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# Production of Furanic Liquid Compounds from Cellulosic Biomass Based on Molten Salts and Catalysis

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# Production of Furanic Liquid Compounds from Cellulosic Biomass Based on Molten Salts and Catalysis

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Worcester Polytechnic Institute

A Major Qualifying Project  
submitted to the faculty of  
WORCESTER POLYTECHNIC INSTITUTE  
In partial fulfillment of the requirements for the  
Degree of Bachelor of Science

By

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Ryan O'Hara

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Approved:

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This report represents the work of three WPI undergraduate students submitted to the faculty as evidence of completion of a degree requirement. WPI routinely publishes these reports on its web site without editorial or peer review.

## **Abstract:**

Organic materials from once-living organisms (referred to as “biomass”) have been shown to yield simpler organic gaseous and liquid compounds when broken down thermally, catalytically, or chemically. Some of these compounds can be further processed into liquid biofuels such as ethanol. Ionic liquids have been shown to aid in the breakdown of biomass into these intermediate compounds. The purpose of this project was to determine whether molten salts, a cheaper alternative to ionic liquids, could also yield these intermediates when used with or without catalysts. During the course of this study, it was found that some combinations of molten salt eutectics and catalysts were very effective in the breakdown of biomass into furanic compounds. The low cost of the molten salts, therefore, promises processes based on them to be cost-effective for converting biomass into biofuels.

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## Table of Contents:

Abstract.....	2
Acknowledgements.....	3
Table of Contents.....	4
Table of Figures.....	8
List of Tables.....	11
Executive Summary.....	12
1 Introduction.....	15
1.1 World Energy Issues.....	15
1.2 Fossil Fuels.....	16
1.3 Renewable/Synthetic Fuels.....	17
1.4 Waste Generation.....	18
1.5 Pollution Reduction.....	19
1.6 Fuels from Biomass.....	19
2 Literature Review.....	23
2.1 Biomass.....	23
2.1.1 Types of Biomass.....	23
2.1.2 Biomass Cycle.....	26
2.1.3 Biomass Fuel Viability.....	27
2.2 Common Fuel-Producing Biomass Reactions.....	29
2.2.1 Hydrolysis.....	29
2.2.2 Gasification.....	29

2.2.3	Pyrolysis.....	30
2.3	Ionic Liquids.....	33
2.3.1	Applications of Ionic Liquids.....	33
2.3.2	Strengths and Weaknesses of Ionic Liquid Usage.....	34
2.4	Molten Salts and Catalysts.....	35
2.4.1	Comparison of the Practicality of Molten Salts and Ionic Liquids.....	35
2.4.2	Previous Research completed at WPI.....	35
2.4.3	Additional Catalysis.....	36
3	Methodology.....	38
3.1	Objectives.....	38
3.2	Initial Property Testing – Benchtop Experiments.....	39
3.2.1	The Molten Salt Solvents.....	39
3.2.2	The Acid/Base Catalytic Compounds.....	40
3.3	Flow Reactor Setup.....	41
3.3.1	Reactor Flow Layout.....	41
3.3.2	Design Specifications of the Reactor.....	42
3.3.3	Heat/Temperature Control Unit.....	43
3.3.4	Gas/Flow Control Calibration.....	44
3.4	Reactor GC Operation Specifications and Calibration.....	46
3.5	Flow Reaction Setup and Procedure.....	47
3.6	Liquid Product Retrieval/Purification.....	48
3.7	GC/Mass Spec Operation Specifications and Calibration.....	49
3.8	Safety Precautions.....	50

4	Results and Discussion.....	52
4.1	Benchtop Results.....	52
4.1.1	Molten Salt Solvent Testing.....	52
4.1.2	Acid/Base Catalytic Compound Testing.....	53
4.1.3	Effects on Flow Reactor Trials.....	56
4.2	Flow Reactor Trials.....	57
4.2.1	Produced Liquids from Cellulose Decomposition.....	57
4.2.2	Liquid Optimization.....	60
4.2.3	Error Analysis.....	60
4.2.4	Gaseous Product Analysis Using the Reactor GC.....	62
4.2.5	Lignocellulose Reactions.....	65
4.3	Liquid Product Analysis.....	67
4.3.1	Interpreting Spectra of the GC/Mass Spec.....	68
4.3.2	Analysis of Liquid Product Distribution.....	71
4.3.3	Char Production and Reaction Mass Balance.....	82
4.4	Equipment Performance.....	83
4.4.1	Flow Reactor Performance.....	83
4.4.2	Performance of Analysis/Masurement Equipment.....	85
5	Conclusions.....	86
5.1	Quantitative Liquid Analysis.....	86
5.2	Qualitative Product Distribution.....	88
6	Recommendations.....	89
6.1	Flow Testing Changes.....	89

6.2	Varied Media Usage.....	90
6.3	Project Scaling.....	91
7	References.....	92
	Appendices.....	I
	Appendix A – Raw Measurements.....	I
	Appendix B – Raw GC Data.....	III
	Appendix C – Raw Mass Spec Data.....	X
	Appendix D – Product Molecular Structures.....	XVI
	Appendix E – Testing Compound Chemical Data.....	XVIII



## List of Figures:

Figure 1: Bio-oil product distribution for the chloride eutectic/ZSM-5 system.....	13
Figure 2: The bio-oil product distribution of cellulose pyrolysis.....	14
Figure 3: Energy consumption by fuel.....	16
Figure 4: Production of liquid fuels from biomass.....	17
Figure 5: Municipal solid waste generation rates.....	18
Figure 6: Routes of biomass degradation by products.....	20
Figure 7: List of reaction pathways for syngas and natural gas.....	21
Figure 8: Acetic acid and levoglucosan.....	21
Figure 9: Plant cell wall structure.....	24
Figure 10: Structure of lignin.....	24
Figure 11: Unit structure of hemicellulose.....	25
Figure 12: The biomass cycle.....	26
Figure 13: Land consumption for biomass fueling.....	27
Figure 14: Energy subsidies by type and fuel.....	28
Figure 15: Products of cellulose pyrolysis.....	31
Figure 16: Proposed mechanism of cellulose pyrolysis.....	32
Figure 17: 1-butyl-3-methylimidazolium and hexafluorophosphate ionic liquid.....	33
Figure 18: A variety of different ionic liquid systems.....	34
Figure 19: Molecular geometry of ZSM-5.....	37
Figure 20: Phosphomolybdic acid.....	37
Figure 21: Benchtop electric furnace.....	39
Figure 22: Sodium hydroxide and ZSM-5 benchtop.....	40

Figure 23: Principle reactor flow diagram.....	41
Figure 24: Principle reactor.....	42
Figure 25: Reaction chamber of the principle reactor.....	42
Figure 26: The gas inlet line.....	43
Figure 27: The Watlow ceramic fiber heater.....	44
Figure 28: The setpoint temperature control unit.....	44
Figure 29: MKS flow controller display panel.....	45
Figure 30: MKS flow controller setpoint dial.....	45
Figure 31: SRI 8610 gas chromatogram.....	46
Figure 32: 2-mL graduated pipette.....	48
Figure 33: The Gateway GC/Mass Spec.....	49
Figure 34: The ionizing unit of the Agilent 5975C mass spectrometer.....	50
Figure 35: Progression of the sodium hydroxide benchtop trial.....	52
Figure 36: Nickel (II) hydroxide before and after benchtop heating.....	53
Figure 37: Stepwise benchtop testing of ZSM-5/sodium hydroxide mixture.....	54
Figure 38: Benchtop reaction of phosphomolybdic acid.....	55
Figure 39: Zinc acetate after decomposition.....	56
Figure 40: Reactor GC graph for cellulose with the chloride eutectic and ZSM-5.....	63
Figure 41: Reactor GC graph for cellulose with the chloride eutectic and ZSM-5 rerun.....	64
Figure 42: Sawdust and grass clippings prior to testing.....	65
Figure 43: Reactor char for the sawdust trial and grass clippings trial.....	66
Figure 44: Array of reactor liquid products.....	67
Figure 45: GC graph from GC/Mass Spec. for chloride eutectic/ZSM-5.....	69

Figure 46: Mass spectrometer spectrum for furfural peak for chloride eutectic/ZSM-5 run.....	70
Figure 47: Product distribution run 32 – cellulose with no catalysts.....	71
Figure 48: Product distribution run 31 – cellulose/ZSM-5 with no molten salt.....	72
Figure 49: Product distribution run 30 – chlorides.....	73
Figure 50: Product distribution run 29 – chlorides and ZSM-5.....	73
Figure 51: Product distribution run 27 – chlorides and sodium hydrogen phosphate.....	74
Figure 52: Product distribution run 34 – chlorides and ZSM-5 (half salt).....	75
Figure 53: Product distribution run 35 – chlorides and ZSM-5 (half ZSM-5) .....	75
Figure 54: Product distribution run 36 – chlorides, ZSM-5 and nickel (II) hydroxide.....	76
Figure 55: Product distribution run 16 – carbonates and nickel (II) hydroxide.....	77
Figure 56: Product distribution run 20 – hydroxides and phosphomolybdic acid.....	78
Figure 57: Product distribution run 11 – hydroxides and ZSM-5.....	79
Figure 58: Product distribution run 15 – carbonates and ZSM-5.....	79
Figure 59: Product distribution run 33 – carbonates.....	80
Figure 60: Product distribution run 26 – hydroxides and nickel (II) hydroxide.....	81
Figure 61: Bottom face of reactor tube post-experimental.....	83
Figure 62: Visible wear and tear on rubber stoppers.....	84
Figure 63: Steel vessel sparger.....	90

## List of Tables:

Table 1: Results listed by salt.....	58
Table 2: Results listed by percent yield.....	59
Table 3: Results of runs with varied amounts of salts and catalysts.....	60
Table 4: Repeated experiments with carbonate eutectic salt.....	61
Table 5: Runs analyzed using GC/Mass Spec. ....	68
Table 6: Product mass balance by phase.....	82
Table 7: Average mass of liquid produced by salt.....	86
Table 8: Average mass of liquid produced by catalyst.....	86
Table 9: Results listed by percent yield.....	87

## Executive Summary:

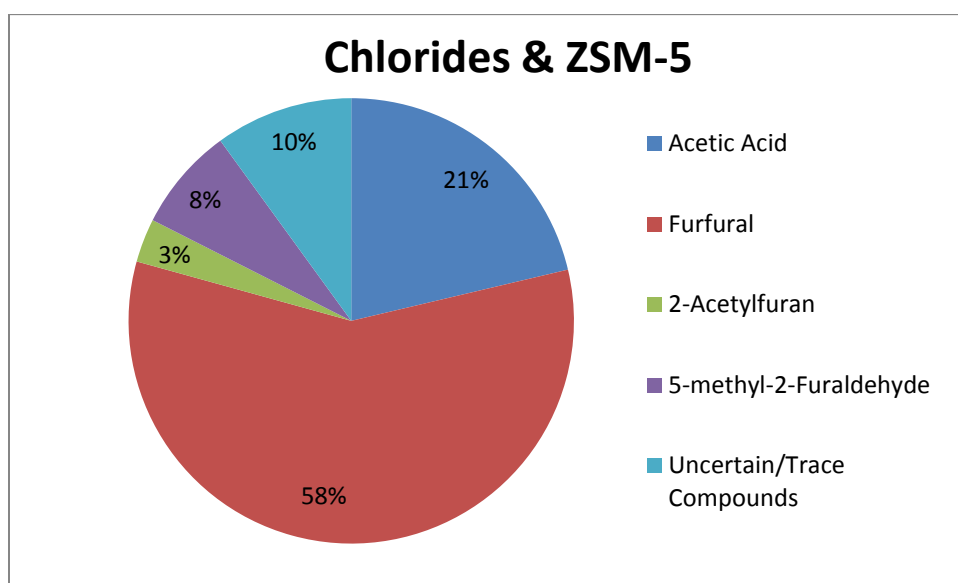
Over the last few centuries, the energy need of mankind has grown massively, and has been generally sustained by the burning of fossil fuels to generate electricity. The major flaw with this scenario however, is that the world's supply of fossil fuels is being rapidly exhausted, and known petroleum deposits will be depleted in the next 50 years at the present rate of consumption (Demirbas 1). Due to inability to replenish these fossil fuels, renewable energy sources have become an integral part of modern research.

Biomass, specifically organic plant based matter, has been a hot topic in recent energy research because of its carbon neutrality and renewability. When looking at the thermochemical conversion of biomass to fuels, the two major types of products to be analyzed are syngas and bio-oil. These products are produced through various reactions, such as pyrolysis, which involves the heating of the biomass to 300-600°C in an oxygen-free environment. Generally, bio-oils produced from cellulose pyrolysis have a wide array of mixture components that are not easily isolated. The focus of this project is to determine the feasibility of producing an optimized bio-oil through pyrolysis reactions involving the use of various molten salts and catalytic compounds.

Previous project work at WPI in both 2009 and 2010 studied the effects of molten salts on various reactions involving biomass. The 2010 project group tested various reactions in order to optimize and analyze the production of syngas. Due to the focus on gaseous products by previous groups, this project focused on liquid optimization, as liquid products are also more economically feasible from a transportation and distribution standpoint.

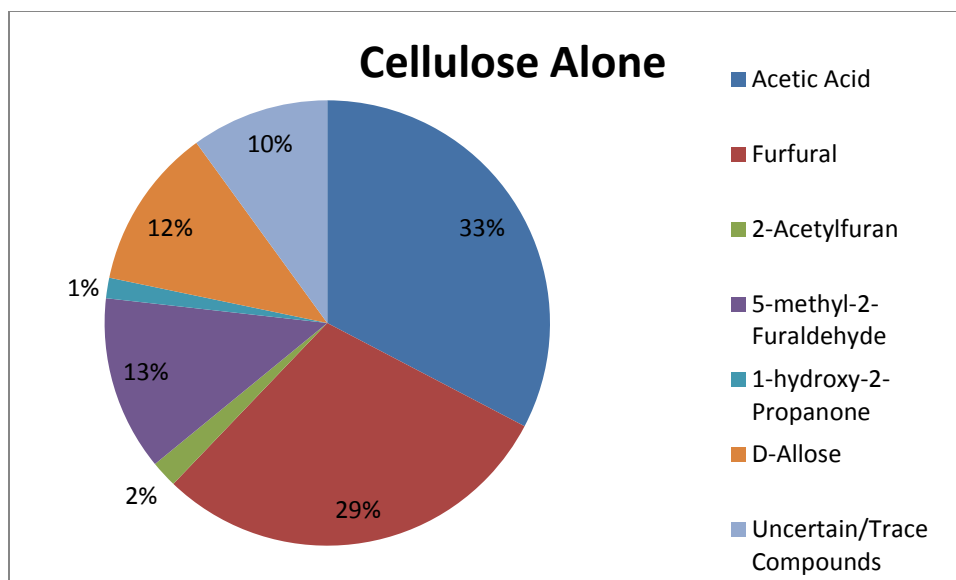
The goal of this project was to optimize, both qualitatively and quantitatively, production of liquid bio-oil through the pyrolysis of biomass (specifically purified cellulose) using molten

salt solvents and various catalytic compounds. This was accomplished by testing the cellulose in a set environment with roughly 20 different combinations of molten salt and catalyst media. After testing the various combinations of molten salts and catalysts, we discovered our optimal system of a chloride eutectic molten salt solvent combined with the ZSM-5 compound acting as a Brønsted acid catalyst. This system was chosen because after testing it provided the largest yield of liquid products at 46%, as well as one of the most refined distributions of compounds, as seen in Figure 1 below.



*Fig. 1: Bio-oil Product Distribution for the Chloride Eutectic/ZSM-5 System*

The success of the chloride eutectic and ZSM-5 system can be seen when compared to the product distribution of bio-oil produced from a pyrolysis reaction that involved no molten salts or catalytic compounds. Figure 2 on the following page shows the bio-oil product distribution of a pyrolysis system that involved no molten salt media, which can be seen to contain a much larger variation of materials.



*Fig 2: The Bio-oil Product Distribution of Cellulose Pyrolysis*

The results of the testing showed that the combined molten salt/catalyst media can successfully refine bio-oil produced in through the pyrolysis of purified cellulose. If this line of research was to be continued, we recommended that a CSTR-style reactor be used as opposed to the semi-batch reactor currently used in testing. We would also recommend further investigation on other types of lignocellulosic biomass, particularly more typical products from everyday life. Further analysis of materials such as sawdust, recyclable paper, yard trimmings, and plastic using a similar molten salt/catalyst media was highly recommended.

While yields as high as 46% showed that our tested systems were effective in producing liquid products, there are many other potential issues with the system that can hinder industrialization of the pilot process. These issues should be researched and addressed before further changes are made.

## 1. Introduction

One of the most important issues in the twenty-first century is the rising costs of energy. Global demand for energy is always increasing, while reserves of limited fossil fuels continue to be depleted. There are also growing concerns over pollution and increasing greenhouse gas emissions from this increased energy demand (ExxonMobil).

In order to insure better energy security and the lowering of pollution, alternative sources of energy must be pursued. The current energy market is dominated by fossil fuels, such as petroleum, coal and natural gas. These sources have a finite amount of materials. Renewable energy resources do not suffer from the same limitations as fossil fuel energy sources. These potential energy sources include solar, wind, hydroelectric, and biomass (Budenholzer).

Petroleum fuel sources, such as gasoline, still dominate the transportation sector. Liquid fuels are much easier to store and transport. Most forms of renewable energy are ill adapted to be used for transportation purposes (Ableson). Biomass shows potential because of its ability to be turned into liquid fuels, such as biodiesel and ethanol (Huber). Liquid fuel sources derived from lignocellulosic biomass could help reduce our dependence on oil for gasoline.

### 1.1 World energy issues

There are many issues facing the world regarding energy. As third world countries develop they require more and more energy. This puts a strain on current energy markets. More countries are competing for the same limited resources. Developing countries also have an increase in automobiles on the road, which increases the need for transportation fuels (Carr).

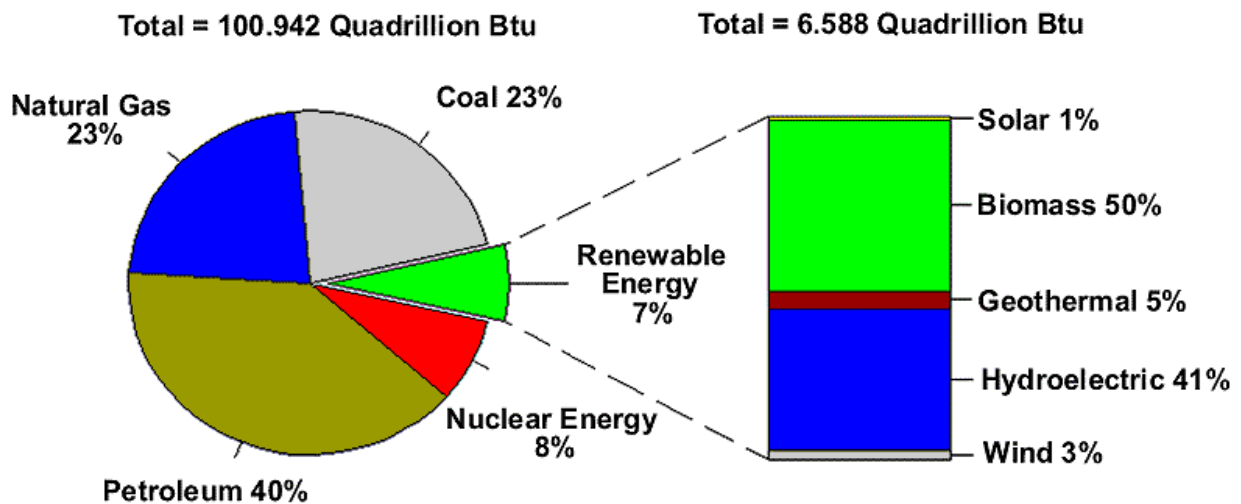
The world's supply of fossil fuels is decreasing. It is believed that the world is nearing its peak oil production, after which oil production will continuously decline. Eventually, the world



will need to change its infrastructure to utilize alternative fuel sources (Whipple). Different geographic locations will need to implement different alternative energy sources based on their available resources.

## 1.2 Fossil fuels

The main source of energy for electricity generation, heating, and transportation all come from fossil fuels. Figure 3 shows the energy consumption in the United States by fuel source in 2005. Fossil fuels, which include coal, natural gas, and petroleum, make up a combined 86 percent of fuel use. Renewable sources only make up seven percent of energy used (EIA). Fossil fuels are still a very important source of energy and will continue to be for years to come.



*Fig. 3: Energy Consumption by Fuel (EIA)*

The use of fossil fuels has many drawbacks. Fossil fuels are one of the largest contributors to greenhouse gases in the atmosphere. It is believed that excessive carbon dioxide

emission can lead to global climate change. Coal, used primarily for electricity generation, is one of the largest producers of carbon dioxide.

Fossil fuels are also a limited resource. There is a finite amount of them and once they are gone they cannot be replenished. While there is still enough fossil fuel for years to come, they will eventually run out. As the amount of fossil fuels decreases there will be an accompanying increase in price, which could put strain on the economies of different countries.

### 1.3 Renewable/Synthetic Fuels

The production of renewable and synthetic fuels is a possible means of alleviating global reliance on fossil fuels. Renewable energy sources, such as solar, hydroelectric, and wind are possible ways to produce electricity. This could reduce the need to burn coal and natural gas for electricity generation. Geothermal energy is a possible way to produce thermal energy for heating, which would divert energy consumption from heating oil and natural gas (Budenholzer).

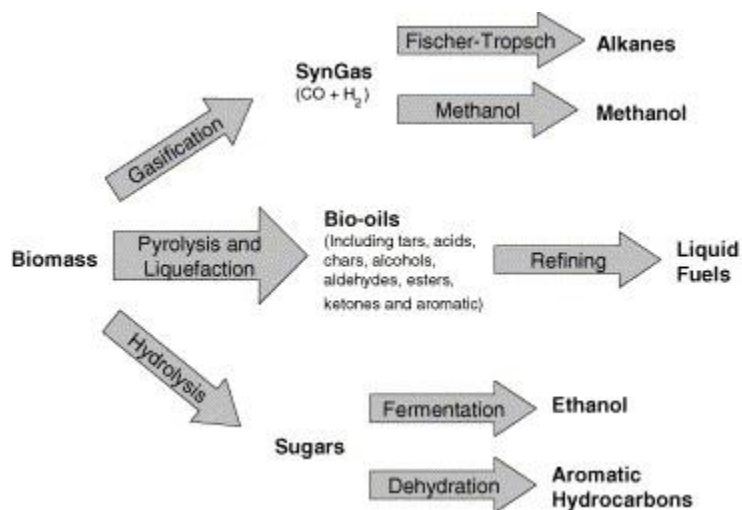


Fig. 4: Production of Liquid Fuels from Biomass (Huber)

The transportation infrastructure is designed to handle large volumes of liquid fuels. Technologies that convert solid and gaseous renewable into liquid fuels are needed to reduce

fossil fuel consumption. Liquid fuels can be produced from synthesis gas, or syngas, which is a mixture of carbon monoxide and hydrogen (Huber). Figure 4 shows various reaction pathways in which biomass can be converted into liquid fuels. Biomass can first be converted into syngas, which can then be used directly as a fuel or further converted into liquid products. Liquid fuels can also be produced from the conversion of biomass into bio-oils or fermentable sugars (Huber).

### 1.4 Waste Generation

Waste generation is a problem facing the United States. Figure 5 shows municipal solid waste generation rates. In 2010 approximately 250 million tons of solid waste was generated. Of this, over 85 million tons was recycled or composted (EPA). As the population increases, generation of solid waste will also increase.

