 %.

On the contrary, with phenol the conversion was higher at subcritical conditions than at much harsher conditions. This could also be due to the fact that more phenol is formed from guaiacol at the higher operating conditions which increase its concentration in the product phase. However, phenol did show a strong preference for oil composition. A lesser oil composition (25 wt.%) gave higher conversions when compared to 50 wt.%. This was also confirmed by the statistical analysis. Catechol conversion on the other hand did not show any preference for operating condition nor oil composition. Instead its conversion was more dependent on reaction time. The shortest reaction time (30 min) gave an average conversion of 97.014 % while extended treatment reduced the conversions. This can be explained from the fact that phenol gets converted to catechol and other substituted phenols during the longer reaction time which could be a logical explanation for the reduced conversions.

Vanillin is also known to contribute significantly to coking of catalysts. It was very evident that as a result of the treatment vanillin was nearly completely converted. This was observed at all operating temperatures and for all oil compositions. Guaiacol is one of the likely products from vanillin. Other products are likely 2-methoxy phenol and 4-methyl 2-methoxy phenol. Levoglucosan which is formed as a product from the decomposition of glucose, another coke precursor, was also completely removed as a result of the treatment. This was true for all operating conditions and for all oil compositions.

Acetic acid remained stable during the treatment. Formation of acetic acid was generally observed during the first one hour of treatment. During the extended treatment two distinctly different trends were observed at subcritical and supercritical conditions.

At 300 °C, acetic acid formation was observed even during the longer treatment while it was observed to have been consumed during the longer reaction time at 380 and 420 °C. Another interesting observation was that acetic acid formation was very less during the shortest reaction time (30 min).

Experiments using methanol as co-solvent did not have any significant impact on the conversion of compounds of interest or on the product distribution except with oleic acid. A very interesting fact that was observed with all the experiments was that significant amount of oleic acid was formed when methanol was used as co-solvent. In its absence, no evidence of oleic acid formation was observed.

The current study has revealed that supercritical water treatment can efficiently eliminate certain compounds which are known to impart undesirable characteristics like coking of catalysts. It has been identified that shortest reaction time (30 min) gave the best results and a higher oil composition in initial charge was preferred for higher conversion of furfural, which is the biggest contributor to coking. Thus the best operating conditions for the treatment were identified and the product distribution after supercritical water treatment was ascertained.

5.3 PATH FORWARD

Although the characteristics of the product after supercritical water treatment seem to be better due to the absence or reduced concentration of many undesirable components, the water tends to form a homogeneous phase with the treated oil. This in turn will reduce the calorific value or heating value of treated bio oil. Hence an efficient way to remove water from the system must be ascertained. One possible technique to use could be concentration method.[2.8] This technique involves concentration of bio-oil by means of evaporation in a Buchi Rotavapor apparatus held under vacuum at relatively low temperature (about 40 °C). This can also remove the volatiles which would otherwise cause undesirable effects like lowering of flash point of bio-oil.

Another perspective of the current study could be to examine the rheological properties of the bio-oil before and after treatment. An elemental composition determination can provide a better picture of whether the oxygen content has been reduced in the bio-oil as a result of the treatment.

APPENDIX A

SAMPLE CALCULATIONS

Quantitative analysis using GC-MS gives the concentration of each compound of interest in µg/mL (i.e.) micro grams of the compound of interest that would be present in 10 mL of the solvent. Hence an explanation of how the conversions were computed from these data is furnished here for further clarity.

Suppose:

C_1 : Concentration of the compound of interest obtained from quantitative analysis using GC-MS of untreated bio oil (µg/mL)

C_2 : Concentration of the compound of interest obtained from quantitative analysis using GC-MS of liquid product sample (µg/mL)

S_1 : Grams of untreated bio-oil sample dissolved in 10 mL of solvent

S_2 : Grams of treated liquid product sample dissolved in 10 mL of solvent

F : Mass of bio-oil charged initially (g)

P : Mass of liquid product collected after treatment (g)

A.1 Composition in feed:

To calculate the composition of the compound of interest in feed, it is important to know the total mass of bio-oil that was charged into the reactor. The calculation is performed:

$$\text{Mass of compound (g) present in 1 g of sample} = \frac{C_1\left(\frac{\mu g}{mL}\right)\times 10(mL)\times 10^{-6}\left(\frac{g}{\mu g}\right)}{S_1\left(\frac{g}{10mL}\right)}$$

Hence the total mass of compound that would be present in F grams of total initial charge is calculated:

Mass of compound (g) present in initial charge = $\dfrac{C_1\left(\dfrac{\mu g}{mL}\right)\times 10(mL)\times 10^{-6}\left(\dfrac{g}{\mu g}\right)}{S_1\left(\dfrac{g}{10mL}\right)}\times F(g)$

This mass of the compound of interest in initial charge is x_f.

A.2 Composition in product phase:

To calculate the composition of the compound of interest in the product phase, it is important to know the total mass of liquid product that was recovered from the experiment. The calculation is performed:

Mass of compound (g) present in 1 g of liquid product =

$$\frac{C_2\left(\dfrac{\mu g}{mL}\right)\times 10(mL)\times 10^{-6}\left(\dfrac{g}{\mu g}\right)}{S_2\left(\dfrac{g}{10mL}\right)}$$

Hence the total mass of compound that would be present in P grams of total liquid product obtained is calculated:

Mass of compound (g) present in initial charge = $\dfrac{C_2\left(\dfrac{\mu g}{mL}\right)\times 10(mL)\times 10^{-6}\left(\dfrac{g}{\mu g}\right)}{S_2\left(\dfrac{g}{10mL}\right)}\times P(g)$

This mass of the compound of interest in initial charge is x_p.

A.3 Conversion calculation:

Conversion of the compound of interest as a result of the treatment is calculated:

$$\text{Conversion (\%)} = \frac{x_f - x_p}{x_f} \times 100$$

APPENDIX B

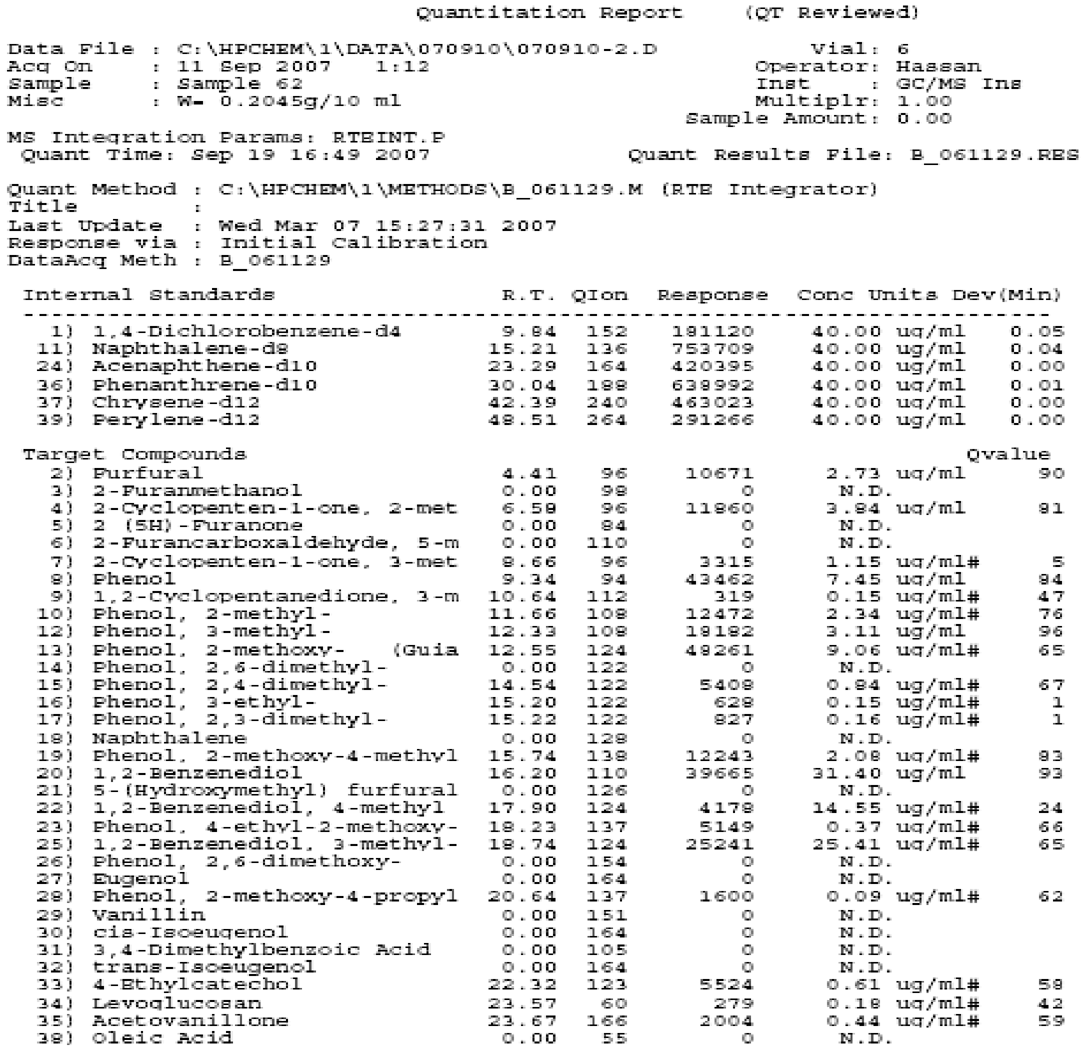
GC-MS DATA OF BIO-OIL

EXPERIMENTAL

RESULTS

B.1 Quantitative report of treated liquid samples

Experiment no.	: 62
Oil composition in bio oil-water mixture	: 25 wt.%
Reaction temperature	: 300 °C
Reaction time	: 1 h



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                          Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\070910\070910-2.D            Vial: 6
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Sample    : Sample 62                                 Inst    : GC/MS Ins
Misc      : W= 0.2045g/10 ml                          Multiplr: 1.00
                                                 Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Sep 19 16:49 2007             Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                   R.T. QIon  Response  Conc Units Dev(Min)
 -------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4          9.84  152   181120    40.00 ug/ml    0.05
  11) Naphthalene-d8                 15.21  136   753709    40.00 ug/ml    0.04
  24) Acenaphthene-d10               23.29  164   420395    40.00 ug/ml    0.00
  36) Phenanthrene-d10               30.04  188   638992    40.00 ug/ml    0.01
  37) Chrysene-d12                   42.39  240   463023    40.00 ug/ml    0.00
  39) Perylene-d12                   48.51  264   291266    40.00 ug/ml    0.00

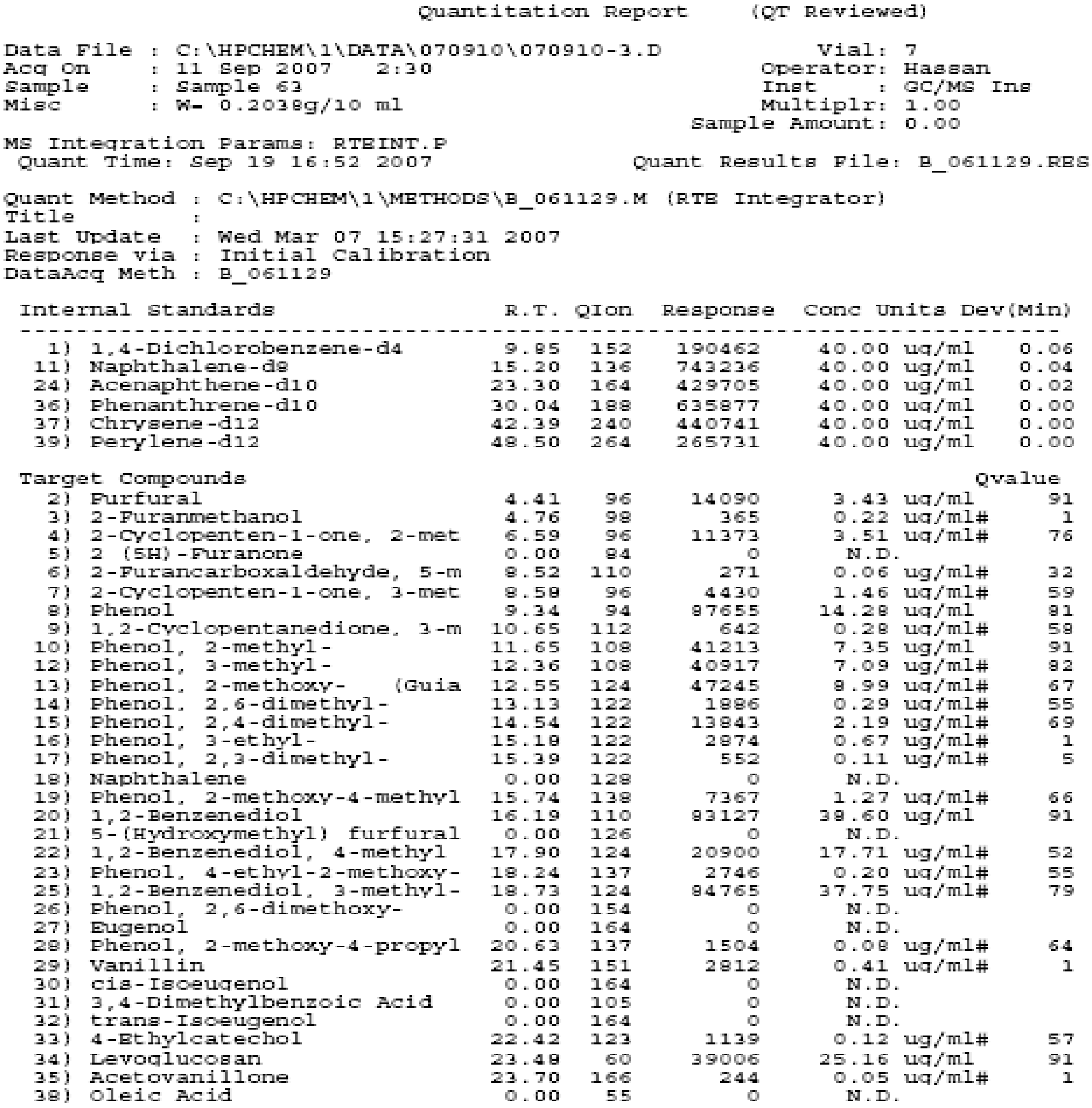
 Target Compounds                                                     Qvalue
   2) Furfural                        4.41   96    10671     2.73 ug/ml     90
   3) 2-Furanmethanol                 0.00   98        0      N.D.
   4) 2-Cyclopenten-1-one, 2-met      6.58   96    11860     3.84 ug/ml     81
   5) 2 (5H)-Furanone                 0.00   84        0      N.D.
   6) 2-Furancarboxaldehyde, 5-m      0.00  110        0      N.D.
   7) 2-Cyclopenten-1-one, 3-met      8.66   96     3315     1.15 ug/ml#     5
   8) Phenol                          9.34   94    43462     7.45 ug/ml     94
   9) 1,2-Cyclopentanedione, 3-m     10.64  112      319     0.15 ug/ml#    47
  10) Phenol, 2-methyl-              11.66  108    12472     2.34 ug/ml#    76
  12) Phenol, 3-methyl-              12.33  108    18182     3.11 ug/ml     96
  13) Phenol, 2-methoxy-   (Guia     12.55  124    48261     9.06 ug/ml#    65
  14) Phenol, 2,6-dimethyl-           0.00  122        0      N.D.
  15) Phenol, 2,4-dimethyl-          14.54  122     5408     0.84 ug/ml#    67
  16) Phenol, 3-ethyl-               15.20  122      628     0.15 ug/ml#     1
  17) Phenol, 2,3-dimethyl-          15.22  122      827     0.16 ug/ml#     1
  18) Naphthalene                     0.00  128        0      N.D.
  19) Phenol, 2-methoxy-4-methyl     15.74  138    12243     2.08 ug/ml#    83
  20) 1,2-Benzenediol                16.20  110    39665    31.40 ug/ml     93
  21) 5-(Hydroxymethyl) furfural      0.00  126        0      N.D.
  22) 1,2-Benzenediol, 4-methyl      17.90  124     4178    14.55 ug/ml#    24
  23) Phenol, 4-ethyl-2-methoxy-     18.23  137     5149     0.37 ug/ml#    66
  25) 1,2-Benzenediol, 3-methyl-     18.74  124    25241    25.41 ug/ml#    65
  26) Phenol, 2,6-dimethoxy-          0.00  154        0      N.D.
  27) Eugenol                         0.00  164        0      N.D.
  28) Phenol, 2-methoxy-4-propyl     20.64  137     1600     0.09 ug/ml#    62
  29) Vanillin                        0.00  151        0      N.D.
  30) cis-Isoeugenol                  0.00  164        0      N.D.
  31) 3,4-Dimethylbenzoic Acid        0.00  105        0      N.D.
  32) trans-Isoeugenol                0.00  164        0      N.D.
  33) 4-Ethylcatechol                22.32  123     5524     0.61 ug/ml#    58
  34) Levoglucosan                   23.57   60      279     0.18 ug/ml#    42
  35) Acetovanillone                 23.67  166     2004     0.44 ug/ml#    59
  38) Oleic Acid                      0.00   55        0      N.D.
```

Experiment no. : 63

Oil composition in bio oil-water mixture : 25 wt.%

Reaction temperature : 380 °C

Reaction time : 1 h



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                              Quantitation Report    (QT Reviewed)

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Misc      : W- 0.2038g/10 ml                          Multiplr: 1.00
                                                 Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Sep 19 16:52 2007              Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
 ----------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4         9.85  152    190462    40.00 ug/ml    0.06
  11) Naphthalene-d8                15.20  136    743236    40.00 ug/ml    0.04
  24) Acenaphthene-d10              23.30  164    429705    40.00 ug/ml    0.02
  36) Phenanthrene-d10              30.04  188    635877    40.00 ug/ml    0.00
  37) Chrysene-d12                  42.39  240    440741    40.00 ug/ml    0.00
  39) Perylene-d12                  48.50  264    265731    40.00 ug/ml    0.00

 Target Compounds                                                      Qvalue
   2) Furfural                       4.41   96     14090     3.43 ug/ml     91
   3) 2-Furanmethanol                4.76   98       365     0.22 ug/ml#     1
   4) 2-Cyclopenten-1-one, 2-met     6.59   96     11373     3.51 ug/ml#    76
   5) 2 (5H)-Furanone                0.00   84         0      N.D.
   6) 2-Furancarboxaldehyde, 5-m     8.52  110       271     0.06 ug/ml#    32
   7) 2-Cyclopenten-1-one, 3-met     8.58   96      4430     1.46 ug/ml#    59
   8) Phenol                         9.34   94     87655    14.28 ug/ml     91
   9) 1,2-Cyclopentanedione, 3-m    10.65  112       642     0.28 ug/ml#    58
  10) Phenol, 2-methyl-             11.65  108     41213     7.35 ug/ml     91
  12) Phenol, 3-methyl-             12.36  108     40917     7.09 ug/ml#    82
  13) Phenol, 2-methoxy-   (Guia    12.55  124     47245     8.99 ug/ml#    67
  14) Phenol, 2,6-dimethyl-         13.13  122      1886     0.29 ug/ml#    55
  15) Phenol, 2,4-dimethyl-         14.54  122     13843     2.19 ug/ml#    69
  16) Phenol, 3-ethyl-              15.18  122      2874     0.67 ug/ml#     1
  17) Phenol, 2,3-dimethyl-         15.39  122       552     0.11 ug/ml#     5
  18) Naphthalene                    0.00  128         0      N.D.
  19) Phenol, 2-methoxy-4-methyl    15.74  138      7367     1.27 ug/ml#    66
  20) 1,2-Benzenediol               16.19  110     83127    38.60 ug/ml     91
  21) 5-(Hydroxymethyl) furfural     0.00  126         0      N.D.
  22) 1,2-Benzenediol, 4-methyl     17.90  124     20900    17.71 ug/ml#    52
  23) Phenol, 4-ethyl-2-methoxy-    18.24  137      2746     0.20 ug/ml#    55
  25) 1,2-Benzenediol, 3-methyl-    18.73  124     84765    37.75 ug/ml#    79
  26) Phenol, 2,6-dimethoxy-         0.00  154         0      N.D.
  27) Eugenol                        0.00  164         0      N.D.
  28) Phenol, 2-methoxy-4-propyl    20.63  137      1504     0.08 ug/ml#    64
  29) Vanillin                      21.45  151      2812     0.41 ug/ml#     1
  30) cis-Isoeugenol                 0.00  164         0      N.D.
  31) 3,4-Dimethylbenzoic Acid       0.00  105         0      N.D.
  32) trans-Isoeugenol               0.00  164         0      N.D.
  33) 4-Ethylcatechol               22.42  123      1139     0.12 ug/ml#    57
  34) Levoglucosan                  23.48   60     39006    25.16 ug/ml     91
  35) Acetovanillone                23.70  166       244     0.05 ug/ml#     1
  38) Oleic Acid                     0.00   55         0      N.D.
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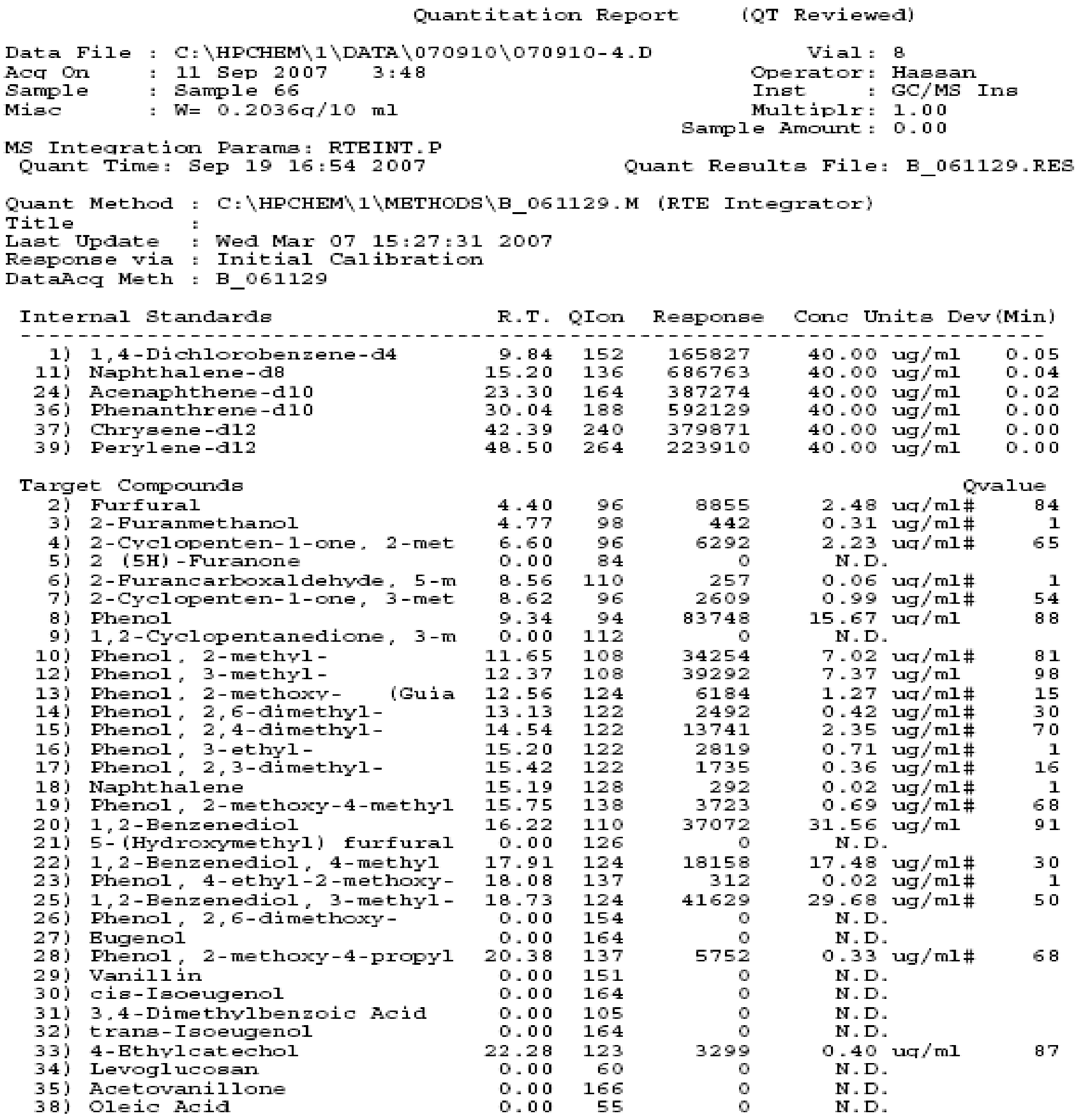
Experiment no. : 66

Oil composition in bio oil-water mixture : 25 wt.%

Reaction temperature : 420 °C

Reaction time : 1 h



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                            Quantitation Report     (QT Reviewed)

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                                                Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Sep 19 16:54 2007              Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                         R.T. QIon  Response  Conc Units Dev(Min)
 -----------------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4                9.84  152   165827    40.00 ug/ml    0.05
  11) Naphthalene-d8                       15.20  136   686763    40.00 ug/ml    0.04
  24) Acenaphthene-d10                     23.30  164   387274    40.00 ug/ml    0.02
  36) Phenanthrene-d10                     30.04  188   592129    40.00 ug/ml    0.00
  37) Chrysene-d12                         42.39  240   379871    40.00 ug/ml    0.00
  39) Perylene-d12                         48.50  264   223910    40.00 ug/ml    0.00

 Target Compounds                                                          Qvalue
   2) Furfural                              4.40   96     8855     2.48 ug/ml#    84
   3) 2-Furanmethanol                       4.77   98      442     0.31 ug/ml#     1
   4) 2-Cyclopenten-1-one, 2-met            6.60   96     6292     2.23 ug/ml#    65
   5) 2 (5H)-Furanone                       0.00   84        0      N.D.
   6) 2-Furancarboxaldehyde, 5-m            8.56  110      257     0.06 ug/ml#     1
   7) 2-Cyclopenten-1-one, 3-met            8.62   96     2609     0.99 ug/ml#    54
   8) Phenol                                9.34   94    83748    15.67 ug/ml     88
   9) 1,2-Cyclopentanedione, 3-m            0.00  112        0      N.D.
  10) Phenol, 2-methyl-                    11.65  108    34254     7.02 ug/ml#    81
  12) Phenol, 3-methyl-                    12.37  108    39292     7.37 ug/ml     98
  13) Phenol, 2-methoxy-   (Guia           12.56  124     6184     1.27 ug/ml#    15
  14) Phenol, 2,6-dimethyl-                13.13  122     2492     0.42 ug/ml#    30
  15) Phenol, 2,4-dimethyl-                14.54  122    13741     2.35 ug/ml#    70
  16) Phenol, 3-ethyl-                     15.20  122     2819     0.71 ug/ml#     1
  17) Phenol, 2,3-dimethyl-                15.42  122     1735     0.36 ug/ml#    16
  18) Naphthalene                          15.19  128      292     0.02 ug/ml#     1
  19) Phenol, 2-methoxy-4-methyl           15.75  138     3723     0.69 ug/ml#    68
  20) 1,2-Benzenediol                      16.22  110    37072    31.56 ug/ml     91
  21) 5-(Hydroxymethyl) furfural            0.00  126        0      N.D.
  22) 1,2-Benzenediol, 4-methyl            17.91  124    18158    17.48 ug/ml#    30
  23) Phenol, 4-ethyl-2-methoxy-           18.08  137      312     0.02 ug/ml#     1
  25) 1,2-Benzenediol, 3-methyl-           18.73  124    41629    29.68 ug/ml#    50
  26) Phenol, 2,6-dimethoxy-                0.00  154        0      N.D.
  27) Eugenol                               0.00  164        0      N.D.
  28) Phenol, 2-methoxy-4-propyl           20.38  137     5752     0.33 ug/ml#    68
  29) Vanillin                              0.00  151        0      N.D.
  30) cis-Isoeugenol                        0.00  164        0      N.D.
  31) 3,4-Dimethylbenzoic Acid              0.00  105        0      N.D.
  32) trans-Isoeugenol                      0.00  164        0      N.D.
  33) 4-Ethylcatechol                      22.28  123     3299     0.40 ug/ml     87
  34) Levoglucosan                          0.00   60        0      N.D.
  35) Acetovanillone                        0.00  166        0      N.D.
  38) Oleic Acid                            0.00   55        0      N.D.
```
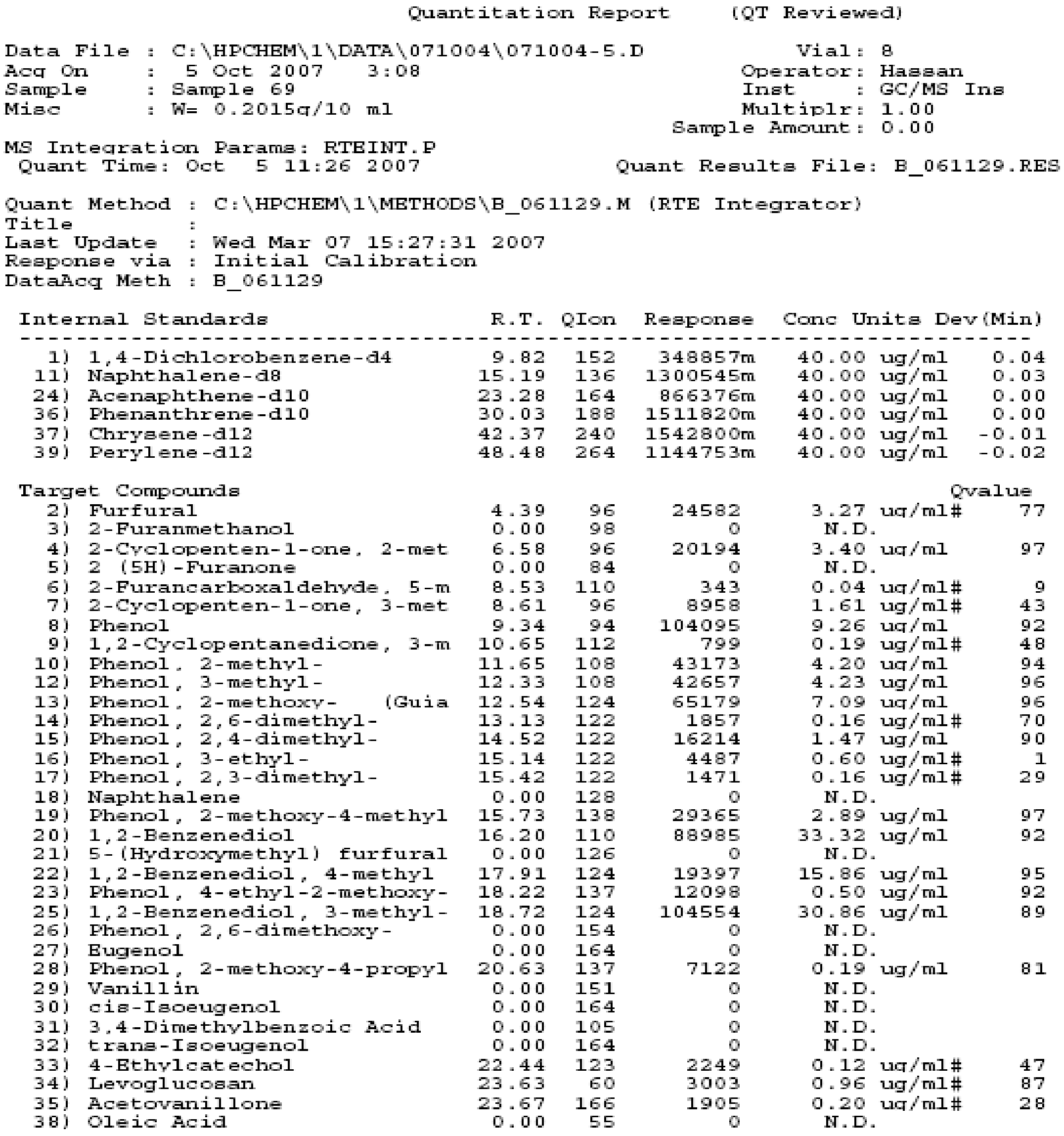