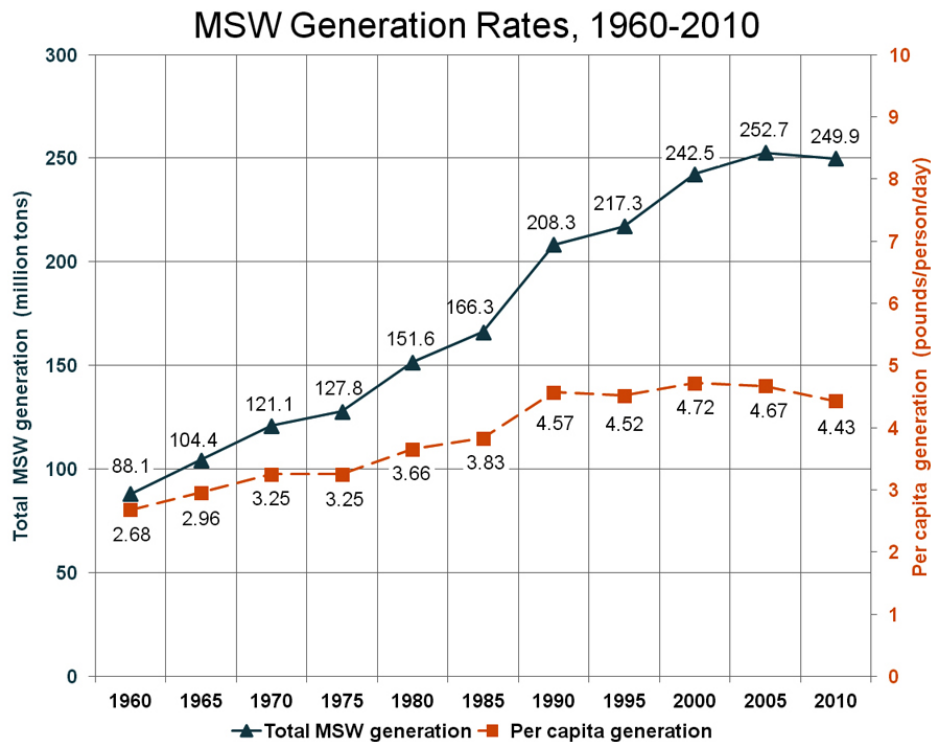


Fig. 5: Municipal Solid Waste Generation Rates (EPA 2012)

Municipal solid waste is primarily disposed of in landfills. Some waste is also incinerated in order to recover some of the wasted energy (EPA). The vast quantity of waste generated makes it appealing to develop ways to recover the unused energy. One possible solution is to break down municipal biomass and plastics into useable fuels. This would allow for a reduction in waste accumulation as well produce useable fuel.

## **1.5 Pollution Reduction**

Pollution is a major problem facing industrialized countries. The use of fossil fuels release greenhouse gases, such as carbon dioxide. The burning of fossil fuels also produces  $\text{NO}_x$ ,  $\text{SO}_2$ , and particulate matter. These pollutants can lead to problems such as ground level ozone formation and acid rain. Acid rain can harm animal and plant life as well as damage buildings and statues (EPA). Pollution also leads to reduced air quality, which can have negative consequences on human health. Technology like gas scrubbers and carbon sequestration can help reduce the amount of pollution released into the environment. Another way to reduce pollution is to convert to cleaner sources of energy (EPA).

## **1.6 Fuels from Biomass**

When looking to break down lignocellulosic biomass, a few different approaches can be taken. Throughout history biomass has been used in combustion reactions in order to produce heat for many different applications. However, biomass can be degraded for more than just heat. Various methods of decomposition, such as thermochemical, biochemical, and even mechanical processes have the ability to convert biomass into different usable products. Some processes,

such as gasification and pyrolysis, provide the environment required to break lignocellulose down into containable compounds that can be converted to usable biofuels (Letcher, 166).

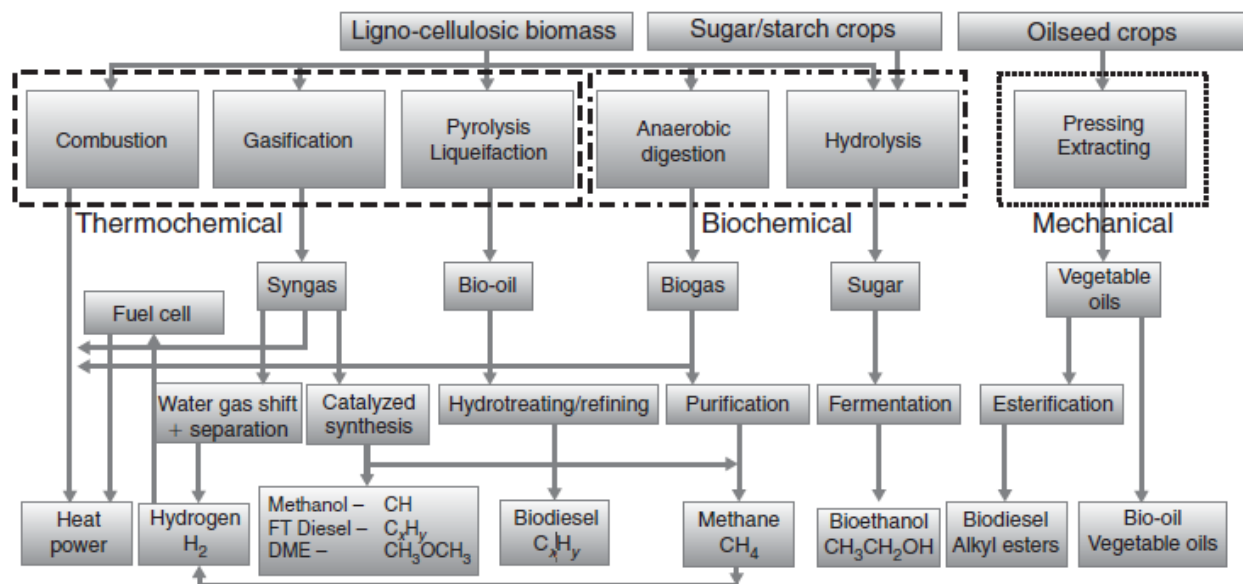


Fig. 6: Routes of Biomass Degradation by Products (Letcher, 166)

The gaseous product of this thermochemical cellulose degradation is known as syngas. Syngas consists of gas mixture containing mainly carbon monoxide (CO) and hydrogen gas (H<sub>2</sub>), but usually is accompanied by methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>), and carbon dioxide (CO<sub>2</sub>) [Pradeep 5014]. Syngas finds use due to the fact it can be converted into methanol and ethanol, one of the most usable liquid fuels in major industry. This process was coined by the German scientists Franz Fisher and Hans Tropsch in 1923, and involves the catalytic conversion of syngas into hydrocarbons and alcohols (Demirbas 2007). Since then many other processes have been discovered which can convert syngas into usable fuels, as seen in Figure 7 on the following page.

The second major thermochemical product of cellulose degradation is the liquid bio-oil. Bio-oil is a corrosive, acidic liquid that contains about 40wt. % oxygen (Letcher, 165). This bio-

oil is similar to crude oil, and has a heating value of 17 MJ/kg which is about 60% of the heating value for diesel by volume (Letcher, 166). Bio-oil is mainly produced by means of pyrolysis, as it

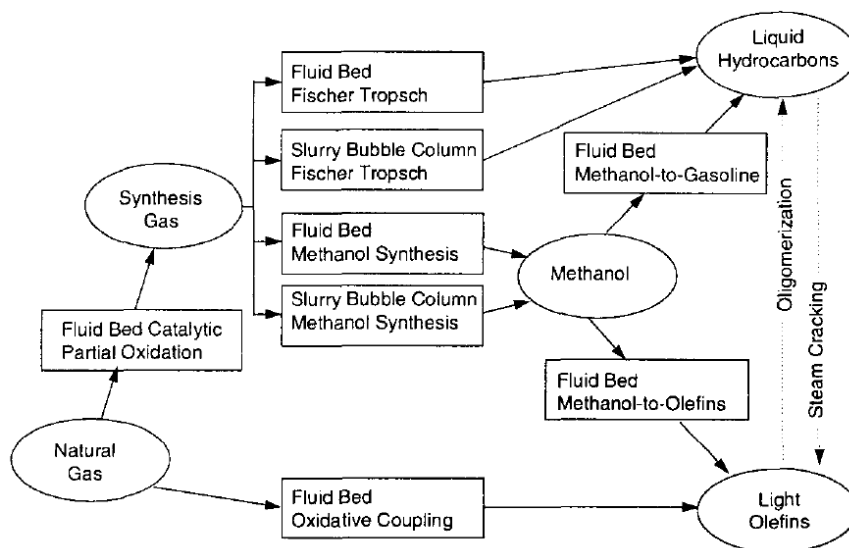


Fig. 7: List of Reaction Pathways for Syngas and Natural Gas (Krishna)

requires an oxygen-free environment to form effectively. Bio-oil, while an economical liquid fuel, has many issues that bar it from becoming a readily acceptable replacement for fossil fuels.

One of the major drawbacks of bio-oils is the fact that it is a mixture of a wide, varying array of compounds. The contents of bio-oil can range from extremely simple molecules such as acetic acid, to extremely complex structures such as levoglucosan, shown below (Mohan 852).

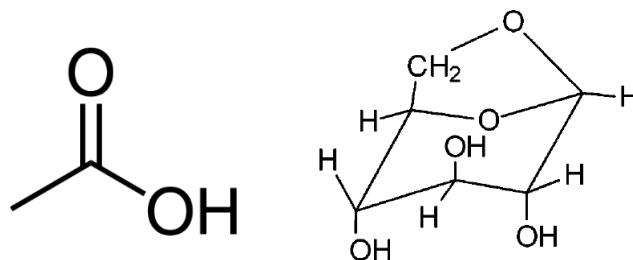


Fig. 8: Acetic Acid (Left) and Levoglucosan (Right)

Research has shown that heavily ionic media has the ability to more effectively decompose cellulose. Ionic liquids have been heavily tested, and been shown to greatly increase biomass reactivity. Ionic liquids, while extremely effective at providing an ionic media to promote cellulose degradation, are also extremely expensive. The cost of these compounds restrict them to usage in reactions where they are 100% retrievable, as any industrial process that involved the loss of an ionic liquid would be extremely difficult to economically support.

Through the use of molten salt media, a potential replacement for ionic liquids has been presented. These salts provide a potential reactive medium that would allow the cellulose to more effectively break down and eliminate the diversity of materials in the resulting bio-oil. The major restriction on molten salts is the need to heat the system to over 300°C in order for the mixtures of salts to melt. This factor however, can be overlooked when comparing the drastic difference in price between the ionic liquids and molten salts.

## **2. Literature Review**

### **2.1 Biomass**

Biomass is defined as organic matter that is relatively recently deceased, from which biofuels can be obtained. Biofuels are the result of carbon fixation (when CO<sub>2</sub> is converted into organic compounds) performed by biologic entities (Oxford English Dictionary). Mankind has been using biomass as a source of fuel for hundreds of years in the form of wood for heating and cooking purposes. Between 1810 and 1867, approximately 5 billion cords of wood was consumed for fuel in fireplaces, industrial furnaces, steamboats, and for railroads. (Cleveland, 330)

#### **2.1.1 Types of Biomass**

As biomass is a result of carbon fixation, there are several different compounds that can rightly qualify as biomass. Generally, this selection is limited to compounds that underwent carbon fixation and are carbon neutral on a short-term time scale. Fossil fuels are not considered biofuels, even though they are a result of this same process. This is because their carbon fixation occurred so long ago and it causes their burning to release a lot more CO<sub>2</sub> at once. After discarding fossil fuels, when looking for a cheap, readily available form of biomass, lignocellulosic biomass is a perfect choice, as it is found in nearly every form of plant life on the planet. Lignocellulosic biomass consists of three major types of media: lignin, hemicellulose, and cellulose.

The first major type of lignocellulosic biomass is lignin. Lignin is an integral structure in plants, as it provides rigidity through the cell walls. If the lignin in wood was biodegraded, the



wood would lose its major structure. The degradation of lignin is mandatory to purify and

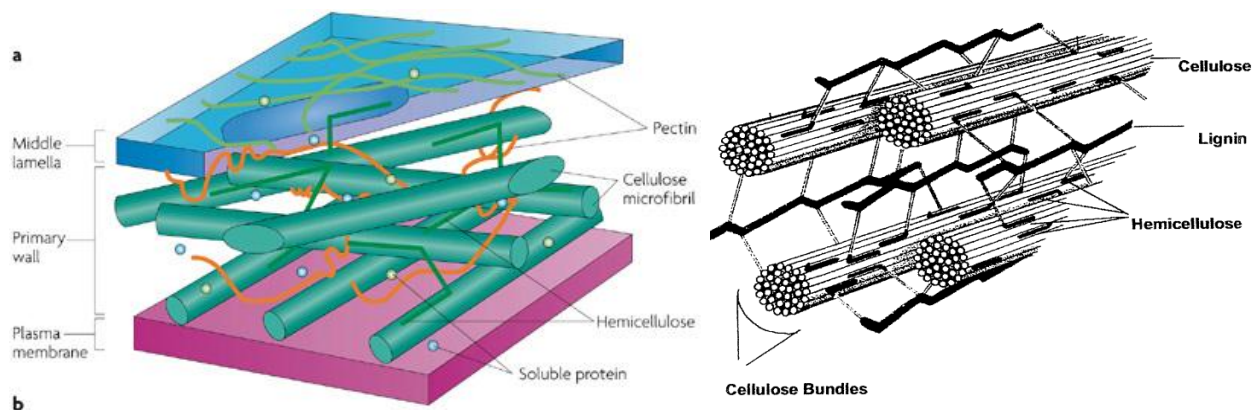


Fig. 9: Plant Cell Wall Structure (All three types of lignocellulosic visible)

process the other two major types of lignocellulosic biomass, hemicellulose and cellulose. Lignin is known to consistently produce the largest amount of energy when decomposed (Yang et. Al.), however several problems such as unmanageable byproducts often cause lignin to be less sought after than the more simplistic cellulose.

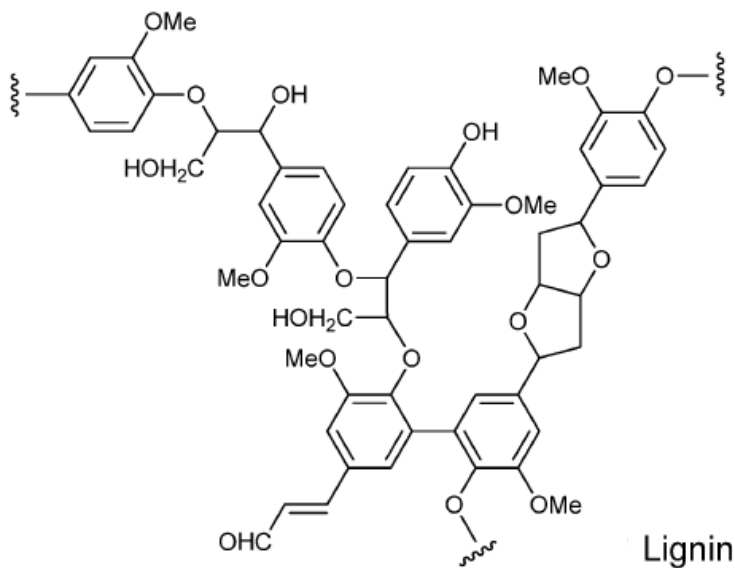
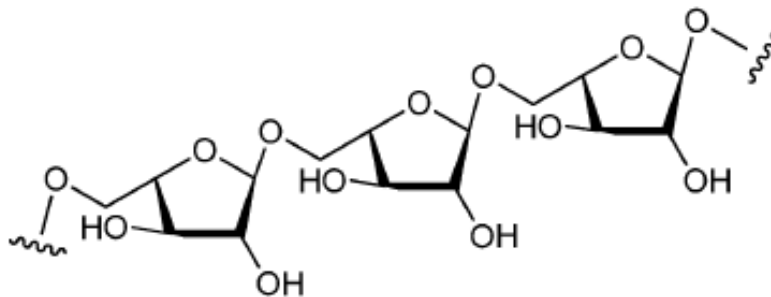


Fig. 10: The Structure of Lignin

Hemicellulose is the second major type of lignocellulosic biomass that can be purified from plant matter. Hemicellulose consists of short, branched 5 or 6 membered sugar units that often link between lignin and cellulose in a plant cell wall. Hemicellulose is the least sturdy of the three major types of lignocellulose, and is generally the least used in experimentation (Yang et. al.). This lack of use is typically due to the dramatically varying branched structures of hemicellulose, whose released energy can vary a great degree.



## Hemicellulose

*Fig. 11: The Unit Structure of Hemicellulose*

Cellulose is the final type of lignocellulosic biomass, and is also the most prolific organic structure on earth. Cellulose is extremely cheap, and has a very consistent structure, especially compared to the highly varying hemicellulose. While it does not provide as much energy per chain as lignin, cellulose burns much cleaner, and when degraded generally leaves much more manageable waste (Yang et. al.). Another major difference between cellulose and its lignocellulose counterparts is the prevalence of oxygen. Cellulose contains over 50% oxygen by mass, and depending on the environment it is placed in, this can either be beneficial or detrimental.

### 2.1.2 The Biomass Cycle

The burning of lignocellulose and other types of biomass is a carbon neutral process. Carbon energy is absorbed from the atmosphere by organic matter and is stored in the molecular bonds of the biomass. When the biomass is degraded, it breaks down, releases the stored energy, and creates syngas and bio-oil (CremLTD). These products can be used as fuel sources, allowing that carbon energy to be harnessed and used. Since the energy was initially from the outside atmosphere, and is being re-released into its initial environment, the system causes no major change in atmospheric carbon levels. This cycle cannot be noted for fossil fuels, since they are not readily replenishable and increase the total atmospheric carbon level.



Fig. 12: The Biomass (Carbon) Cycle

### 2.1.3 Biomass Fuel Viability

One of the major issues posed by using biomass as a fuel source is the difficulty of obtaining a large, cheap, consistent source of fuel. The amount of biomass needed to meet the energy standards of America is massive, and securing the space needed to create that amount of biomass provides a great challenge as well (Akinici, 3485). Figure 13 below shows the (sometimes astronomical) amount of land needed for biomass to replace diesel and motor gasoline as the main fuel source for automotive use.

Plant	Land area needed to replace transportation diesel consumption		Land area needed to replace sum of diesel and motor gasoline consumption	
	(km <sup>2</sup> )	(% US land)	(km <sup>2</sup> )	(% US land)
Corn	12,166,420	133	45,917,664	501
Oat	9,640,060	105	36,382,849	397
Cotton	6,462,018	71	24,388,503	266
Soybean	4,704,349	51	17,754,830	194
Safflower	2,693,330	29	10,164,979	111
Sunflower	2,205,164	24	8,322,577	91
Peanut	1,982,170	22	7,480,968	82
Rapeseed	1,764,131	19	6,658,061	73
Jojoba	1,154,536	13	4,357,370	48
Microalgae	120,831	1	456,032	5

Data from Tickell (2000), USDA. Agricultural Research Service (2002), U.S.DOE, EIA, Annual Energy Review (2006), Central Intelligence Agency, (2001), and NREL (1998a, b).

*Fig. 13: Land Consumption for Biomass Fueling (Akinici 3485)*

Biomass as a whole also requires resources to grow and harvest, and with current purification processes provides a low energy turnout. As shown in Figure 13 however, the use of microalgae has potential to supply the nation with a much needed source of biomass. While microalgae is the most promising perspective fuel source, there are no current methods of

promoting sustained microalgae growth in large bodies of water. Many of the major strains fall prey to zooplankton feeding or lack of ability to grow in high alkalinity water. One strain of algae known as Spirulina has potential to be a successful source, however it is plagued by extremely low reproduction rates, and likely could not support the energy needs without reproduction stimulation (Bordage 26).

While biomass acting as a total replacement for fossil fuel energy is not going to appear anytime in the near future, America has certainly begun to embrace renewable biofuels and other renewable sources of energy. Figure 14 shows that over the last 20 years usage of renewable energy has skyrocketed, and as research on biofuels and other sources of renewable energy continues, the commercial success of renewable energy will continue to grow. (EIA, xii)

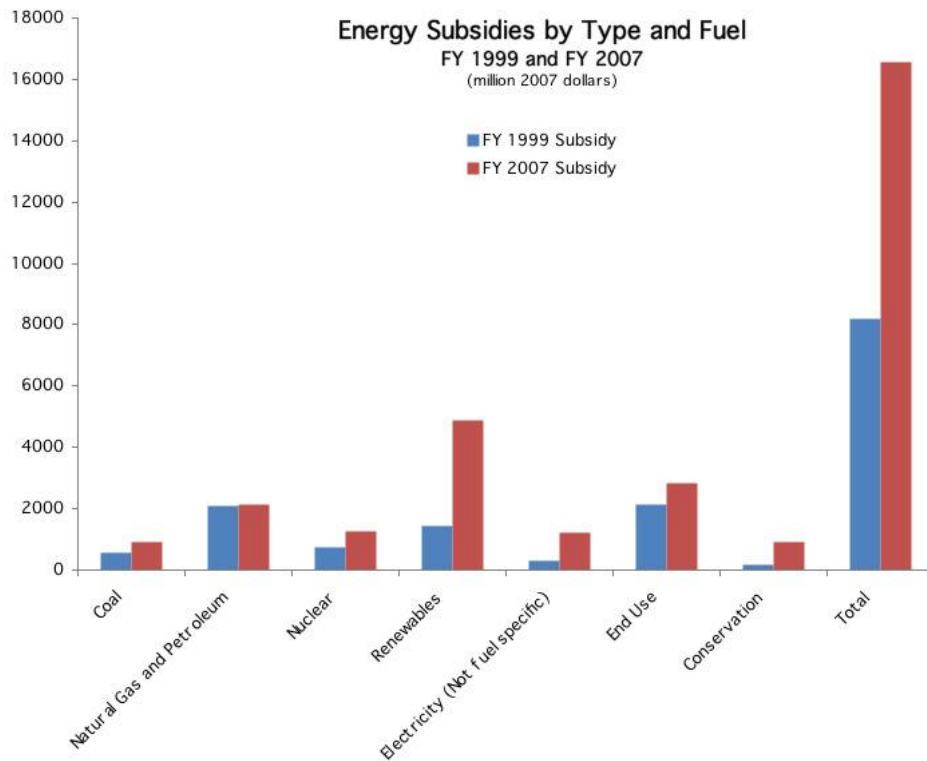


Fig. 14: Energy Subsidies by Type and Fuel (1999-2007)

## 2.2 Common Processes for Producing Fuel from Biomass

There are several reactions that can produce fuel from biomass. These include hydrolysis, pyrolysis, and gasification. Liquid and gaseous products can be produced by these reactions. They can also be catalyzed by the use of acids.

### 2.2.1 Hydrolysis

Hydrolysis is a reaction in which organic materials are broken down into smaller pieces using water. The cellulose and hemicelluloses in biomass can be broken down into simple sugars via hydrolysis. These sugars can then be fermented using yeast in order to produce ethanol, a potential biofuel.

Biomass hydrolysis can be catalyzed in many different ways. Hydrolysis can be catalyzed using acids to lower the pH. Enzymes known as cellulases can also act as catalysts in the breakdown of cellulose into basic sugars. These enzymes can be produced from various forms of fungi, such as *Trichoderma reesei*. Hydrolysis can also be catalyzed in very alkali solutions, such as a sodium hydroxide solution (Talebnia).

### 2.2.2 Gasification

Gasification is a process in which solid or liquid carbon containing materials, such as biomass or coal, is converted into a gas in the presence of oxygen or water vapor, which consists of CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. During gasification pyrolysis partially breaks down the biomass into gaseous products due to extreme temperatures. Partial oxidation also occurs, which occurs when the biomass is reacted with less than the stoichiometric amount of oxygen required for complete combustion (Huber).

Two other important reactions that occur during biomass gasification are methanation and water-gas shift reactions. During methanation carbon monoxide and hydrogen react to form methane and water. In the water-gas shift reaction water and carbon monoxide react to form hydrogen and carbon dioxide (Huber).

### 2.2.3 Pyrolysis

Pyrolysis is a chemical reaction in which organic compounds are broken down via the application of heat in the absence of oxygen. The resulting thermal decomposition reaction produces solid in the form of char, as well as liquid and gaseous products. The main gas products that can be produced are carbon dioxide, carbon monoxide, and hydrogen. Many different types of liquid products can condense and be obtained through pyrolysis reactions.

Cellulose pyrolysis is a complex reaction. The overall reaction is endothermic. The rate at which the cellulose is heated has an effect on the product distribution. The production of charcoal is favored under conditions with lower temperatures and longer residence times. At long residence times and high temperatures there is an increase in the production of gaseous products. Under rapid heating, or fast pyrolysis, mostly liquid products form. In order to maximize the amount of liquid products produced, a high heating rate and short residence times would be desired (Bridgewater).

Figure 15 shows products that can be obtained from the pyrolysis of cellulose. The two biggest products are solid char, and acetic acid. Carbon dioxide and carbon monoxide gas are also produced (Lin). Potential liquid products include mostly water with small proportions of acetaldehyde, propion aldehyde, furural, acetone, and methanol (Demibras).

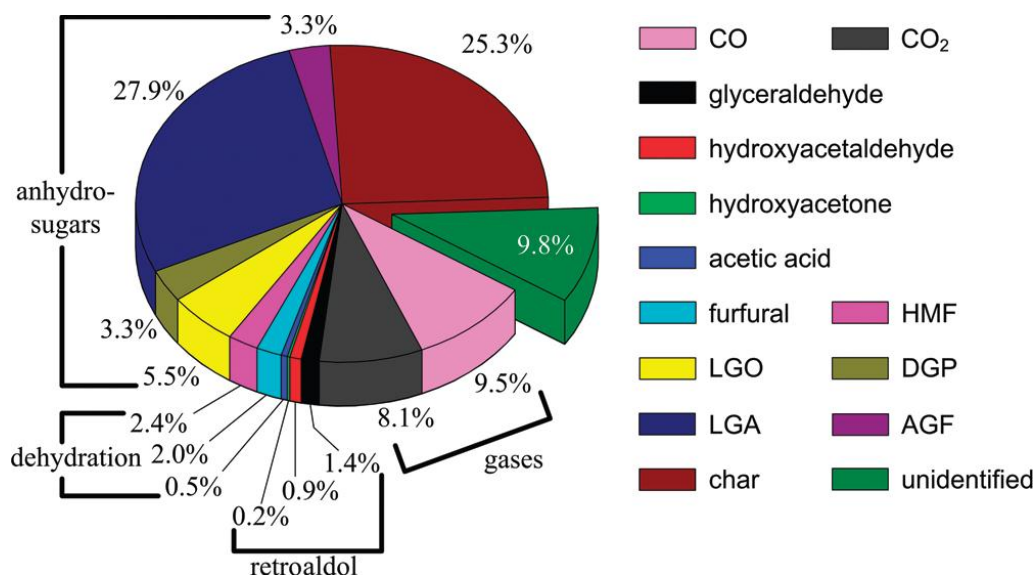


Fig. 15: Products of Cellulose Pyrolysis

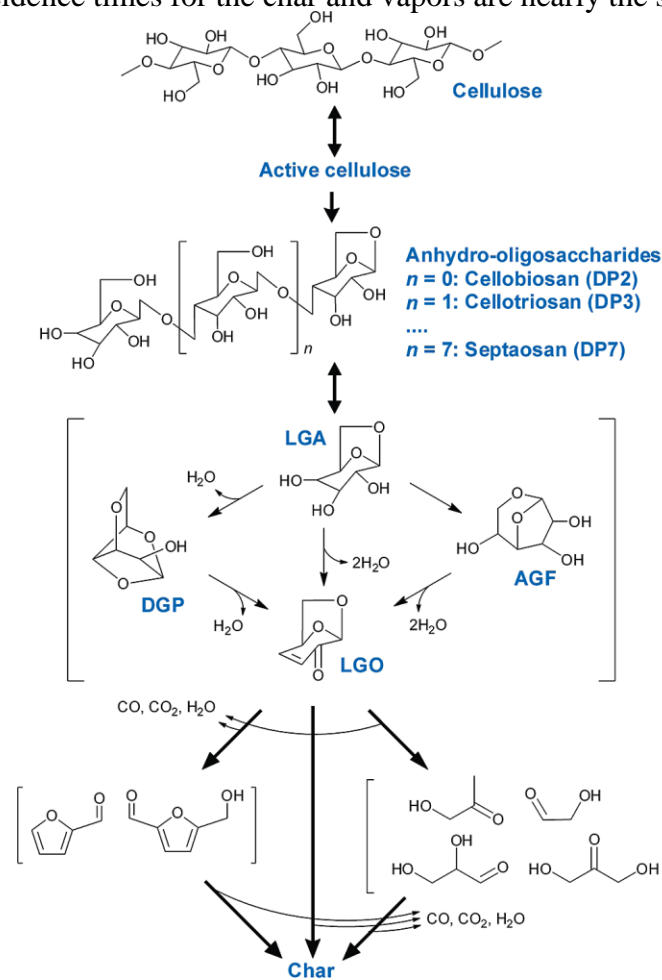
Figure 16 shows a potential reaction mechanism for the pyrolysis of cellulose. In the first step, cellulose undergoes depolymerization and decomposes to oligosaccharides with shorter chain lengths. This continues until the anhydro-monosaccharide levoglucosan, or LGA, is formed. Levoglucosan can undergo a number of isomerization and dehydration reactions to form other anhydro-monosaccharides, which react to form other hydrocarbons (Mohan 852). Eventually, all products can be converted to char.

There are many industrial uses for pyrolysis. Pyrolysis can be used for turning wood into charcoal or coal into coke. It is also used in the production of carbon fiber. Fibers made from material such as rayon or polyacrylonitrile are heated with extreme temperature to drive out non-carbon molecules resulting in carbon fiber (Chung).

Several different reactors are used for industrial scale fast pyrolysis. One type of reactor commonly used is the bubbling fluidized bed reactor. Residence times are higher for char than for the vapors, which are controlled by the fluidizing gas flow rate. Small particle sizes are required for the reactor to achieve the high heating rates. Circulating fluidized beds are also



used. The main difference between circulating fluidized bed reactors and bubbling fluidized bed reactors is that the residence times for the char and vapors are nearly the same (Bridgewater).

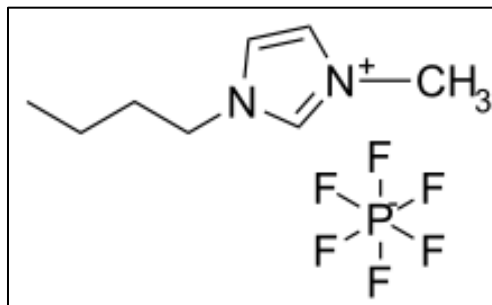


*Fig. 16: Proposed Mechanism of Cellulose Pyrolysis*

A different method for pyrolysis is ablative pyrolysis. In ablative pyrolysis of biomass wood chips are contacted against a heated surface under pressure. Rotating blades are used to press the wood chips to the reactor surface. A liquid film is formed on the hot surface, which is removed by friction. This allows for much larger particle sizes than those required for pyrolysis in fluidized beds (Meire).

## 2.3 Ionic Liquids

Ionic liquids are generally defined as ionic compounds that are liquid at room temperature, or at least below 100 °C. They are usually composed of an organic cation and an inorganic anion. Because they are completely composed of ions, they act as unique reaction media and have many applications.



*Fig. 17: 1-Butyl-3-Methylimidazolium and Hexafluorophosphate Ionic Liquid*

### 2.3.1 General Applications of Ionic Liquids

Because the chemical species making up ionic liquids are ions, the interactive forces between them are much stronger than typical interactions between polar molecules, or Van der Waals interactions. These relatively strong positive and negative charges make ionic liquids very good solvents for a variety of compounds (A. Berthod). Since the cation is usually an organic molecule, it would be relatively simple, in most cases, to design a solvent system that would be useful for specific reaction conditions (ChemicalVision2020).

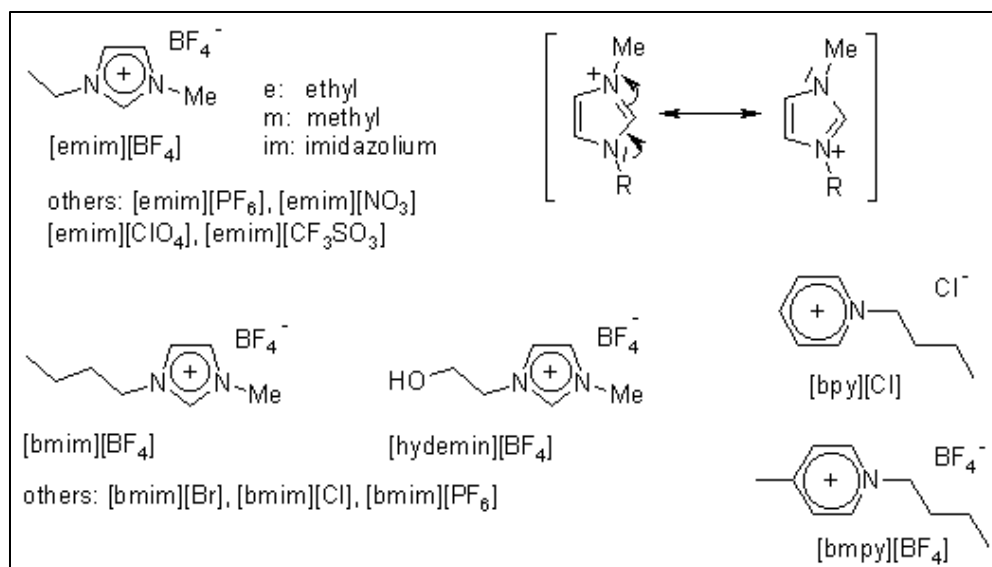


Fig. 18: A Variety of Different Ionic Liquid Systems

Due to their strong interactive forces, ionic liquids also have very low vapor pressures. This could be useful for replacing industrial chemicals that are harmful to the environment. If an ionic liquid can be designed to perform the same function as a volatile, toxic solvent, that harmful solvent would no longer have to be used. Their low vapor pressures also mean that, if the ionic liquid designed were to be toxic as well, very little would enter the atmosphere. Loss of the fluids through vaporization during use would also be very small.

### 2.3.2 Drawbacks of Ionic Liquids

Because ionic compounds that are liquid at room temperature are unusual, ionic liquids tend to be expensive, on the order of magnitude of \$1,000 per kilogram (ChemicalVision2020). This is the major problem with the use of ionic liquids. Research is currently being done to try to find cheap yet effective ionic liquids. Some have been created that contain simple methyl and ethyl sulfate anions (J. Holbrey et. al.). However, the processes used to create them can be

complicated. The limited number and variety of these low-cost ionic liquids also means that they cannot be modified as much in order to increase their suitability for the chemical systems in which they are needed.

## **2.4 Molten Salts and Catalysts**

Salts that must be heated substantially in order to enter the liquid phase are referred to as molten salts when in their liquid form. Most common salts fall into this category such as sodium chloride, lithium carbonate, potassium hydroxide, etc.

### **2.4.1 Comparison of the Practicality of Molten Salts and Ionic Liquids**

In comparison to ionic liquids, molten salts are much cheaper. Ionic liquids can cost on the order of \$1,000 per kilogram. In contrast, the same amount of some salts used as molten salts can be purchased for only a few dollars at a grocery store. The other main difference between the two is that molten salts must be heated to a high temperature in order to become liquid, while ionic liquids are liquid at much lower temperatures. This means that, in order to use molten salts, a certain energy investment is required, as well as a high temperature. Since most salts have to be heated up a few hundred degrees, the ability of any lab equipment to operate at these temperatures must also be taken into consideration.

### **2.4.2 Previous Research Completed at WPI**

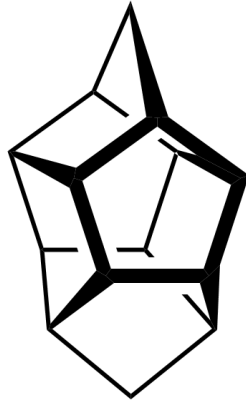
An MQP group in 2009 studied the gasification of biomass using molten salts. They analyzed various compositions of molten salt eutectics of carbonates and hydroxides. They then

determined eutectics of the carbonates that would produce a reasonably low melting point mixture that could be used in the reactor for the biomass.

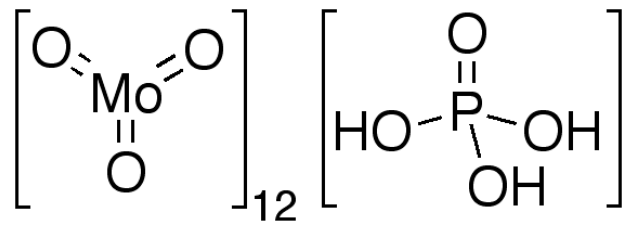
Another MQP group studied some of the reactions of molten salts with biomass materials in 2010. The focus of their project was on the gas products obtained from reactions of these materials. They studied a variety of reactions, as gasification, pyrolysis, thermal depolymerization, and transesterification. They thoroughly analyzed the gaseous products formed in order to determine what gases were formed and the amount of each present.

### 2.4.3 Additional Catalysts

The idea behind the use of molten salts and ionic liquids in reacting biomass is that the molecules in biomass, such as cellulose, which consist of long polysaccharides, will be broken down into smaller molecules at lower temperatures than in pyrolysis because of the ionic nature of the salts. Some additional catalysts could be used in order to cause the biomass to not only breakdown, but reform into other, larger molecular weight compounds. These catalysts can also serve as a method to reduce the large span of chemicals that are present in the produced bio-oil. These compounds generally provide the cellulose with an acidic or basic media that mixes well with the molten salt, as it will promote reactivity with the varying bonds in the glucose chains. Two promising commercially available catalysts that could potentially reform these products are ZSM-5 (Fig. 19), which can be used as a Brønsted acid and provides reaction pores due to its cyclic structure, and Nickel (II) Hydroxide (solid), which provides the reaction with a source of hydroxide ions and the reactive nickel media. Sodium hydrogen phosphate, phosphomolybdic acid (Fig. 20), zinc acetate, zinc chloride, and aluminum chloride have also been considered as potential candidates to promote cellulose reactivity and are included in this study.



*Fig. 19: Molecular Geometry of ZSM-5*



*Fig. 20: Phosphomolybdic Acid*

### 3. Methodology

#### 3.1 Objectives

This study had the following goals:

- Testing the effect of the following molten salt solvents in the pyrolysis reaction of cellulose (specifically focusing on produced liquids):
  - Sodium/Potassium/Lithium Hydroxide
  - Sodium/Potassium/Lithium Carbonate
  - Sodium/Potassium Bicarbonate
  - Sodium/Potassium/Lithium/Zinc Chloride
- Testing the effect of the following acid/base compounds and their effect in combination with molten salt solvents in the pyrolysis reaction of cellulose:
  - Nickel Hydroxide
  - Aluminum Chloride
  - Zinc Chloride
  - Zinc Acetate
  - Sodium Hydrogen Phosphate
  - Phosphomolybdic Acid
  - Zeolite Socony Mobil – 5 (ZSM-5)
- Examining the effects of varying ratios between the cellulose and charged compounds
- Analyzing and optimizing the reactor trials both quantitatively and qualitatively with the examined compounds
- Comparing the effects of batch and semi-batch reactor setups

- Examining consistency of produced products/data

## 3.2 Initial Property Testing – Benchtop Experiments

In order to determine whether or not our various materials would effectively degrade/reconstruct cellulose in the intended reactor environment, initial tests were run on each compound using an electric furnace. The furnace, as seen in Figure 21, can be set using a power control meter on the front panel, and heated to well over 500°C. Initially, the cellulose is tested in the heater alone. This allows one to examine any effect the temperature has on the biomass without any outside interference. From there, each trial was conducted separately in the heater, and allowed to sit overnight.



*Fig. 21: The Benchtop Electric Furnace (in GH 220)*

### 3.2.1 The Molten Salt Solvents

Initially, each molten salt solvent was tested by adding 7.5-10g of each material to a ceramic crucible and placing it into the heater. The power setting on the furnace was then increased every 10 minutes until the compound melted or decomposed, or the furnace reaches the 90% mark on the power control scale. If the compound added to the reactor successfully



melted into a stable liquid state, the ceramic crucible and the liquid molten salt was removed from the furnace, and cellulose quickly added. Once the rapid addition of cellulose was complete, any observations were recorded, and the next sample prepared. After each salt was tested separately, tests were run using eutectics of several molten salts, in order to determine differences when reacted with cellulose.

### 3.2.2 The Acid/Base Catalytic Compounds

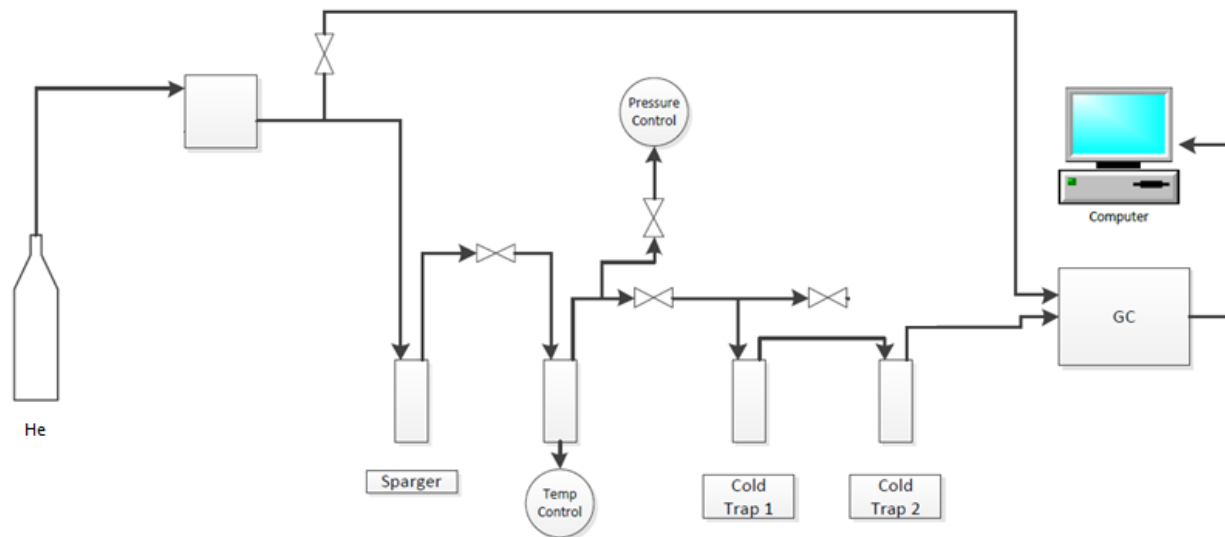
Following the testing of the molten salt solvents, the acid/base catalytic compounds were tested in a similar manner in the electric furnace. Following the running of each compound's individual trial, each compound was placed in another crucible, and mixed thoroughly with a molten salt solvent (Fig. 22). This allowed us to observe any potential reactions between the two compounds in an environment similar to that of the principle reaction. In addition, trials were run where cellulose is premixed in the crucible before entering the heater, to observe if any potential reactions occurred in the mixture as the temperature increased.



*Fig. 22: Sodium Hydroxide and ZSM-5 Benchtop Testing*

### 3.3 Flow Reactor Setup

#### 3.3.1 Reactor Flow Layout



*Fig. 23: Flow Reactor Flow Diagram*

The above system was used as the flow reactor system for all of our experimental trials. Helium was used as the reactor carrier gas. The helium was supplied by a compressed air tank, and pushed into the system through a gas flow meter manufactured by MKS Instruments. Once passing through the flow controller, the gas could either enter the reactor, or bypass the system and travel straight to the gas chromatograph (GC).

When entering the reactor system, the gas must first pass through our steel vessel sparger, which allowed us to purge any possible impurities out of the inlet line, even at extremely high pressures. From there, the gas was pushed through the main reactor, and then outwards towards two downstream cold traps, as seen in Figure 24. These cold traps consisted of two Erlenmeyer flasks, the first of which was submerged in a beaker of room temperature water, the second in a contained ice bath. These cold traps served two separate purposes. Their major purpose was to

condense and collect liquid vapors produced during the reaction, but they also served as a method to purge impurities out of the produced gas stream prior to entry into the GC.

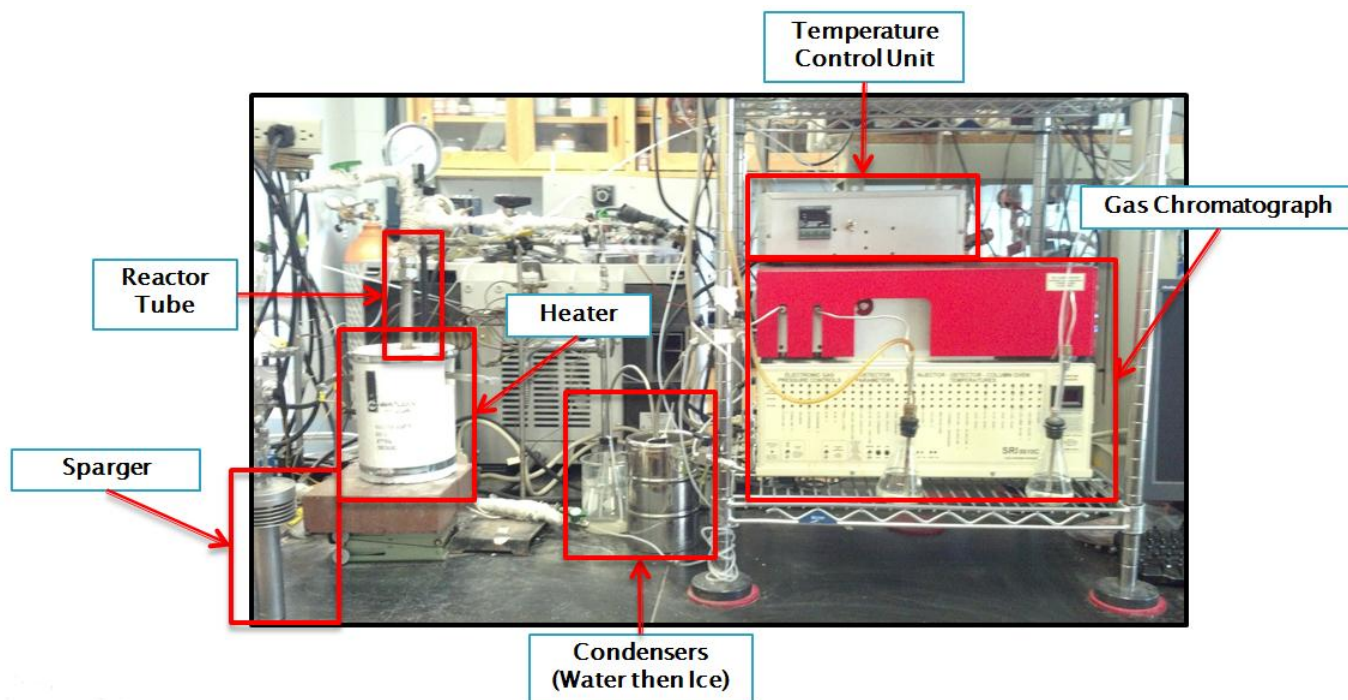


Fig. 24: The Flow Reactor

### 3.3.2 Design Specifications of the Reactor

The reactor of the flow unit was a  $\frac{3}{4}$ " stainless steel cylinder that measured 14" in length (as seen in Figure 25). The reactor tube was sealed by a Swagelok  $\frac{3}{4}$ " -  $\frac{1}{4}$ " reducing union on the upper face, and a  $\frac{3}{4}$ " ferrule cap on the bottom face. The pressure rating of the

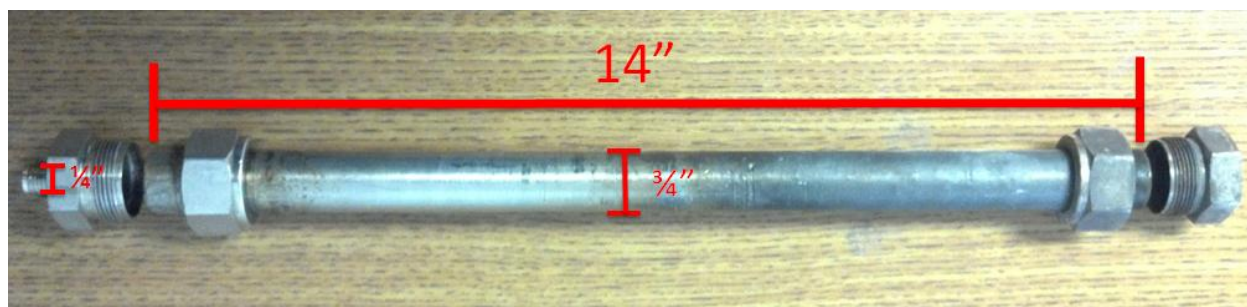


Fig. 25: Reaction Chamber of the Flow Reactor

reactor was well over 1000psi, although our trials never came remotely close to that limit. The gas inlet for the reactor tube protruded 8” into the cylinder from the reducing union, pumping helium near the bottom of the tube in order to push out any gases and vaporized liquids during the reaction (see Fig. 26). Depending on the materials used, the materials charged in the reactor could fill the cylinder as far as the gas inlet.