Experiment no. : 69

Oil composition in bio oil-water mixture : 25 wt.%

Reaction temperature : 300 °C

Reaction time : 5 h



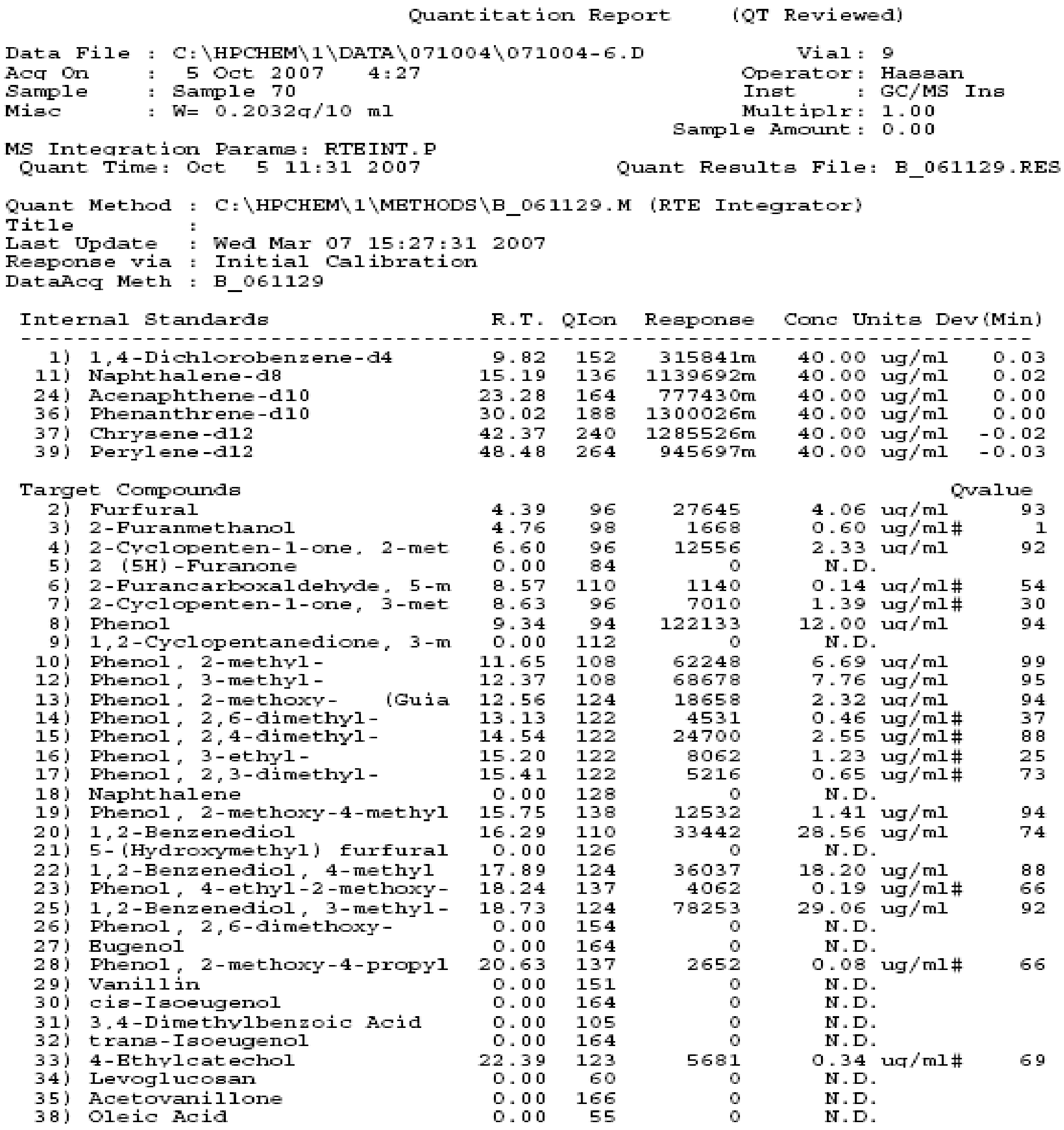
```
                        Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071004\071004-5.D              Vial: 8
Acq On    :  5 Oct 2007    3:08                         Operator: Hassan
Sample    : Sample 69                                   Inst     : GC/MS Ins
Misc      : W= 0.2015g/10 ml                            Multiplr: 1.00
                                                   Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Oct  5 11:26 2007              Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                 R.T. QIon  Response  Conc Units Dev(Min)
 -------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4       9.82  152   348857m   40.00 ug/ml   0.04
  11) Naphthalene-d8              15.19  136  1300545m   40.00 ug/ml   0.03
  24) Acenaphthene-d10            23.28  164   866376m   40.00 ug/ml   0.00
  36) Phenanthrene-d10            30.03  188  1511820m   40.00 ug/ml   0.00
  37) Chrysene-d12                42.37  240  1542800m   40.00 ug/ml  -0.01
  39) Perylene-d12                48.48  264  1144753m   40.00 ug/ml  -0.02

 Target Compounds                                                   Qvalue
   2) Furfural                     4.39   96    24582     3.27 ug/ml#    77
   3) 2-Furanmethanol              0.00   98        0      N.D.
   4) 2-Cyclopenten-1-one, 2-met   6.58   96    20194     3.40 ug/ml     97
   5) 2 (5H)-Furanone              0.00   84        0      N.D.
   6) 2-Furancarboxaldehyde, 5-m   8.53  110      343     0.04 ug/ml#     9
   7) 2-Cyclopenten-1-one, 3-met   8.61   96     8958     1.61 ug/ml#    43
   8) Phenol                       9.34   94   104095     9.26 ug/ml     92
   9) 1,2-Cyclopentanedione, 3-m  10.65  112      799     0.19 ug/ml#    48
  10) Phenol, 2-methyl-           11.65  108    43173     4.20 ug/ml     94
  12) Phenol, 3-methyl-           12.33  108    42657     4.23 ug/ml     96
  13) Phenol, 2-methoxy-   (Guia  12.54  124    65179     7.09 ug/ml     96
  14) Phenol, 2,6-dimethyl-       13.13  122     1857     0.16 ug/ml#    70
  15) Phenol, 2,4-dimethyl-       14.52  122    16214     1.47 ug/ml     90
  16) Phenol, 3-ethyl-            15.14  122     4487     0.60 ug/ml#     1
  17) Phenol, 2,3-dimethyl-       15.42  122     1471     0.16 ug/ml#    29
  18) Naphthalene                  0.00  128        0      N.D.
  19) Phenol, 2-methoxy-4-methyl  15.73  138    29365     2.89 ug/ml     97
  20) 1,2-Benzenediol             16.20  110    88985    33.32 ug/ml     92
  21) 5-(Hydroxymethyl) furfural   0.00  126        0      N.D.
  22) 1,2-Benzenediol, 4-methyl   17.91  124    19397    15.86 ug/ml     95
  23) Phenol, 4-ethyl-2-methoxy-  18.22  137    12098     0.50 ug/ml     92
  25) 1,2-Benzenediol, 3-methyl-  18.72  124   104554    30.86 ug/ml     89
  26) Phenol, 2,6-dimethoxy-       0.00  154        0      N.D.
  27) Eugenol                      0.00  164        0      N.D.
  28) Phenol, 2-methoxy-4-propyl  20.63  137     7122     0.19 ug/ml     81
  29) Vanillin                     0.00  151        0      N.D.
  30) cis-Isoeugenol               0.00  164        0      N.D.
  31) 3,4-Dimethylbenzoic Acid     0.00  105        0      N.D.
  32) trans-Isoeugenol             0.00  164        0      N.D.
  33) 4-Ethylcatechol             22.44  123     2249     0.12 ug/ml#    47
  34) Levoglucosan                23.63   60     3003     0.96 ug/ml#    87
  35) Acetovanillone              23.67  166     1905     0.20 ug/ml#    28
  38) Oleic Acid                   0.00   55        0      N.D.
```

Experiment no. : 70

Oil composition in bio oil-water mixture : 25 wt.%

Reaction temperature : 380 °C

Reaction time : 5 h



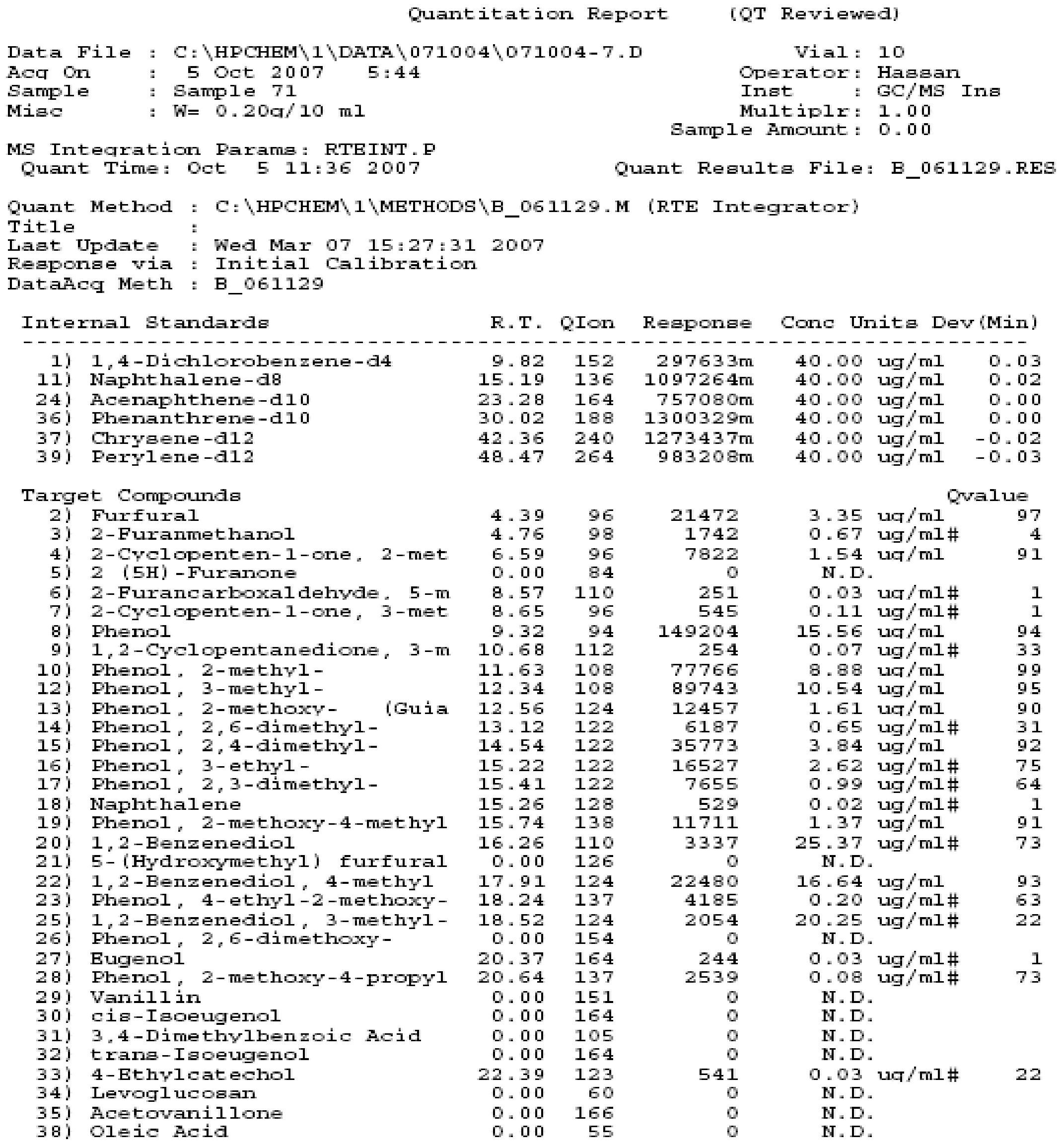
```
                                 Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071004\071004-6.D          Vial: 9
Acq On    :  5 Oct 2007   4:27                      Operator: Hassan
Sample    : Sample 70                               Inst    : GC/MS Ins
Misc      : W= 0.2032g/10 ml                        Multiplr: 1.00
                                               Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Oct  5 11:31 2007             Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
 ----------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4         9.82  152   315841m   40.00 ug/ml    0.03
  11) Naphthalene-d8                15.19  136  1139692m   40.00 ug/ml    0.02
  24) Acenaphthene-d10              23.28  164   777430m   40.00 ug/ml    0.00
  36) Phenanthrene-d10              30.02  188  1300026m   40.00 ug/ml    0.00
  37) Chrysene-d12                  42.37  240  1285526m   40.00 ug/ml   -0.02
  39) Perylene-d12                  48.48  264   945697m   40.00 ug/ml   -0.03

 Target Compounds                                                    Qvalue
   2) Furfural                       4.39   96     27645    4.06 ug/ml     93
   3) 2-Furanmethanol                4.76   98      1668    0.60 ug/ml#     1
   4) 2-Cyclopenten-1-one, 2-met     6.60   96     12556    2.33 ug/ml     92
   5) 2 (5H)-Furanone                0.00   84         0     N.D.
   6) 2-Furancarboxaldehyde, 5-m     8.57  110      1140    0.14 ug/ml#    54
   7) 2-Cyclopenten-1-one, 3-met     8.63   96      7010    1.39 ug/ml#    30
   8) Phenol                         9.34   94    122133   12.00 ug/ml     94
   9) 1,2-Cyclopentanedione, 3-m     0.00  112         0     N.D.
  10) Phenol, 2-methyl-             11.65  108     62248    6.69 ug/ml     99
  12) Phenol, 3-methyl-             12.37  108     68678    7.76 ug/ml     95
  13) Phenol, 2-methoxy-   (Guia    12.56  124     18658    2.32 ug/ml     94
  14) Phenol, 2,6-dimethyl-         13.13  122      4531    0.46 ug/ml#    37
  15) Phenol, 2,4-dimethyl-         14.54  122     24700    2.55 ug/ml#    88
  16) Phenol, 3-ethyl-              15.20  122      8062    1.23 ug/ml#    25
  17) Phenol, 2,3-dimethyl-         15.41  122      5216    0.65 ug/ml#    73
  18) Naphthalene                    0.00  128         0     N.D.
  19) Phenol, 2-methoxy-4-methyl    15.75  138     12532    1.41 ug/ml     94
  20) 1,2-Benzenediol               16.29  110     33442   28.56 ug/ml     74
  21) 5-(Hydroxymethyl) furfural     0.00  126         0     N.D.
  22) 1,2-Benzenediol, 4-methyl     17.89  124     36037   18.20 ug/ml     88
  23) Phenol, 4-ethyl-2-methoxy-    18.24  137      4062    0.19 ug/ml#    66
  25) 1,2-Benzenediol, 3-methyl-    18.73  124     78253   29.06 ug/ml     92
  26) Phenol, 2,6-dimethoxy-         0.00  154         0     N.D.
  27) Eugenol                        0.00  164         0     N.D.
  28) Phenol, 2-methoxy-4-propyl    20.63  137      2652    0.08 ug/ml#    66
  29) Vanillin                       0.00  151         0     N.D.
  30) cis-Isoeugenol                 0.00  164         0     N.D.
  31) 3,4-Dimethylbenzoic Acid       0.00  105         0     N.D.
  32) trans-Isoeugenol               0.00  164         0     N.D.
  33) 4-Ethylcatechol               22.39  123      5681    0.34 ug/ml#    69
  34) Levoglucosan                   0.00   60         0     N.D.
  35) Acetovanillone                 0.00  166         0     N.D.
  38) Oleic Acid                     0.00   55         0     N.D.
```

Experiment no. : 71

Oil composition in bio oil-water mixture : 25 wt.%

Reaction temperature : 420 °C

Reaction time : 5 h



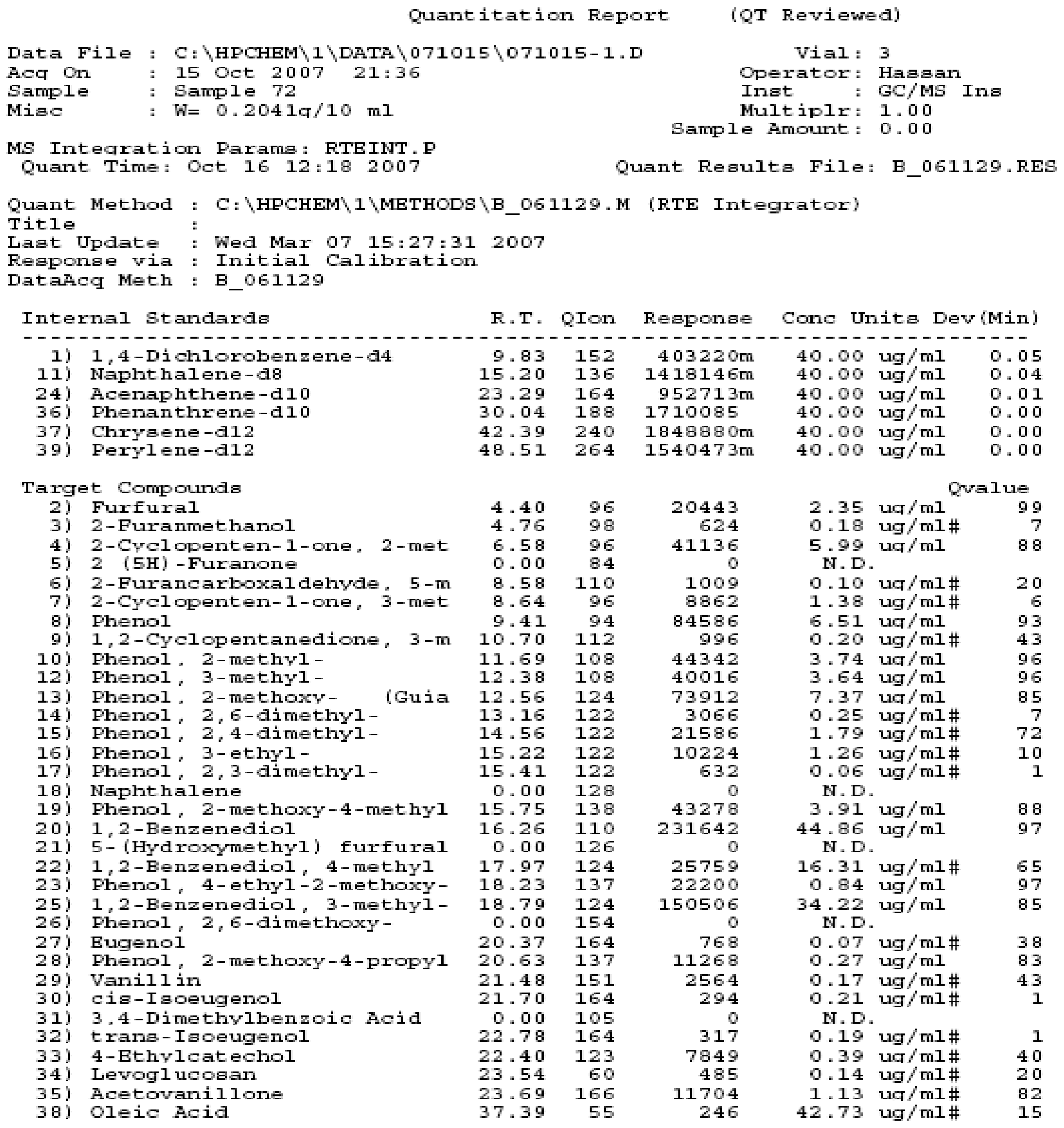
```
                               Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071004\071004-7.D            Vial: 10
Acq On    :  5 Oct 2007   5:44                        Operator: Hassan
Sample    : Sample 71                                 Inst    : GC/MS Ins
Misc      : W= 0.20g/10 ml                            Multiplr: 1.00
                                                 Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Oct  5 11:36 2007              Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
 -----------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4         9.82  152   297633m   40.00 ug/ml    0.03
  11) Naphthalene-d8                15.19  136  1097264m   40.00 ug/ml    0.02
  24) Acenaphthene-d10              23.28  164   757080m   40.00 ug/ml    0.00
  36) Phenanthrene-d10              30.02  188  1300329m   40.00 ug/ml    0.00
  37) Chrysene-d12                  42.36  240  1273437m   40.00 ug/ml   -0.02
  39) Perylene-d12                  48.47  264   983208m   40.00 ug/ml   -0.03

 Target Compounds                                                     Qvalue
   2) Furfural                       4.39   96    21472     3.35 ug/ml      97
   3) 2-Furanmethanol                4.76   98     1742     0.67 ug/ml#      4
   4) 2-Cyclopenten-1-one, 2-met     6.59   96     7822     1.54 ug/ml      91
   5) 2 (5H)-Furanone                0.00   84        0      N.D.
   6) 2-Furancarboxaldehyde, 5-m     8.57  110      251     0.03 ug/ml#      1
   7) 2-Cyclopenten-1-one, 3-met     8.65   96      545     0.11 ug/ml#      1
   8) Phenol                         9.32   94   149204    15.56 ug/ml      94
   9) 1,2-Cyclopentanedione, 3-m    10.68  112      254     0.07 ug/ml#     33
  10) Phenol, 2-methyl-             11.63  108    77766     8.88 ug/ml      99
  12) Phenol, 3-methyl-             12.34  108    89743    10.54 ug/ml      95
  13) Phenol, 2-methoxy-   (Guia    12.56  124    12457     1.61 ug/ml      90
  14) Phenol, 2,6-dimethyl-         13.12  122     6187     0.65 ug/ml#     31
  15) Phenol, 2,4-dimethyl-         14.54  122    35773     3.84 ug/ml      92
  16) Phenol, 3-ethyl-              15.22  122    16527     2.62 ug/ml#     75
  17) Phenol, 2,3-dimethyl-         15.41  122     7655     0.99 ug/ml#     64
  18) Naphthalene                   15.26  128      529     0.02 ug/ml#      1
  19) Phenol, 2-methoxy-4-methyl    15.74  138    11711     1.37 ug/ml      91
  20) 1,2-Benzenediol               16.26  110     3337    25.37 ug/ml#     73
  21) 5-(Hydroxymethyl) furfural     0.00  126        0      N.D.
  22) 1,2-Benzenediol, 4-methyl     17.91  124    22480    16.64 ug/ml      93
  23) Phenol, 4-ethyl-2-methoxy-    18.24  137     4185     0.20 ug/ml#     63
  25) 1,2-Benzenediol, 3-methyl-    18.52  124     2054    20.25 ug/ml#     22
  26) Phenol, 2,6-dimethoxy-         0.00  154        0      N.D.
  27) Eugenol                       20.37  164      244     0.03 ug/ml#      1
  28) Phenol, 2-methoxy-4-propyl    20.64  137     2539     0.08 ug/ml#     73
  29) Vanillin                       0.00  151        0      N.D.
  30) cis-Isoeugenol                 0.00  164        0      N.D.
  31) 3,4-Dimethylbenzoic Acid       0.00  105        0      N.D.
  32) trans-Isoeugenol               0.00  164        0      N.D.
  33) 4-Ethylcatechol               22.39  123      541     0.03 ug/ml#     22
  34) Levoglucosan                   0.00   60        0      N.D.
  35) Acetovanillone                 0.00  166        0      N.D.
  38) Oleic Acid                     0.00   55        0      N.D.
```