*Fig. 26: The Gas Inlet Line*

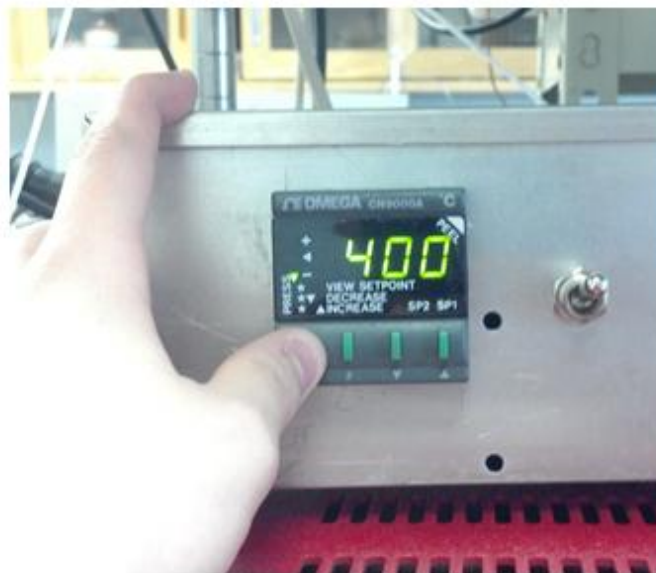
### **3.3.3 Heat and Temperature Control**

The heating of the system was provided by a Watlow Ceramic Fiber Heater. The heater is a cylinder with a vacant central space that can provide the system reactor with 360° of heating (see Figure 27). The cylinder consists of two semicircular halves which separate in order to insert larger objects. In order to ensure that our reactor was secure, the heater was fastened with metal bands in order to avoid heater separation.

The power source of the heater was a set-point temperature control unit (Figure 28) that uses an external thermocouple to control the voltage output to the reactor. The thermocouple was wrapped around the reactor tube roughly four inches from the base of the tube, allowing reasonable temperature control of the inside materials.



*Fig. 27 (Left): The Watlow Ceramic Fiber Heater*



*Fig. 28 (Right): The Process Set-point Temperature Control Unit*

Along with the mechanical temperature control, the system also included insulation to avoid unnecessary heat loss. Looking closely at Figure 24 (page 42), the insulation of all reactor lines can be seen, both preceding and following the reactor. Glass wool was also used to insulate the openings in the ceramic heater, as the spaces were significantly wider than the reactor tube. This simple insulation reduced the heat lost to the outside environment, maintained desired internal temperature, and also provided safety to the experimental team, reducing the chances of accidental burns from heated lines.

### **3.3.4 Gas/Flow Control and Calibration**

The gas flow through the flow reactor originated from a compressed helium tank in GH 222. The tank was set to release 50 psig at all times, in order to ensure pressure consistency for every trial. From the tank, the helium was pushed through an MKS flow controller. The MKS

flow controller, as seen in Figure 29 below, was calibrated to allow roughly 90 sccm of helium to flow from the tank side to the reactor side of the process. In order to calibrate the flow controller, calculating the system set point was necessary, and was found using the following equations:

$$\text{INTENDED FLOW}/\text{MAX FLOW} = \% \text{FULL SCALE} \quad (\text{X})$$

$$\text{SET POINT SETTING} = \% \text{FULL SCALE} \times 10/\text{GCF}_{\text{HELIUM}} \quad (\text{X})$$



*Fig. 29 (Top): The MKS Flow Controller Display Panel*

*Fig. 30 (Bottom): The MKS Flow Controller Set-point Dial*

Our process used a 100sccm flow controller, with intention to run around 90sccm of helium throughout our experiments. The GCF, or Gas Correction Factor, for helium was provided by the MKS manual, at 1.25. This allowed the calculation of the set point value, with ours resulting with the value of 720. This was input into the system by adjusting the dial seen in Figure 30. To input a set-point value of 720, the larger primary setting is set to “7” by fully rotating the dial,

then the secondary setting is adjusted until the dial is in the “20” position. Once set, the MKS was locked in position for the entirety of our flow testing.

### 3.4 Reactor GC Calibration and Specifications

The helium flow through our flow reactor carried all gases produced during the heating period out of the system through the SRI 8610C Gas Chromatograph. This GC was equipped with a TCD detector attached to a 60/80 Carboxen 1000 separation column. This column was chosen because of its ability to separate common gases such as O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> and CO.



*Fig. 31: The SRI 8610 Gas Chromatograph (TCD Detector shown as the grey box in the top right of the image)*

The GC TCD was programmed to begin analysis at 50°C, and ramp up at a 10° per minute rate, until a temperature of 200°C was reached. This ensured any lingering liquids in the sample would be vaporized, protecting columns integrity. The GC was tested to ensure that simple gases could be identified, using injected samples of air, methane, and CO.

Helium was chosen as the carrier gas for both our reactor and the GC. Helium was used over Nitrogen and Hydrogen in order to prevent any outside interference with the reacting

cellulose. Hydrogen is also extremely flammable, and the 400+°C environment is not stable for such a volatile carrier gas. Helium was chosen over argon as it is lighter, and much more readily available, and the GC was pre-calibrated to function using a Helium carrier.

### 3.5 Flow Reaction Setup and Procedure

The procedure for the reactor trials was approached as follows:

1. The reactor tube was charged with cellulose and any molten salts and catalysts desired for that run. The cellulose was measured to be roughly 5.1g for every trial, with the molten salt solvent ranging from 5.8-6.0g depending on the compound. When acidic/basic catalytic compounds were used, they were added in quantities of around 2g, depending on the specific trial.
2. The system was next sealed completely, with the exception of the GC outlet, and flushed with helium for 10 minutes to make sure little to no oxygen was present in the system to interfere with the reaction.
3. The heater/temperature control unit was then turned on, and the set-point was set to the desired temperature. With the exception of the runs involving carbonate solvents, the temperature was set to 400°C for all trials. Due to the high melting point of the carbonates, the set-point for those trials was raised to 430°C, to ensure melting.
4. Next the gas chromatograph was initiated and took a sample 5 minutes after the temperature set-point was reached. It took another sample 20 minutes later. This set the total reaction time to 45 minutes.



5. Once the reaction had run to completion, the heater was separated from the reactor tube, and the system was allowed to cool for 15 minutes. This allowed time for any remaining vapors to condense prior to collection.
6. Once the system had fully cooled, any produced liquid products were collected from the two condensing flasks downstream of the reactor tube.
7. The lines immediately preceding and following the cold traps, as well the line between, were thoroughly cleaned and purged of any liquid residue.
8. The reactor tube was then unsealed, its contents examined, and cleaned thoroughly. The flasks were then cleaned, and the system was reassembled for the next run.

### 3.6 Liquid Product Retrieval and Purification

After completed reactions, any produced liquids were collected and were analyzed. Liquids produced in the reaction chamber were vaporized due to the high temperature, and pushed out of the tube into the cold traps. After the system cooled down post-reaction, the liquids were retrieved from the cold traps. This was most easily accomplished using a long 2mL pipette (see Figure 32 below), filling the syringe with 0.4mL of air, 0.5mL of sample, and a finally 0.1mL of air. This process avoids too large of a buildup of liquid inside of the syringe, preventing the loss of any product. This also provides an easy method of removal from the narrow necked Erlenmeyer flasks.



*Fig. 32: 2mL Graduated Pipette*

After the liquid was retrieved, they were placed into simple 1-dram vials, where the mass of the liquid was measured, and the volume of liquid can be compared to preceding trials. Prior to analyzing the liquids further, they were filtered into 2mL septum vials using an Agilent Technology EconoFilter, in order to ensure no solid particles remained in the product solution.

### 3.7 Gateway GC/Mass Spec Calibration and Specifications

In order to gain qualitative data on the product liquids, a GC/Mass Spec was used in order to separate and identify the various fluids in the reaction products. This Agilent Technology 7890 Gas Chromatograph (picture in Figure 33 below) uses a fused silica column in order to separate and detect the various liquids in each liquid sample. The liquids were injected

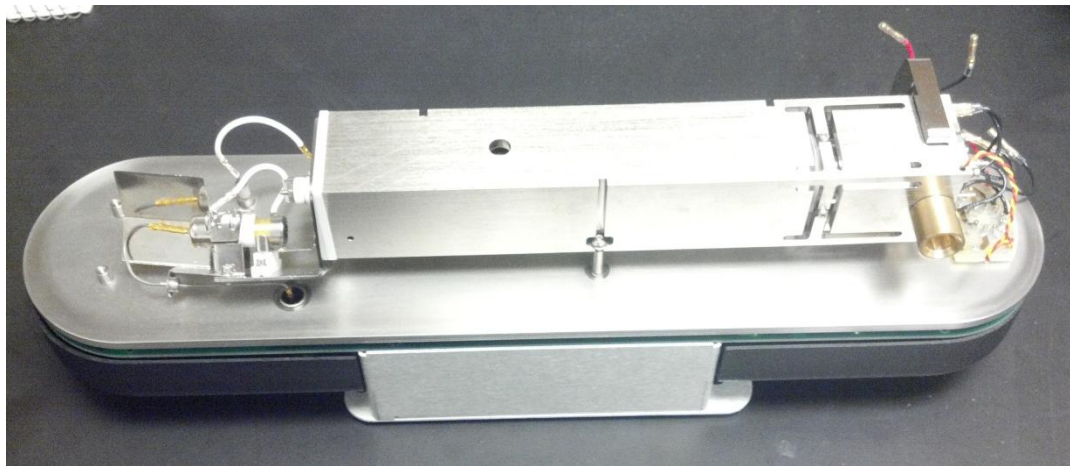


*Fig. 33: The Gateway GC/Mass Spec*

into the GC at a 200:1 ratio, ensuring that overloading the GC with pure sample was not a possibility. The GC was set to run initially at 250°C, but slowly ramped up to a final temperature

of 400°C after 12 minutes. This ramp ending in our reaction temperature ensured that all of the product liquids would vaporize, preventing damage to the column.

After passing through the GC, each portion of the separated liquid entered into the Agilent 5975C Mass Spectrometer. The Mass Spec unit uses a central unit with an electron beam to charge the particles of the injected sample, and then subsequently separates them based on a mass-to-charge ratio by induced electron fields. The ions are then sorted and processed into mass spectra, which are recorded and compared to similar spectra. This spectra database allows the mass spectrometer to correctly identify the makeup of the sample with often over 95% assurance.



*Fig. 34: The Ionizing Unit of the Agilent 5975C Mass Spectrometer*

### **3.8 Safety Procedures**

Many aspects of the testing process throughout the scope of the project presented a danger to both the team and the environment, and precautionary measures were taken extremely seriously. This project involved very heavy use of heat, which needed to be addressed to ensure the safety of all group members. Whenever items were being moved in proximity to either the electric furnace, ceramic heater, or running gas chromatograph, heat resistant gloves were used.

With respect to the handling of chemicals, the utmost care was taken when dealing with the reactor tube, liquid products, and trials involving phosphomolybdic acid as their contents were variable, potentially dangerous, or both. With the exception of very common products (such as sodium chloride and sodium bicarbonate) latex gloves, safety goggles, and lab-appropriate clothing was worn at all times when in contact, or in proximity of the chemicals. When the benchtop experiments were being run, all testing was done in a vented fume hood with a sealable door, preventing any resulting fumes from collecting in the high-traffic room. In order to ensure no dangerous gases were escaping from the flow reactor, every major line downstream of the reactor was checked and tightened (if possible), between experimental runs.

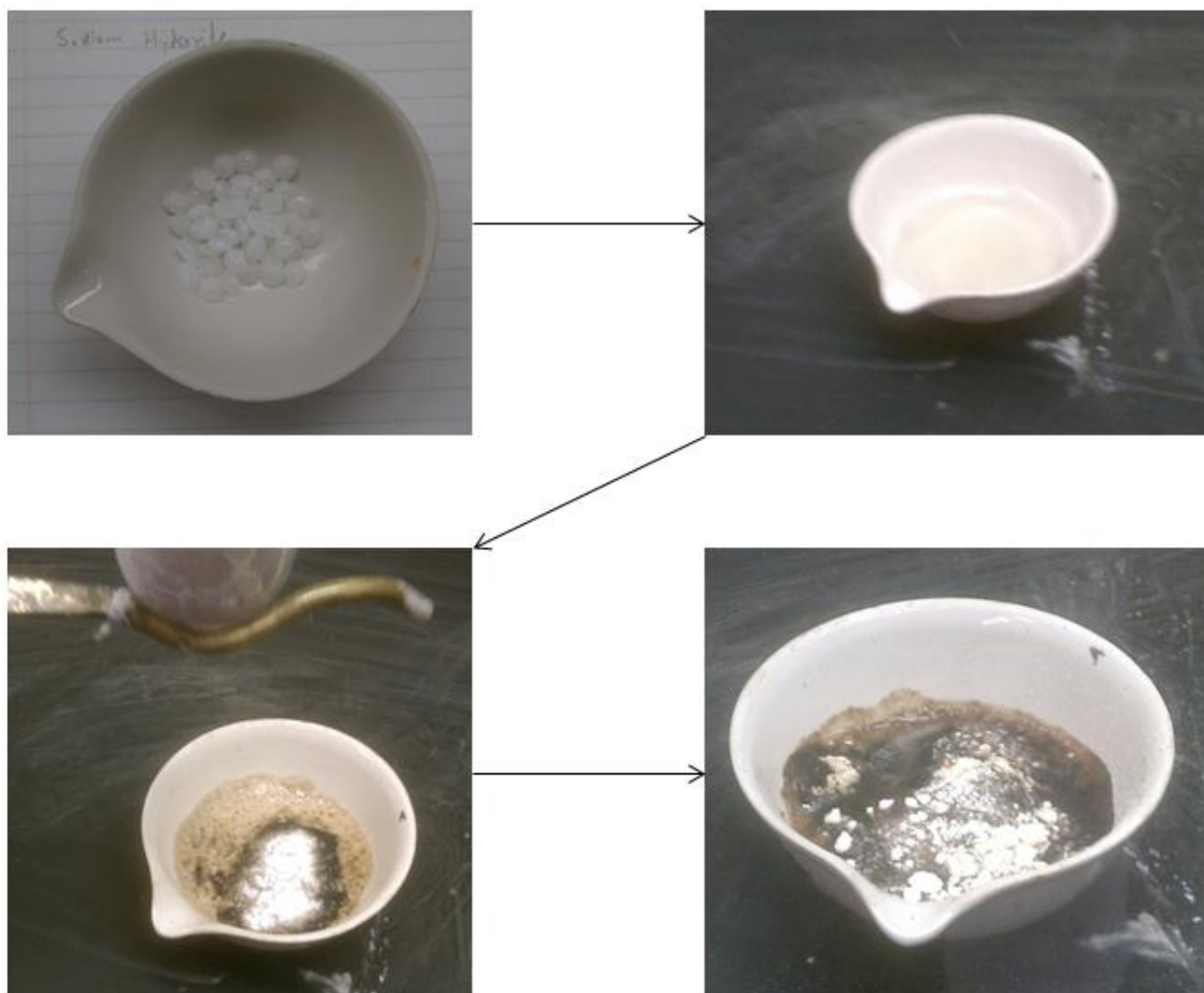
Waste from the project was separated carefully into municipal waste and hazardous waste, in order to ensure the proper disposal of all chemicals. Special care was also taken around all of the equipment in GH 222 and the Gateway building, to ensure that the integrity of all used equipment was maintained for future use.

## 4. Results and Discussion

### 4.1 Benchtop Testing Results

#### 4.1.1 Molten Salt Solvent Testing

The molten salt solvents were tested one by one in the benchtop process. The hydroxide and chloride salts gave rather consistent results, as they all melted in the electric furnace and produced visible decomposition (seen in Figure 35 below) of the cellulose after it was introduced into the system. The carbonates however, were more difficult to successfully melt.



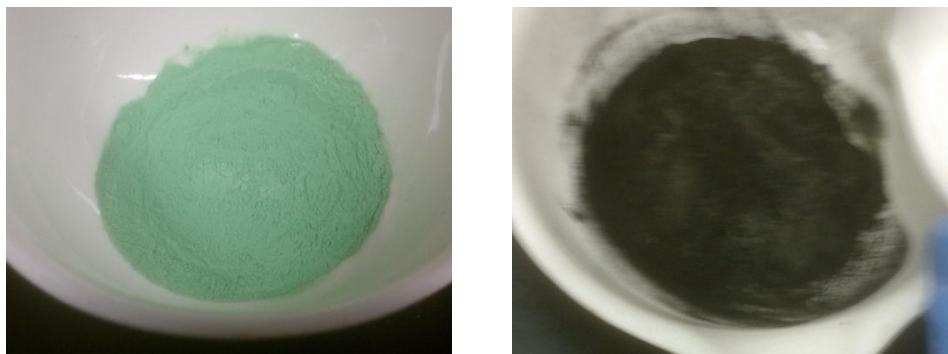
*Fig. 35: The Progression of the Sodium Hydroxide Benchtop Trial*

In order to successfully melt the carbonate solvents, the necessity to create a eutectic mixture of the compounds arose. The remaining carbonates were combined into a 34.3 wt%  $\text{NaCO}_3$ , 51.2 wt%  $\text{KCO}_3$ , and 14.4 wt%  $\text{LiCO}_3$  mixture. This eutectic mixture of carbonates lowered the universal melting point of the solvents to around our  $400^\circ\text{C}$  goal. Due to the success of the carbonate eutectic mixture, mixtures of the hydroxide and chloride salts were made as well, in order to maximize system potential when flow reactor trials began.

The only two molten salt solvents that did not effectively melt were the sodium bicarbonate and potassium bicarbonate. These salts, even in mixture, could not completely liquefy in the electric furnace.

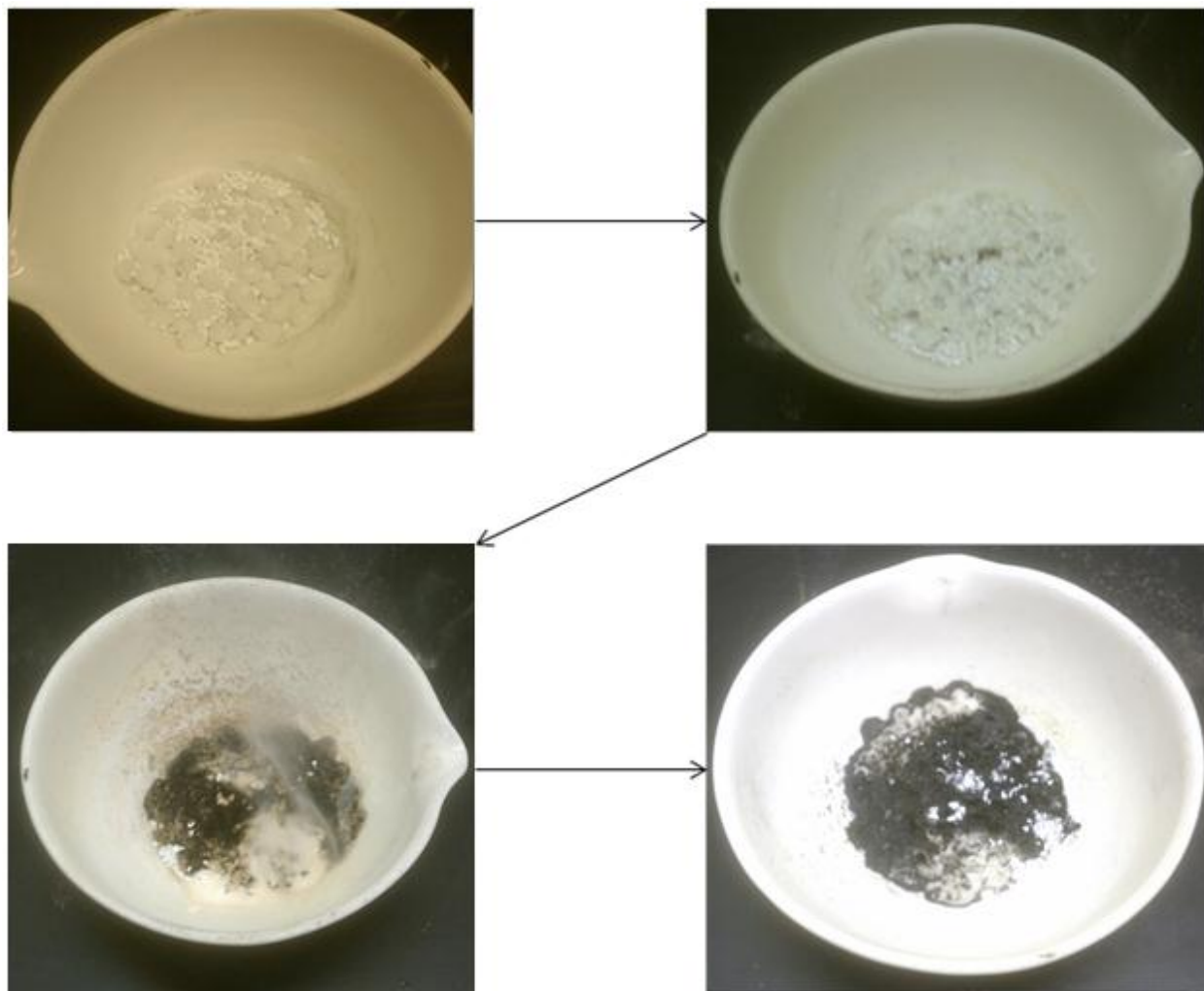
#### 4.1.2 Acid/Base Catalytic Compound Testing

The initial testing of the acid/base compounds provided several different results. When the nickel hydroxide ( $\text{NiOH}$ ), sodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ), and Zeolite Socony Mobil – 5 (ZSM-5) were heated in the electric furnace by themselves, it was not possible to liquefy them. Due to this, there was little reaction that occurred when combined with the cellulose upon removal from the reactor. In order to disperse the compounds and promote reaction, these three compounds were placed in the electric heater after being mixed with a molten salt solvent, before the cellulose was introduced to the molten salt media.



*Fig. 36: NiOH Before (left) and After (right) Benchtop Heating*

When mixed with sodium hydroxide, the nickel hydroxide and sodium hydrogen phosphate did little to change the visible decomposition of the cellulose when added to the media. When the cellulose was added to these media, similarly to the independent sodium hydroxide reaction, the decomposition visibly took place and produced smoke over a 10-15 second period before settling. When the cellulose was added to the ZSM-5/NaOH media however (as seen in Figure 37 below), the reaction was prolonged, and produced much less smoke, visibly decomposing for 45-50 seconds.



*Fig. 37: The Stepwise Benchtop Testing of a ZSM-5/NaOH Mixture*

Unlike the ZSM-5, nickel hydroxide, and sodium hydrogen phosphate, the phosphomolybdic acid partially melted in the electric furnace when set to 90% power. When the cellulose was introduced to the semi-liquefied phosphomolybdic acid, the media immediately decomposed the cellulose, bubbled up, and hardened in a 10-12 second timeframe. The smoke produced was very similar to the standard solvent trials, coming out in puffs over a 10 second window. Over the 10 second reaction window, the yellow compound also turned green at the points of contact with the cellulose, as seen in Figure 38 below.