Experiment no. : 72

Oil composition in bio oil-water mixture : 25 wt.% bio oil + 5 wt.% methanol

Reaction temperature : 300 °C

Reaction time : 1 h



```
                              Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071015\071015-1.D             Vial: 3
Acq On    : 15 Oct 2007   21:36                        Operator: Hassan
Sample    : Sample 72                                  Inst    : GC/MS Ins
Misc      : W= 0.2041g/10 ml                           Multiplr: 1.00
                                                  Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Oct 16 12:18 2007               Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                 R.T. QIon  Response  Conc Units Dev(Min)
 -------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4        9.83  152   403220m   40.00 ug/ml   0.05
  11) Naphthalene-d8               15.20  136  1418146m   40.00 ug/ml   0.04
  24) Acenaphthene-d10             23.29  164   952713m   40.00 ug/ml   0.01
  36) Phenanthrene-d10             30.04  188  1710085    40.00 ug/ml   0.00
  37) Chrysene-d12                 42.39  240  1848880m   40.00 ug/ml   0.00
  39) Perylene-d12                 48.51  264  1540473m   40.00 ug/ml   0.00

 Target Compounds                                                   Qvalue
   2) Furfural                      4.40   96    20443     2.35 ug/ml     99
   3) 2-Furanmethanol               4.76   98      624     0.18 ug/ml#     7
   4) 2-Cyclopenten-1-one, 2-met    6.58   96    41136     5.99 ug/ml     88
   5) 2 (5H)-Furanone               0.00   84        0     N.D.
   6) 2-Furancarboxaldehyde, 5-m    8.58  110     1009     0.10 ug/ml#    20
   7) 2-Cyclopenten-1-one, 3-met    8.64   96     8862     1.38 ug/ml#     6
   8) Phenol                        9.41   94    84586     6.51 ug/ml     93
   9) 1,2-Cyclopentanedione, 3-m   10.70  112      996     0.20 ug/ml#    43
  10) Phenol, 2-methyl-            11.69  108    44342     3.74 ug/ml     96
  12) Phenol, 3-methyl-            12.38  108    40016     3.64 ug/ml     96
  13) Phenol, 2-methoxy-   (Guia   12.56  124    73912     7.37 ug/ml     85
  14) Phenol, 2,6-dimethyl-        13.16  122     3066     0.25 ug/ml#     7
  15) Phenol, 2,4-dimethyl-        14.56  122    21586     1.79 ug/ml#    72
  16) Phenol, 3-ethyl-             15.22  122    10224     1.26 ug/ml#    10
  17) Phenol, 2,3-dimethyl-        15.41  122      632     0.06 ug/ml#     1
  18) Naphthalene                   0.00  128        0     N.D.
  19) Phenol, 2-methoxy-4-methyl   15.75  138    43278     3.91 ug/ml     88
  20) 1,2-Benzenediol              16.26  110   231642    44.86 ug/ml     97
  21) 5-(Hydroxymethyl) furfural    0.00  126        0     N.D.
  22) 1,2-Benzenediol, 4-methyl    17.97  124    25759    16.31 ug/ml#    65
  23) Phenol, 4-ethyl-2-methoxy-   18.23  137    22200     0.84 ug/ml     97
  25) 1,2-Benzenediol, 3-methyl-   18.79  124   150506    34.22 ug/ml     85
  26) Phenol, 2,6-dimethoxy-        0.00  154        0     N.D.
  27) Eugenol                      20.37  164      768     0.07 ug/ml#    38
  28) Phenol, 2-methoxy-4-propyl   20.63  137    11268     0.27 ug/ml     83
  29) Vanillin                     21.48  151     2564     0.17 ug/ml#    43
  30) cis-Isoeugenol               21.70  164      294     0.21 ug/ml#     1
  31) 3,4-Dimethylbenzoic Acid      0.00  105        0     N.D.
  32) trans-Isoeugenol             22.78  164      317     0.19 ug/ml#     1
  33) 4-Ethylcatechol              22.40  123     7849     0.39 ug/ml#    40
  34) Levoglucosan                 23.54   60      485     0.14 ug/ml#    20
  35) Acetovanillone               23.69  166    11704     1.13 ug/ml#    82
  38) Oleic Acid                   37.39   55      246    42.73 ug/ml#    15
```

Experiment no. : 73

Oil composition in bio oil-water mixture : 25 wt.% bio oil + 5 wt.% methanol

Reaction temperature : 380 °C

Reaction time : 1 h

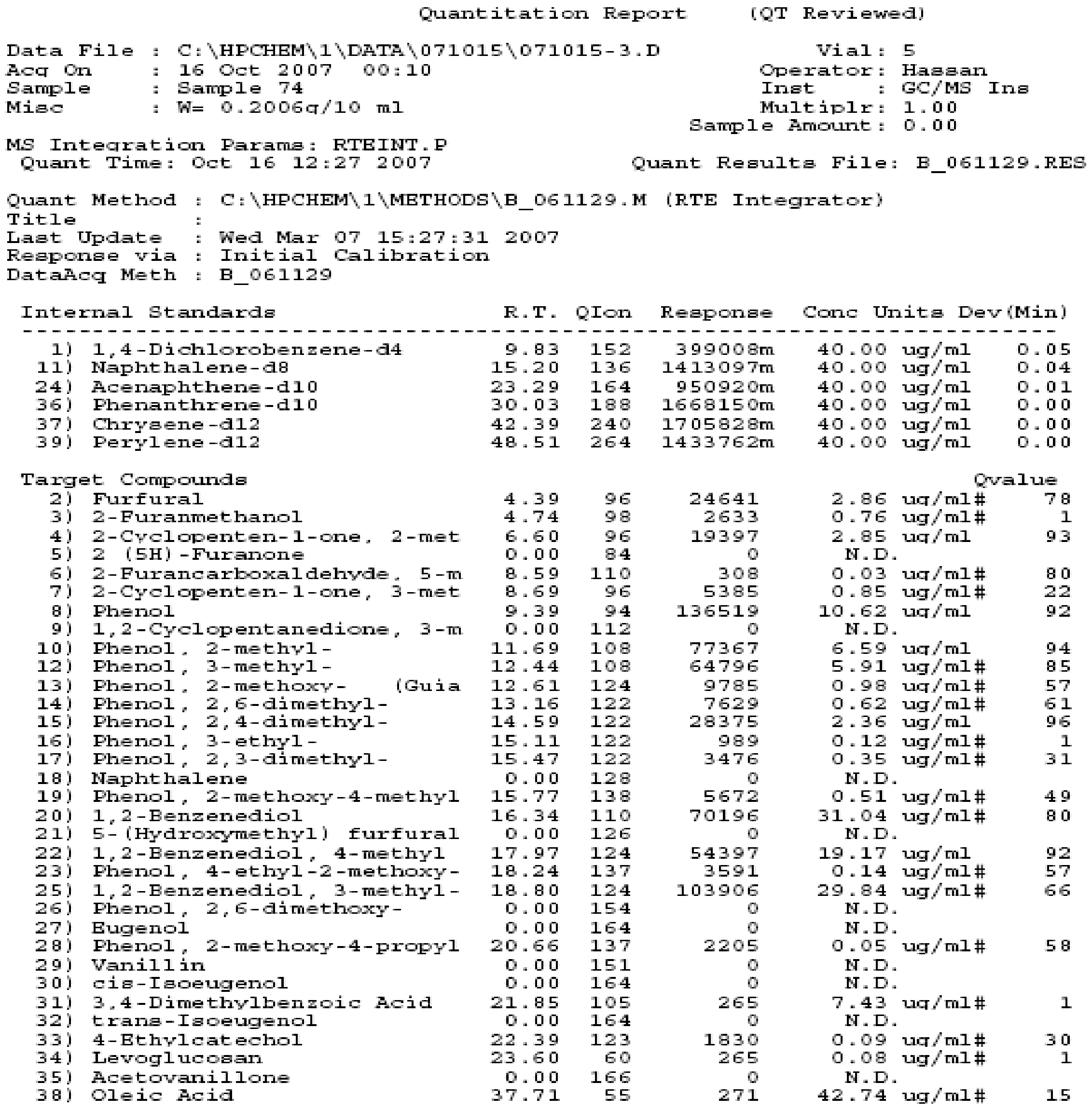
```
                            Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071015\071015-2.D             Vial: 4
Acq On    : 15 Oct 2007   22:53                        Operator: Hassan
Sample    : Sample 73                                  Inst     : GC/MS Ins
Misc      : W= 0.2041g/10 ml                           Multiplr: 1.00
                                                  Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Oct 16 12:23 2007               Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
 ------------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4        9.83  152   422220m   40.00 ug/ml    0.04
  11) Naphthalene-d8               15.19  136  1460251m   40.00 ug/ml    0.03
  24) Acenaphthene-d10             23.29  164   994795m   40.00 ug/ml    0.00
  36) Phenanthrene-d10             30.04  188  1782326m   40.00 ug/ml    0.01
  37) Chrysene-d12                 42.40  240  1874838m   40.00 ug/ml    0.01
  39) Perylene-d12                 48.51  264  1548278m   40.00 ug/ml    0.00

 Target Compounds                                                   Qvalue
   2) Furfural                      4.41   96    16427     1.80 ug/ml      97
   3) 2-Furanmethanol               4.76   98     1500     0.41 ug/ml#      1
   4) 2-Cyclopenten-1-one, 2-met    6.59   96    25648     3.57 ug/ml      92
   5) 2 (5H)-Furanone               0.00   84        0     N.D.
   6) 2-Furancarboxaldehyde, 5-m    0.00  110        0     N.D.
   7) 2-Cyclopenten-1-one, 3-met    0.00   96        0     N.D.
   8) Phenol                        9.41   94   113975     8.38 ug/ml      90
   9) 1,2-Cyclopentanedione, 3-m    0.00  112        0     N.D.
  10) Phenol, 2-methyl-            11.70  108    63753     5.13 ug/ml      98
  12) Phenol, 3-methyl-            12.43  108    52591     4.64 ug/ml      92
  13) Phenol, 2-methoxy-   (Guia   12.57  124    35775     3.47 ug/ml#     82
  14) Phenol, 2,6-dimethyl-        13.17  122     5642     0.45 ug/ml#     27
  15) Phenol, 2,4-dimethyl-        14.59  122    23975     1.93 ug/ml#     60
  16) Phenol, 3-ethyl-             15.18  122     2027     0.24 ug/ml#      1
  17) Phenol, 2,3-dimethyl-        15.44  122     5095     0.49 ug/ml#     89
  18) Naphthalene                   0.00  128        0     N.D.
  19) Phenol, 2-methoxy-4-methyl   15.77  138    15044     1.32 ug/ml#     77
  20) 1,2-Benzenediol              16.29  110   132979    36.07 ug/ml      96
  21) 5-(Hydroxymethyl) furfural    0.00  126        0     N.D.
  22) 1,2-Benzenediol, 4-methyl    17.96  124    60861    19.61 ug/ml      91
  23) Phenol, 4-ethyl-2-methoxy-   18.24  137     8169     0.30 ug/ml      86
  25) 1,2-Benzenediol, 3-methyl-   18.79  124   190542    37.24 ug/ml      93
  26) Phenol, 2,6-dimethoxy-        0.00  154        0     N.D.
  27) Eugenol                       0.00  164        0     N.D.
  28) Phenol, 2-methoxy-4-propyl   20.64  137     5985     0.14 ug/ml#     65
  29) Vanillin                     21.53  151      239     0.02 ug/ml#      1
  30) cis-Isoeugenol                0.00  164        0     N.D.
  31) 3,4-Dimethylbenzoic Acid     21.86  105      277     7.43 ug/ml#     20
  32) trans-Isoeugenol              0.00  164        0     N.D.
  33) 4-Ethylcatechol              22.13  123     3493     0.16 ug/ml      81
  34) Levoglucosan                 23.72   60      297     0.08 ug/ml#     42
  35) Acetovanillone               23.72  166     1027     0.10 ug/ml#      1
  38) Oleic Acid                   37.22   55      290    42.74 ug/ml#     33
```

Experiment no. : 74

Oil composition in bio oil-water mixture : 25 wt.% bio oil + 5 wt.% methanol

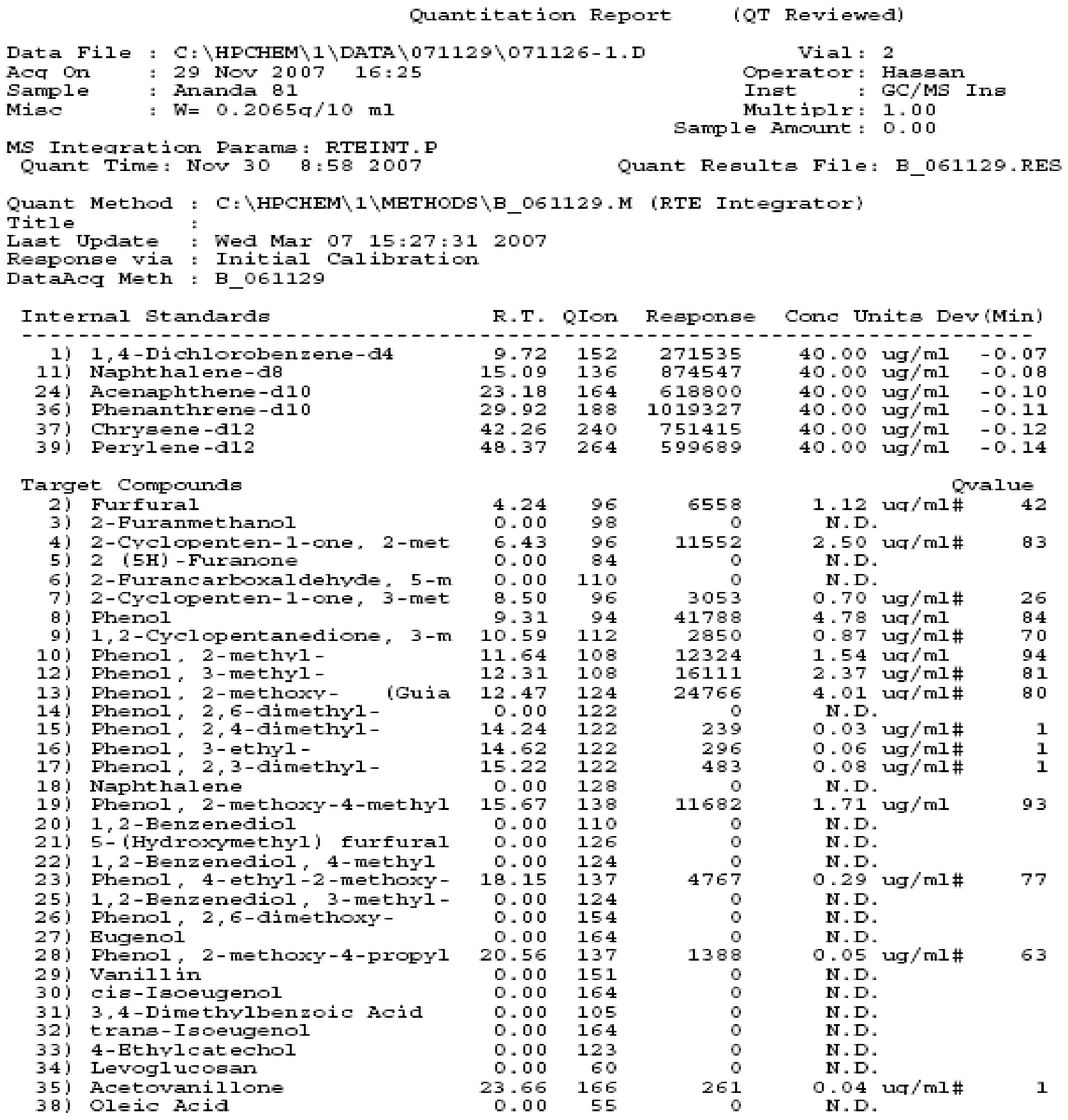
Reaction temperature : 420 °C

Reaction time : 1 h



```
                             Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071015\071015-3.D          Vial: 5
Acq On    : 16 Oct 2007  00:10                      Operator: Hassan
Sample    : Sample 74                               Inst    : GC/MS Ins
Misc      : W= 0.2006g/10 ml                        Multiplr: 1.00
                                               Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Oct 16 12:27 2007              Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                 R.T. QIon  Response  Conc Units Dev(Min)
 ----------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4        9.83  152   399008m   40.00 ug/ml    0.05
  11) Naphthalene-d8               15.20  136  1413097m   40.00 ug/ml    0.04
  24) Acenaphthene-d10             23.29  164   950920m   40.00 ug/ml    0.01
  36) Phenanthrene-d10             30.03  188  1668150m   40.00 ug/ml    0.00
  37) Chrysene-d12                 42.39  240  1705828m   40.00 ug/ml    0.00
  39) Perylene-d12                 48.51  264  1433762m   40.00 ug/ml    0.00

 Target Compounds                                                   Qvalue
   2) Furfural                      4.39   96     24641    2.86 ug/ml#    78
   3) 2-Furanmethanol               4.74   98      2633    0.76 ug/ml#     1
   4) 2-Cyclopenten-1-one, 2-met    6.60   96     19397    2.85 ug/ml     93
   5) 2 (5H)-Furanone               0.00   84         0     N.D.
   6) 2-Furancarboxaldehyde, 5-m    8.59  110       308    0.03 ug/ml#    80
   7) 2-Cyclopenten-1-one, 3-met    8.69   96      5385    0.85 ug/ml#    22
   8) Phenol                        9.39   94    136519   10.62 ug/ml     92
   9) 1,2-Cyclopentanedione, 3-m    0.00  112         0     N.D.
  10) Phenol, 2-methyl-            11.69  108     77367    6.59 ug/ml     94
  12) Phenol, 3-methyl-            12.44  108     64796    5.91 ug/ml#    85
  13) Phenol, 2-methoxy-   (Guia   12.61  124      9785    0.98 ug/ml#    57
  14) Phenol, 2,6-dimethyl-        13.16  122      7629    0.62 ug/ml#    61
  15) Phenol, 2,4-dimethyl-        14.59  122     28375    2.36 ug/ml     96
  16) Phenol, 3-ethyl-             15.11  122       989    0.12 ug/ml#     1
  17) Phenol, 2,3-dimethyl-        15.47  122      3476    0.35 ug/ml#    31
  18) Naphthalene                   0.00  128         0     N.D.
  19) Phenol, 2-methoxy-4-methyl   15.77  138      5672    0.51 ug/ml#    49
  20) 1,2-Benzenediol              16.34  110     70196   31.04 ug/ml#    80
  21) 5-(Hydroxymethyl) furfural    0.00  126         0     N.D.
  22) 1,2-Benzenediol, 4-methyl    17.97  124     54397   19.17 ug/ml     92
  23) Phenol, 4-ethyl-2-methoxy-   18.24  137      3591    0.14 ug/ml#    57
  25) 1,2-Benzenediol, 3-methyl-   18.80  124    103906   29.84 ug/ml#    66
  26) Phenol, 2,6-dimethoxy-        0.00  154         0     N.D.
  27) Eugenol                       0.00  164         0     N.D.
  28) Phenol, 2-methoxy-4-propyl   20.66  137      2205    0.05 ug/ml#    58
  29) Vanillin                      0.00  151         0     N.D.
  30) cis-Isoeugenol                0.00  164         0     N.D.
  31) 3,4-Dimethylbenzoic Acid     21.85  105       265    7.43 ug/ml#     1
  32) trans-Isoeugenol              0.00  164         0     N.D.
  33) 4-Ethylcatechol              22.39  123      1830    0.09 ug/ml#    30
  34) Levoglucosan                 23.60   60       265    0.08 ug/ml#     1
  35) Acetovanillone                0.00  166         0     N.D.
  38) Oleic Acid                   37.71   55       271   42.74 ug/ml#    15
```

Experiment no.	: 81
Oil composition in bio oil-water mixture	: 25 wt.%
Reaction temperature	: 300 °C
Reaction time	: 0.5 h



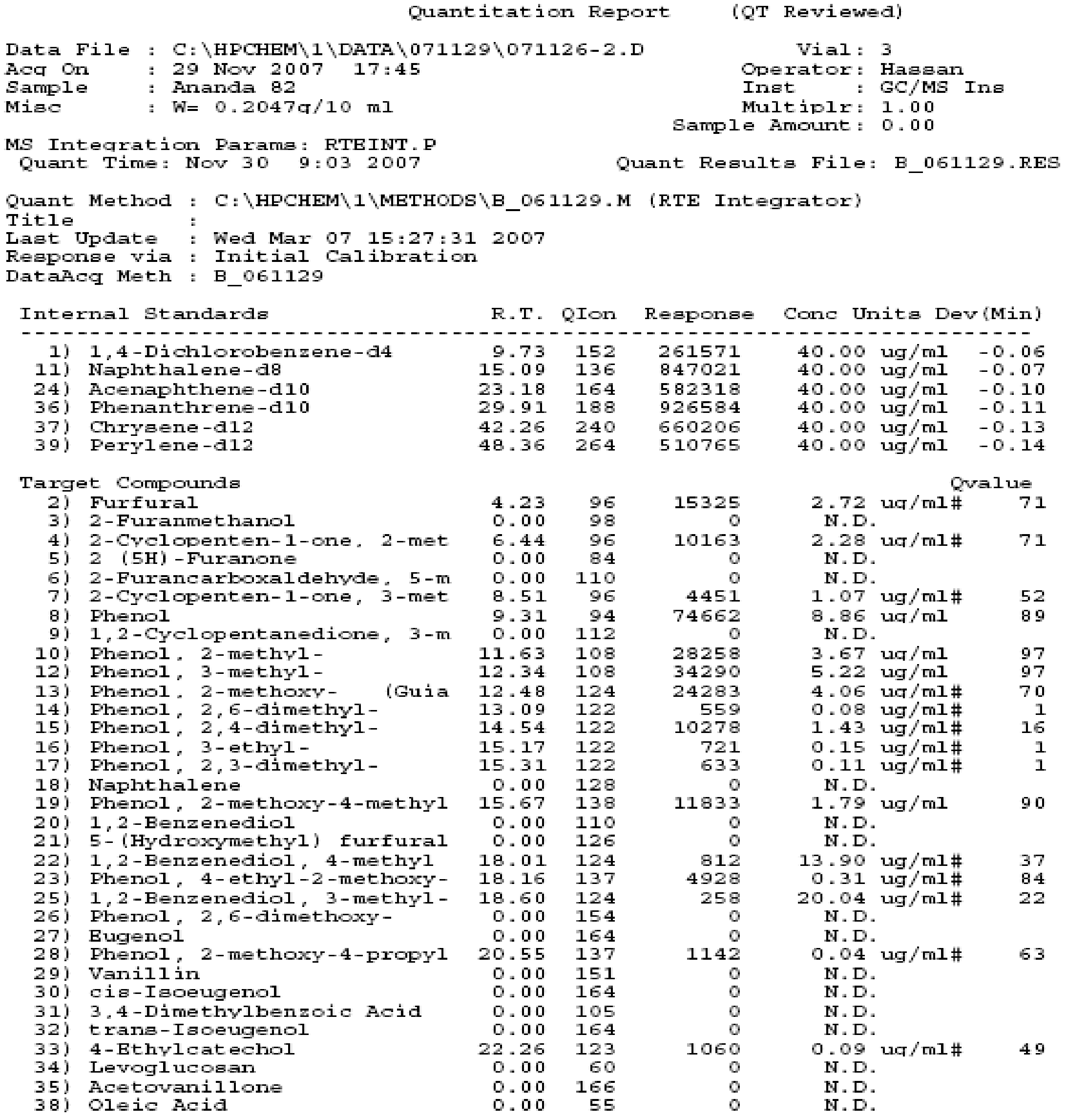
```
                              Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071129\071126-1.D           Vial: 2
Acq On    : 29 Nov 2007  16:25                       Operator: Hassan
Sample    : Ananda 81                                Inst    : GC/MS Ins
Misc      : W= 0.2065g/10 ml                         Multiplr: 1.00
                                                Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Nov 30  8:58 2007             Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
 --------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4       9.72  152   271535    40.00 ug/ml  -0.07
  11) Naphthalene-d8              15.09  136   874547    40.00 ug/ml  -0.08
  24) Acenaphthene-d10            23.18  164   618800    40.00 ug/ml  -0.10
  36) Phenanthrene-d10            29.92  188  1019327    40.00 ug/ml  -0.11
  37) Chrysene-d12                42.26  240   751415    40.00 ug/ml  -0.12
  39) Perylene-d12                48.37  264   599689    40.00 ug/ml  -0.14

 Target Compounds                                                   Qvalue
   2) Furfural                     4.24   96     6558    1.12 ug/ml#    42
   3) 2-Furanmethanol              0.00   98        0     N.D.
   4) 2-Cyclopenten-1-one, 2-met   6.43   96    11552    2.50 ug/ml#    83
   5) 2 (5H)-Furanone              0.00   84        0     N.D.
   6) 2-Furancarboxaldehyde, 5-m   0.00  110        0     N.D.
   7) 2-Cyclopenten-1-one, 3-met   8.50   96     3053    0.70 ug/ml#    26
   8) Phenol                       9.31   94    41788    4.78 ug/ml     84
   9) 1,2-Cyclopentanedione, 3-m  10.59  112     2850    0.87 ug/ml#    70
  10) Phenol, 2-methyl-           11.64  108    12324    1.54 ug/ml     94
  12) Phenol, 3-methyl-           12.31  108    16111    2.37 ug/ml#    81
  13) Phenol, 2-methoxy-   (Guia  12.47  124    24766    4.01 ug/ml#    80
  14) Phenol, 2,6-dimethyl-        0.00  122        0     N.D.
  15) Phenol, 2,4-dimethyl-       14.24  122      239    0.03 ug/ml#     1
  16) Phenol, 3-ethyl-            14.62  122      296    0.06 ug/ml#     1
  17) Phenol, 2,3-dimethyl-       15.22  122      483    0.08 ug/ml#     1
  18) Naphthalene                  0.00  128        0     N.D.
  19) Phenol, 2-methoxy-4-methyl  15.67  138    11682    1.71 ug/ml     93
  20) 1,2-Benzenediol              0.00  110        0     N.D.
  21) 5-(Hydroxymethyl) furfural   0.00  126        0     N.D.
  22) 1,2-Benzenediol, 4-methyl    0.00  124        0     N.D.
  23) Phenol, 4-ethyl-2-methoxy-  18.15  137     4767    0.29 ug/ml#    77
  25) 1,2-Benzenediol, 3-methyl-   0.00  124        0     N.D.
  26) Phenol, 2,6-dimethoxy-       0.00  154        0     N.D.
  27) Eugenol                      0.00  164        0     N.D.
  28) Phenol, 2-methoxy-4-propyl  20.56  137     1388    0.05 ug/ml#    63
  29) Vanillin                     0.00  151        0     N.D.
  30) cis-Isoeugenol               0.00  164        0     N.D.
  31) 3,4-Dimethylbenzoic Acid     0.00  105        0     N.D.
  32) trans-Isoeugenol             0.00  164        0     N.D.
  33) 4-Ethylcatechol              0.00  123        0     N.D.
  34) Levoglucosan                 0.00   60        0     N.D.
  35) Acetovanillone              23.66  166      261    0.04 ug/ml#     1
  38) Oleic Acid                   0.00   55        0     N.D.
```

Experiment no. : 82

Oil composition in bio oil-water mixture : 25 wt.%

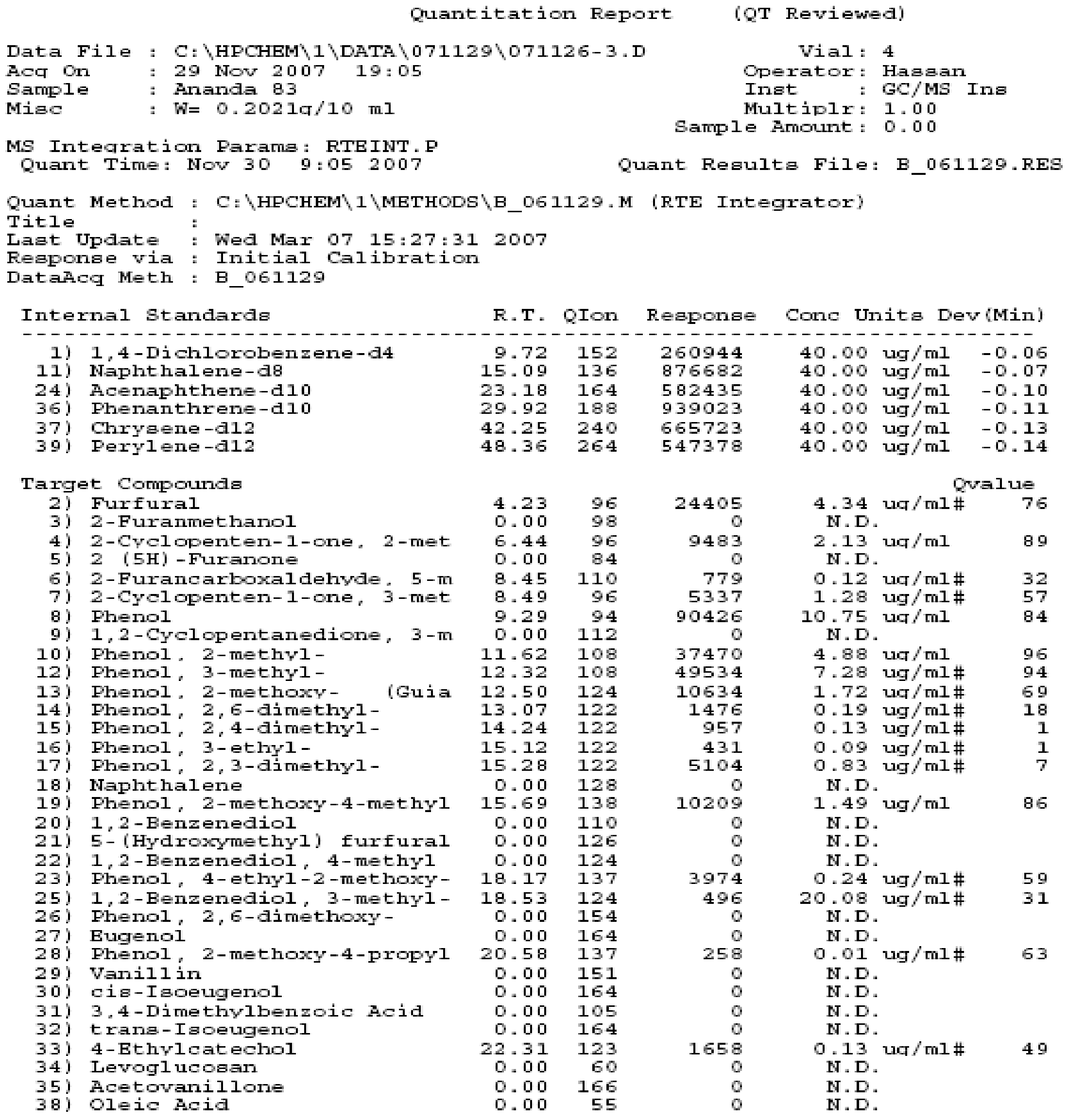
Reaction temperature : 380 °C

Reaction time : 0.5 h



```
                              Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071129\071126-2.D           Vial: 3
Acq On    : 29 Nov 2007  17:45                       Operator: Hassan
Sample    : Ananda 82                                Inst    : GC/MS Ins
Misc      : W= 0.2047g/10 ml                         Multiplr: 1.00
                                                Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Nov 30  9:03 2007              Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
 -------------------------------------------------------------------------
   1) 1,4-Dichlorobenzene-d4        9.73  152   261571    40.00 ug/ml  -0.06
  11) Naphthalene-d8               15.09  136   847021    40.00 ug/ml  -0.07
  24) Acenaphthene-d10             23.18  164   582318    40.00 ug/ml  -0.10
  36) Phenanthrene-d10             29.91  188   926584    40.00 ug/ml  -0.11
  37) Chrysene-d12                 42.26  240   660206    40.00 ug/ml  -0.13
  39) Perylene-d12                 48.36  264   510765    40.00 ug/ml  -0.14

 Target Compounds                                                   Qvalue
   2) Furfural                      4.23   96    15325     2.72 ug/ml#    71
   3) 2-Furanmethanol               0.00   98        0      N.D.
   4) 2-Cyclopenten-1-one, 2-met    6.44   96    10163     2.28 ug/ml#    71
   5) 2 (5H)-Furanone               0.00   84        0      N.D.
   6) 2-Furancarboxaldehyde, 5-m    0.00  110        0      N.D.
   7) 2-Cyclopenten-1-one, 3-met    8.51   96     4451     1.07 ug/ml#    52
   8) Phenol                        9.31   94    74662     8.86 ug/ml     89
   9) 1,2-Cyclopentanedione, 3-m    0.00  112        0      N.D.
  10) Phenol, 2-methyl-            11.63  108    28258     3.67 ug/ml     97
  12) Phenol, 3-methyl-            12.34  108    34290     5.22 ug/ml     97
  13) Phenol, 2-methoxy-   (Guia   12.48  124    24283     4.06 ug/ml#    70
  14) Phenol, 2,6-dimethyl-        13.09  122      559     0.08 ug/ml#     1
  15) Phenol, 2,4-dimethyl-        14.54  122    10278     1.43 ug/ml#    16
  16) Phenol, 3-ethyl-             15.17  122      721     0.15 ug/ml#     1
  17) Phenol, 2,3-dimethyl-        15.31  122      633     0.11 ug/ml#     1
  18) Naphthalene                   0.00  128        0      N.D.
  19) Phenol, 2-methoxy-4-methyl   15.67  138    11833     1.79 ug/ml     90
  20) 1,2-Benzenediol               0.00  110        0      N.D.
  21) 5-(Hydroxymethyl) furfural    0.00  126        0      N.D.
  22) 1,2-Benzenediol, 4-methyl    18.01  124      812    13.90 ug/ml#    37
  23) Phenol, 4-ethyl-2-methoxy-   18.16  137     4928     0.31 ug/ml#    84
  25) 1,2-Benzenediol, 3-methyl-   18.60  124      258    20.04 ug/ml#    22
  26) Phenol, 2,6-dimethoxy-        0.00  154        0      N.D.
  27) Eugenol                       0.00  164        0      N.D.
  28) Phenol, 2-methoxy-4-propyl   20.55  137     1142     0.04 ug/ml#    63
  29) Vanillin                      0.00  151        0      N.D.
  30) cis-Isoeugenol                0.00  164        0      N.D.
  31) 3,4-Dimethylbenzoic Acid      0.00  105        0      N.D.
  32) trans-Isoeugenol              0.00  164        0      N.D.
  33) 4-Ethylcatechol              22.26  123     1060     0.09 ug/ml#    49
  34) Levoglucosan                  0.00   60        0      N.D.
  35) Acetovanillone                0.00  166        0      N.D.
  38) Oleic Acid                    0.00   55        0      N.D.
```

Experiment no.	: 83
Oil composition in bio oil-water mixture	: 25 wt.%
Reaction temperature	: 420 °C
Reaction time	: 0.5 h



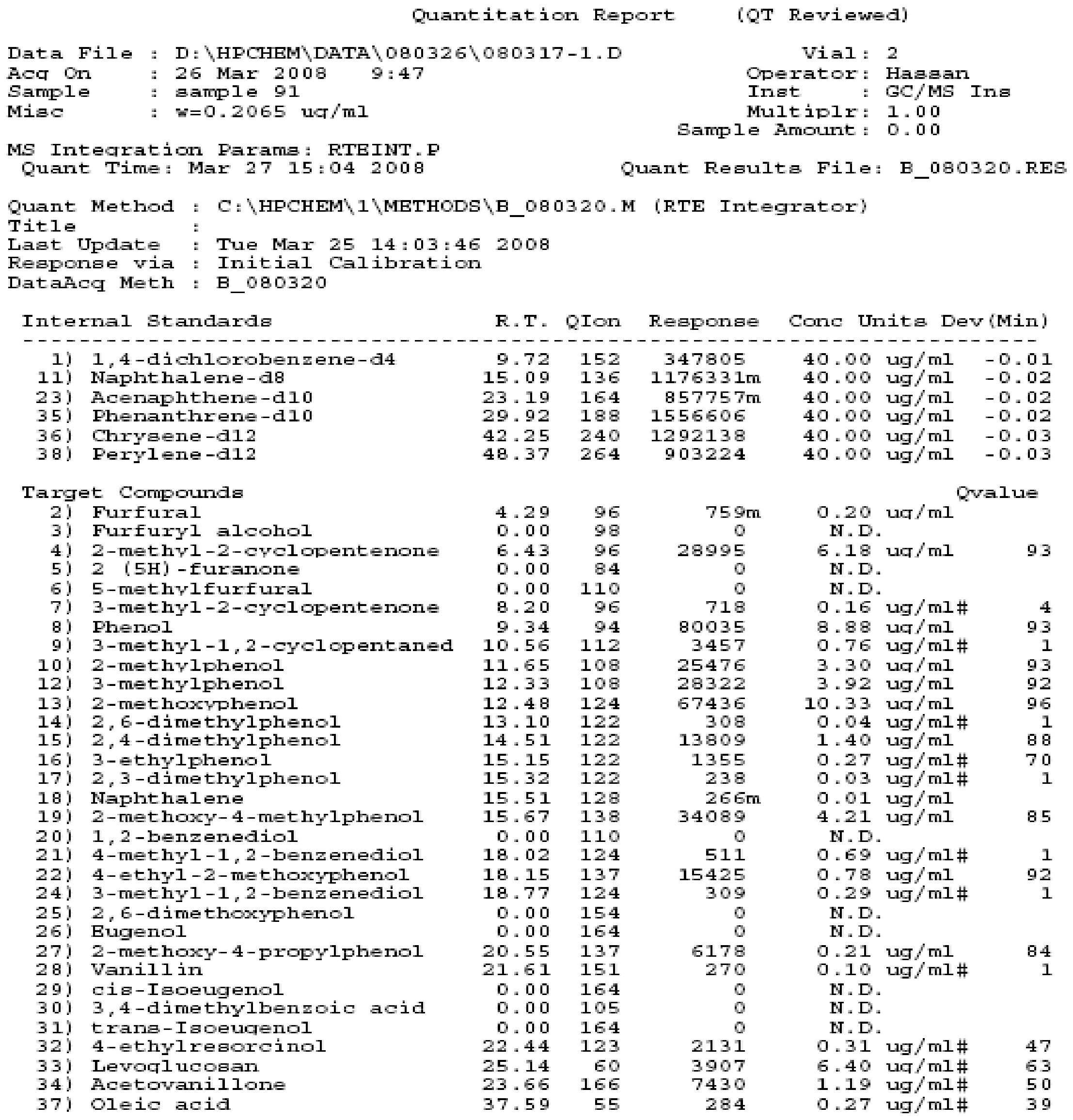
```
                        Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\071129\071126-3.D            Vial: 4
Acq On    : 29 Nov 2007   19:05                       Operator: Hassan
Sample    : Ananda 83                                 Inst    : GC/MS Ins
Misc      : W= 0.2021g/10 ml                          Multiplr: 1.00
                                                 Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Nov 30   9:05 2007              Quant Results File: B_061129.RES

Quant Method : C:\HPCHEM\1\METHODS\B_061129.M (RTE Integrator)
Title        :
Last Update  : Wed Mar 07 15:27:31 2007
Response via : Initial Calibration
DataAcq Meth : B_061129

 Internal Standards                 R.T. QIon  Response  Conc Units Dev(Min)
-------------------------------------------------------------------------------
  1) 1,4-Dichlorobenzene-d4         9.72  152   260944    40.00 ug/ml  -0.06
 11) Naphthalene-d8                15.09  136   876682    40.00 ug/ml  -0.07
 24) Acenaphthene-d10              23.18  164   582435    40.00 ug/ml  -0.10
 36) Phenanthrene-d10              29.92  188   939023    40.00 ug/ml  -0.11
 37) Chrysene-d12                  42.25  240   665723    40.00 ug/ml  -0.13
 39) Perylene-d12                  48.36  264   547378    40.00 ug/ml  -0.14

 Target Compounds                                                     Qvalue
  2) Furfural                       4.23   96    24405     4.34 ug/ml#    76
  3) 2-Furanmethanol                0.00   98        0      N.D.
  4) 2-Cyclopenten-1-one, 2-met     6.44   96     9483     2.13 ug/ml     89
  5) 2 (5H)-Furanone                0.00   84        0      N.D.
  6) 2-Furancarboxaldehyde, 5-m     8.45  110      779     0.12 ug/ml#    32
  7) 2-Cyclopenten-1-one, 3-met     8.49   96     5337     1.28 ug/ml#    57
  8) Phenol                         9.29   94    90426    10.75 ug/ml     84
  9) 1,2-Cyclopentanedione, 3-m     0.00  112        0      N.D.
 10) Phenol, 2-methyl-             11.62  108    37470     4.88 ug/ml     96
 12) Phenol, 3-methyl-             12.32  108    49534     7.28 ug/ml#    94
 13) Phenol, 2-methoxy-    (Guia   12.50  124    10634     1.72 ug/ml#    69
 14) Phenol, 2,6-dimethyl-         13.07  122     1476     0.19 ug/ml#    18
 15) Phenol, 2,4-dimethyl-         14.24  122      957     0.13 ug/ml#     1
 16) Phenol, 3-ethyl-              15.12  122      431     0.09 ug/ml#     1
 17) Phenol, 2,3-dimethyl-         15.28  122     5104     0.83 ug/ml#     7
 18) Naphthalene                    0.00  128        0      N.D.
 19) Phenol, 2-methoxy-4-methyl    15.69  138    10209     1.49 ug/ml     86
 20) 1,2-Benzenediol                0.00  110        0      N.D.
 21) 5-(Hydroxymethyl) furfural     0.00  126        0      N.D.
 22) 1,2-Benzenediol, 4-methyl      0.00  124        0      N.D.
 23) Phenol, 4-ethyl-2-methoxy-    18.17  137     3974     0.24 ug/ml#    59
 25) 1,2-Benzenediol, 3-methyl-    18.53  124      496    20.08 ug/ml#    31
 26) Phenol, 2,6-dimethoxy-         0.00  154        0      N.D.
 27) Eugenol                        0.00  164        0      N.D.
 28) Phenol, 2-methoxy-4-propyl    20.58  137      258     0.01 ug/ml#    63
 29) Vanillin                       0.00  151        0      N.D.
 30) cis-Isoeugenol                 0.00  164        0      N.D.
 31) 3,4-Dimethylbenzoic Acid       0.00  105        0      N.D.
 32) trans-Isoeugenol               0.00  164        0      N.D.
 33) 4-Ethylcatechol               22.31  123     1658     0.13 ug/ml#    49
 34) Levoglucosan                   0.00   60        0      N.D.
 35) Acetovanillone                 0.00  166        0      N.D.
 38) Oleic Acid                     0.00   55        0      N.D.
```

Experiment no. : 91

Oil composition in bio oil-water mixture : 50 wt.%

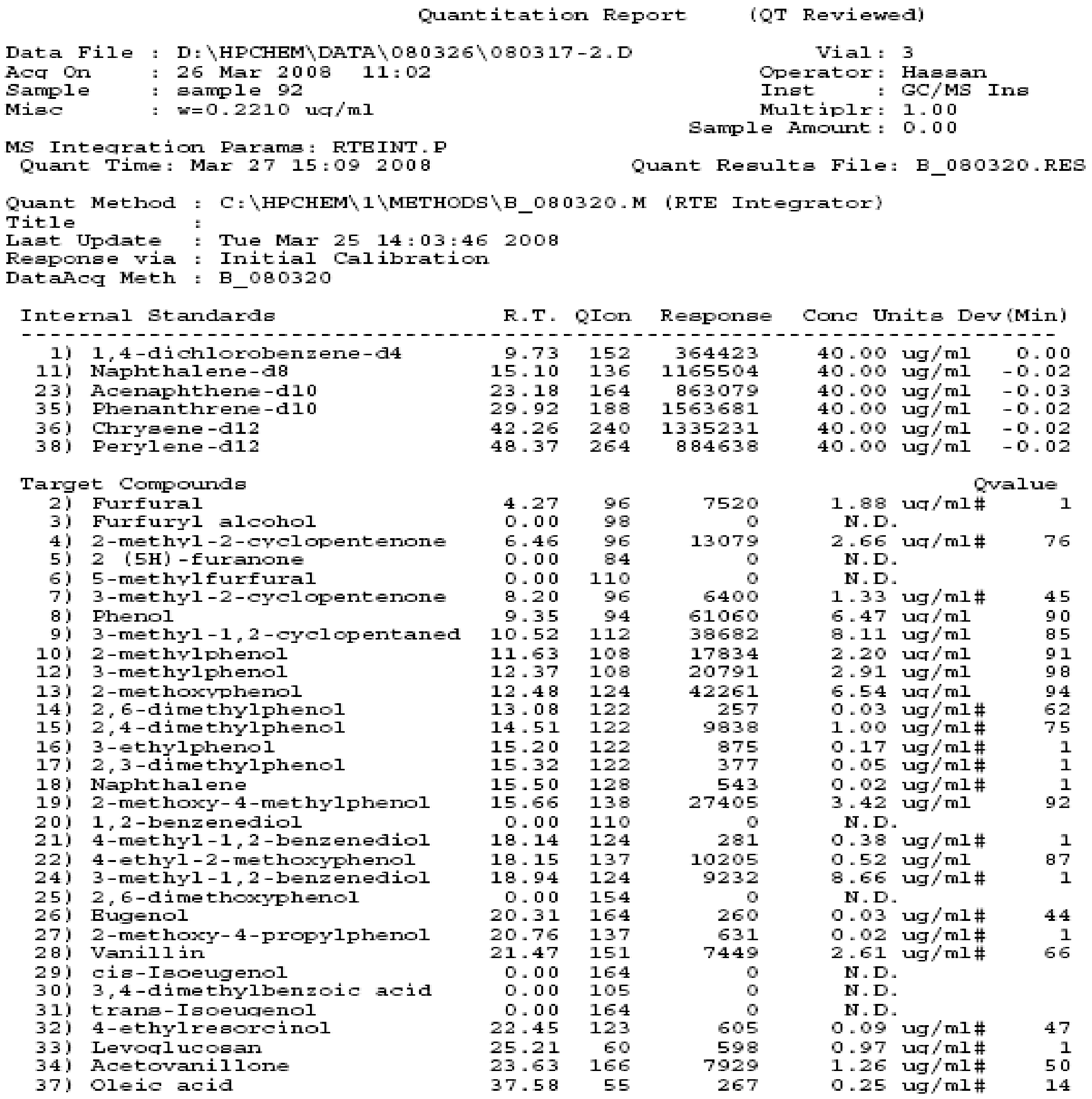
Reaction temperature : 300 °C

Reaction time : 0.5 h



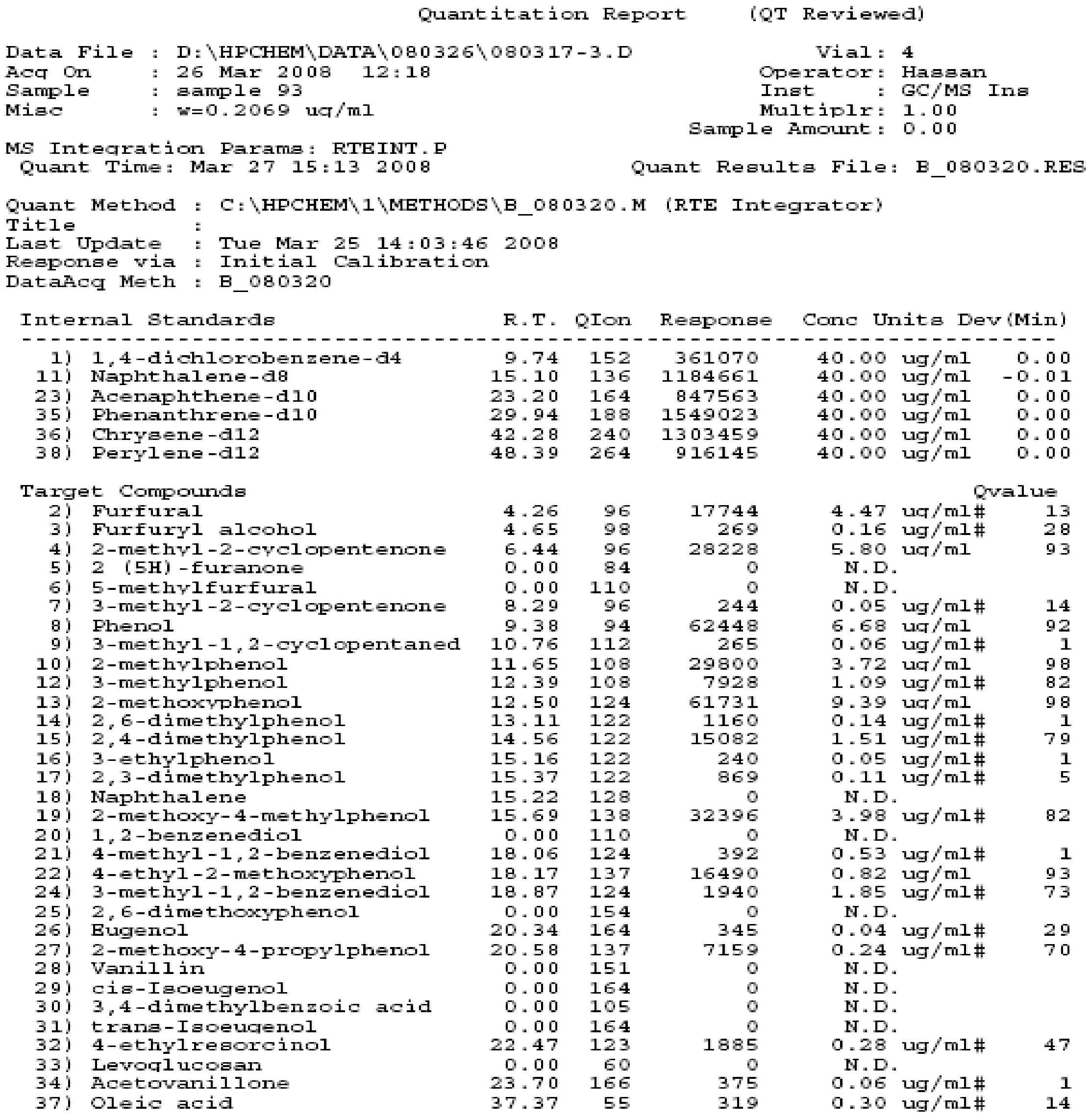
```
                         Quantitation Report    (QT Reviewed)

Data File : D:\HPCHEM\DATA\080326\080317-1.D             Vial: 2
Acq On    : 26 Mar 2008   9:47                       Operator: Hassan
Sample    : sample 91                                Inst    : GC/MS Ins
Misc      : w=0.2065 ug/ml                           Multiplr: 1.00
                                                Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Mar 27 15:04 2008              Quant Results File: B_080320.RES

Quant Method : C:\HPCHEM\1\METHODS\B_080320.M (RTE Integrator)
Title        :
Last Update  : Tue Mar 25 14:03:46 2008
Response via : Initial Calibration
DataAcq Meth : B_080320

 Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
 -------------------------------------------------------------------------
   1) 1,4-dichlorobenzene-d4       9.72  152   347805    40.00 ug/ml  -0.01
  11) Naphthalene-d8              15.09  136  1176331m   40.00 ug/ml  -0.02
  23) Acenaphthene-d10            23.19  164   857757m   40.00 ug/ml  -0.02
  35) Phenanthrene-d10            29.92  188  1556606    40.00 ug/ml  -0.02
  36) Chrysene-d12                42.25  240  1292138    40.00 ug/ml  -0.03
  38) Perylene-d12                48.37  264   903224    40.00 ug/ml  -0.03

 Target Compounds                                                   Qvalue
   2) Furfural                     4.29   96      759m    0.20 ug/ml
   3) Furfuryl alcohol             0.00   98        0      N.D.
   4) 2-methyl-2-cyclopentenone    6.43   96    28995     6.18 ug/ml     93
   5) 2 (5H)-furanone              0.00   84        0      N.D.
   6) 5-methylfurfural             0.00  110        0      N.D.
   7) 3-methyl-2-cyclopentenone    8.20   96      718     0.16 ug/ml#     4
   8) Phenol                       9.34   94    80035     8.88 ug/ml     93
   9) 3-methyl-1,2-cyclopentaned  10.56  112     3457     0.76 ug/ml#     1
  10) 2-methylphenol              11.65  108    25476     3.30 ug/ml     93
  12) 3-methylphenol              12.33  108    28322     3.92 ug/ml     92
  13) 2-methoxyphenol             12.48  124    67436    10.33 ug/ml     96
  14) 2,6-dimethylphenol          13.10  122      308     0.04 ug/ml#     1
  15) 2,4-dimethylphenol          14.51  122    13809     1.40 ug/ml     88
  16) 3-ethylphenol               15.15  122     1355     0.27 ug/ml#    70
  17) 2,3-dimethylphenol          15.32  122      238     0.03 ug/ml#     1
  18) Naphthalene                 15.51  128      266m    0.01 ug/ml
  19) 2-methoxy-4-methylphenol    15.67  138    34089     4.21 ug/ml     85
  20) 1,2-benzenediol              0.00  110        0      N.D.
  21) 4-methyl-1,2-benzenediol    18.02  124      511     0.69 ug/ml#     1
  22) 4-ethyl-2-methoxyphenol     18.15  137    15425     0.78 ug/ml     92
  24) 3-methyl-1,2-benzenediol    18.77  124      309     0.29 ug/ml#     1
  25) 2,6-dimethoxyphenol          0.00  154        0      N.D.
  26) Eugenol                      0.00  164        0      N.D.
  27) 2-methoxy-4-propylphenol    20.55  137     6178     0.21 ug/ml     84
  28) Vanillin                    21.61  151      270     0.10 ug/ml#     1
  29) cis-Isoeugenol               0.00  164        0      N.D.
  30) 3,4-dimethylbenzoic acid     0.00  105        0      N.D.
  31) trans-Isoeugenol             0.00  164        0      N.D.
  32) 4-ethylresorcinol           22.44  123     2131     0.31 ug/ml#    47
  33) Levoglucosan                25.14   60     3907     6.40 ug/ml#    63
  34) Acetovanillone              23.66  166     7430     1.19 ug/ml#    50
  37) Oleic acid                  37.59   55      284     0.27 ug/ml#    39
```