*Fig. 38: The Benchtop Reaction of Phosphomolybdic Acid (before & after)*

The final two tested compounds, zinc acetate and aluminum chloride, were the most volatile of the tested acid/base catalytic compounds. Both materials not only changed phase, but completely decomposed from a solid to a gas at around 70% furnace capacity. While the zinc acetate slowly began to decompose and produce smoke, the aluminum chloride decomposed extremely rapidly once the furnace reached around 200°C. Further research showed that an external pressure of slightly over 3 atmospheres of pressure was required to cause the aluminum chloride to melt without totally decomposing (Schläfer).





*Fig. 39: Zinc Acetate After Decomposition (Note: Produced smoke blackened the crucible)*

#### **4.1.3 Effects on Flow Reactor Trials**

The benchtop testing provided insight into the basic properties of our tested compounds. Through benchtop testing it was determined that eutectic mixtures of the carbonate, chloride, and hydroxide subgroups would be useful in the flow trials, as it would both reduce the melting point of the solvent and increase reactivity. The lack of full liquefaction when testing the bicarbonate compounds led to their removal from the flow trials. It was also determined from these trials that the catalytic species nickel hydroxide, sodium hydrogen phosphate, and ZSM-5 must be introduced in combination with a molten salt solvent. The volatility of the zinc acetate and aluminum chloride also led to their removal from usage in the flow trials, as instability in a closed off environment could lead to pressure rise, or uncontrollable reactions.

## 4.2 Flow Reactor Trials

### 4.2.1 Produced Liquids from Cellulose Decomposition Reactions

The liquids obtained from each run were weighed in order to determine their masses. These values were compared to the amount of cellulose initially charged to the reactor and percent yields were calculated. These can be found in Table 1, listed by salt used, then by catalyst. They are also listed in Table 2, in order of percent yield. The term “percent yield” as used in this document is intended to mean the mass fraction of charged cellulose in the reactor that was converted to liquid products. The amount of catalyst used for all of these runs, when there was one present, was 2 grams. Runs 1-8 were performed under a batch setup, in which helium was not constantly flowing through the system. Very low amounts of liquids were obtained from this and the data from them was not used. The system was then changed to an open, flowing reactor system. Other runs had problems such as the bottom cap of the reactor tube not being tightened securely. This caused no products to form and so the runs were discarded when all of the results were being tabulated. These are the reasons there are some discontinuities in the run numbers.

Table 1: Results Listed by Salt

Run #	Salt	Catalyst	Cellulose (g)	Liquid (g)	%Yield
32	N/A	N/A	5.4	1.8	33
31	N/A	ZSM-5	5.3	1.7	32
12	Hydroxides	N/A	5.0	0.1	2.0
11	Hydroxides	ZSM-5	5.1	0.8	16
18	Hydroxides	Ni(OH) <sub>2</sub>	5.1	0.4	7.8
19	Hydroxides	Na <sub>2</sub> HPO <sub>4</sub>	5.2	0.2	3.8
20	Hydroxides	phosphomolybdic	5.4	1.8	33
30	Chlorides	N/A	5.1	1.8	35
29	Chlorides	ZSM-5	5.2	2.4	46
36	Chlorides	ZSM-5 & Ni(OH) <sub>2</sub>	5.2	2.2	42
26	Chlorides	Ni(OH) <sub>2</sub>	5.3	1.8	34
27	Chlorides	Na <sub>2</sub> HPO <sub>4</sub>	5.2	2.3	44
28	Chlorides	phosphomolybdic	5.3	0.1	1.9
13	Carbonates	N/A	5.2	0.1	1.9
14	Carbonates	N/A	5.1	0.1	2.0
33	Carbonates	N/A	5.2	0.1	1.9
15	Carbonates	ZSM-5	5.1	0.6	12
16	Carbonates	Ni(OH) <sub>2</sub>	5.2	1.4	27
17	Carbonates	Na <sub>2</sub> HPO <sub>4</sub>	5.2	0.6	12
9	Carbonates	phosphomolybdic	5.1	0.2	3.9

Table 2: Results Listed by Percent Yield

Run #	Salt	Catalyst	Cellulose (g)	Liquid (g)	%Yield
29	Chlorides	ZSM-5	5.2	2.4	46
27	Chlorides	Na <sub>2</sub> HPO <sub>4</sub>	5.2	2.3	44
36	Chlorides	ZSM-5 & Ni(OH) <sub>2</sub>	5.2	2.2	42
30	Chlorides	N/A	5.1	1.8	35
26	Chlorides	Ni(OH) <sub>2</sub>	5.3	1.8	34
32	N/A	N/A	5.4	1.8	33
20	Hydroxides	phosphomolybdic	5.4	1.8	33
31	N/A	ZSM-5	5.3	1.7	32
16	Carbonates	Ni(OH) <sub>2</sub>	5.2	1.4	27
11	Hydroxides	ZSM-5	5.1	0.8	16
15	Carbonates	ZSM-5	5.1	0.6	12
17	Carbonates	Na <sub>2</sub> HPO <sub>4</sub>	5.2	0.6	12
18	Hydroxides	Ni(OH) <sub>2</sub>	5.1	0.4	7.8
9	Carbonates	phosphomolybdic	5.1	0.2	3.9
19	Hydroxides	Na <sub>2</sub> HPO <sub>4</sub>	5.2	0.2	3.8
12	Hydroxides	N/A	5	0.1	2
14	Carbonates	N/A	5.1	0.1	2
28	Chlorides	phosphomolybdic	5.3	0.1	1.9
13	Carbonates	N/A	5.2	0.1	1.9
33	Carbonates	N/A	5.2	0.1	1.9

The amount of liquid and percent yield was usually highest when a eutectic mixture of chloride salts was used. The hydroxide eutectic and carbonate eutectic mixtures performed about equally, but neither yielded as much product overall as the chlorides. In the absence of an additional catalyst, the yields were usually much lower. The only exception to this was the pyrolysis of cellulose run in which cellulose was used with no catalyst or salt. The reason for this may have been that, in the absence of a molten salt, the cellulose was not broken down into gasses as much as in the other reactions, causing most of the products to be larger, heavier

molecules. This also explains why the presence of ZSM-5 did not seem to have much of an effect. The ZSM-5 would normally take the smaller, broken down products of the cellulose and reform them into larger molecular weight products. However, this cannot occur if there are almost no smaller, broken down products to begin with.

#### 4.2.2 Liquid Optimization

In order to further study the effect of the molten salts and catalysts used on the formation of the products resulting from the decomposition of cellulose, 3 runs were performed in which the amount of salt and catalyst were varied. The results of these runs are summarized in Table 3.

*Table 3: Results of Runs with Varied Amounts of Salts and Catalysts*

Run	Cellulose (g)	Salt	Salt Mass (g)	Catalyst	Catalyst Mass (g)	Liquid (g)	%Yield
29	5.2	Chlorides	6.0	ZSM-5	2.0	2.4	46
34	5.2	Chlorides	3.0	ZSM-5	2.0	1.9	37
35	5.2	Chlorides	6.0	ZSM-5	1.0	2	38

The results show that when less of the chloride eutectic mixture was used, a smaller amount of product formed. The same was seen when less ZSM-5 was used. This data suggests that the chloride salts and the catalysts did indeed have an effect on how much product was formed and shows that the catalysts did affect the reaction.

#### 4.2.3 Error Analysis

In order to roughly determine how reproducible the results of these experiments were, one was chosen and performed a total of 3 times. This was the experiment in which the carbonate eutectic mixture was used as the salt with no additional catalyst (Runs 13, 14, and 33). The results of these runs are summarized in Table 4.

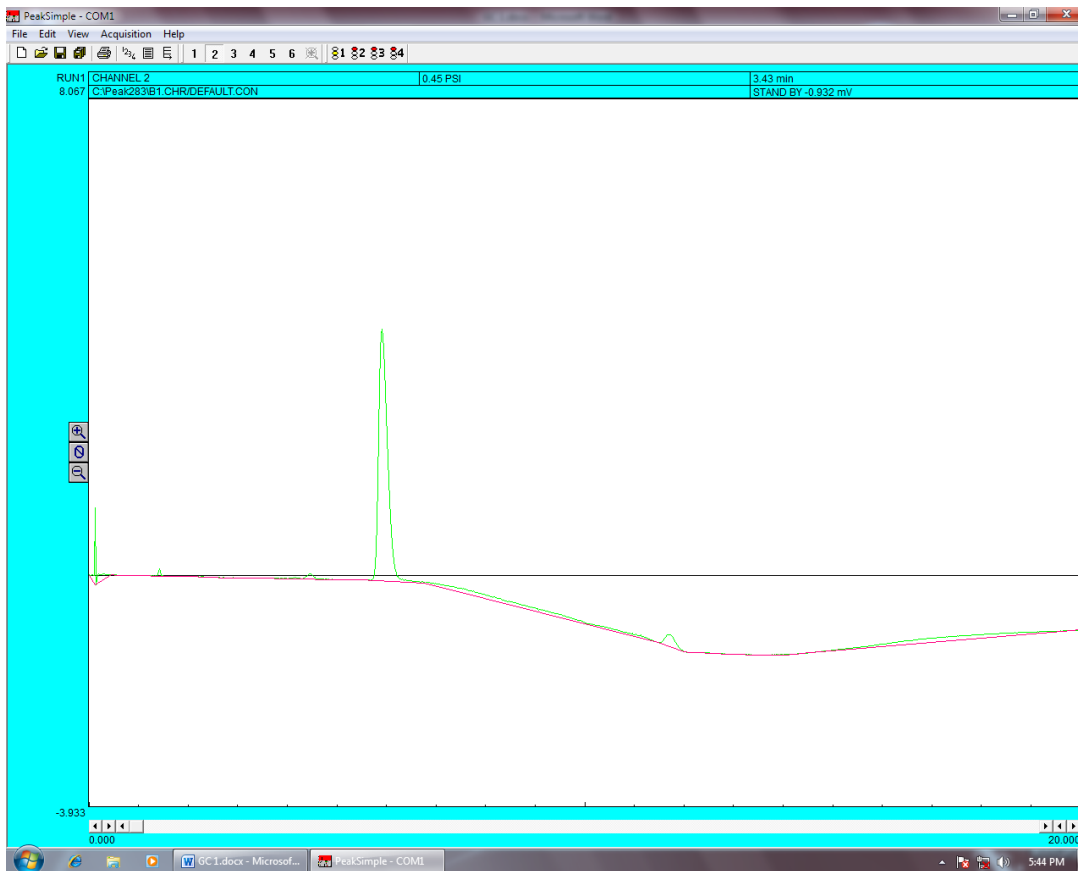
*Table 4: Repeated Experiments with Carbonate Eutectic Salt and No Additional Catalyst*

<b>Run #</b>	<b>Salt</b>	<b>Catalyst</b>	<b>Cellulose (g)</b>	<b>Liquid (g)</b>	<b>%Yield</b>
13	Carbonates	N/A	5.2	0.1	1.9
14	Carbonates	N/A	5.1	0.1	2.0
33	Carbonates	N/A	5.8	0.1	1.7

The amount of liquid collected and the yield of each run was approximately the same. This suggests that the reaction proceeded in a similar manner each time it was performed and that the results were not random. Since all other runs were performed in the same way, but with different salts and/or catalysts, it is reasonable to expect that they would also demonstrate the same degree of reproducibility.

#### 4.2.4 Gaseous Product Analysis Using the Reactor System Gas Chromatograph

As the pyrolysis reactions were taking place in the reactor tube, a gas chromatograph was used to analyze the resulting gaseous products that flowed out. The expectation was that the products observed would be similar in composition to syn gas (carbon monoxide and hydrogen), along with carbon dioxide. The gas chromatograph was setup so that it would take a sample 5 minutes after the reactor tube temperature reached the set point, and again 20 minutes later. The resulting graphs, however, were mostly inconclusive. For example, in Figures 40 and 41, the gas chromatograph plots shown are both for the run in which a chloride eutectic mixture was used with ZSM-5 as a catalyst, but the two graphs do not look very similar. The green line is the data line, which should show a peak whenever a compound eluted from the column. The red line is a base line generated by the Peak Simple software. Most of the graphs obtained contained very few, very broad peaks. Some were also large and negative. It is very likely that many of the runs yielded similar gaseous products. However, the times at which peaks appeared never seemed to match up for different runs, even though some of them should correspond to the same compounds. Valuable information was unable to be attained from any of the graphs obtained from the gas chromatograph attached to the reactor system. Future groups should investigate these gaseous products more carefully while collecting the liquid products in order to get a complete idea of what products are being formed from the reaction of the cellulose. Appropriate columns and calibrated GC peaks should be used.



*Fig. 40: Reactor GC Graph for Cellulose with the Chloride Eutectic and ZSM-5*



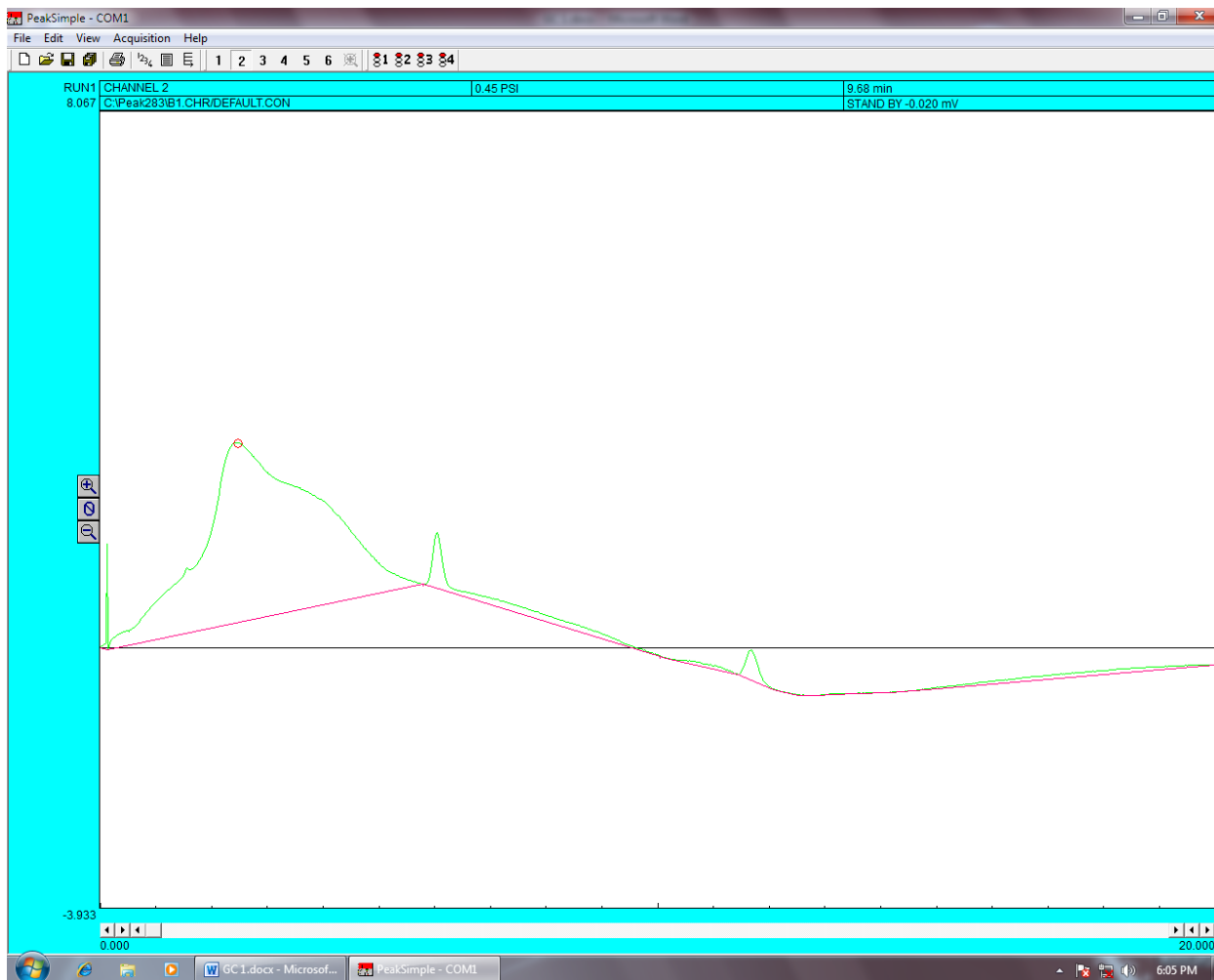
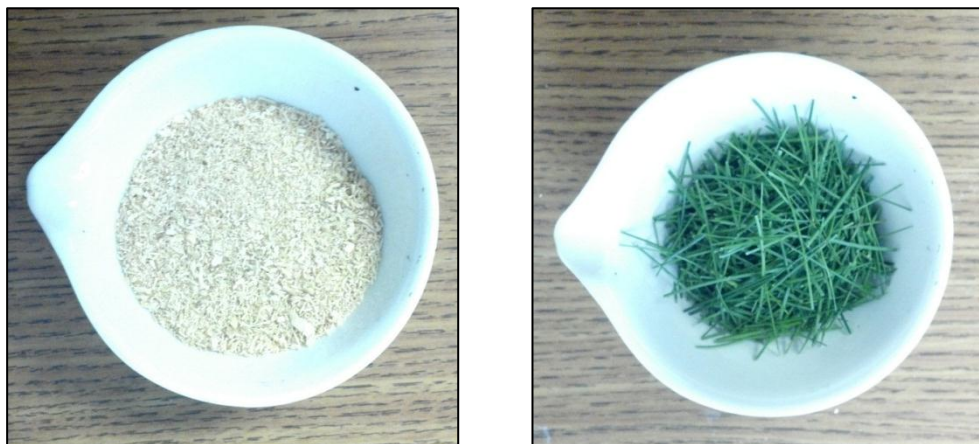


Fig. 41: Reactor GC Graph for Cellulose with the Chloride Eutectic and ZSM-5 (Rerun)

#### 4.2.5 Lignocellulose Reactions

Two additional runs were also completed using different forms of biomass other than pure cellulose. This testing allowed us to view the liquid yield in a unpurified lignocellulosic form of biomass. The setup and procedure followed were the same as in previous runs. The first material tested was industrial sawdust from assorted untreated wood. This test was done in order to examine the effect of our optimal material system (Chloride Eutectic & ZSM-5) on a sturdy, industrially realistic material. The second compound tested was a collection of dried grass clippings. Grass clippings were chosen because yard trimmings are a very common municipal waste, and are a good example of readily available plant matter. The collected compounds can be seen in Figure 42 below.

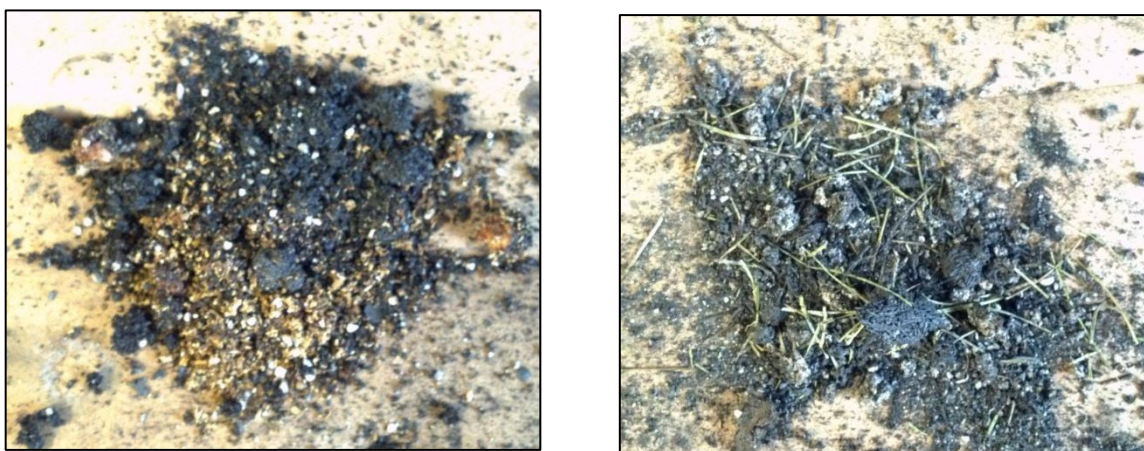


*Fig. 42: Sawdust (Left) and Grass Clippings (Right) Prior to Testing*

Due to the low density compared to the microcrystalline cellulose, only 4.5 g of sawdust was charged in the reactor tube, to avoid filling the chamber up past the gas inlet tube. For similar reasons, in the second run, only 4.0g of grass clippings were used. In both trials the standard 6.0g of the chloride eutectic and 2.0g of the ZSM-5 were used.

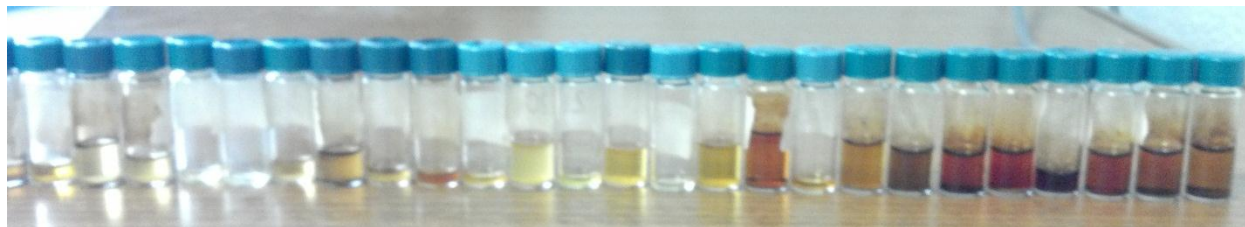
Pictures of the char for each run and of the reactants can be seen in Figure 43 below. For the run in which sawdust was used, 0.6 g of liquid were obtained, giving a yield of 13%. For the

run in which the grass was used, 2.4 g of liquid were obtained, giving an astonishing yield of 60%. However, because the grass was relatively freshly cut, it had very high water content. This means that a large portion of the liquid formed was most likely just water. The sawdust, in comparison to the cellulose, did not yield as much product when reacted with the same catalysts. The fresh-cut grass did yield more liquid, but until it is analyzed by the GC/Mass Spectrometer, it is unknown whether the liquid is composed mostly of actual products from the reaction, or water.



*Fig. 43: Reactor Char for the Sawdust Trial (Left) and Grass Clippings Trial (Right)*

### 4.3 Liquid Product Analysis



*Fig. 44: Array of Reactor Liquid Products*

The liquid samples obtained from many of the experiments were brought to Gateway Park and analyzed using the Gas Chromatograph and Mass Spectrometer. Due to time constraints surrounding usage of the machine, only experiments that yielded relatively large amounts of liquid products were analyzed. These included runs 11, 15, 16, 20, 26, 27, and 29 through 36. The details of these runs are reproduced in Table 5. To reiterate, runs 34 and 35 contained the same mixture as run 29 except that half the amount of salt was used for run 34 and half the amount of ZSM-5 was used for run 35.