Experiment no.	: 92
Oil composition in bio oil-water mixture	: 25 wt.%
Reaction temperature	: 300 °C
Reaction time	: 0 h (To examine effect of heating cycle)



```
                          Quantitation Report    (QT Reviewed)

Data File : D:\HPCHEM\DATA\080326\080317-2.D              Vial: 3
Acq On    : 26 Mar 2008   11:02                       Operator: Hassan
Sample    : sample 92                                 Inst    : GC/MS Ins
Misc      : w=0.2210 ug/ml                            Multiplr: 1.00
                                                 Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Mar 27 15:09 2008            Quant Results File: B_080320.RES

Quant Method : C:\HPCHEM\1\METHODS\B_080320.M (RTE Integrator)
Title        :
Last Update  : Tue Mar 25 14:03:46 2008
Response via : Initial Calibration
DataAcq Meth : B_080320

 Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
 ---------------------------------------------------------------------------
   1) 1,4-dichlorobenzene-d4         9.73  152    364423    40.00 ug/ml   0.00
  11) Naphthalene-d8                15.10  136   1165504    40.00 ug/ml  -0.02
  23) Acenaphthene-d10              23.18  164    863079    40.00 ug/ml  -0.03
  35) Phenanthrene-d10              29.92  188   1563681    40.00 ug/ml  -0.02
  36) Chrysene-d12                  42.26  240   1335231    40.00 ug/ml  -0.02
  38) Perylene-d12                  48.37  264    884638    40.00 ug/ml  -0.02

 Target Compounds                                                     Qvalue
   2) Furfural                       4.27   96      7520     1.88 ug/ml#     1
   3) Furfuryl alcohol               0.00   98         0      N.D.
   4) 2-methyl-2-cyclopentenone      6.46   96     13079     2.66 ug/ml#    76
   5) 2 (5H)-furanone                0.00   84         0      N.D.
   6) 5-methylfurfural               0.00  110         0      N.D.
   7) 3-methyl-2-cyclopentenone      8.20   96      6400     1.33 ug/ml#    45
   8) Phenol                         9.35   94     61060     6.47 ug/ml     90
   9) 3-methyl-1,2-cyclopentaned    10.52  112     38682     8.11 ug/ml     85
  10) 2-methylphenol                11.63  108     17834     2.20 ug/ml     91
  12) 3-methylphenol                12.37  108     20791     2.91 ug/ml     98
  13) 2-methoxyphenol               12.48  124     42261     6.54 ug/ml     94
  14) 2,6-dimethylphenol            13.08  122       257     0.03 ug/ml#    62
  15) 2,4-dimethylphenol            14.51  122      9838     1.00 ug/ml#    75
  16) 3-ethylphenol                 15.20  122       875     0.17 ug/ml#     1
  17) 2,3-dimethylphenol            15.32  122       377     0.05 ug/ml#     1
  18) Naphthalene                   15.50  128       543     0.02 ug/ml#     1
  19) 2-methoxy-4-methylphenol      15.66  138     27405     3.42 ug/ml     92
  20) 1,2-benzenediol                0.00  110         0      N.D.
  21) 4-methyl-1,2-benzenediol      18.14  124       281     0.38 ug/ml#     1
  22) 4-ethyl-2-methoxyphenol       18.15  137     10205     0.52 ug/ml     87
  24) 3-methyl-1,2-benzenediol      18.94  124      9232     8.66 ug/ml#     1
  25) 2,6-dimethoxyphenol            0.00  154         0      N.D.
  26) Eugenol                       20.31  164       260     0.03 ug/ml#    44
  27) 2-methoxy-4-propylphenol      20.76  137       631     0.02 ug/ml#     1
  28) Vanillin                      21.47  151      7449     2.61 ug/ml#    66
  29) cis-Isoeugenol                 0.00  164         0      N.D.
  30) 3,4-dimethylbenzoic acid       0.00  105         0      N.D.
  31) trans-Isoeugenol               0.00  164         0      N.D.
  32) 4-ethylresorcinol             22.45  123       605     0.09 ug/ml#    47
  33) Levoglucosan                  25.21   60       598     0.97 ug/ml#     1
  34) Acetovanillone                23.63  166      7929     1.26 ug/ml#    50
  37) Oleic acid                    37.58   55       267     0.25 ug/ml#    14
```

Experiment no.	: 93
Oil composition in bio oil-water mixture	: 25 wt.%
Reaction temperature	: 380 °C
Reaction time	: 0 h (To examine effect of heating cycle)



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                         Quantitation Report    (QT Reviewed)

Data File : D:\HPCHEM\DATA\080326\080317-3.D              Vial: 4
Acq On    : 26 Mar 2008   12:18                       Operator: Hassan
Sample    : sample 93                                 Inst    : GC/MS Ins
Misc      : w=0.2069 ug/ml                            Multiplr: 1.00
                                                 Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Mar 27 15:13 2008              Quant Results File: B_080320.RES

Quant Method : C:\HPCHEM\1\METHODS\B_080320.M (RTE Integrator)
Title        :
Last Update  : Tue Mar 25 14:03:46 2008
Response via : Initial Calibration
DataAcq Meth : B_080320

 Internal Standards                 R.T. QIon  Response  Conc Units Dev(Min)
 ----------------------------------------------------------------------------
   1) 1,4-dichlorobenzene-d4        9.74  152   361070    40.00 ug/ml    0.00
  11) Naphthalene-d8               15.10  136  1184661    40.00 ug/ml   -0.01
  23) Acenaphthene-d10             23.20  164   847563    40.00 ug/ml    0.00
  35) Phenanthrene-d10             29.94  188  1549023    40.00 ug/ml    0.00
  36) Chrysene-d12                 42.28  240  1303459    40.00 ug/ml    0.00
  38) Perylene-d12                 48.39  264   916145    40.00 ug/ml    0.00

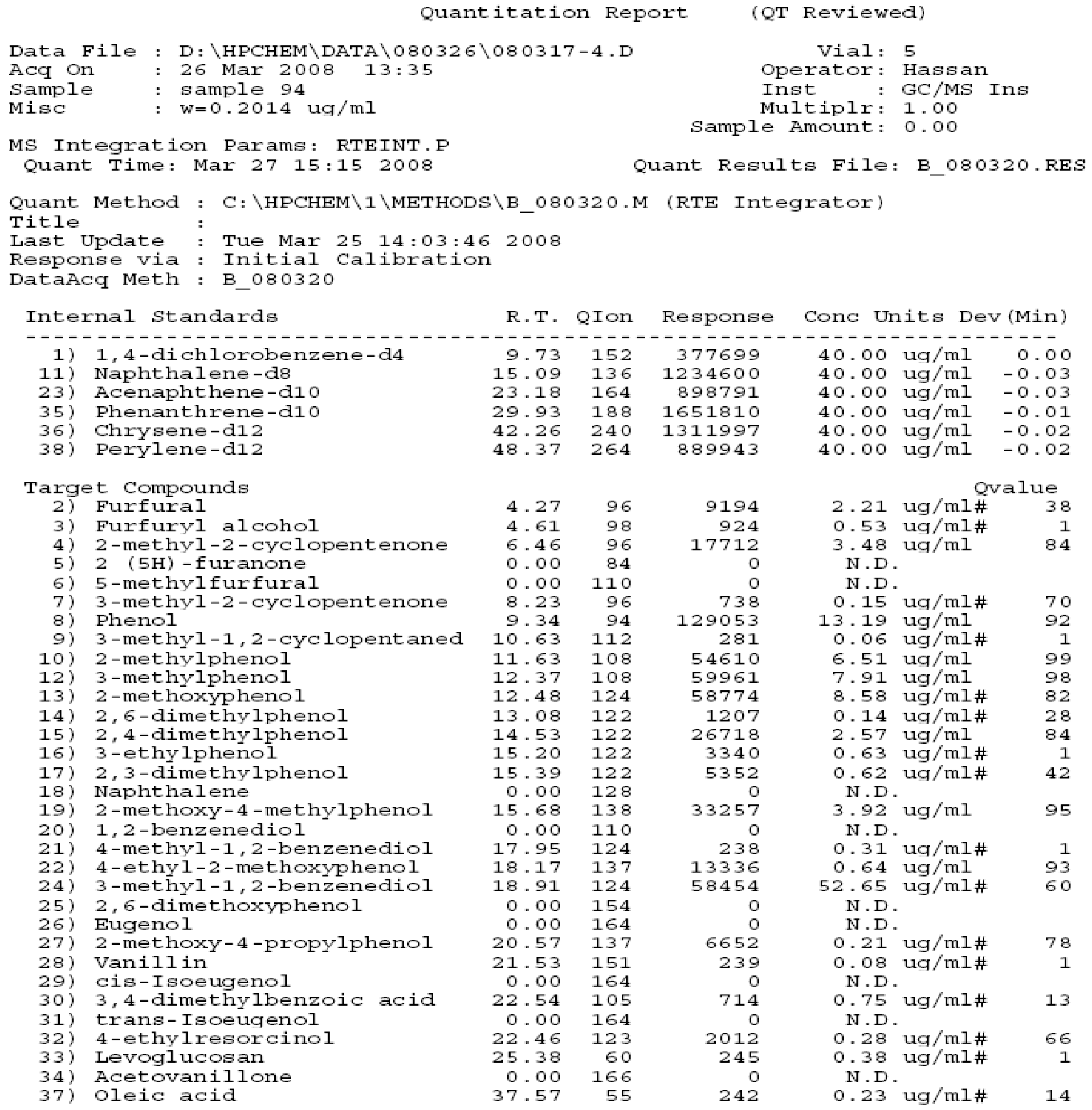
 Target Compounds                                                     Qvalue
   2) Furfural                      4.26   96    17744     4.47 ug/ml#     13
   3) Furfuryl alcohol              4.65   98      269     0.16 ug/ml#     28
   4) 2-methyl-2-cyclopentenone     6.44   96    28228     5.80 ug/ml      93
   5) 2 (5H)-furanone               0.00   84        0      N.D.
   6) 5-methylfurfural              0.00  110        0      N.D.
   7) 3-methyl-2-cyclopentenone     8.29   96      244     0.05 ug/ml#     14
   8) Phenol                        9.38   94    62448     6.68 ug/ml      92
   9) 3-methyl-1,2-cyclopentaned   10.76  112      265     0.06 ug/ml#      1
  10) 2-methylphenol               11.65  108    29800     3.72 ug/ml      98
  12) 3-methylphenol               12.39  108     7928     1.09 ug/ml#     82
  13) 2-methoxyphenol              12.50  124    61731     9.39 ug/ml      98
  14) 2,6-dimethylphenol           13.11  122     1160     0.14 ug/ml#      1
  15) 2,4-dimethylphenol           14.56  122    15082     1.51 ug/ml#     79
  16) 3-ethylphenol                15.16  122      240     0.05 ug/ml#      1
  17) 2,3-dimethylphenol           15.37  122      869     0.11 ug/ml#      5
  18) Naphthalene                  15.22  128        0      N.D.
  19) 2-methoxy-4-methylphenol     15.69  138    32396     3.98 ug/ml#     82
  20) 1,2-benzenediol               0.00  110        0      N.D.
  21) 4-methyl-1,2-benzenediol     18.06  124      392     0.53 ug/ml#      1
  22) 4-ethyl-2-methoxyphenol      18.17  137    16490     0.82 ug/ml      93
  24) 3-methyl-1,2-benzenediol     18.87  124     1940     1.85 ug/ml#     73
  25) 2,6-dimethoxyphenol           0.00  154        0      N.D.
  26) Eugenol                      20.34  164      345     0.04 ug/ml#     29
  27) 2-methoxy-4-propylphenol     20.58  137     7159     0.24 ug/ml#     70
  28) Vanillin                      0.00  151        0      N.D.
  29) cis-Isoeugenol                0.00  164        0      N.D.
  30) 3,4-dimethylbenzoic acid      0.00  105        0      N.D.
  31) trans-Isoeugenol              0.00  164        0      N.D.
  32) 4-ethylresorcinol            22.47  123     1885     0.28 ug/ml#     47
  33) Levoglucosan                  0.00   60        0      N.D.
  34) Acetovanillone               23.70  166      375     0.06 ug/ml#      1
  37) Oleic acid                   37.37   55      319     0.30 ug/ml#     14
```

Experiment no. : 94

Oil composition in bio oil-water mixture : 50 wt.%

Reaction temperature : 380 °C

Reaction time : 0.5 h



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                        Quantitation Report    (QT Reviewed)

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Acq On    : 26 Mar 2008   13:35                     Operator: Hassan
Sample    : sample 94                               Inst    : GC/MS Ins
Misc      : w=0.2014 ug/ml                          Multiplr: 1.00
                                               Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Mar 27 15:15 2008             Quant Results File: B_080320.RES

Quant Method : C:\HPCHEM\1\METHODS\B_080320.M (RTE Integrator)
Title        :
Last Update  : Tue Mar 25 14:03:46 2008
Response via : Initial Calibration
DataAcq Meth : B_080320

 Internal Standards                   R.T. QIon  Response  Conc Units Dev(Min)
 ------------------------------------------------------------------------------
   1) 1,4-dichlorobenzene-d4          9.73  152   377699    40.00 ug/ml    0.00
  11) Naphthalene-d8                 15.09  136  1234600    40.00 ug/ml   -0.03
  23) Acenaphthene-d10               23.18  164   898791    40.00 ug/ml   -0.03
  35) Phenanthrene-d10               29.93  188  1651810    40.00 ug/ml   -0.01
  36) Chrysene-d12                   42.26  240  1311997    40.00 ug/ml   -0.02
  38) Perylene-d12                   48.37  264   889943    40.00 ug/ml   -0.02

 Target Compounds                                                      Qvalue
   2) Furfural                        4.27   96     9194     2.21 ug/ml#    38
   3) Furfuryl alcohol                4.61   98      924     0.53 ug/ml#     1
   4) 2-methyl-2-cyclopentenone       6.46   96    17712     3.48 ug/ml     84
   5) 2 (5H)-furanone                 0.00   84        0      N.D.
   6) 5-methylfurfural                0.00  110        0      N.D.
   7) 3-methyl-2-cyclopentenone       8.23   96      738     0.15 ug/ml#    70
   8) Phenol                          9.34   94   129053    13.19 ug/ml     92
   9) 3-methyl-1,2-cyclopentaned     10.63  112      281     0.06 ug/ml#     1
  10) 2-methylphenol                 11.63  108    54610     6.51 ug/ml     99
  12) 3-methylphenol                 12.37  108    59961     7.91 ug/ml     98
  13) 2-methoxyphenol                12.48  124    58774     8.58 ug/ml#    82
  14) 2,6-dimethylphenol             13.08  122     1207     0.14 ug/ml#    28
  15) 2,4-dimethylphenol             14.53  122    26718     2.57 ug/ml     84
  16) 3-ethylphenol                  15.20  122     3340     0.63 ug/ml#     1
  17) 2,3-dimethylphenol             15.39  122     5352     0.62 ug/ml#    42
  18) Naphthalene                     0.00  128        0      N.D.
  19) 2-methoxy-4-methylphenol       15.68  138    33257     3.92 ug/ml     95
  20) 1,2-benzenediol                 0.00  110        0      N.D.
  21) 4-methyl-1,2-benzenediol       17.95  124      238     0.31 ug/ml#     1
  22) 4-ethyl-2-methoxyphenol        18.17  137    13336     0.64 ug/ml     93
  24) 3-methyl-1,2-benzenediol       18.91  124    58454    52.65 ug/ml#    60
  25) 2,6-dimethoxyphenol             0.00  154        0      N.D.
  26) Eugenol                         0.00  164        0      N.D.
  27) 2-methoxy-4-propylphenol       20.57  137     6652     0.21 ug/ml#    78
  28) Vanillin                       21.53  151      239     0.08 ug/ml#     1
  29) cis-Isoeugenol                  0.00  164        0      N.D.
  30) 3,4-dimethylbenzoic acid       22.54  105      714     0.75 ug/ml#    13
  31) trans-Isoeugenol                0.00  164        0      N.D.
  32) 4-ethylresorcinol              22.46  123     2012     0.28 ug/ml#    66
  33) Levoglucosan                   25.38   60      245     0.38 ug/ml#     1
  34) Acetovanillone                  0.00  166        0      N.D.
  37) Oleic acid                     37.57   55      242     0.23 ug/ml#    14
```
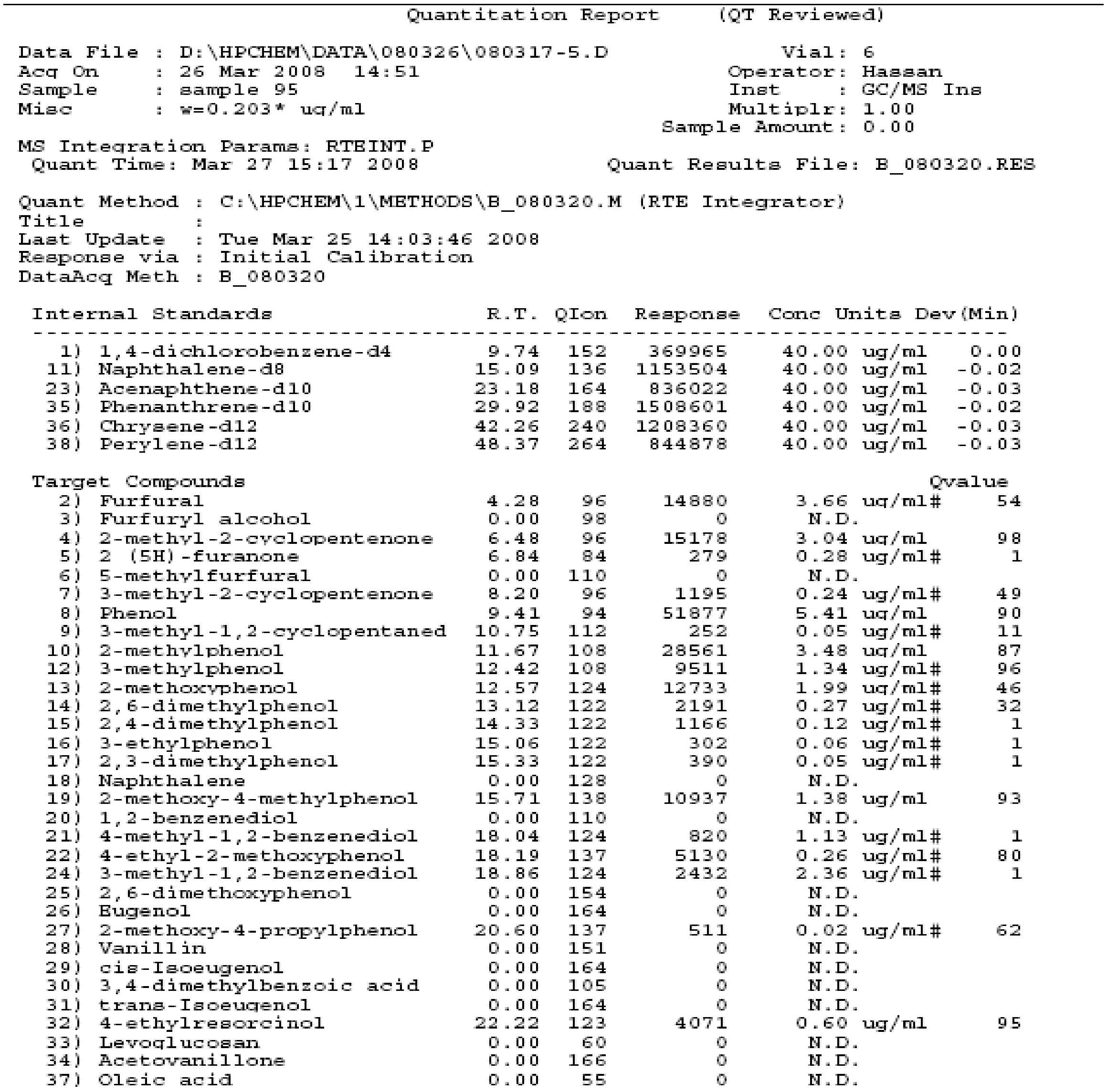

Experiment no.	: 95
Oil composition in bio oil-water mixture	: 25 wt.%
Reaction temperature	: 420 °C
Reaction time	: 0 h (To examine effect of heating cycle)



```
                         Quantitation Report    (QT Reviewed)

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 Acq On    : 26 Mar 2008  14:51                        Operator: Hassan
 Sample    : sample 95                                 Inst    : GC/MS Ins
 Misc      : w=0.203* ug/ml                            Multiplr: 1.00
                                                  Sample Amount: 0.00
 MS Integration Params: RTEINT.P
  Quant Time: Mar 27 15:17 2008              Quant Results File: B_080320.RES

 Quant Method : C:\HPCHEM\1\METHODS\B_080320.M (RTE Integrator)
 Title        :
 Last Update  : Tue Mar 25 14:03:46 2008
 Response via : Initial Calibration
 DataAcq Meth : B_080320

  Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
  -------------------------------------------------------------------------
    1) 1,4-dichlorobenzene-d4       9.74  152   369965    40.00 ug/ml   0.00
   11) Naphthalene-d8              15.09  136  1153504    40.00 ug/ml  -0.02
   23) Acenaphthene-d10            23.18  164   836022    40.00 ug/ml  -0.03
   35) Phenanthrene-d10            29.92  188  1508601    40.00 ug/ml  -0.02
   36) Chrysene-d12                42.26  240  1208360    40.00 ug/ml  -0.03
   38) Perylene-d12                48.37  264   844878    40.00 ug/ml  -0.03

  Target Compounds                                                  Qvalue
    2) Furfural                     4.28   96    14880     3.66 ug/ml#    54
    3) Furfuryl alcohol             0.00   98        0      N.D.
    4) 2-methyl-2-cyclopentenone    6.48   96    15178     3.04 ug/ml     98
    5) 2 (5H)-furanone              6.84   84      279     0.28 ug/ml#     1
    6) 5-methylfurfural             0.00  110        0      N.D.
    7) 3-methyl-2-cyclopentenone    8.20   96     1195     0.24 ug/ml#    49
    8) Phenol                       9.41   94    51877     5.41 ug/ml     90
    9) 3-methyl-1,2-cyclopentaned  10.75  112      252     0.05 ug/ml#    11
   10) 2-methylphenol              11.67  108    28561     3.48 ug/ml     87
   12) 3-methylphenol              12.42  108     9511     1.34 ug/ml#    96
   13) 2-methoxyphenol             12.57  124    12733     1.99 ug/ml#    46
   14) 2,6-dimethylphenol          13.12  122     2191     0.27 ug/ml#    32
   15) 2,4-dimethylphenol          14.33  122     1166     0.12 ug/ml#     1
   16) 3-ethylphenol               15.06  122      302     0.06 ug/ml#     1
   17) 2,3-dimethylphenol          15.33  122      390     0.05 ug/ml#     1
   18) Naphthalene                  0.00  128        0      N.D.
   19) 2-methoxy-4-methylphenol    15.71  138    10937     1.38 ug/ml     93
   20) 1,2-benzenediol              0.00  110        0      N.D.
   21) 4-methyl-1,2-benzenediol    18.04  124      820     1.13 ug/ml#     1
   22) 4-ethyl-2-methoxyphenol     18.19  137     5130     0.26 ug/ml#    80
   24) 3-methyl-1,2-benzenediol    18.86  124     2432     2.36 ug/ml#     1
   25) 2,6-dimethoxyphenol          0.00  154        0      N.D.
   26) Eugenol                      0.00  164        0      N.D.
   27) 2-methoxy-4-propylphenol    20.60  137      511     0.02 ug/ml#    62
   28) Vanillin                     0.00  151        0      N.D.
   29) cis-Isoeugenol               0.00  164        0      N.D.
   30) 3,4-dimethylbenzoic acid     0.00  105        0      N.D.
   31) trans-Isoeugenol             0.00  164        0      N.D.
   32) 4-ethylresorcinol           22.22  123     4071     0.60 ug/ml     95
   33) Levoglucosan                 0.00   60        0      N.D.
   34) Acetovanillone               0.00  166        0      N.D.
   37) Oleic acid                   0.00   55        0      N.D.
```
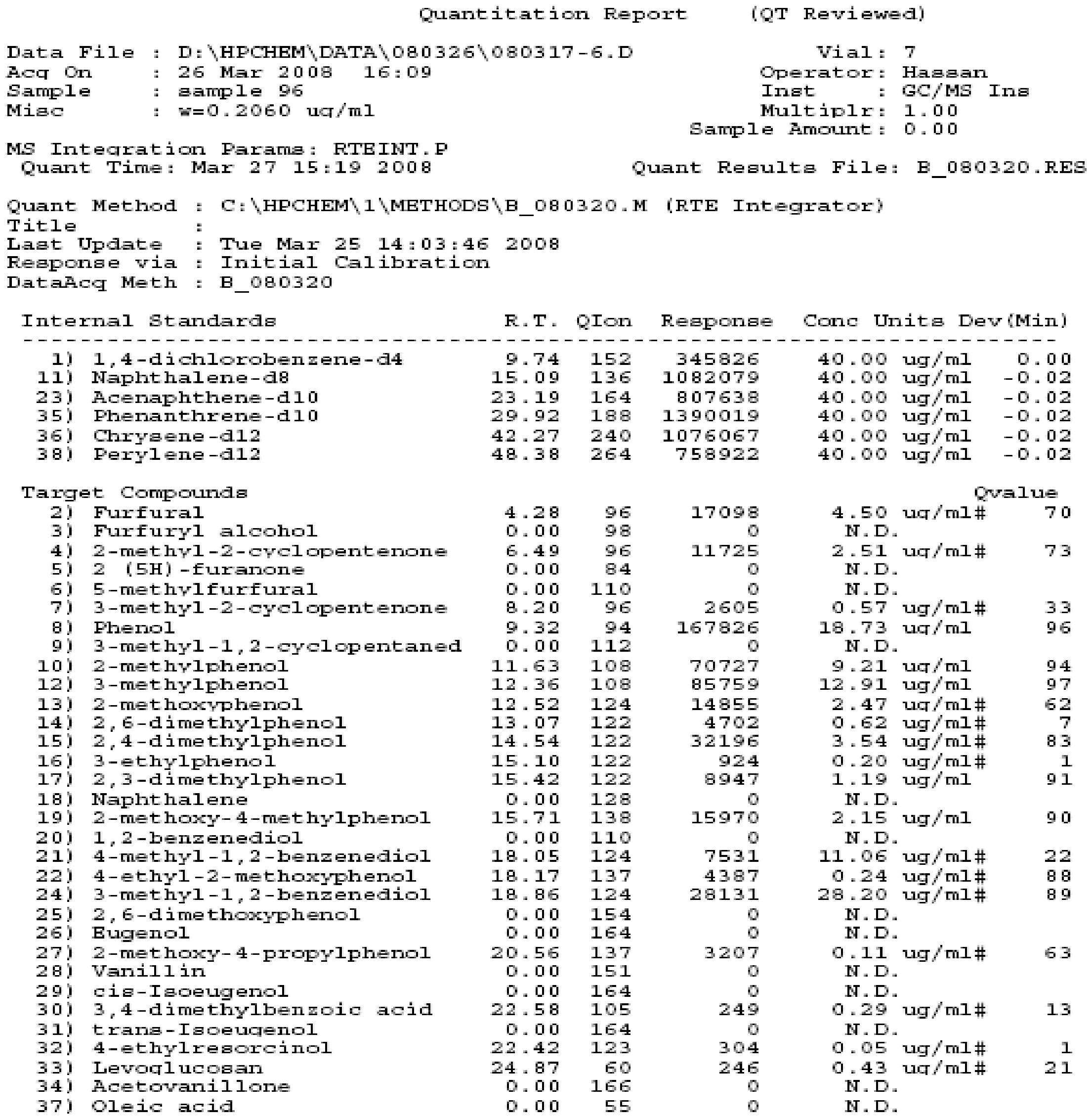

Experiment no.	: 96
Oil composition in bio oil-water mixture	: 50 wt.%
Reaction temperature	: 420 °C
Reaction time	: 0.5 h



```
                               Quantitation Report    (QT Reviewed)

Data File : D:\HPCHEM\DATA\080326\080317-6.D                 Vial: 7
Acq On    : 26 Mar 2008   16:09                          Operator: Hassan
Sample    : sample 96                                    Inst    : GC/MS Ins
Misc      : w=0.2060 ug/ml                               Multiplr: 1.00
                                                    Sample Amount: 0.00
MS Integration Params: RTEINT.P
 Quant Time: Mar 27 15:19 2008                 Quant Results File: B_080320.RES

Quant Method : C:\HPCHEM\1\METHODS\B_080320.M (RTE Integrator)
Title        :
Last Update  : Tue Mar 25 14:03:46 2008
Response via : Initial Calibration
DataAcq Meth : B_080320

 Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
 ------------------------------------------------------------------------------
   1) 1,4-dichlorobenzene-d4         9.74  152   345826    40.00 ug/ml    0.00
  11) Naphthalene-d8                15.09  136  1082079    40.00 ug/ml   -0.02
  23) Acenaphthene-d10              23.19  164   807638    40.00 ug/ml   -0.02
  35) Phenanthrene-d10              29.92  188  1390019    40.00 ug/ml   -0.02
  36) Chrysene-d12                  42.27  240  1076067    40.00 ug/ml   -0.02
  38) Perylene-d12                  48.38  264   758922    40.00 ug/ml   -0.02

 Target Compounds                                                      Qvalue
   2) Furfural                       4.28   96    17098     4.50 ug/ml#    70
   3) Furfuryl alcohol               0.00   98        0     N.D.
   4) 2-methyl-2-cyclopentenone      6.49   96    11725     2.51 ug/ml#    73
   5) 2 (5H)-furanone                0.00   84        0     N.D.
   6) 5-methylfurfural               0.00  110        0     N.D.
   7) 3-methyl-2-cyclopentenone      8.20   96     2605     0.57 ug/ml#    33
   8) Phenol                         9.32   94   167826    18.73 ug/ml     96
   9) 3-methyl-1,2-cyclopentaned     0.00  112        0     N.D.
  10) 2-methylphenol                11.63  108    70727     9.21 ug/ml     94
  12) 3-methylphenol                12.36  108    85759    12.91 ug/ml     97
  13) 2-methoxyphenol               12.52  124    14855     2.47 ug/ml#    62
  14) 2,6-dimethylphenol            13.07  122     4702     0.62 ug/ml#     7
  15) 2,4-dimethylphenol            14.54  122    32196     3.54 ug/ml#    83
  16) 3-ethylphenol                 15.10  122      924     0.20 ug/ml#     1
  17) 2,3-dimethylphenol            15.42  122     8947     1.19 ug/ml     91
  18) Naphthalene                    0.00  128        0     N.D.
  19) 2-methoxy-4-methylphenol      15.71  138    15970     2.15 ug/ml     90
  20) 1,2-benzenediol                0.00  110        0     N.D.
  21) 4-methyl-1,2-benzenediol      18.05  124     7531    11.06 ug/ml#    22
  22) 4-ethyl-2-methoxyphenol       18.17  137     4387     0.24 ug/ml#    88
  24) 3-methyl-1,2-benzenediol      18.86  124    28131    28.20 ug/ml#    89
  25) 2,6-dimethoxyphenol            0.00  154        0     N.D.
  26) Eugenol                        0.00  164        0     N.D.
  27) 2-methoxy-4-propylphenol      20.56  137     3207     0.11 ug/ml#    63
  28) Vanillin                       0.00  151        0     N.D.
  29) cis-Isoeugenol                 0.00  164        0     N.D.
  30) 3,4-dimethylbenzoic acid      22.58  105      249     0.29 ug/ml#    13
  31) trans-Isoeugenol               0.00  164        0     N.D.
  32) 4-ethylresorcinol             22.42  123      304     0.05 ug/ml#     1
  33) Levoglucosan                  24.87   60      246     0.43 ug/ml#    21
  34) Acetovanillone                 0.00  166        0     N.D.
  37) Oleic acid                     0.00   55        0     N.D.
```

APPENDIX C

GRAPHICAL DATA

C.1 Effect of composition at 300 °C

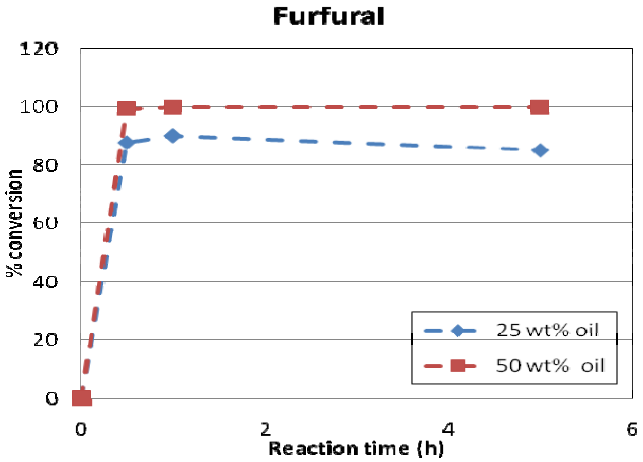


Figure C.1 Effect of bio-oil composition on furfural conversion at 300 °C

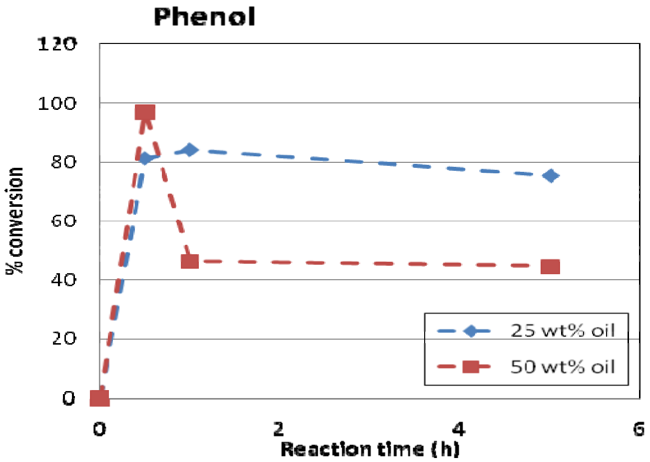


Figure C.2 Effect of bio-oil composition on conversion of phenol at 300 °C

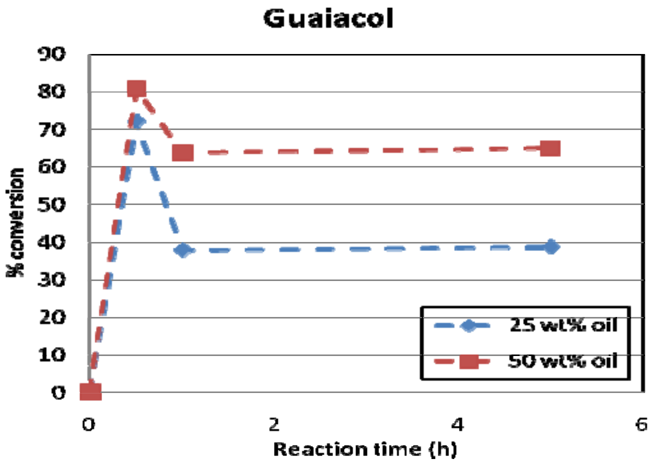


Figure C.3 Effect of bio-oil composition on conversion of guaiacol at 300 °C

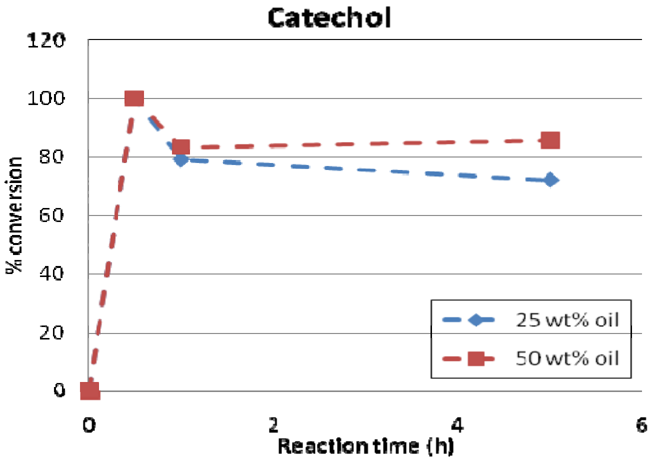


Figure C.4 Effect of bio-oil composition on conversion of catechol at 300 °C

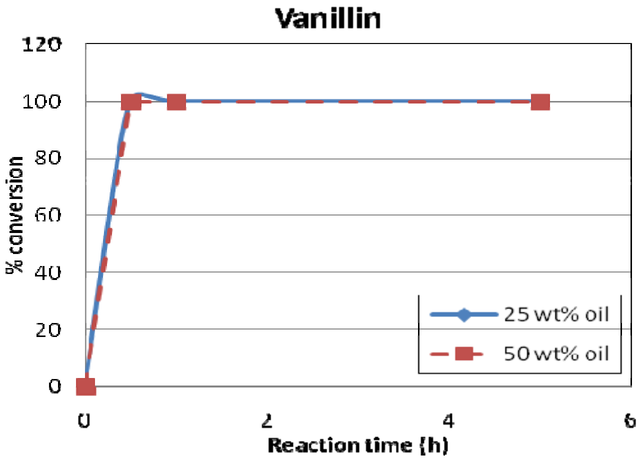


Figure C.5 Effect of bio-oil composition on conversion of vanillin at 300 °C

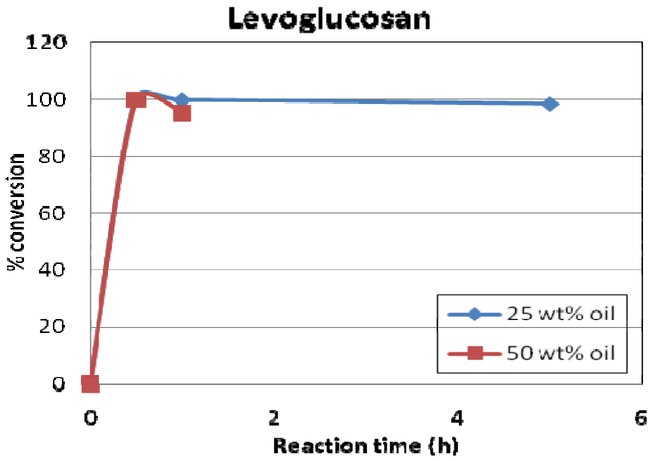


Figure C.6 Effect of bio-oil composition on conversion of levoglucosan at 300 °C

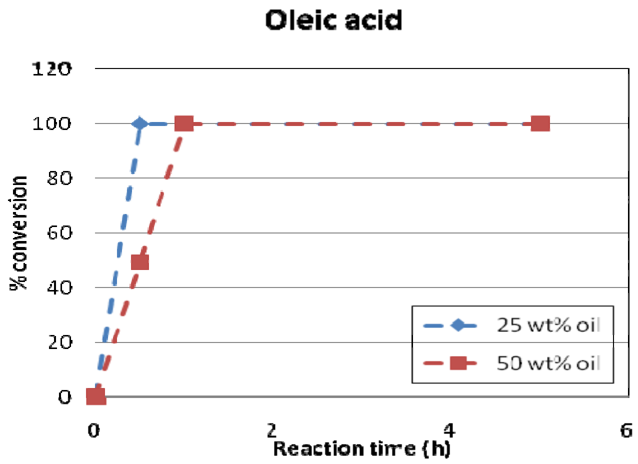


Figure C.7 Effect of bio-oil composition on conversion of oleic acid at 300 °C

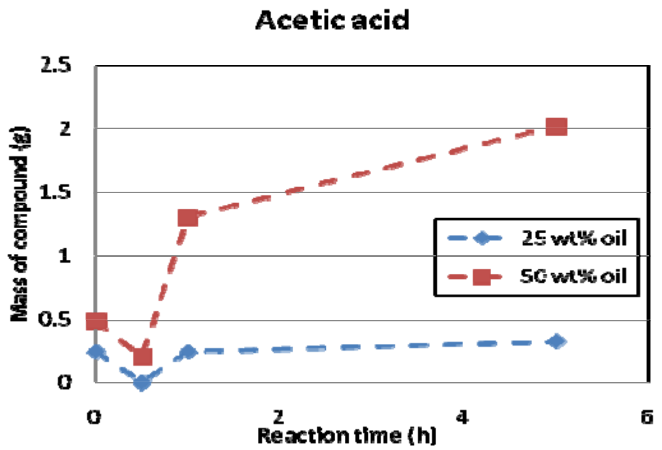


Figure C.8 Effect of bio-oil composition on acetic acid formation at 300 °C

C.2 Effect of oil composition at 380 °C

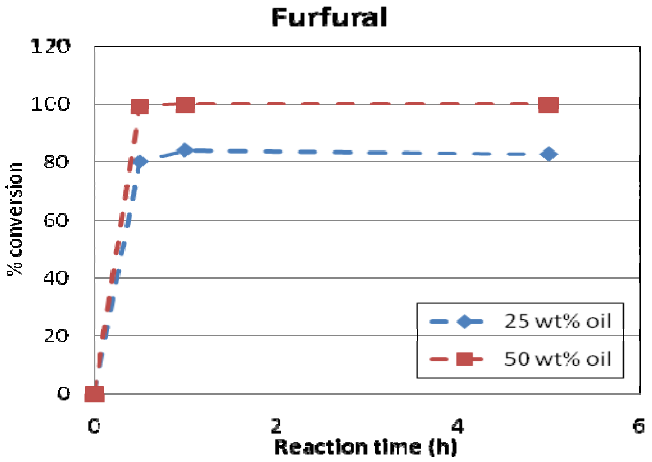


Figure C.9 Effect of bio-oil composition on conversion of furfural at 380 °C

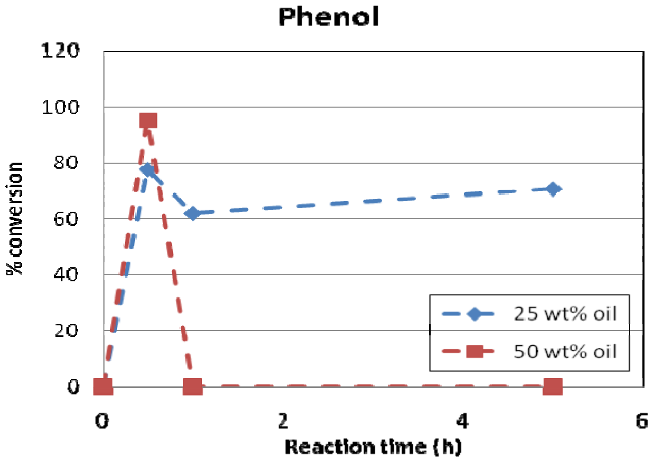


Figure C.10 Effect of bio-oil composition on conversion of phenol at 380 °C

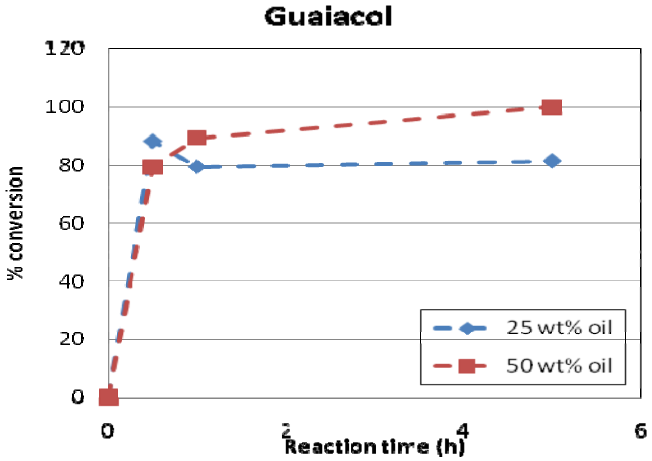


Figure C.11 Effect of bio-oil composition on conversion of guaiacol at 380 °C

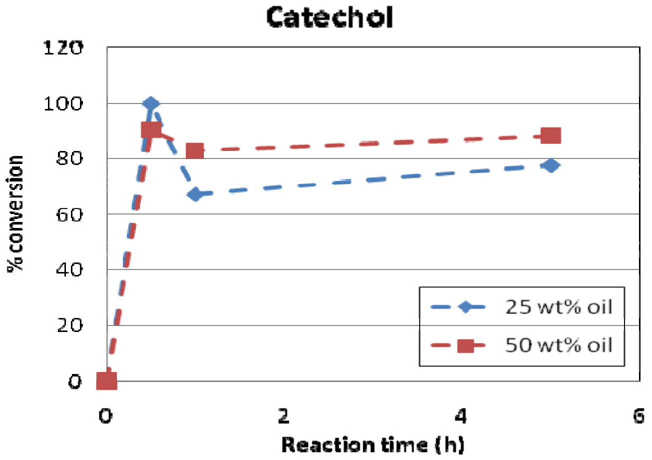


Figure C.12 Effect of bio-oil composition on conversion of catechol at 380 °C

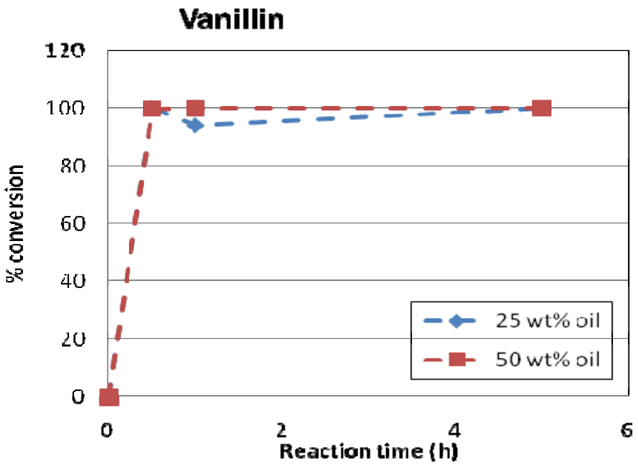


Figure C.13 Effect of bio-oil composition on conversion of vanillin at 380 °C

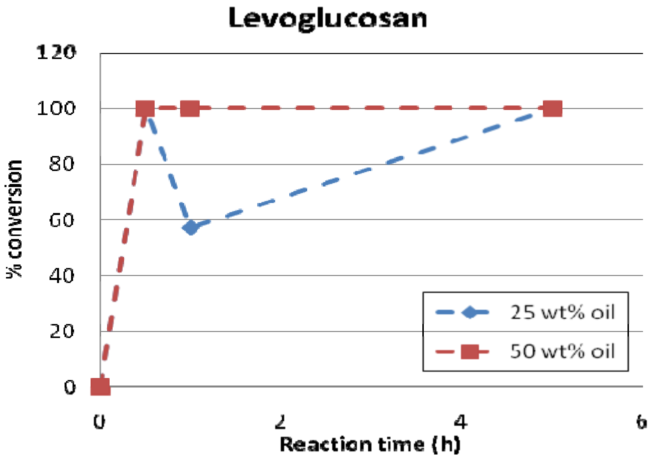


Figure C.14 Effect of bio-oil composition on conversion of levoglucosan at 380 °C

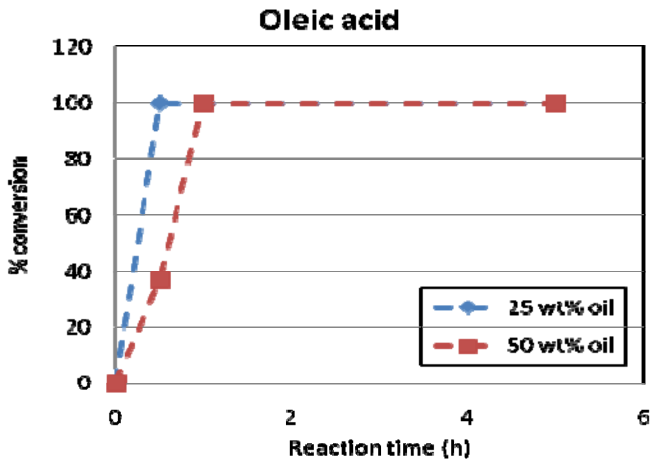


Figure C.15 Effect of bio-oil composition on conversion of oleic acid at 380 °C

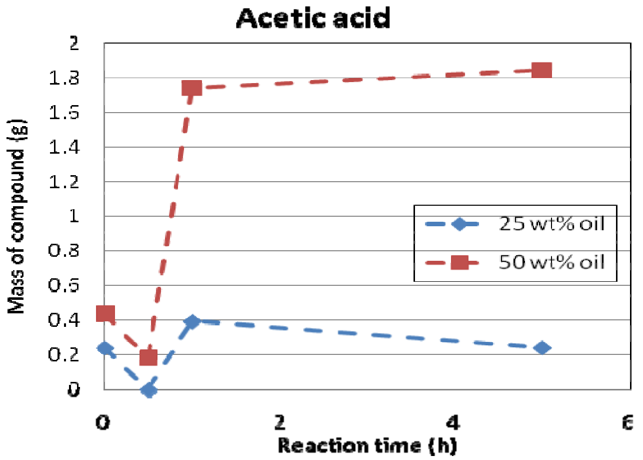


Figure C.16 Effect of bio-oil composition on acetic acid formation at 380 °C

C.3 Effect of temperature with 50 wt% oil

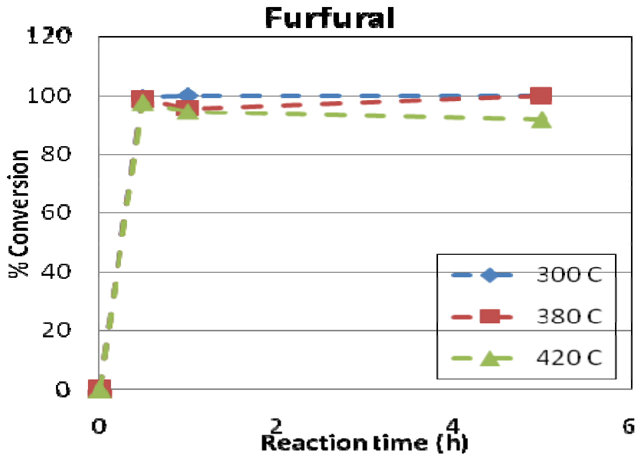


Figure C.17 Effect of operating temperature on furfural conversion with 50 wt% oil

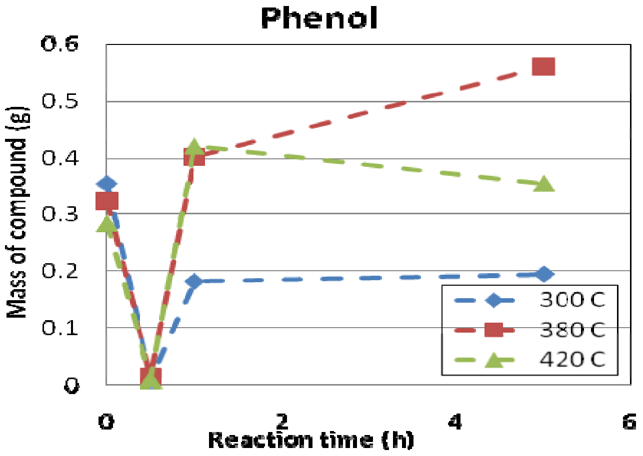


Figure C.18 Effect of operating temperature on phenol formation with 50 wt% oil

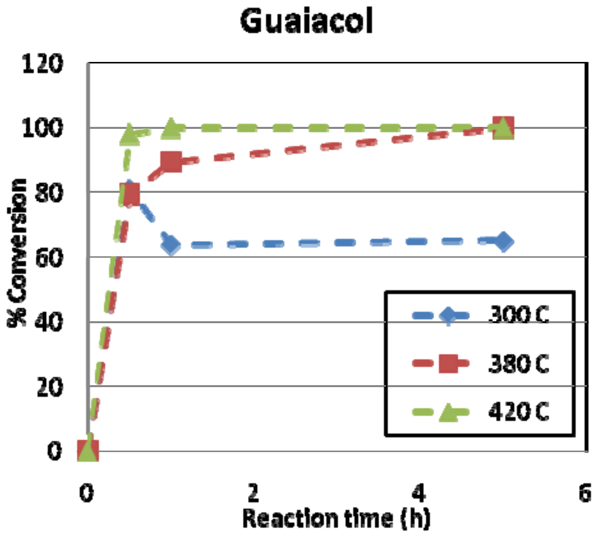


Figure C.19 Effect of operating temperature on conversion of guaiacol with 50 wt% oil

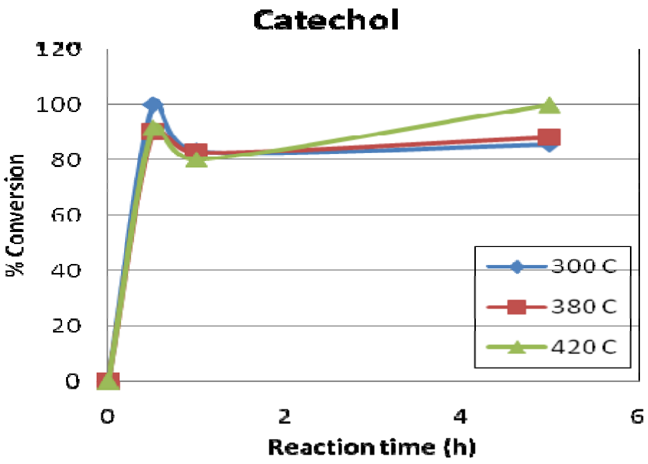


Figure C.20 Effect of operating temperature on conversion of catechol with 50 wt% oil

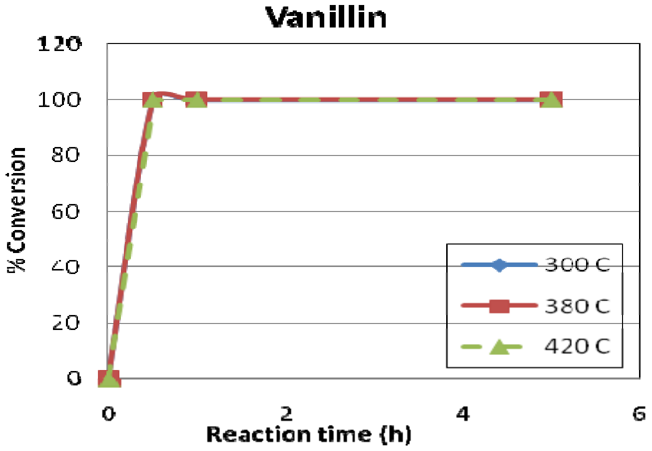


Figure C.21 Effect of operating temperature on conversion of vanillin with 50 wt% oil

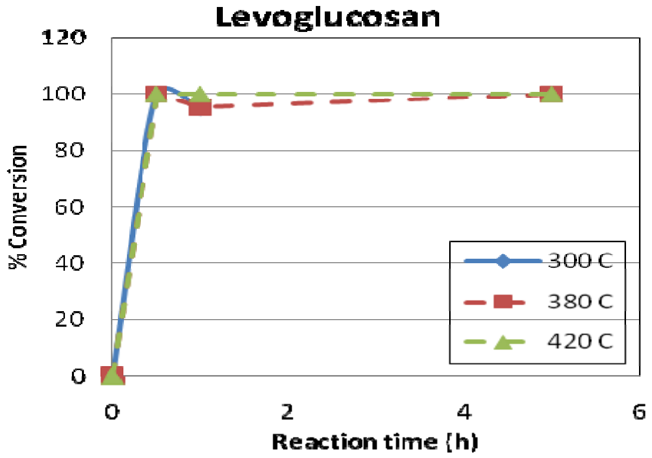


Figure C.22 Effect of operating temperature on conversion of levoglucosan with 50 wt% oil

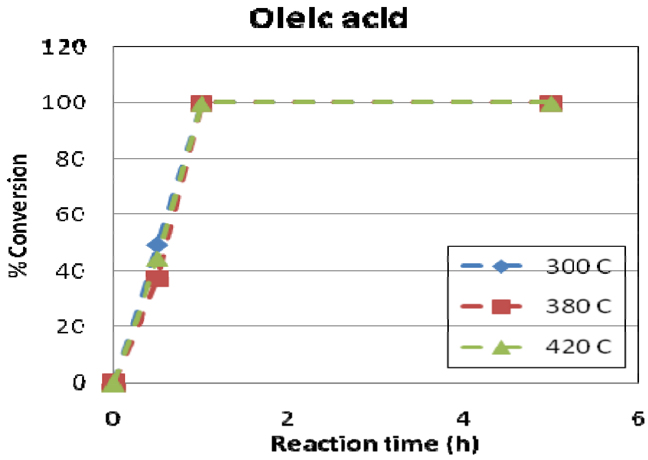


Figure C.23 Effect of operating temperature on conversion of oleic acid with 50 wt% oil

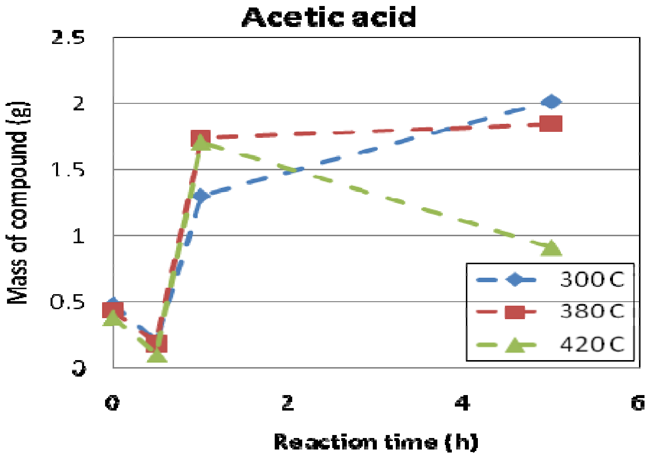


Figure C.24 Effect of operating temperature on acetic acid formation with 50 wt% oil

APPENDIX D

STATISTICAL ANALYSIS

D.1 Objective

The objective of performing statistical analysis was to narrow down on the best process conditions on the basis of desirable product composition and the effectiveness in conversion of undesirable components. Three different ANOVA algorithms were employed to understand the influence of each process parameter on the conversions. A two-way Anova was deployed to study the effect of operating temperature and reaction time. Two different One-way Anova experiments were performed to study effects of initial oil composition and use of methanol as co-solvent. Eight compounds viz. furfural, guaiacol, vanillin, phenol, catechol, levoglucosan, acetic acid and oleic acid were used in the analysis.