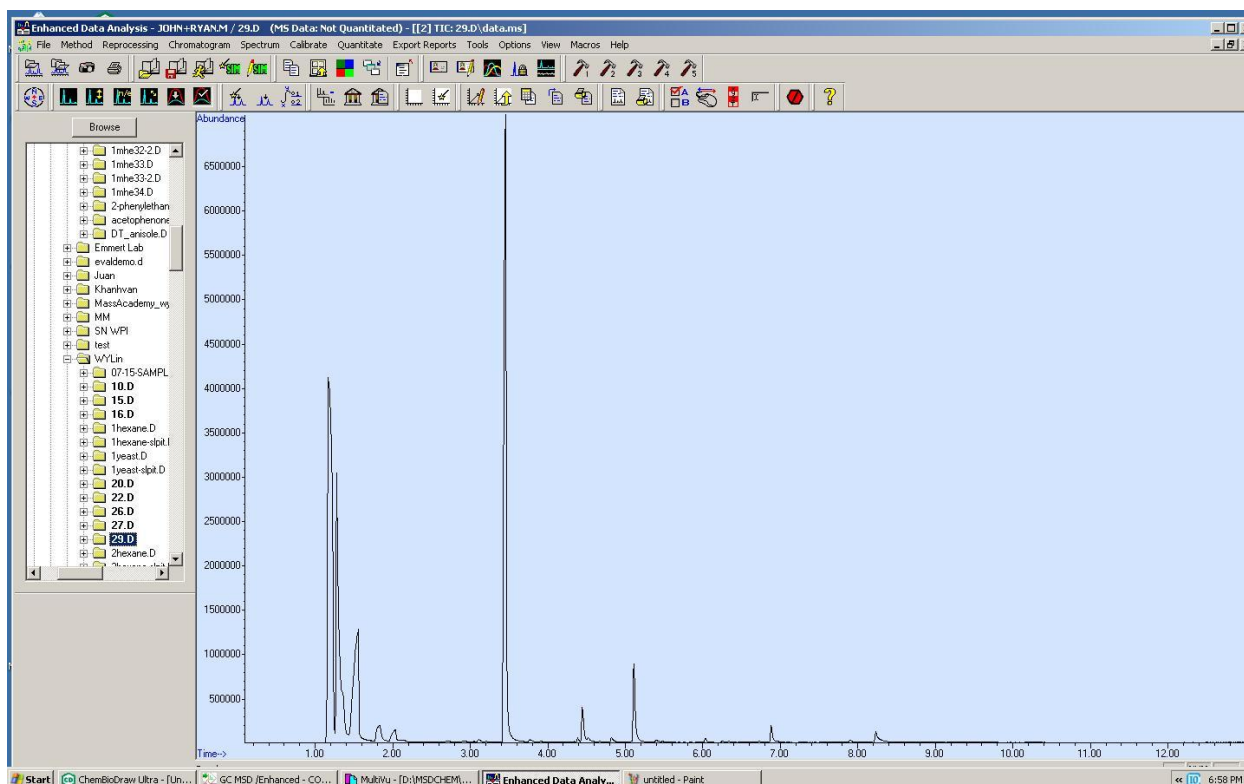
Table 5: Runs Analyzed Using GC/Mass Spectrometer

Run #	Salt	Catalyst	Cellulose (g)	Liquid (g)	%Yield
11	Hydroxides	ZSM-5	5.1	0.8	16
15	Carbonates	ZSM-5	5.1	0.6	12
16	Carbonates	Ni(OH) <sub>2</sub>	5.2	1.4	27
20	Hydroxides	phosphomolybdic	5.4	1.8	33
26	Chlorides	Ni(OH) <sub>2</sub>	5.3	1.8	34
27	Chlorides	Na <sub>2</sub> HPO <sub>4</sub>	5.2	2.3	44
29	Chlorides	ZSM-5	5.2	2.4	46
30	Chlorides	N/A	5.1	1.8	35
31	N/A	ZSM-5	5.3	1.7	32
32	N/A	N/A	5.4	1.8	33
33	Carbonates	N/A	5.2	0.1	1.9
34	Chlorides (3 grams)	ZSM-5	5.2	1.9	37
35	Chlorides	ZSM-5 (1 gram)	5.2	2	38
36	Chlorides	ZSM-5 & Ni(OH) <sub>2</sub>	5.2	2.2	42

The distribution of products was determined using the areas under the peaks on the GC graphs to determine relative molar ratios. The areas under small peaks and unidentified peaks were approximated and combined. These can be seen in Figures 47-61 in Section 4.3.2. Molecular structures of all compounds listed can be found in Appendix D.

#### 4.3.1 Interpreting Spectra of the Combined GC/Mass Spectrometer

When a sample is analyzed by the GC/Mass Spectrometer, the compounds in the sample are first separated in the column in the gas chromatograph. A graph of the peaks is displayed on the computer to which the machine is connected. An example of this graph can be seen in Figure 45, which shows the results for run 29 in which the chloride eutectic and ZSM-5 were used.



*Fig. 45: GC Graph from GC/Mass Spec. for Chloride Eutectic and ZSM-5*

After separation of the compounds in the gas chromatograph, each substance is analyzed in the mass spectrometer to try to determine its identity. When a peak is selected on the computer using the mouse, two graphs produced by the mass spectrometer are displayed. An example of these graphs can be seen in Figure 46, again using run 29 as an example. The top graph shows the fragmentation pattern of the sample and the bottom shows how well the pattern of the substance matches those the computer already has in its database. The percent likelihood of each identification is displayed, along with the full name of the compound and a diagram of its molecular structure. In Fig. 46, after clicking on the peak at ~3.5 in Fig. 45, the peak is identified as furfural with a 95% probability.

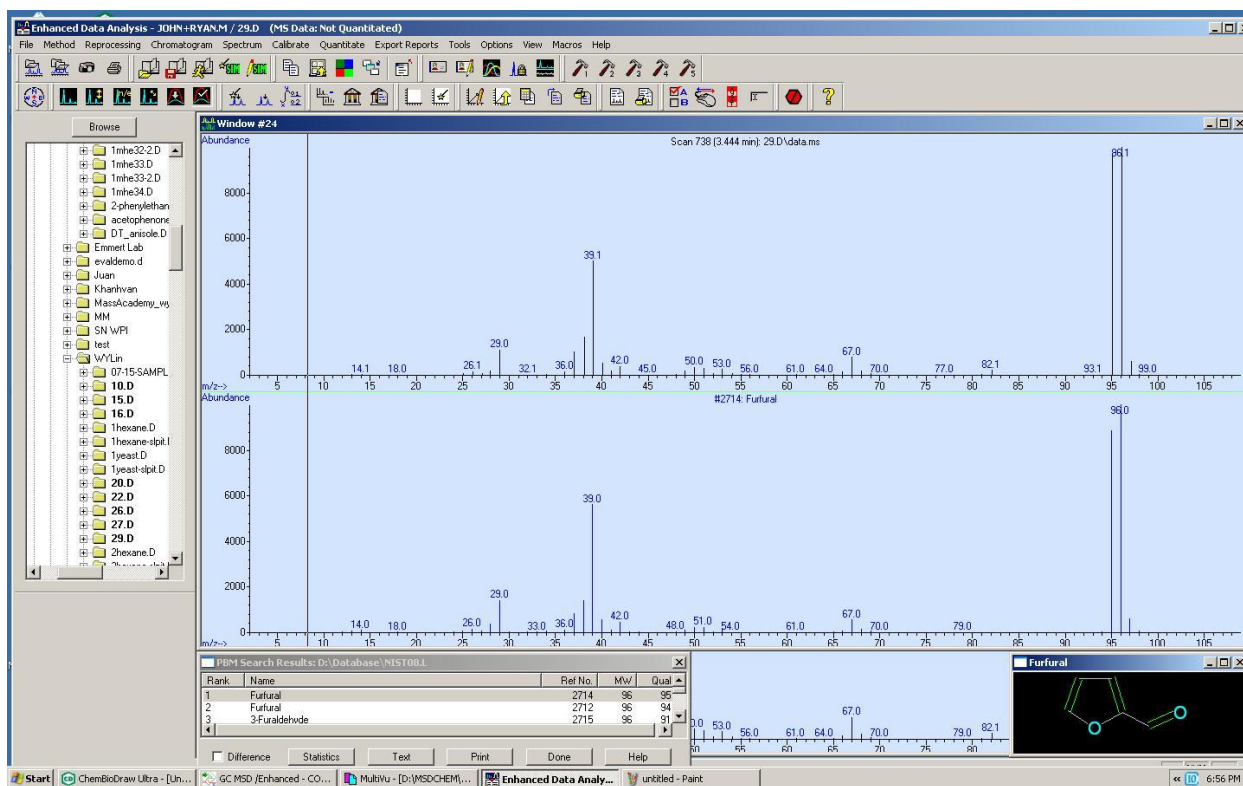


Fig. 46: Mass Spectrometer Spectrum for Furfural Peak for Chloride Eutectic and ZSM-5 Run

### 4.3.2 Analysis of Liquid Product Distribution

When cellulose was subjected to pyrolysis in the absence of a molten salt or other catalyst (run 32), there was a relatively large distribution of products, as seen in Figure 47. Furfural was produced but in a much lower mole fraction compared to other runs in which it was formed. The fraction of the liquid products that was identified as acetic acid was much larger than most of the other runs analyzed. When cellulose was subjected to pyrolysis in the absence of a molten salt but in the presence of ZSM-5 (run 31), a slightly larger percentage of the products formed was furfural or furfural analogues, as seen in Figure 48. The amount of acetic acid was smaller. Presumably, this is because the ZSM-5 caused more of the smaller products being produced to reform into larger products. This would mean larger compounds such as furfural would be more likely to form and smaller compounds such as acetic acid would be less likely to form than if the ZSM-5 were not present.

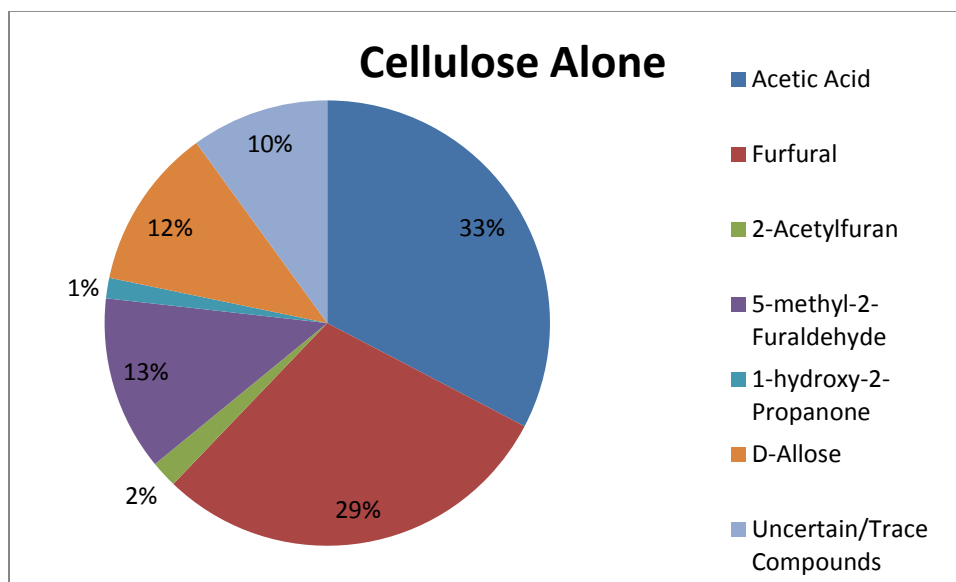


Fig. 47: Product Distribution Run 32 – Cellulose with No Catalysts (Yield: 1.8 g)



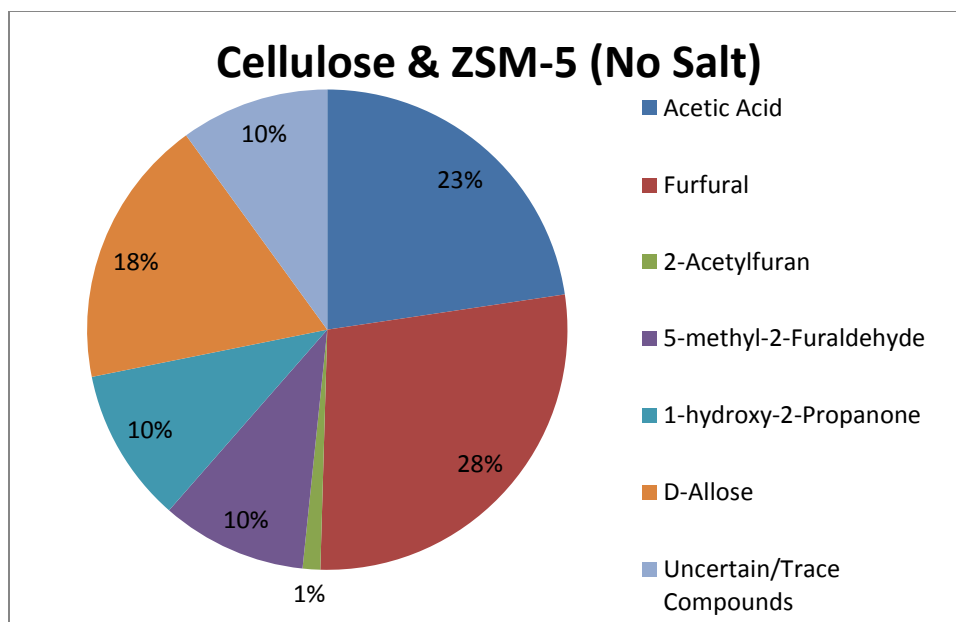


Fig. 48: Product Distribution Run 31 – Cellulose & ZSM-5 with No Molten Salt (Yield: 1.7 g)

The use of the chloride eutectic mixture and ZSM-5 catalyst (run 29) resulted in the largest amount of liquid produced at 2.4 g (see Figure 50). It had one of the highest mole fractions of furfural and produced the greatest yield of liquid products. The use of the chloride eutectic mixture without any additional catalysts (run 30) yielded a very similar distribution of products (see Figure 49). However, the overall amount of liquid product obtained was not as high. Use of the chloride eutectic mixture with other catalyst besides ZSM-5 still resulted in the production of furfural, but not as much was produced and the total amount of liquid produced was also smaller.

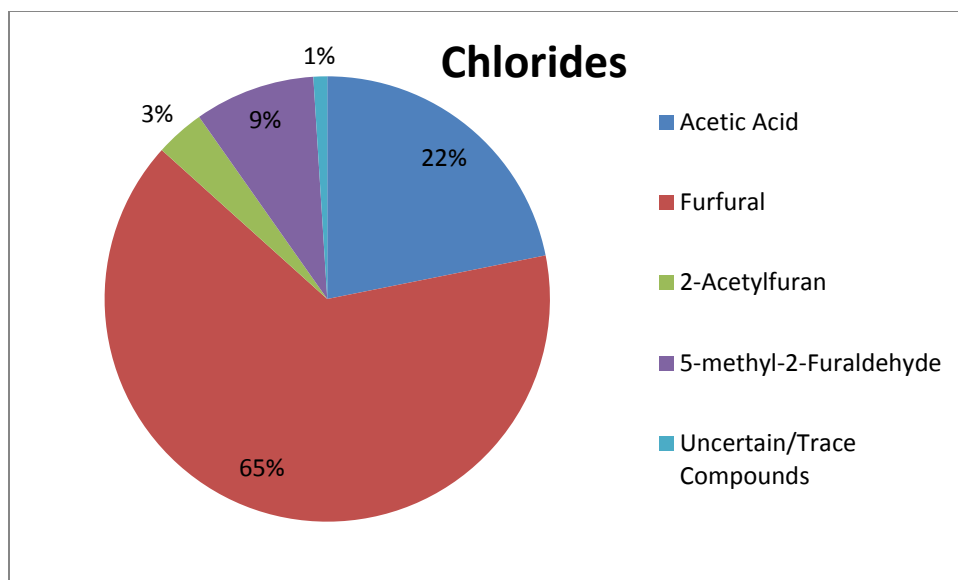


Fig. 49: Product Distribution Run 30 – Chlorides (Yield: 1.8 g)

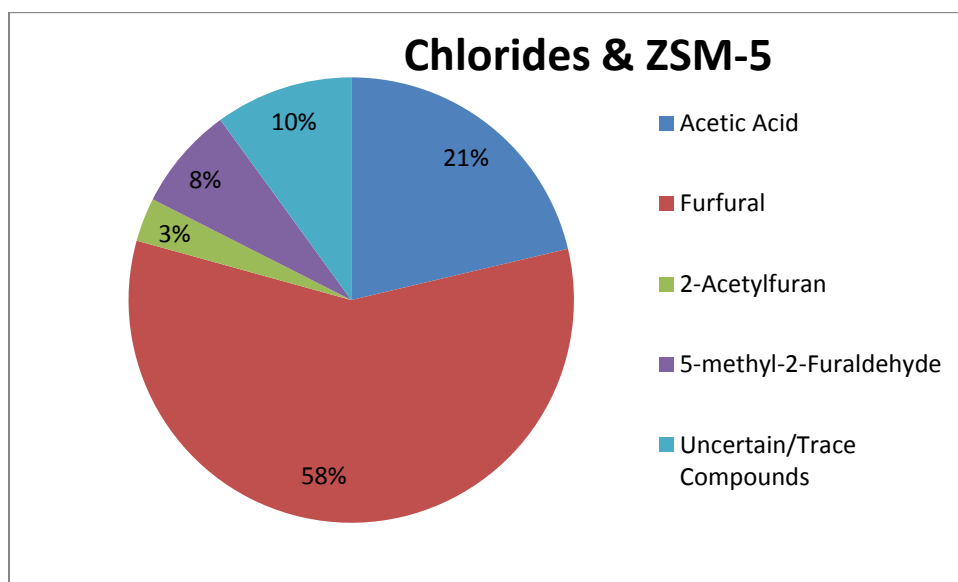
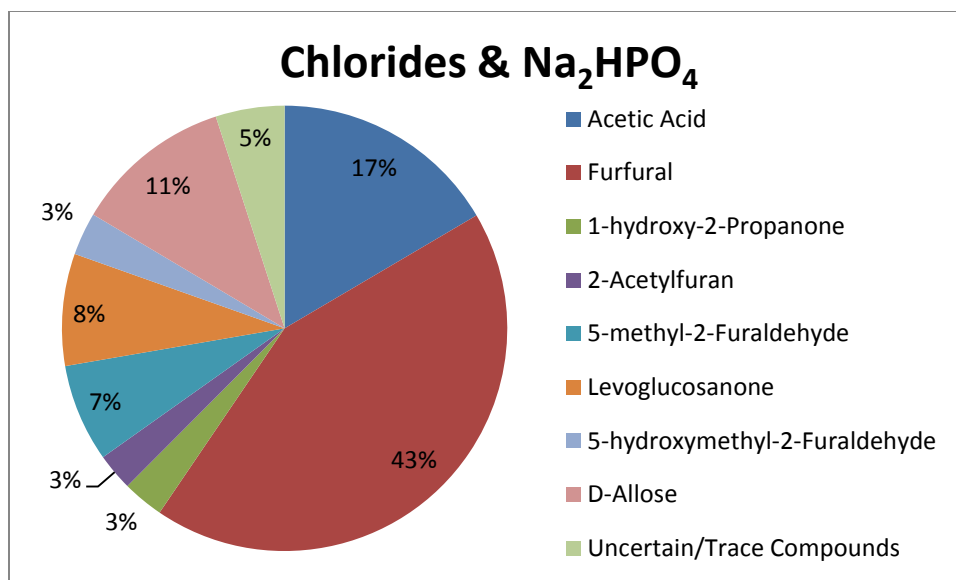
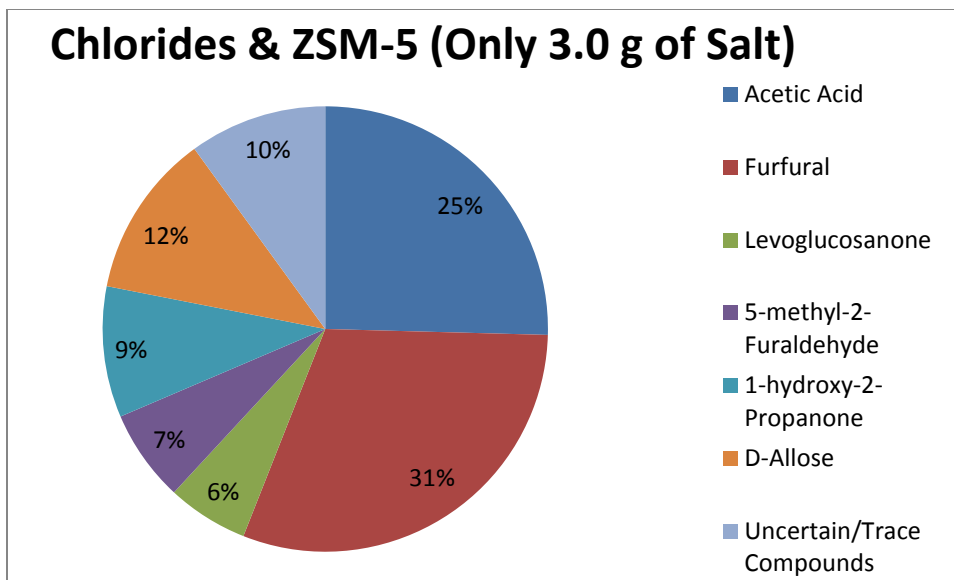


Fig. 50: Product Distribution Run 29 – Chlorides & ZSM-5 (Yield: 2.4 g)

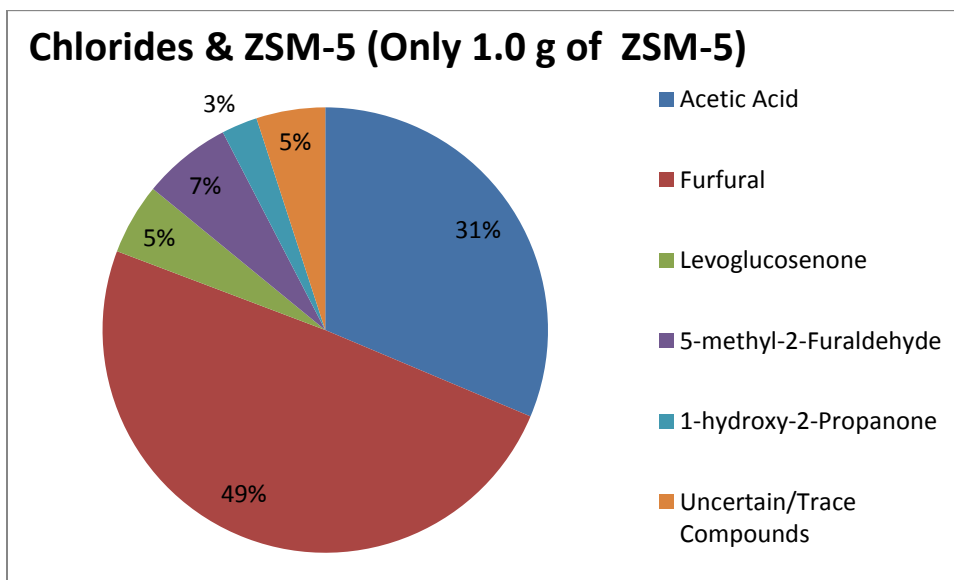


*Fig. 51: Product Distribution Run 27 – Chlorides & Na<sub>2</sub>HPO<sub>4</sub> (Yield: 2.3 g)*

For runs 34 and 35, the chloride eutectic mixture and ZSM-5 were used. However, in run 34, the amount of chloride eutectic only was cut in half (3.0 g) and in run 35, the amount of ZSM-5 only was cut in half (1.0 g). When half the chloride eutectic mixture was used, the results were very similar to when cellulose and ZSM-5 were used without any salt present (run 31). When half the amount of ZSM-5 was used, it was similar to when the standard amount of 2.0 g was used except that there was less furfural and more acetic acid. Again, this is presumably because the role of the ZSM-5 is to cause more, larger products to form; when less is present, smaller products are formed in larger yields.



*Fig. 52: Product Distribution Run 34 – Chlorides & ZSM-5 (half the normal amount of salt)  
(Yield: 1.9 g)*



*Fig. 53: Product Distribution Run 35 – Chlorides & ZSM-5 (half the normal amount of ZSM-5)  
(Yield: 2.0 g)*

In run 36, the chloride mixture was used along with a mixture of ZSM-5 and nickel (II) hydroxide (1.0 g each). The results of this run were very similar to run 35 in which the chloride eutectic mixture was used with 1.0 g of ZSM-5. This seems to indicate that the presence of the nickel (II) hydroxide either did not have much of an effect on the reaction. When the chloride eutectic mixture was used along with the nickel (II) hydroxide, 1.8 g of product were produced, indicating that, in the absence of ZSM-5, the nickel (II) hydroxide did have an effect on the reaction. However, GC/Mass Spec. data for this run are not available for a further comparison of the runs.