D.2 Two-way ANOVA - temperature and reaction time

Effect of temperature:

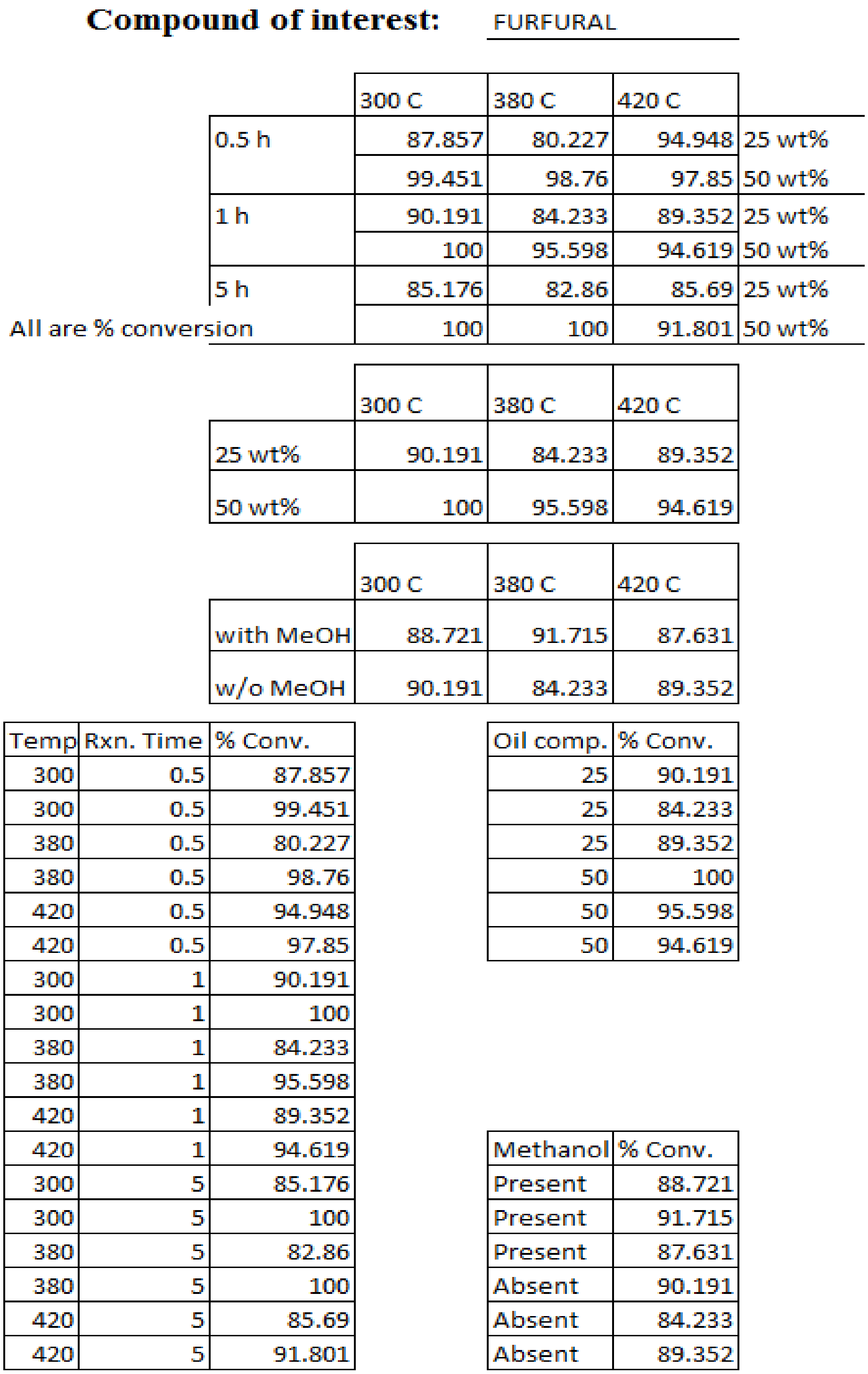
$H_o : \mu_{300C} = \mu_{380C} = \mu_{420C}$

$H_a : \mu_{300C} \neq \mu_{380C} \neq \mu_{420C}$

Two statistical methods namely Tukey and Scheffe were employed for analysis. The Null hypothesis (H_o) was tested at 90 % significance level.

For a better understanding, the complete procedure is elaborately explained for Furfural.

Table D.1 Anova program input



Compound of interest: FURFURAL

	300 C	380 C	420 C	
0.5 h	87.857	80.227	94.948	25 wt%
	99.451	98.76	97.85	50 wt%
1 h	90.191	84.233	89.352	25 wt%
	100	95.598	94.619	50 wt%
5 h	85.176	82.86	85.69	25 wt%
	100	100	91.801	50 wt%

All are % conversion

	300 C	380 C	420 C
25 wt%	90.191	84.233	89.352
50 wt%	100	95.598	94.619

	300 C	380 C	420 C
with MeOH	88.721	91.715	87.631
w/o MeOH	90.191	84.233	89.352

Temp	Rxn. Time	% Conv.
300	0.5	87.857
300	0.5	99.451
380	0.5	80.227
380	0.5	98.76
420	0.5	94.948
420	0.5	97.85
300	1	90.191
300	1	100
380	1	84.233
380	1	95.598
420	1	89.352
420	1	94.619
300	5	85.176
300	5	100
380	5	82.86
380	5	100
420	5	85.69
420	5	91.801

Oil comp.	% Conv.
25	90.191
25	84.233
25	89.352
50	100
50	95.598
50	94.619

Methanol	% Conv.
Present	88.721
Present	91.715
Present	87.631
Absent	90.191
Absent	84.233
Absent	89.352

```
SAS OUTPUT:                          The SAS System          22:01 Tuesday, April 1, 2008   1

                                        The GLM Procedure

                                     Class Level Information

                             Class              Levels    Values

                             temperature             3    300 380 420

                             reactiontime            3    0.5 1 5


                             Number of Observations Read          18
                             Number of Observations Used          18

                                        The GLM Procedure

Dependent Variable: conversion   Conversion of furfural (in %)

                                               Sum of
       Source                      DF         Squares     Mean Square    F Value    Pr > F

       Model                        8     106.7393680      13.3424210       0.19    0.9866

       Error                        9     645.1552105      71.6839123

       Corrected Total             17     751.8945785


                     R-Square     Coeff Var      Root MSE    conversion Mean

                     0.141961      9.188366      8.466635           92.14517


       Source                      DF       Type I SS     Mean Square    F Value    Pr > F

       temperature                  2     37.22183100     18.61091550       0.26    0.7769
       reactiontime                 2     15.65108400      7.82554200       0.11    0.8977
       temperatu*reactionti         4     53.86645300     13.46661325       0.19    0.9388


       Source                   DF     Type III SS     Mean Square    F Value    Pr > F
       temperature              2     37.22183100     18.61091550       0.26    0.7769
       reactiontime             2     15.65108400      7.82554200       0.11    0.8977
       temperatu*reactionti     4     53.86645300     13.46661325       0.19    0.9388
```

```
                   The GLM Procedure
                  Least Squares Means
       Adjustment for Multiple Comparisons: Tukey

                         conversion      LSMEAN
        temperature          LSMEAN      Number

        300              93.7791667           1
        380              90.2796667           2
        420              92.3766667           3


       Least Squares Means for effect temperature
          Pr > |t| for H0: LSMean(i)=LSMean(j)

             Dependent Variable: conversion

     i/j              1             2             3

        1                      0.7605        0.9559
        2        0.7605                      0.9046
        3        0.9559        0.9046


                 conversion
temperature          LSMEAN      95% Confidence Limits

300               93.779167       85.960044   101.598289
380               90.279667       82.460544    98.098789
420               92.376667       84.557544   100.195789


       Least Squares Means for Effect temperature

              Difference         Simultaneous 95%
                 Between       Confidence Limits for
  i    j           Means        LSMean(i)-LSMean(j)

  1    2        3.499500      -10.148441    17.147441
  1    3        1.402500      -12.245441    15.050441
  2    3       -2.097000      -15.744941    11.550941


                   The GLM Procedure
                  Least Squares Means
      Adjustment for Multiple Comparisons: Scheffe

                         conversion      LSMEAN
        temperature          LSMEAN      Number

        300              93.7791667           1
        380              90.2796667           2
        420              92.3766667           3

       Least Squares Means for effect temperature
          Pr > |t| for H0: LSMean(i)=LSMean(j)
```

```
             Dependent Variable: conversion

     i/j              1             2             3

        1                      0.7794        0.9599
        2        0.7794                      0.9129
        3        0.9599        0.9129


                 conversion
temperature          LSMEAN      95% Confidence Limits

300               93.779167       85.960044   101.598289
380               90.279667       82.460544    98.098789
420               92.376667       84.557544   100.195789


       Least Squares Means for Effect temperature

              Difference         Simultaneous 95%
                 Between      Confidence Limits for
  i    j           Means       LSMean(i)-LSMean(j)

  1    2        3.499500      -10.762856    17.761856
  1    3        1.402500      -12.859856    15.664856
  2    3       -2.097000      -16.359356    12.165356


                   The GLM Procedure
                  Least Squares Means
       Adjustment for Multiple Comparisons: Tukey

                          conversion       LSMEAN
        reactiontime          LSMEAN       Number

        0.5               93.1821667            1
        1                 92.3321667            2
        5                 90.9211667            3


      Least Squares Means for effect reactiontime
          Pr > |t| for H0: LSMean(i)=LSMean(j)

             Dependent Variable: conversion

     i/j              1             2             3

        1                      0.9835        0.8901
        2        0.9835                      0.9553
        3        0.8901        0.9553
```

```
                  conversion
reactiontime          LSMEAN      95% Confidence Limits

0.5                93.182167      85.363044   101.001289
1                  92.332167      84.513044   100.151289
5                  90.921167      83.102044    98.740289


       Least Squares Means for Effect reactiontime

               Difference         Simultaneous 95%
                  Between      Confidence Limits for
   i    j           Means       LSMean(i)-LSMean(j)

   1    2        0.850000      -12.797941    14.497941
   1    3        2.261000      -11.386941    15.908941
   2    3        1.411000      -12.236941    15.058941


                    The GLM Procedure
                   Least Squares Means
       Adjustment for Multiple Comparisons: Scheffe

                           conversion      LSMEAN
         reactiontime          LSMEAN      Number

         0.5               93.1821667           1
         1                 92.3321667           2
         5                 90.9211667           3


       Least Squares Means for effect reactiontime
           Pr > |t| for H0: LSMean(i)=LSMean(j)

              Dependent Variable: conversion

      i/j              1             2             3

         1                      0.9850        0.8997
         2        0.9850                      0.9594
         3        0.8997        0.9594


                  conversion
reactiontime          LSMEAN      95% Confidence Limits

0.5                93.182167      85.363044   101.001289
1                  92.332167      84.513044   100.151289
5                  90.921167      83.102044    98.740289


       Least Squares Means for Effect reactiontime

               Difference         Simultaneous 95%
                  Between      Confidence Limits for
   i    j           Means       LSMean(i)-LSMean(j)
```

```
      1    2        0.850000      -13.412356    15.112356
      1    3        2.261000      -12.001356    16.523356
      2    3        1.411000      -12.851356    15.673356
                    The UNIVARIATE Procedure
                         Variable:  ry

                            Moments

N                          18    Sum Weights                 18
Mean                        0    Sum Observations             0
Std Deviation      6.16038201    Variance            37.9503065
Skewness                    0    Kurtosis            -1.4385601
Uncorrected SS     645.155211    Corrected SS        645.155211
Coeff Variation             .    Std Error Mean      1.45201596


                   Basic Statistical Measures

         Location                    Variability

     Mean            0     Std Deviation            6.16038
     Median    -711E-17    Variance                37.95031
     Mode            .     Range                   18.53300
                           Interquartile Range     11.36500


                   Tests for Location: Mu0=0

        Test           -Statistic-    -----p Value------

        Student's t    t         0    Pr > |t|    1.0000
        Sign           M         0    Pr >= |M|   1.0000
        Signed Rank    S         0    Pr >= |S|   1.0000


                      Tests for Normality

   Test                  --Statistic---    -----p Value------

   Shapiro-Wilk          W      0.935175    Pr < W      0.2392
   Kolmogorov-Smirnov    D      0.120357    Pr > D     >0.1500
   Cramer-von Mises      W-Sq   0.064414    Pr > W-Sq  >0.2500
   Anderson-Darling      A-Sq   0.400829    Pr > A-Sq  >0.2500


                    Quantiles (Definition 5)

                     Quantile      Estimate

                     100% Max        9.2665
                     99%             9.2665
                     95%             9.2665
                     90%             8.5700
                     75% Q3          5.6825
                     50% Median     -0.0000
```

```
                  The UNIVARIATE Procedure
                       Variable:  ry

                  Quantiles (Definition 5)

                   Quantile      Estimate

                   25% Q1         -5.6825
                   10%            -8.5700
                   5%             -9.2665
                   1%             -9.2665
                   0% Min         -9.2665


                    Extreme Observations

          -----Lowest-----        -----Highest----

            Value      Obs           Value      Obs

          -9.2665        3          5.6825       10
          -8.5700       15          5.7970        2
          -7.4120       13          7.4120       14
          -5.7970        1          8.5700       16
          -5.6825        9          9.2665        4
```

STATISTICAL INFERENCE:

P-value for temperature comparison is 0.26 which is greater than α (i.e.) significance level which is 0.10 (90%). Hence we fail to reject Null hypothesis (H_o) . Thus at the 90 % significance level, there is no significant difference between the conversions of Furfural at 300, 380 and 420 °C.

P-value for reaction time comparison is 0.11 which is greater than α (i.e.) significance level which is 0.10 (90%). Hence we fail to reject Null hypothesis (H_o) . Thus at the 90 % significance level, there is no significant difference between the conversions of Furfural for 0.5, 1 and 5 hours reaction time.

D.3 One-way ANOVA- effect of oil composition

$H_o : \mu_{25wt\%} = \mu_{50wt\%}$

$H_a : \mu_{25wt\%} \neq \mu_{50wt\%}$

Three statistical methods namely Tukey, Scheffe and Bonferroni were employed for analysis. The Null hypothesis (H_o) was tested at 90 % significance level.

For a better understanding, the complete procedure is elaborately explained for Furfural.

SAS CODE:

```
data furfuraloilcomp;
input oilcomp conversion;
cards;
25     90.191
25     84.233
25     89.352
50     100.0
50     95.598
50     94.619
run;

data methods;
tukey=probmc('range',.,.95,4,2)/sqrt(2);
bonferroni=tinv(1-.05/2,4);
scheffe=sqrt(finv(.95,1,4)*1);
run;

proc print data=methods;
run;
quit;

proc glm data=furfuraloilcomp;
class oilcomp;
model conversion=oilcomp;
lsmeans oilcomp/adjust=bon pdiff cl;
lsmeans oilcomp/adjust=tukey pdiff cl;
lsmeans oilcomp/adjust=scheffe pdiff cl;
run;
quit;


data confint;
tukey=probmc('range',.,.95,4,2)/sqrt(2);
bonferroni=tinv(1-.05/2,4);
scheffe=sqrt(finv(.95,1,4)*1);
lowerlimitbonferroni=87.9253333-96.739-
bonferroni*sqrt(9.3080877*(1/3+1/3));
```

```
upperlimitbonferroni=87.9253333-
96.739+bonferroni*sqrt(9.3080877*(1/3+1/3));
lowerlimittukey=87.923333-96.739-tukey*sqrt(9.3080877*(1/3+1/3));
upperlimittukey=87.923333-96.739+tukey*sqrt(9.3080877*(1/3+1/3));
lowerlimitscheffe=87.923333-96.739-scheffe*sqrt(9.3080877*(1/3+1/3));
upperlimitscheffe=87.923333-96.739+scheffe*sqrt(9.3080877*(1/3+1/3));
run;

proc print data=confint;
run;
quit;
```

SAS OUTPUT:

```
                                     The SAS System          22:43 Tuesday, April 1, 2008   1

                             Obs     tukey     bonferroni    scheffe

                              1     2.77645      2.77645     2.77645


                                        The GLM Procedure

                                     Class Level Information

                                  Class         Levels    Values

                                  oilcomp            2    25 50


                             Number of Observations Read           6
                             Number of Observations Used           6
                                        The GLM Procedure

Dependent Variable: conversion

                                               Sum of
      Source                      DF         Squares     Mean Square    F Value    Pr > F

      Model                        1     116.5210802     116.5210802      12.52    0.0241

       Error                        4      37.2323507       9.3080877

       Corrected Total              5     153.7534308


                     R-Square     Coeff Var      Root MSE    conversion Mean

                     0.757844      3.304283      3.050916           92.33217


      Source                      DF       Type I SS     Mean Square    F Value    Pr > F

      oilcomp                      1     116.5210802     116.5210802      12.52    0.0241


      Source                      DF     Type III SS     Mean Square    F Value    Pr > F

      oilcomp                      1     116.5210802     116.5210802      12.52    0.0241
```

```
                 The GLM Procedure
                Least Squares Means
  Adjustment for Multiple Comparisons: Bonferroni

                                  H0:LSMean1=
                    conversion      LSMean2
       oilcomp          LSMEAN       Pr > |t|

       25           87.9253333         0.0241
       50           96.7390000


             conversion
oilcomp          LSMEAN      95% Confidence Limits

25            87.925333       83.034772    92.815895
50            96.739000       91.848439   101.629561


       Least Squares Means for Effect oilcomp

            Difference         Simultaneous 95%
               Between      Confidence Limits for
i    j           Means       LSMean(i)-LSMean(j)

1    2       -8.813667      -15.729965    -1.897369
                 The GLM Procedure
                Least Squares Means
     Adjustment for Multiple Comparisons: Tukey

                                  H0:LSMean1=
                    conversion      LSMean2
       oilcomp          LSMEAN       Pr > |t|

       25           87.9253333         0.0241
       50           96.7390000


             conversion
oilcomp          LSMEAN      95% Confidence Limits

25            87.925333       83.034772    92.815895
50            96.739000       91.848439   101.629561


       Least Squares Means for Effect oilcomp

            Difference         Simultaneous 95%
               Between      Confidence Limits for
i    j           Means       LSMean(i)-LSMean(j)

1    2       -8.813667      -15.729968    -1.897365
                 The GLM Procedure
                Least Squares Means
    Adjustment for Multiple Comparisons: Scheffe
```

```
                                         H0:LSMean1=
                          conversion      LSMean2
             oilcomp          LSMEAN       Pr > |t|

             25           87.9253333        0.0241
             50           96.7390000


                   conversion
      oilcomp          LSMEAN      95% Confidence Limits

      25             87.925333       83.034772    92.815895
      50             96.739000       91.848439   101.629561


             Least Squares Means for Effect oilcomp

                  Difference         Simultaneous 95%
                     Between      Confidence Limits for
      i    j           Means       LSMean(i)-LSMean(j)

      1    2       -8.813667      -15.729965    -1.897369
```

```
                                      l          u
                                      o          p
                                      w          p
                                      e          e                                l          u
                                      r          r                                o          p
                                      l          l          l          u          w          p
                                      i          i          o          p          e          e
                                      m          m          w          p          r          r
                                      i          i          e          e          l          l
                                      t          t          r          r          i          i
                 b                    b          b          l          l          m          m
                 o                    o          o          i          i          i          i
                 n                    n          n          m          m          t          t
                 f         s          f          f          i          i          s          s
                 e         c          e          e          t          t          c          c
       t         r         h          r          r          t          t          h          h
       u         r         e          r          r          u          u          e          e
O      k         o         f          o          o          k          k          f          f
b      e         n         f          n          n          e          e          f          f
s      y         i         e          i          i          y          y          e          e

1   2.77645   2.77645   2.77645   -15.7300   -1.89737   -15.7320   -1.89937   -15.7320   -1.89937
```

STATISTICAL INFERENCE:

P-value for oil composition comparison between 25 wt% and 50 wt% is 0.0241 which is lesser than α (i.e.) significance level which is 0.10 (90%). Hence we reject the Null hypothesis (H_o) and accept the alternate hypothesis (H_a). Thus at the 90 % significance level, there is enough evidence to suggest that there is difference between the conversions of Furfural with 25 wt% and 50 wt% with higher oil composition favoring higher conversion of Furfural.

From another perspective the confidence interval for the mean by the three methods are as follows:

1. Tukey : (-15.7320, -1.89937)
2. Scheffe : (-15.7320, -1.89937)
3. Bonferroni : (-15.7300, -1.89737)

From this it can be said that none of the confidence intervals for the mean contain zero within the interval. This confirms that the difference between the two means could never be zero, which justifies the fact that there is significant difference between the conversions with 25 and 50 wt% initial oil composition.

D.4 One-way ANOVA- effect of methanol addition

$H_o : \mu_{MeOH-Present} = \mu_{MeOH-Absent}$

$H_a : \mu_{MeOH-Present} \neq \mu_{MeOH-Absent}$

Three statistical methods namely Tukey, Scheffe and Bonferroni were employed for analysis. The Null hypothesis (H_o) was tested at 90 % significance level.

For a better understanding, the complete procedure is elaborately explained for Furfural.

SAS CODE:

```
data Furfuralmethanoleffect;
input methanol $ conversion;
cards;
present     88.721
present     91.715
present     87.631
absent      90.191
absent      84.233
absent      89.352
run;

data methods;
tukey=probmc('range',.,.95,4,2)/sqrt(2);
bonferroni=tinv(1-.05/2,4);
scheffe=sqrt(finv(.95,1,4)*1);
run;

proc print data=methods;
run;
quit;

proc glm data=Furfuralmethanoleffect;
class methanol;
model conversion=methanol;
lsmeans methanol/adjust=bon pdiff cl;
lsmeans methanol/adjust=tukey pdiff cl;
lsmeans methanol/adjust=scheffe pdiff cl;
run;
quit;

data confint;
tukey=probmc('range',.,.95,4,2)/sqrt(2);
bonferroni=tinv(1-.05/2,4);
scheffe=sqrt(finv(.95,1,4)*1);
lowerlimitbonferroni=87.9253333-89.3556667-
bonferroni*sqrt(7.43641983*(1/3+1/3));
upperlimitbonferroni=87.9253333-
89.3556667+bonferroni*sqrt(7.43641983*(1/3+1/3));
lowerlimittukey=87.923333-89.3556667-tukey*sqrt(7.43641983*(1/3+1/3));
upperlimittukey=87.923333-89.3556667+tukey*sqrt(7.43641983*(1/3+1/3));
lowerlimitscheffe=87.923333-89.3556667-
scheffe*sqrt(7.43641983*(1/3+1/3));
upperlimitscheffe=87.923333-
89.3556667+scheffe*sqrt(7.43641983*(1/3+1/3));
run;

proc print data=confint;
run;
quit;
```

SAS OUTPUT:

```
                                    The SAS System        11:41 Wednesday, April 2, 2008   1

                             Obs     tukey     bonferroni    scheffe

                              1     2.77645      2.77645     2.77645
                                       The GLM Procedure

                                     Class Level Information

                             Class         Levels    Values

                             methanol           2    absent present


                             Number of Observations Read           6
                             Number of Observations Used           6

                                        The GLM Procedure

Dependent Variable: conversion

                                               Sum of
       Source                      DF         Squares     Mean Square    F Value    Pr > F

       Model                        1      3.06878017      3.06878017       0.41    0.5556

       Error                        4     29.74567933      7.43641983

       Corrected Total              5     32.81445950


                     R-Square     Coeff Var      Root MSE    conversion Mean

                     0.093519      3.076449      2.726980           88.64050


      Source                      DF       Type I SS     Mean Square    F Value    Pr > F

      methanol                     1      3.06878017      3.06878017       0.41    0.5556

      Source                      DF     Type III SS     Mean Square    F Value    Pr > F

      methanol                     1      3.06878017      3.06878017       0.41    0.5556
```

```
                    The GLM Procedure
                 Least Squares Means
   Adjustment for Multiple Comparisons: Bonferroni

                                   H0:LSMean1=
                     conversion      LSMean2
       methanol          LSMEAN       Pr > |t|

       absent        87.9253333         0.5556
       present       89.3556667


              conversion
methanol          LSMEAN      95% Confidence Limits

absent         87.925333       83.554035    92.296631
present        89.355667       84.984369    93.726965


       Least Squares Means for Effect methanol

             Difference         Simultaneous 95%
                Between      Confidence Limits for
 i    j           Means       LSMean(i)-LSMean(j)

 1    2       -1.430333       -7.612282     4.751616
                  The GLM Procedure
                 Least Squares Means
      Adjustment for Multiple Comparisons: Tukey

                                   H0:LSMean1=
                     conversion      LSMean2
       methanol          LSMEAN       Pr > |t|

       absent        87.9253333         0.5556
       present       89.3556667


              conversion
methanol          LSMEAN      95% Confidence Limits

absent         87.925333       83.554035    92.296631
present        89.355667       84.984369    93.726965


       Least Squares Means for Effect methanol

             Difference         Simultaneous 95%
                Between      Confidence Limits for
 i    j           Means       LSMean(i)-LSMean(j)

 1    2       -1.430333       -7.612285     4.751619
```

```
                    The GLM Procedure
                 Least Squares Means
     Adjustment for Multiple Comparisons: Scheffe

                                   H0:LSMean1=
                     conversion      LSMean2
       methanol          LSMEAN       Pr > |t|

       absent        87.9253333         0.5556
       present       89.3556667


              conversion
methanol          LSMEAN      95% Confidence Limits

absent         87.925333       83.554035    92.296631
present        89.355667       84.984369    93.726965


       Least Squares Means for Effect methanol

             Difference         Simultaneous 95%
                Between      Confidence Limits for
 i    j           Means       LSMean(i)-LSMean(j)

 1    2       -1.430333       -7.612282     4.751616
```

```
                                       l          u
                                       o          p
                                       w          p
                                       e          e                              l          u
                                       r          r                              o          p
                                       l          l         l          u         w          p
                                       i          i         o          p         e          e
                                       m          m         w          p         r          r
                                       i          i         e          e         l          l
                                       t          t         r          r         i          i
                   b                   b          b         l          l         m          m
                   o                   o          o         i          i         i          i
                   n                   n          n         m          m         t          t
                   f         s         f          f         i          i         s          s
                   e         c         e          e         t          t         c          c
         t         r         h         r          r         t          t         h          h
         u         r         e         r          r         u          u         e          e
  O      k         o         f         o          o         k          k         f          f
  b      e         n         f         n          n         e          e         f          f
  s      y         i         e         i          i         y          y         e          e

  1   2.77645   2.77645   2.77645   -7.61228   4.75162   -7.61429   4.74962   -7.61428   4.74962
```

STATISTICAL INFERENCE:

P-value for oil composition comparison between 25 wt% and 50 wt% is 0.5556 which is greater than α (i.e.) significance level which is 0.10 (90%). Hence we fail to reject the Null hypothesis (H_o). Thus at the 90 % significance level, there is not enough evidence to suggest that there is significant evidence of the influence of methanol addition on the conversion of furfural.

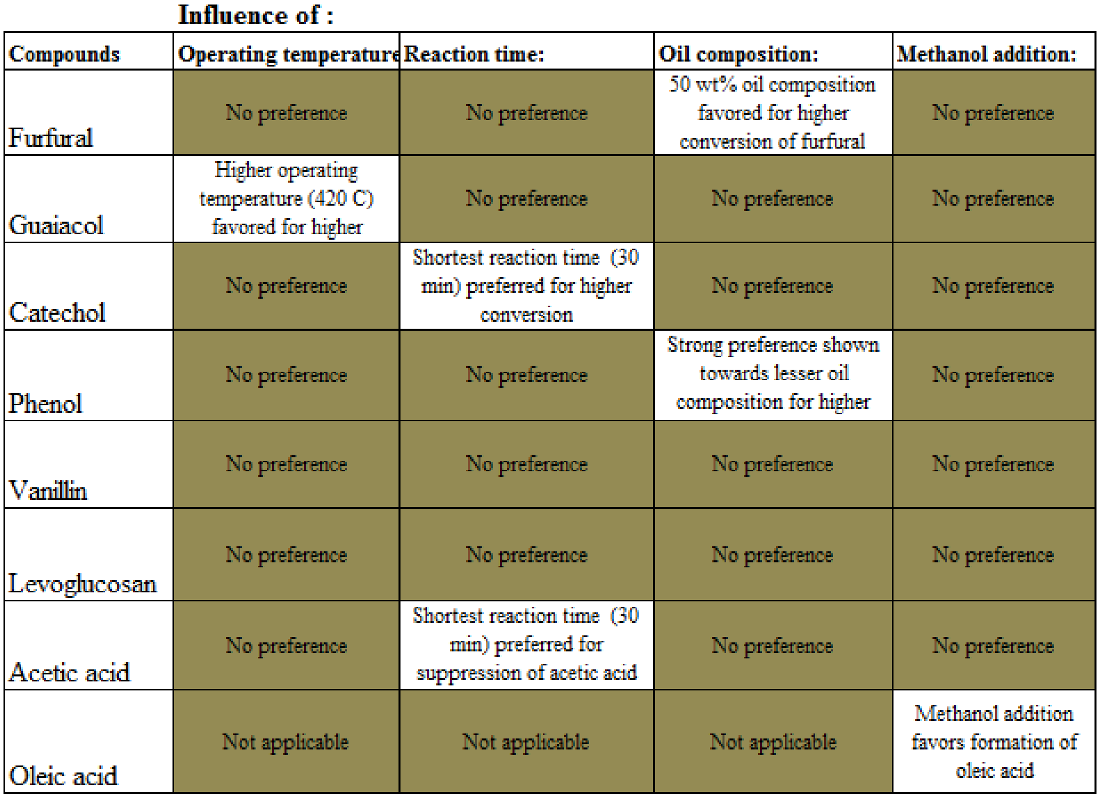
From another perspective the confidence interval for the mean by the three methods are as follows:

1. Tukey : (-7.61429, +4.74962)
2. Bonferroni : (-7.61228, +4.75162)
3. Scheffe : (-7.61428, +4.74962)

From this it can be said that all of the confidence intervals for the mean contain zero within the interval. This confirms that the difference between the two means has an eventuality to become zero, which justifies the fact that there is not enough evidence to suggest that the conversion of furfural is significantly influenced by the presence or absence of methanol.

Given below is the tabulation of all the results from statistical analysis performed for the select compounds.

Table D.2 Tabulation of results from statistical analysis



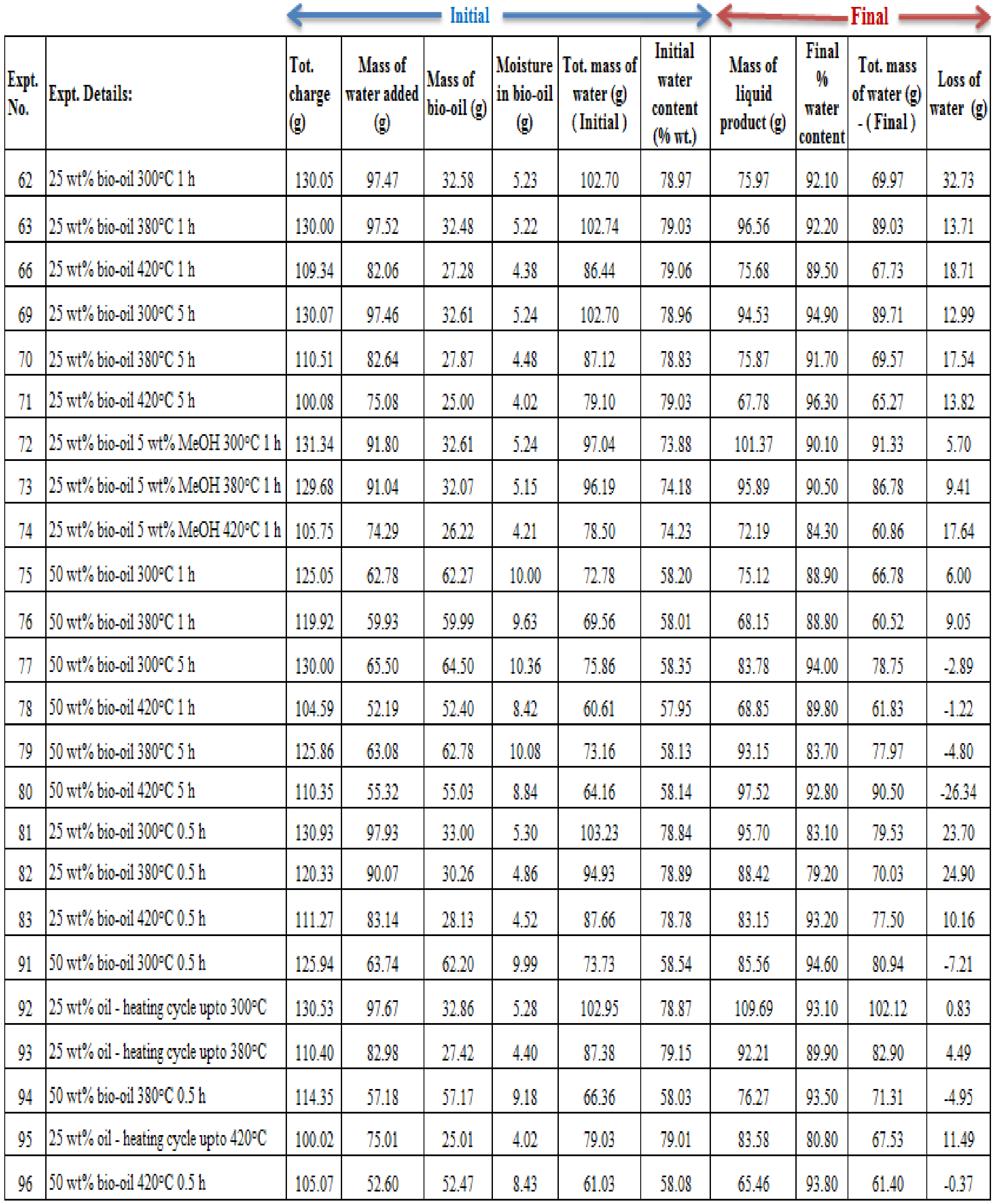
Influence of :

Compounds	**Operating temperature**	**Reaction time:**	**Oil composition:**	**Methanol addition:**
Furfural	No preference	No preference	50 wt% oil composition favored for higher conversion of furfural	No preference
Guaiacol	Higher operating temperature (420 C) favored for higher	No preference	No preference	No preference
Catechol	No preference	Shortest reaction time (30 min) preferred for higher conversion	No preference	No preference
Phenol	No preference	No preference	Strong preference shown towards lesser oil composition for higher	No preference
Vanillin	No preference	No preference	No preference	No preference
Levoglucosan	No preference	No preference	No preference	No preference
Acetic acid	No preference	Shortest reaction time (30 min) preferred for suppression of acetic acid	No preference	No preference
Oleic acid	Not applicable	Not applicable	Not applicable	Methanol addition favors formation of oleic acid

APPENDIX E

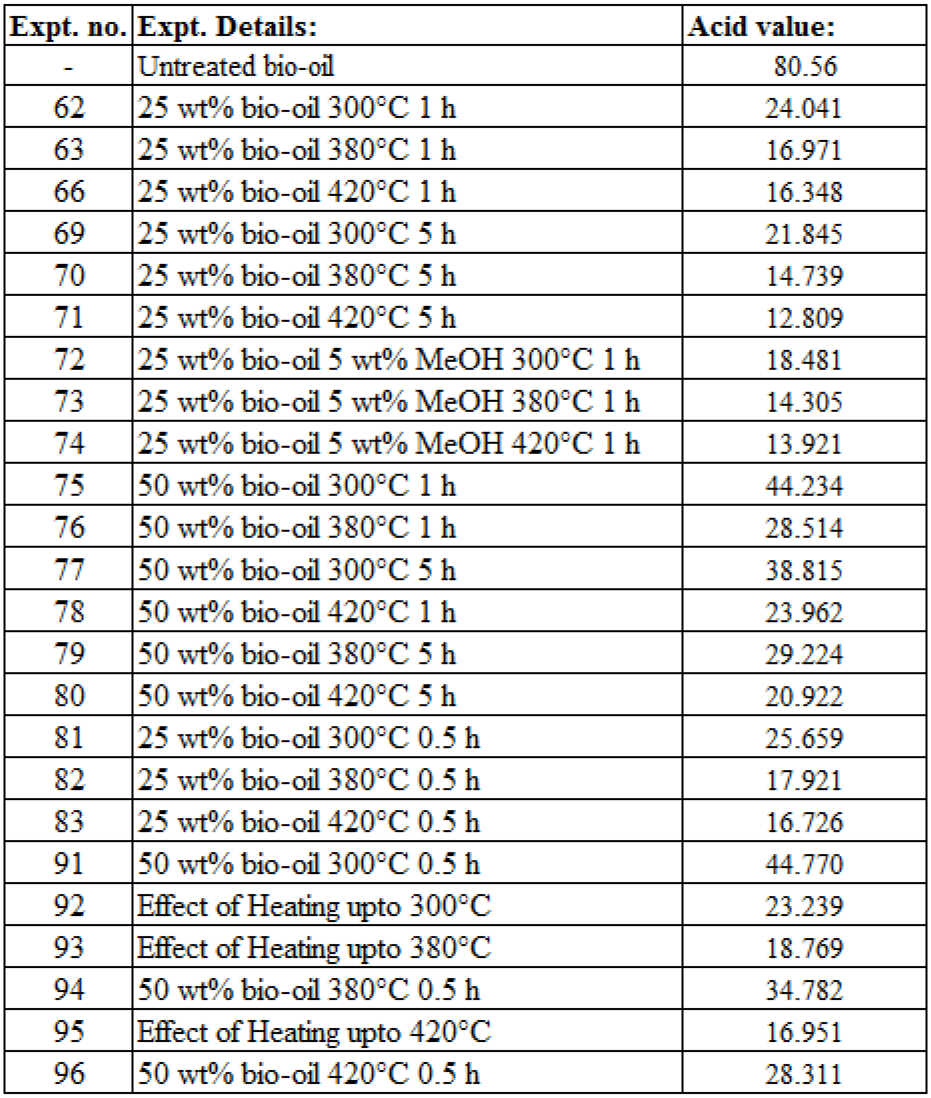
ANALYSIS OF PHYSICAL PROPERTIES

TABLE E.1 WATER CONTENT ANALYSIS



		Initial						Final			
Expt. No.	Expt. Details:	Tot. charge (g)	Mass of water added (g)	Mass of bio-oil (g)	Moisture in bio-oil (g)	Tot. mass of water (g) (Initial)	Initial water content (% wt.)	Mass of liquid product (g)	Final % water content	Tot. mass of water (g) - (Final)	Loss of water (g)
62	25 wt% bio-oil 300°C 1 h	130.05	97.47	32.58	5.23	102.70	78.97	75.97	92.10	69.97	32.73
63	25 wt% bio-oil 380°C 1 h	130.00	97.52	32.48	5.22	102.74	79.03	96.56	92.20	89.03	13.71
66	25 wt% bio-oil 420°C 1 h	109.34	82.06	27.28	4.38	86.44	79.06	75.68	89.50	67.73	18.71
69	25 wt% bio-oil 300°C 5 h	130.07	97.46	32.61	5.24	102.70	78.96	94.53	94.90	89.71	12.99
70	25 wt% bio-oil 380°C 5 h	110.51	82.64	27.87	4.48	87.12	78.83	75.87	91.70	69.57	17.54
71	25 wt% bio-oil 420°C 5 h	100.08	75.08	25.00	4.02	79.10	79.03	67.78	96.30	65.27	13.82
72	25 wt% bio-oil 5 wt% MeOH 300°C 1 h	131.34	91.80	32.61	5.24	97.04	73.88	101.37	90.10	91.33	5.70
73	25 wt% bio-oil 5 wt% MeOH 380°C 1 h	129.68	91.04	32.07	5.15	96.19	74.18	95.89	90.50	86.78	9.41
74	25 wt% bio-oil 5 wt% MeOH 420°C 1 h	105.75	74.29	26.22	4.21	78.50	74.23	72.19	84.30	60.86	17.64
75	50 wt% bio-oil 300°C 1 h	125.05	62.78	62.27	10.00	72.78	58.20	75.12	88.90	66.78	6.00
76	50 wt% bio-oil 380°C 1 h	119.92	59.93	59.99	9.63	69.56	58.01	68.15	88.80	60.52	9.05
77	50 wt% bio-oil 300°C 5 h	130.00	65.50	64.50	10.36	75.86	58.35	83.78	94.00	78.75	-2.89
78	50 wt% bio-oil 420°C 1 h	104.59	52.19	52.40	8.42	60.61	57.95	68.85	89.80	61.83	-1.22
79	50 wt% bio-oil 380°C 5 h	125.86	63.08	62.78	10.08	73.16	58.13	93.15	83.70	77.97	-4.80
80	50 wt% bio-oil 420°C 5 h	110.35	55.32	55.03	8.84	64.16	58.14	97.52	92.80	90.50	-26.34
81	25 wt% bio-oil 300°C 0.5 h	130.93	97.93	33.00	5.30	103.23	78.84	95.70	83.10	79.53	23.70
82	25 wt% bio-oil 380°C 0.5 h	120.33	90.07	30.26	4.86	94.93	78.89	88.42	79.20	70.03	24.90
83	25 wt% bio-oil 420°C 0.5 h	111.27	83.14	28.13	4.52	87.66	78.78	83.15	93.20	77.50	10.16
91	50 wt% bio-oil 300°C 0.5 h	125.94	63.74	62.20	9.99	73.73	58.54	85.56	94.60	80.94	-7.21
92	25 wt% oil - heating cycle upto 300°C	130.53	97.67	32.86	5.28	102.95	78.87	109.69	93.10	102.12	0.83
93	25 wt% oil - heating cycle upto 380°C	110.40	82.98	27.42	4.40	87.38	79.15	92.21	89.90	82.90	4.49
94	50 wt% bio-oil 380°C 0.5 h	114.35	57.18	57.17	9.18	66.36	58.03	76.27	93.50	71.31	-4.95
95	25 wt% oil - heating cycle upto 420°C	100.02	75.01	25.01	4.02	79.03	79.01	83.58	80.80	67.53	11.49
96	50 wt% bio-oil 420°C 0.5 h	105.07	52.60	52.47	8.43	61.03	58.08	65.46	93.80	61.40	-0.37

TABLE E.2 ACID VALUE ANALYSIS



Expt. no.	**Expt. Details:**	**Acid value:**
-	Untreated bio-oil	80.56
62	25 wt% bio-oil 300°C 1 h	24.041
63	25 wt% bio-oil 380°C 1 h	16.971
66	25 wt% bio-oil 420°C 1 h	16.348
69	25 wt% bio-oil 300°C 5 h	21.845
70	25 wt% bio-oil 380°C 5 h	14.739
71	25 wt% bio-oil 420°C 5 h	12.809
72	25 wt% bio-oil 5 wt% MeOH 300°C 1 h	18.481
73	25 wt% bio-oil 5 wt% MeOH 380°C 1 h	14.305
74	25 wt% bio-oil 5 wt% MeOH 420°C 1 h	13.921
75	50 wt% bio-oil 300°C 1 h	44.234
76	50 wt% bio-oil 380°C 1 h	28.514
77	50 wt% bio-oil 300°C 5 h	38.815
78	50 wt% bio-oil 420°C 1 h	23.962
79	50 wt% bio-oil 380°C 5 h	29.224
80	50 wt% bio-oil 420°C 5 h	20.922
81	25 wt% bio-oil 300°C 0.5 h	25.659
82	25 wt% bio-oil 380°C 0.5 h	17.921
83	25 wt% bio-oil 420°C 0.5 h	16.726
91	50 wt% bio-oil 300°C 0.5 h	44.770
92	Effect of Heating upto 300°C	23.239
93	Effect of Heating upto 380°C	18.769
94	50 wt% bio-oil 380°C 0.5 h	34.782
95	Effect of Heating upto 420°C	16.951
96	50 wt% bio-oil 420°C 0.5 h	28.311

TABLE E.3 ELEMENTAL COMPOSITION ANALYSIS

		Initial																Final									
Expt. No.	Expt. Details:	Mass of bio-oil (g)	% C	% H	% N	% O	C (g)	H (g)	N (g)	O (g)	Mass of water (g)	H (g)	O (g)	Tot. initial C (g)	Tot. Initial H (g)	Tot. Initial N (g)	Tot. Initial O (g)	Mass of liquid product (g)	Mass of solid product (g)	% C	% H	% N	% O	Tot. final C (g)	Tot. final H (g)	Tot. final N (g)	Tot. final O (g)
62	25 wt% bio-oil 300°C 1 h	32.58	38.8	6.44	0.39	54.33	12.65	2.10	0.13	17.7	97.47	10.83	86.64	12.65	12.93	0.13	104.34	75.97	16.83	1.93	10.86	1.11	86.10	1.47	8.25	0.84	65.41
63	25 wt% bio-oil 380°C 1 h	32.48	38.8	6.44	0.39	54.33	12.62	2.09	0.13	17.65	97.52	10.84	86.68	12.62	12.93	0.13	104.33	96.56	23.04	3.58	10.92	1.04	84.46	3.46	10.54	1.00	81.55
66	25 wt% bio-oil 420°C 1 h	27.28	38.8	6.44	0.39	54.33	10.6	1.76	0.11	14.82	82.06	9.12	72.94	10.60	10.87	0.11	87.76	75.68	12.80	1.69	11.22	0.32	86.77	1.28	8.49	0.24	65.67
69	25 wt% bio-oil 300°C 5 h	32.61	38.8	6.44	0.39	54.33	12.67	2.10	0.13	17.72	97.46	10.83	86.63	12.67	12.93	0.13	104.35	94.53	11.21	3.58	11.02	1.69	83.71	3.38	10.42	1.60	79.13
70	25 wt% bio-oil 380°C 5 h	27.87	38.8	6.44	0.39	54.33	10.82	1.79	0.11	15.14	82.64	9.18	73.46	10.82	10.98	0.11	88.60	75.87	9.35	3.36	10.69	1.11	84.84	2.55	8.11	0.84	64.37
71	25 wt% bio-oil 420°C 5 h	25.00	38.8	6.44	0.39	54.33	9.71	1.61	0.10	13.58	75.08	8.34	66.74	9.71	9.95	0.10	80.32	67.78	10.35	4.25	8.92	0.93	85.90	2.88	6.05	0.63	58.22
72	25 wt% bio-oil 5 wt% MeOH 300°C 1 h	32.61	38.8	6.44	0.39	54.33	12.67	2.10	0.13	17.72	91.80	10.20	81.60	12.67	12.30	0.13	99.32	101.37	8.28	3.35	10.19	0.24	86.22	3.40	10.33	0.24	87.40
73	25 wt% bio-oil 5 wt% MeOH 380°C 1 h	32.07	38.8	6.44	0.39	54.33	12.46	2.07	0.13	17.42	91.04	10.12	80.92	12.46	12.18	0.13	98.35	95.89	11.78	1.83	9.23	0.26	88.68	1.75	8.85	0.25	85.04
74	25 wt% bio-oil 5 wt% MeOH 420°C 1 h	26.22	38.8	6.44	0.39	54.33	10.18	1.69	0.10	14.25	74.29	8.25	66.04	10.18	9.94	0.10	80.28	72.19	11.75	2.83	11.19	0.73	85.25	2.04	8.08	0.53	61.54
75	50 wt% bio-oil 300°C 1 h	62.27	38.8	6.44	0.39	54.33	24.19	4.01	0.24	33.83	62.78	6.98	55.80	24.19	10.99	0.24	89.64	75.12	-	2.61	10.74	1.56	85.09	1.96	8.07	1.17	63.92
76	50 wt% bio-oil 380°C 1 h	59.99	38.8	6.44	0.39	54.33	23.3	3.86	0.23	32.59	59.93	6.66	53.27	23.30	10.52	0.23	85.86	68.15	16.87	3.00	10.78	0.83	85.39	2.04	7.35	0.57	58.19
77	50 wt% bio-oil 300°C 5 h	64.50	38.8	6.44	0.39	54.33	25.05	4.15	0.25	35.04	65.50	7.28	58.22	25.05	11.43	0.25	93.27	83.78	17.36	2.48	9.24	0.19	88.09	2.08	7.74	0.16	73.80
78	50 wt% bio-oil 420°C 1 h	52.40	38.8	6.44	0.39	54.33	20.35	3.37	0.20	28.47	52.19	5.80	46.39	20.35	9.17	0.20	74.86	68.85	23.00	2.45	8.95	0.13	88.47	1.69	6.16	0.09	60.91
79	50 wt% bio-oil 380°C 5 h	62.78	38.8	6.44	0.39	54.33	24.38	4.04	0.24	34.11	63.08	7.01	56.07	24.38	11.05	0.24	90.18	93.15	17.02	3.19	10.92	0.29	85.60	2.97	10.17	0.27	79.74
80	50 wt% bio-oil 420°C 5 h	55.03	38.8	6.44	0.39	54.33	21.37	3.54	0.21	29.9	55.32	6.15	49.17	21.37	9.69	0.21	79.07	97.52	16.85	2.03	7.82	0.18	89.97	1.98	7.63	0.18	87.74
81	25 wt% bio-oil 300°C 0.5 h	33.00	38.8	6.44	0.39	54.33	12.82	2.13	0.13	17.93	97.93	10.88	87.05	12.82	13.01	0.13	104.98	95.70	16.30	3.46	10.99	0.32	85.23	3.31	10.52	0.31	81.57
82	25 wt% bio-oil 380°C 0.5 h	30.26	38.8	6.44	0.39	54.33	11.75	1.95	0.12	16.44	90.07	10.01	80.06	11.75	11.96	0.12	96.50	88.42	10.35	2.34	11.25	1.03	85.38	2.07	9.95	0.91	75.49
83	25 wt% bio-oil 420°C 0.5 h	28.13	38.8	6.44	0.39	54.33	10.93	1.81	0.11	15.28	83.14	9.24	73.90	10.93	11.05	0.11	89.19	83.15	13.20	1.96	10.76	0.21	87.07	1.63	8.95	0.17	72.40
91	50 wt% bio-oil 300°C 0.5 h	62.20	38.8	6.44	0.39	54.33	24.16	4.01	0.24	33.79	63.74	7.08	56.66	24.16	11.09	0.24	90.45	85.56	21.92	3.95	9.79	0.84	85.42	3.38	8.38	0.72	73.09
92	25 wt% oil - heating cycle upto 300°C	32.86	38.8	6.44	0.39	54.33	12.76	2.12	0.13	17.85	97.67	10.85	86.82	12.76	12.97	0.13	104.67	109.69	11.19	2.25	10.60	1.41	85.74	2.47	11.63	1.55	94.05
93	25 wt% oil - heating cycle upto 380°C	27.42	38.8	6.44	0.39	54.33	10.65	1.77	0.11	14.9	82.98	9.22	73.76	10.65	10.99	0.11	88.66	92.21	11.11	1.81	9.27	0.13	88.79	1.67	8.55	0.12	81.87
94	50 wt% bio-oil 380°C 0.5 h	57.17	38.8	6.44	0.39	54.33	22.2	3.68	0.22	31.06	57.18	6.35	50.83	22.20	10.04	0.22	81.89	76.27	16.73	1.96	11.33	1.03	85.68	1.49	8.64	0.79	65.35
95	25 wt% oil - heating cycle upto 420°C	25.01	38.8	6.44	0.39	54.33	9.714	1.61	0.10	13.59	75.01	8.33	66.68	9.71	9.95	0.10	80.26	83.58	9.33	4.32	10.79	0.42	84.47	3.61	9.02	0.35	70.60
96	50 wt% bio-oil 420°C 0.5 h	52.47	38.8	6.44	0.39	54.33	20.38	3.38	0.20	28.51	52.60	5.84	46.76	20.38	9.22	0.20	75.26	65.46	23.84	2.59	11.03	0.20	86.18	1.70	7.22	0.13	56.41