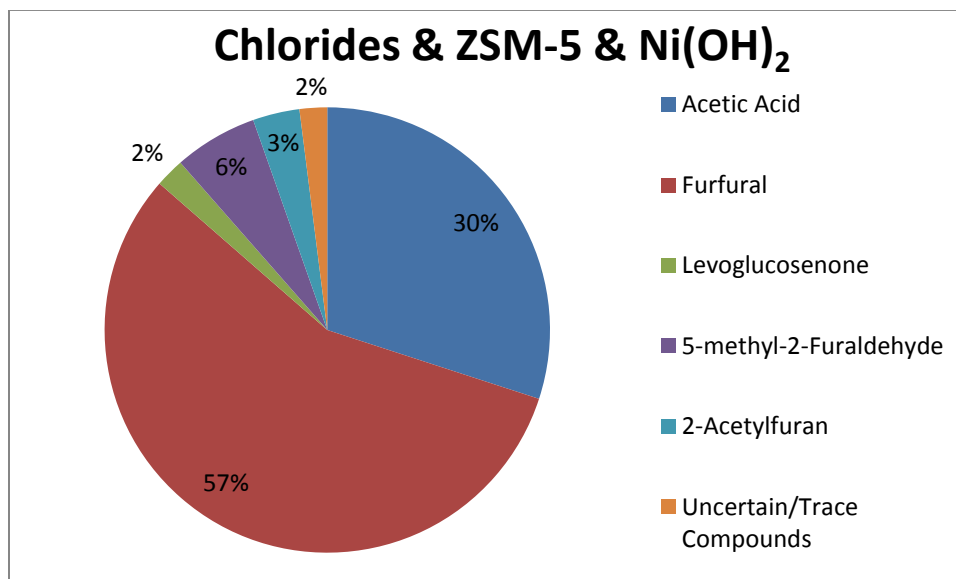


Fig. 54: Product Distribution Run 36 – Chlorides & ZSM-5 & Ni(OH)<sub>2</sub> (Yield: 2.2 g)

Runs 16 and 20 in which the carbonate eutectic with nickel (II) hydroxide, and the hydroxide eutectic with phosphomolybdic acid were used, respectively, resulted in no furfural or furfural analogue formation (see Figures 55 and 56). These runs produced mostly analogues of cyclopentane. When the hydroxide eutectic was mixed with nickel (II) hydroxide (run 26), furfural was produced and there were very few compounds that were only present in trace amounts, as shown in Figure 60. There was also much more acetic acid present. The total amount of liquid formed by this run was 1.8 g, about 2/3 the amount produced by the chloride eutectic and ZSM-5 catalyst.

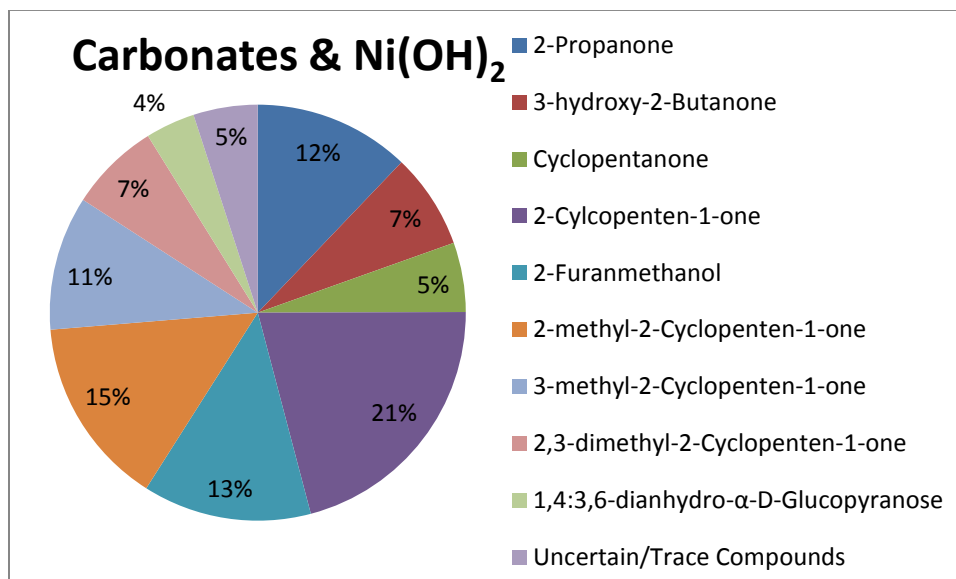
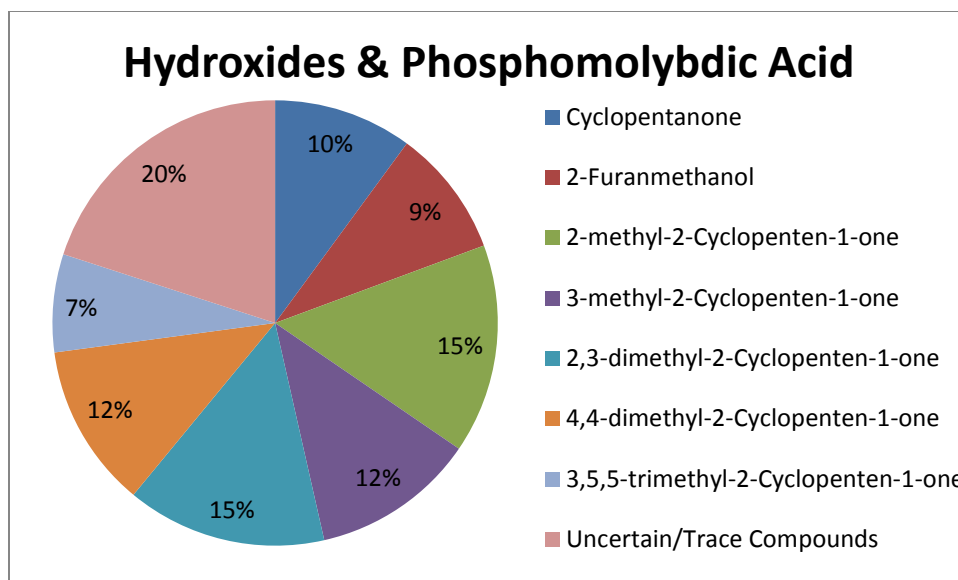


Fig. 55: Product Distribution Run 16 – Carbonates & Ni(OH)<sub>2</sub> (Yield: 1.4 g)



*Fig. 56: Product Distribution Run 20 – Hydroxides & Phosphomolybdic Acid (Yield: 1.8 g)*

Every run in which ZSM-5 was used produced furfural, regardless of the salt used. When it was used with the hydroxide eutectic (run 11), a large mole percentage of the products was furfural, as shown in Figure 57. However, there was a larger distribution of several different products, including some cyclopentane analogues. When ZSM-5 was used with the carbonate eutectic (run 15), a much smaller mole percentage of furfural was formed, as shown in Figure 58. There were also more cyclopentane analogues formed. For both of these runs, the amount of liquid collected was small, 0.8 and 0.6 g, respectively.

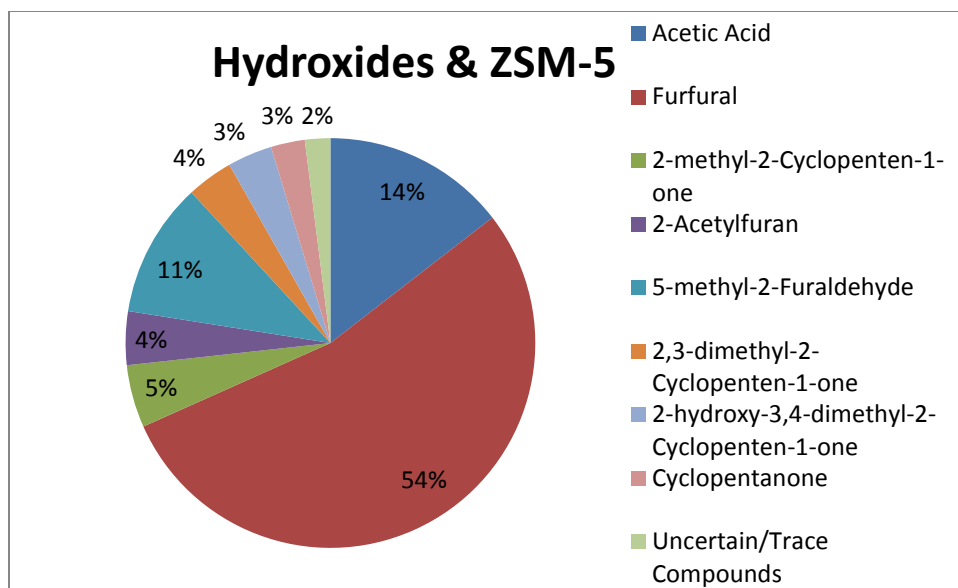


Fig. 57: Product Distribution Run 11 – Hydroxides & ZSM-5 (Yield: 0.8 g)

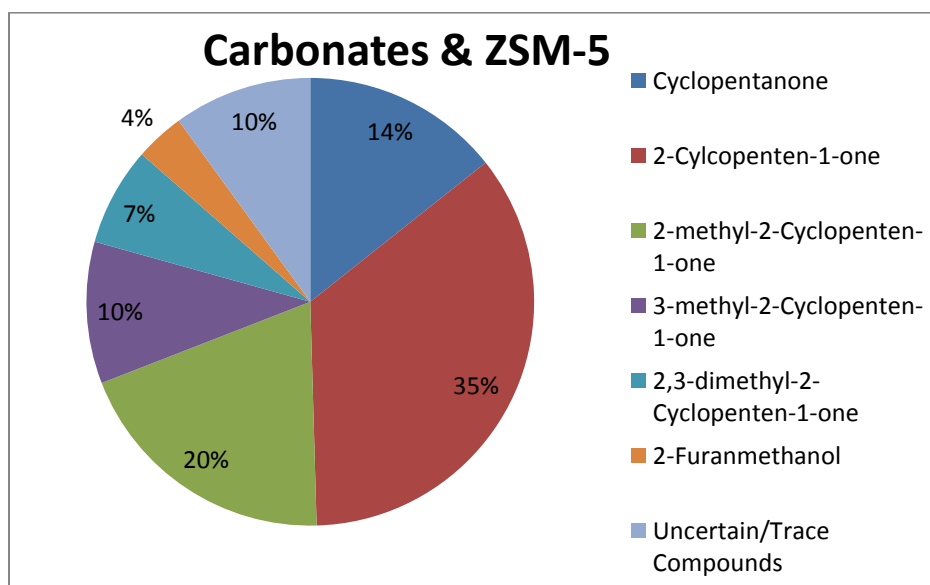
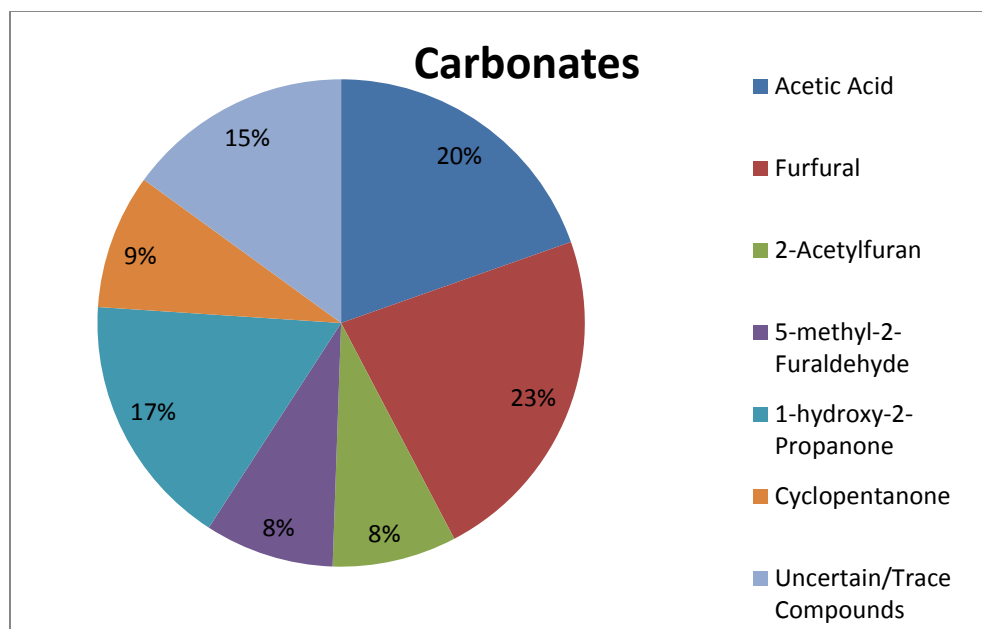


Fig. 58: Product Distribution Run 15 – Carbonates & ZSM-5 (Yield: 0.6 g)



The use of the carbonate eutectic with no additional catalyst yielded some furfural analogues. The mole percentage of furfural and furfural analogues, however, was relatively low and similar amounts of other compounds formed. The total amount of liquid product was also very small, only 0.1 g. These results are summarized in Figure 59.



*Fig. 59: Product Distribution Run 33 – Carbonates (Yield: 0.1 g)*

The use of the hydroxide eutectic mixture with nickel (II) hydroxide as a catalyst (run 26) yielded a fairly large mole percentage of furfural and furfural analogues. There was also a large amount of acetic acid formed. However, the total amount of liquid products formed from this run was relatively small, only about 0.4 g.

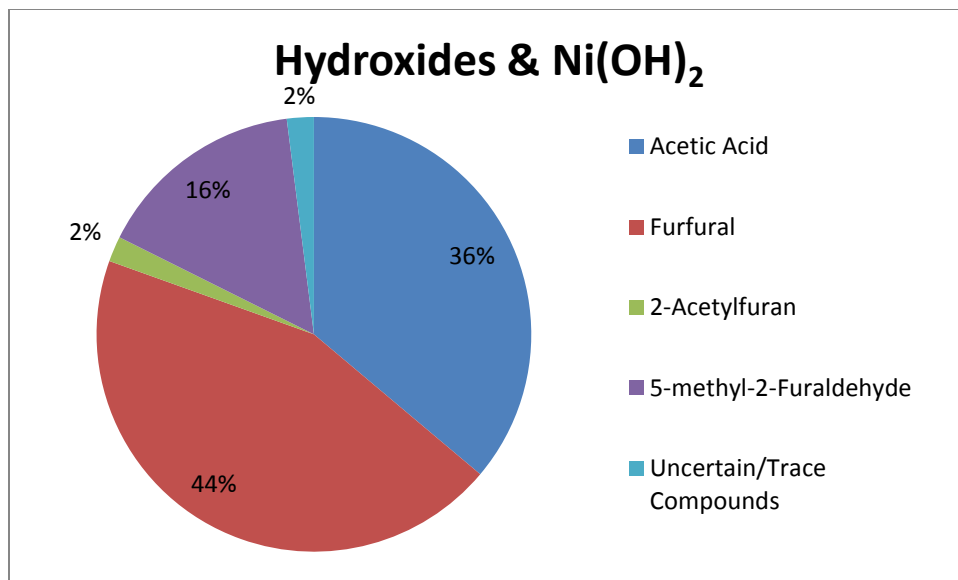


Fig. 60: Product Distribution Run 26 – Hydroxides & Ni(OH)<sub>2</sub> (Yield: 1.8 g)

### 4.3.3 Char Production and Reaction Mass Balance

Char was produced during each run. The amount of char was determined by measuring the reactor before the reaction when it was full of the cellulose, salt, and an additional catalyst if one was used, and subtracting the weight of the reactor after the reaction but before cleaning it out. The resulting amounts of char are listed in Table 6. Due to the fact that the data from the gas chromatograph attached to the reactor system was unreliable, the products in the gas phase could not be determined through any series of measurements. Their suspected masses were calculated using a mass balance.

*Table 6: Product Mass Balance by Phase*

Run #	Empty Reactor	Full Reactor	After Reaction	Char	Liquid Obtained	Charged Material	Suspected Gas Amount
9	409.9	423	417.7	7.8	0.2	13.1	5.1
11	409.8	423.5	420.6	10.8	0.8	13.7	2.1
12	410	421.7	420.6	10.6	0.1	11.7	1
13	410	421.2	419	9	0.1	11.2	2.1
14	410.1	421	418.9	8.8	0	10.9	2.1
15	409.7	422.6	420	10.3	0.6	12.9	2
16	410.1	423.4	419.7	9.6	1.4	13.3	2.3
17	410.1	423.3	420.7	10.6	0.6	13.2	2
18	410.4	424.2	422.4	12	0.4	13.8	1.4
19	410.3	425	424	13.7	0.2	14.7	0.8
20	409	422.1	420.3	11.3	1.8	13.1	0
26	408.9	422.2	418.4	9.5	1.8	13.3	2
27	409	420.9	417.5	8.5	2.3	11.9	1.1
28	409.1	422.7	420.8	11.7	0	13.6	1.9
29	409.5	422.9	419.1	9.6	2.4	13.4	1.4
30	408.8	420.2	417.5	8.7	1.8	11.4	0.9
31	409.1	417	413.6	4.5	1.7	7.9	1.7
32	409.3	414.8	410.3	1	1.8	5.5	2.7
33	408.26	420	416.9	8.64	0.8	11.74	2.3
36	408.5	422	418.3	9.8	2.2	13.5	1.5

## 4.4 Equipment Performance

### 4.4.1 Flow Reactor Performance

Overall the equipment used throughout the biomass testing worked extremely well, with only a few minor problems. However, when looking at the flow reactor, there are a few equipment issues that can be noted. The reactor tube itself sustained some minor damage over the course of the experimental trials. The slight damage can be seen in Figure 61 below, as the tube was often the subject of scratching, torqueing, and hammering in order to remove the bottom cap after experimental trials. Specifically the slight ferrule damage can be noted, as small dents in the ferrule can lead to gases escaping/entering the reactor due to the lack of an ideal seal.



*Fig 61: The bottom face of the reactor tube after the completion of experimental runs*

The sealing of the reactor tube was not the only seal based issue of the flow system. The rubber stoppers sealing the tops of the cold traps were also a performance problem. Initially, there were issues with keeping the stoppers sealed under the pressures reached by the reactor,

however this issue was dealt with through the use of locked cable ties, preventing the stoppers from unsealing. The other issue with the stoppers was their predisposition to wear and tear. In Figure 62 below, the wear on the used stopper 6 (right) is easily visible when compared to the new, unused stopper 5 (left). The stoppers needed to be changed twice throughout the testing period, as their wear eventually caused them to lose the ability to efficiently seal the cold traps.



*Fig 62: The visible wear and tear from usage of the rubber stoppers.*

The final equipment issues pertaining to the process involve the use of various set-point methods of control. The temperature control unit would very often raise the temperature as high as 30°C above the temperature set-point, as well as drop to around 5°C below. This issue can also be seen with the flow controller, as the helium flow would often vary between 87sccm and 93sccm.

#### 4.4.2 Performance of Analysis/Measurement Equipment

Another issue with the testing was the scale used to measure the materials charged into the reactor. The scale used was accurate, however GH 222 has significant airflow due to the fans, vents, AC, heaters, and windows present, and the scale did not have any external shields to protect from airflow. While minor, this could still potentially skew the data if updrafts or downflow was present around the scale.

Looking at the analysis equipment, the Goddard Hall GC required both a new column and replacement filaments before being capable of analyzing samples, however these issues were dealt with well before the testing period, and the GC was working extremely well by the time any testing began. However, useful data of the gaseous byproducts could not be obtained. This should be investigated before any further experiments can be performed. The GC/Mass Spec unit in the WPI Life Sciences building was calibrated and cared for extremely well, and needed no maintenance before or during the testing period.

## 5. Conclusions

### 5.1 Quantitative Analysis of Liquid Production

The use of the chloride eutectic with the ZSM-5 produced the largest amount of liquid. In general, runs in which the chloride eutectic mixture was used produced a larger amount of liquid products than those in which the hydroxides or carbonates were used. The performances of the hydroxides and carbonates were about equal. The use of ZSM-5 as a catalyst usually caused more liquid products to form than most of the other catalysts for any given salt used. Tables 7 and 8 show the average amount of liquid produced from all of the runs for each eutectic used and each catalyst used.

*Table 7: Average Mass of Liquid Produced by Salt*

Salt	Avg. Mass of Liquid Produced (g)
Carbonates	0.58
Hydroxides	0.66
Chlorides	1.38

*Table 8: Average Mass of Liquid Produced by Catalyst*

Catalyst	Avg. Mass of Liquid Produced (g)
ZSM-5	1.27
Ni(OH) <sub>2</sub>	1.20
Na <sub>2</sub> HPO <sub>4</sub>	0.73
Phosphomolybdic Acid	1.03

Table 9: Results Listed by Percent Yield

Run #	Salt	Catalyst	Cellulose (g)	Liquid (g)	%Yield
29	Chlorides	ZSM-5	5.2	2.4	46
27	Chlorides	Na <sub>2</sub> HPO <sub>4</sub>	5.2	2.3	44
36	Chlorides	ZSM-5 & Ni(OH) <sub>2</sub>	5.2	2.2	42
30	Chlorides	N/A	5.1	1.8	35
26	Chlorides	Ni(OH) <sub>2</sub>	5.3	1.8	34
32	N/A	N/A	5.4	1.8	33
20	Hydroxides	phosphomolybdic	5.4	1.8	33
31	N/A	ZSM-5	5.3	1.7	32
16	Carbonates	Ni(OH) <sub>2</sub>	5.2	1.4	27
11	Hydroxides	ZSM-5	5.1	0.8	16
15	Carbonates	ZSM-5	5.1	0.6	12
17	Carbonates	Na <sub>2</sub> HPO <sub>4</sub>	5.2	0.6	12
18	Hydroxides	Ni(OH) <sub>2</sub>	5.1	0.4	7.8
9	Carbonates	phosphomolybdic	5.1	0.2	3.9
19	Hydroxides	Na <sub>2</sub> HPO <sub>4</sub>	5.2	0.2	3.8
12	Hydroxides	N/A	5	0.1	2
14	Carbonates	N/A	5.1	0.1	2
28	Chlorides	phosphomolybdic	5.3	0.1	1.9
13	Carbonates	N/A	5.2	0.1	1.9
33	Carbonates	N/A	5.2	0.1	1.9



## 5.2 Qualitative Analysis of Product Distribution

After comparing the product distributions of all of the runs, the chlorides tended to yield the highest mole percentage of furfural in the liquid products. This includes the mixture of the chloride eutectic with ZSM-5. If the production of furfural is desired from a reaction similar to the ones performed in these experiments, the chlorides would be a better choice than the hydroxides or carbonates.

When comparing runs in which different catalysts were used, the ZSM-5 usually caused the largest mole fraction of furfural to form, as well as furfural analogues. It tended to decrease the amount of acetic acid formed. Little to no cyclopentane analogues formed.

Using different amounts of salt and catalyst seemed to alter the product distribution as well. For all runs except 34 and 35, approximately 5 g of cellulose was reacted in the presence of 6 g of salt and 2 g of an additional catalyst if one was used. In run 34, only 3 g of salt were used. In run 35, only 1 g of an additional catalyst (ZSM-5) was used. The result was that, when half the amount of salt was used, the product distribution was very similar to when cellulose was reacted in the presence of ZSM-5 when no salt was present. When half of the ZSM-5 was used instead, most of the same products were formed as when the full amount of ZSM-5 was used. However, of those same products formed, there were higher mole percentages of the smaller compounds, such as acetic acid, and there were lower mole percentages of the larger compounds, such as furfural and its analogues.

In general, the use of chloride molten salts with an appropriate catalyst were shown to be highly effective in the conversion of cellulosic biomass into liquid compounds.

## 6. Recommendations

The promising results of this project should be followed up with additional research as suggested to determine the viability of using molten salts and catalysts for processing biomass into liquid chemicals as fuels and chemical intermediates.

### 6.1 Flow Testing Changes

When considering the continuation of this project, a few major changes to the flow reactor are recommended. Firstly, in order to promote a more complete mixing of the cellulose, molten salt, and acidic/basic compound, a CSTR style reactor should be considered. This reactor, while providing a much better source of contact between the cellulose would also present the issue of dealing with cleaning the hardened molten salts out of the mixing unit. This would most easily be dealt with by having a mixing unit, cellulose supply line, and helium pump that could be removed while the molten salts were still heated to the point of liquefaction.

Another recommendation for the flow reactor would be the addition of more secure cold traps. Steel vessels that could withstand a higher pressure would be recommended (such as the one seen in Figure 63), allowing the system to be run at a larger variety of environments. The only drawback to the steel vessels would be the increased difficulty of retrieving the liquids produced in the system.



*Figure 63: Steel Vessel for Sparger and potential Cold Trap Usage*

Another recommendation would be the addition of a filter unit that can remove specific phases of material. The process used by the testing team did not filter the solid particles out before any streams left the reactor tube. This lack of filtering in the reactor allowed solid particles to potentially contaminate the liquid products retrieved from the cold traps. Another filtering issue involves the direct product flow through the gas chromatograph after passing through the unit's cold traps. Due to this, it is also recommended that a filter be installed to ensure that no trace solids or liquids be injected into the GC, in order to preserve the unit's integrity.

Finally, it can be noted that the use of gas chromatography for analysis of gaseous compounds in this study was inconclusive, and needs to be more carefully looked at in any future experiments.

## **6.2 Varied Media Usage**

The results of these experiments suggest that molten salts show promise as substances which effectively catalyze the pyrolysis of cellulose. When they were used, fewer products

resulted and more of these products were formed. The next step would be to evaluate how molten salts compare to ionic liquids in terms of how effective they are at affecting the product distribution of the decomposition of cellulose. It is recommended that similar experiments be performed with ionic liquids and the results be compared to those obtained using molten salts. This will make it possible to accurately assess how molten salts perform compared to ionic liquids, and to determine whether they could be used as a suitable, cheaper alternative. Further optimization of molten salt usage in combination with appropriate catalysts needs to be performed along with optimization of reaction conditions (i.e. temperature, etc.).

Another recommendation is to further investigate the more affective systems from our results on more industry friendly biomass, such as wood, discarded organic matter, recycled paper, and plastics. This will provide a more realistic view on products that would be available for feedstock, and would promote the optimization of a useable media.

### **6.3 Pilot Scale Testing**

The next logical step for the testing is to increase the scale of the system in order to more correctly understand the effect of the reaction on a larger amount of biomass. This would be achieved by using the previously recommended CSTR reactor, and building the system on a much larger pilot scale. This would allow the testing team to analyze any issues that could arise when looking to convert the process into a potentially industrial system. This scaling would involve the usage of a much larger quantity of materials, so the necessary funds would also need to be allocated for the endeavor.

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## Appendices

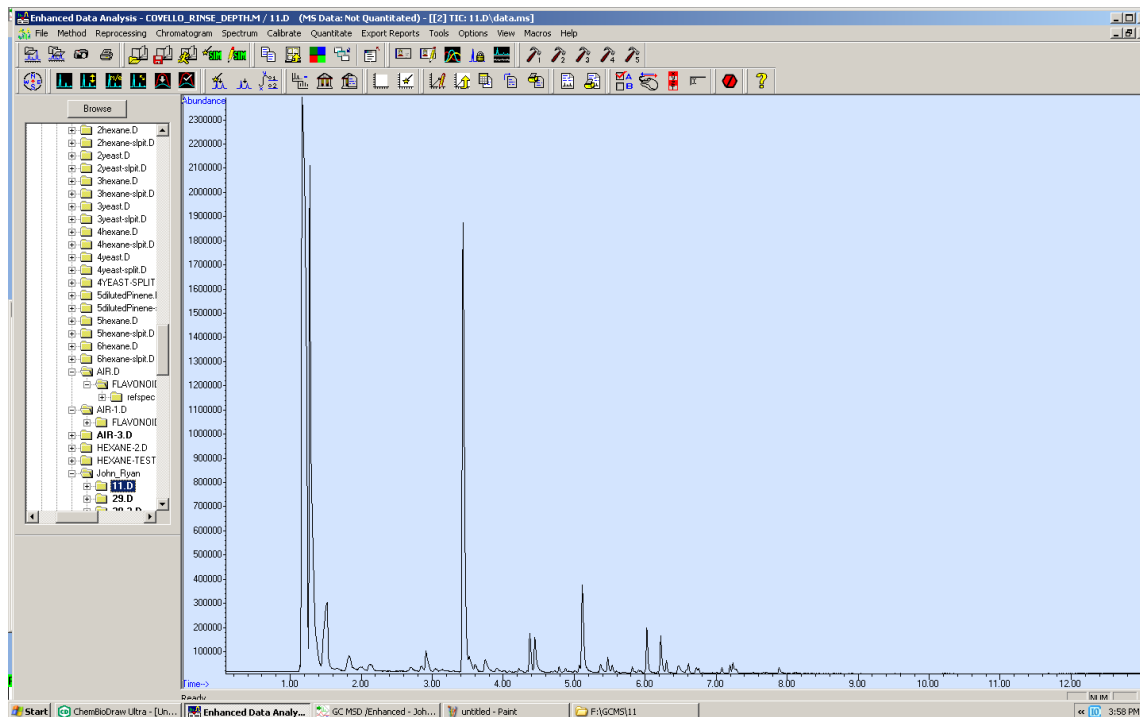
### Appendix A: Measurements

All masses are measured in grams.

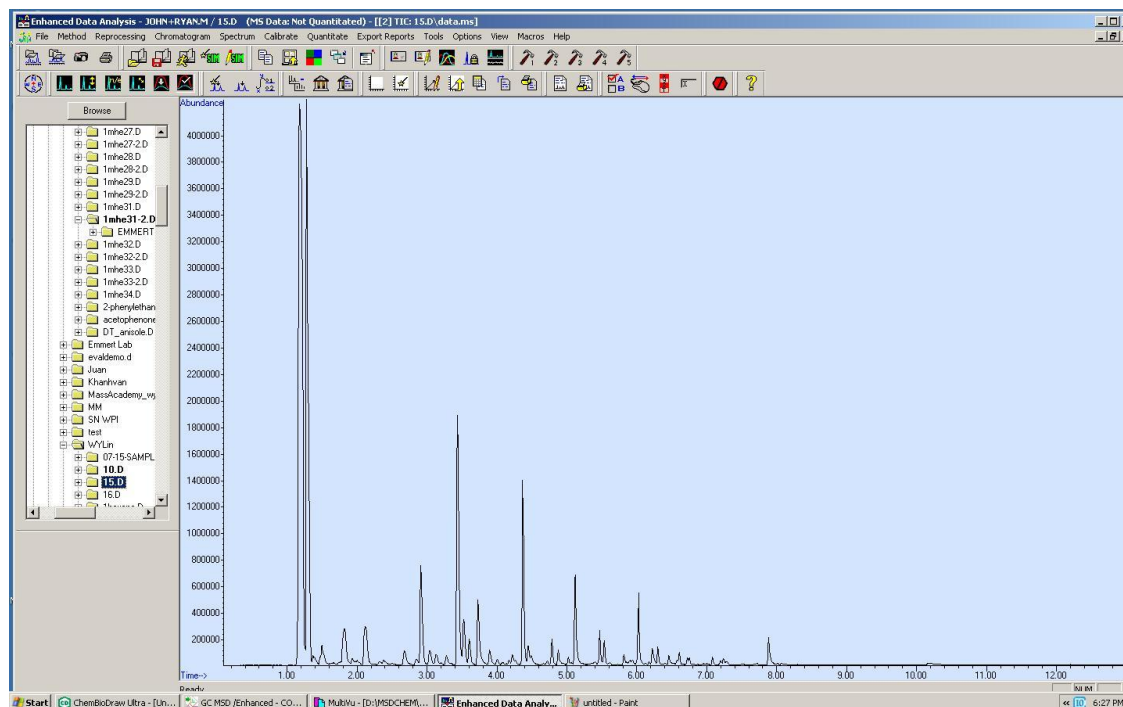
Run	Cellulose Amount	Salt	Salt Weight	Catalyst	Catalyst Weight
9	5.1	Carbonates	6.0	phosphomolybdic	2.5
11	5.1	Hydroxides	6.0	ZSM-5	2.0
12	5	Hydroxides	6.0	N/A	N/A
13	5.2	Carbonates	5.8	N/A	N/A
14	5.1	Carbonates	5.8	N/A	N/A
15	5.1	Carbonates	5.8	ZSM-5	2.0
16	5.2	Carbonates	5.9	Ni(OH) <sub>2</sub>	2.3
17	5.2	Carbonates	5.9	Na <sub>2</sub> HPO <sub>4</sub>	2.1
18	5.1	Hydroxides	6.0	Ni(OH) <sub>2</sub>	2.0
19	5.2	Hydroxides	6.2	Na <sub>2</sub> HPO <sub>4</sub>	2.1
20	5.4	Hydroxides	6.2	phosphomolybdic	2.0
21	5.2	Chlorides	6.0	N/A	N/A
22	5.2	Chlorides	6.0	ZSM-5	2.0
23	5.1	Chlorides	6.1	Ni(OH) <sub>2</sub>	2.0
24	5.1	Chlorides	6.1	Na <sub>2</sub> HPO <sub>4</sub>	2.1
25	5.1	Chlorides	6.0	phosphomolybdic	2.1
26	5.3	Chlorides	6.0	Ni(OH) <sub>2</sub>	2.0
27	5.2	Chlorides	6.0	Na <sub>2</sub> HPO <sub>4</sub>	2.0
28	5.3	Chlorides	6.0	phosphomolybdic	2.2
29	5.2	Chlorides	6.0	ZSM-5	2.0
30	5.1	Chlorides	6.0	N/A	N/A
31	5.3	N/A	N/A	ZSM-5	2.5
32	5.4	N/A	N/A	N/A	N/A
33	5.2	Carbonates	5.8	N/A	N/A
34	5.2	Chlorides	3.0	ZSM-5	2.0
35	5.2	Chlorides	6.0	ZSM-5	1.0
36	5.2	Chlorides	6.2	ZSM-5 & Nickel	2.0

Run	Catalyst Weight	Reactor Empty	Before Reaction	After	Amount Char	Amount Liquids
9	2.5	409.9	423	417.7	0.3	0.2
11	2.0	409.8	423.5	420.6	2.8	0.8
12	N/A	410	421.7	420.6	4.6	0.1
13	N/A	410	421.2	419	3.2	0.1
14	N/A	410.1	421	418.9	3.0	0
15	2.0	409.7	422.6	420	2.5	0.6
16	2.3	410.1	423.4	419.7	1.4	1.4
17	2.1	410.1	423.3	420.7	2.6	0.6
18	2.0	410.4	424.2	422.4	4.0	0.4
19	2.1	410.3	425	424	5.4	0.2
20	2.0	409	422.1	420.3	3.1	1.8
21	N/A	409.5	420.7	419.6	4.1	0.2
22	2.0	409.4	422.4	419.2	1.8	1.8
23	2.0	409.2	424.7	423	5.7	0
24	2.1	409.8	424.1	422.2	4.2	0
25	2.1	409.3	423.4	421.8	4.4	0
26	2.0	408.9	422.2	418.4	1.5	1.8
27	2.0	409	420.9	417.5	0.5	2.3
28	2.2	409.1	422.7	420.8	3.5	0
29	2.0	409.5	422.9	419.1	1.6	2.4
30	N/A	408.8	420.2	417.5	2.7	1.8
31	2.5	409.1	417	413.6	2.0	1.7
32	N/A	409.3	414.8	410.3	1.0	1.8
33	N/A	408.26	420	416.9	2.8	0.8
34	2.0	408.3	418.4	415.2	1.9	1.9
35	1.0	407.2	420.2	417	2.8	2
36	2.0	408.5	422	418.3	1.6	2.2

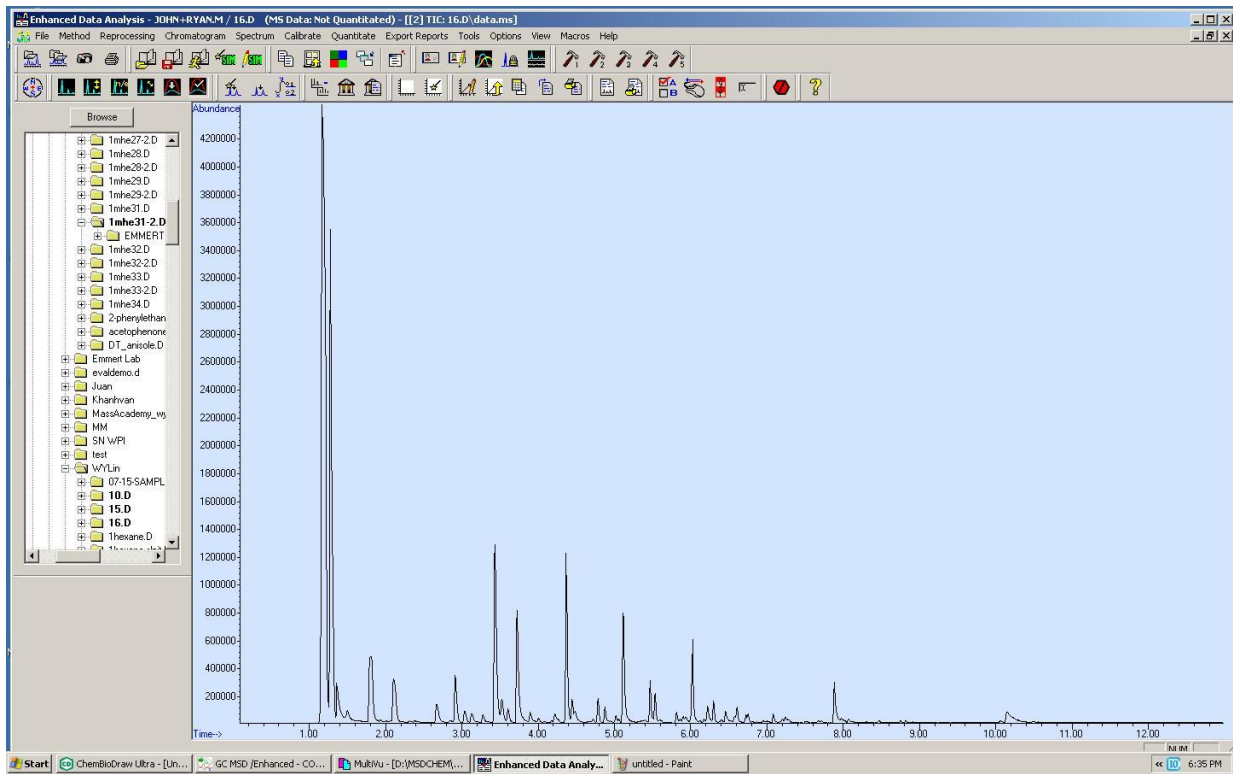
## Appendix B: Raw Gas Chromatograph Data from the GC/Mass Spectrometer



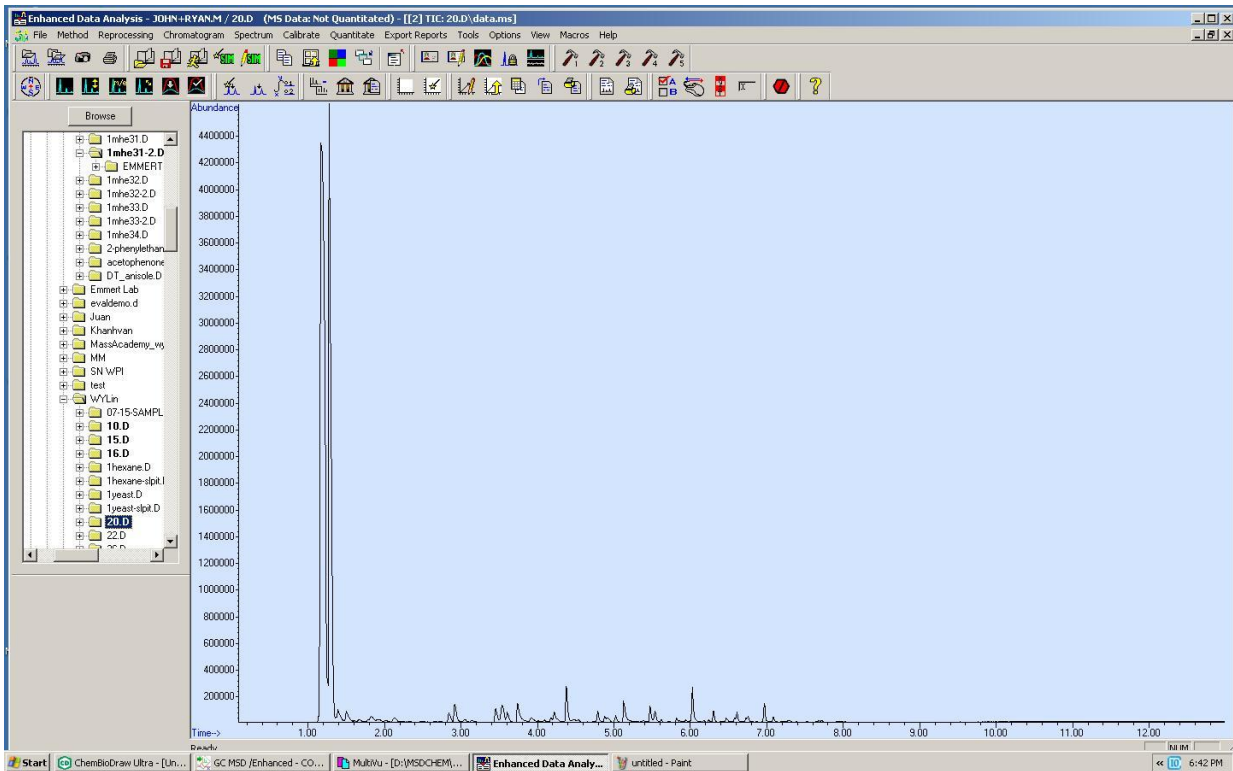
Run 11: Hydroxides and ZSM-5



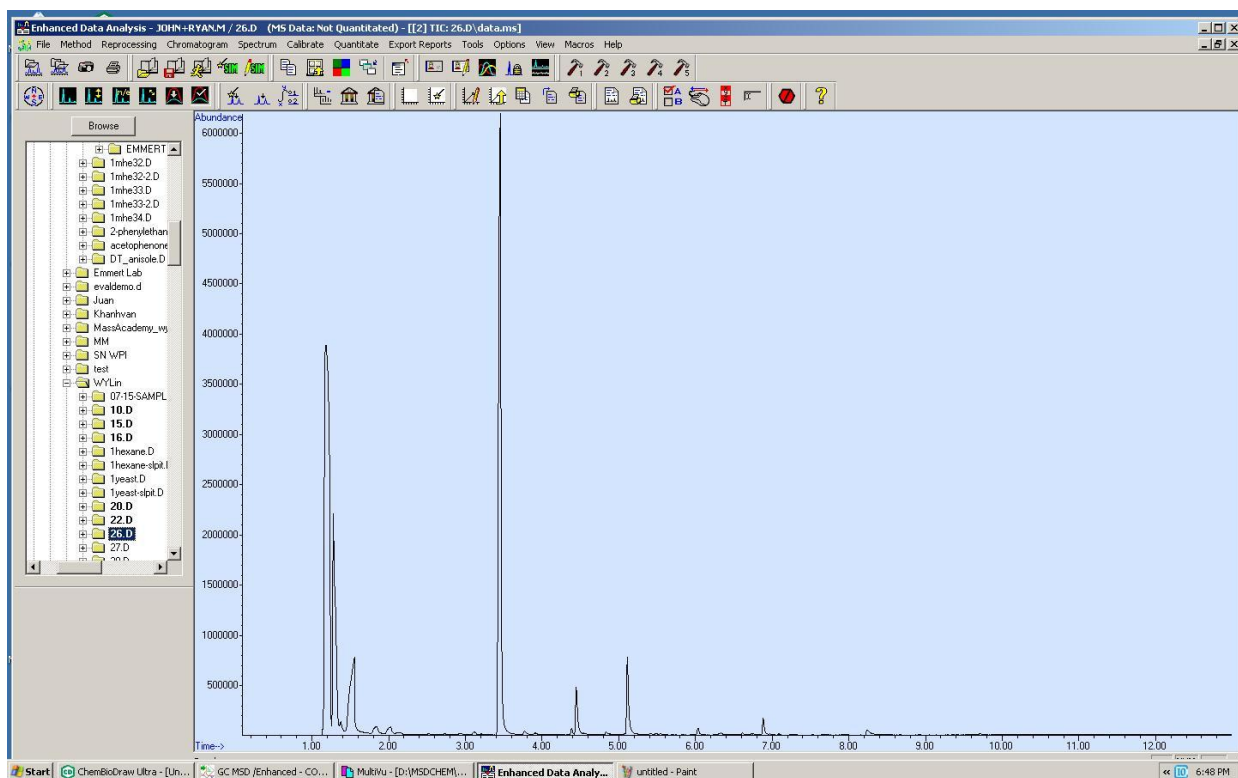
Run 15: Carbonates and ZSM-5



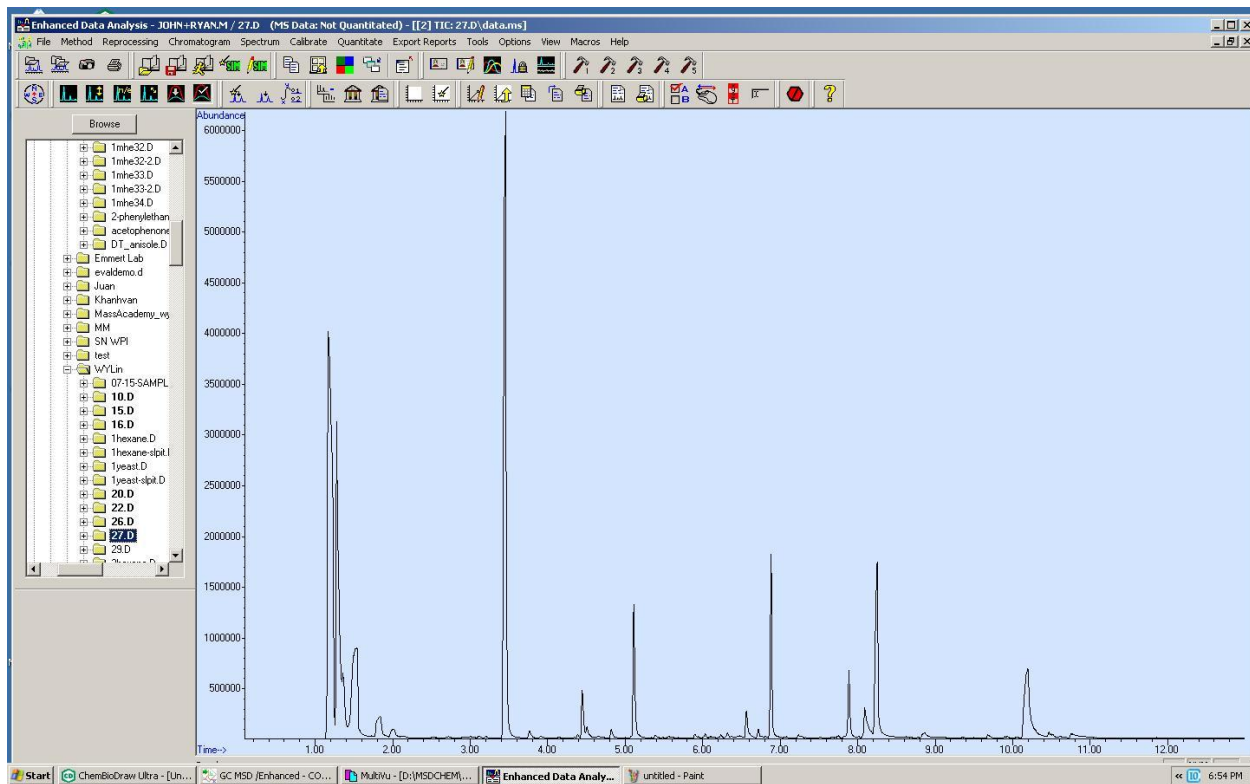
Run 16: Carbonates and Ni(OH)<sub>2</sub>



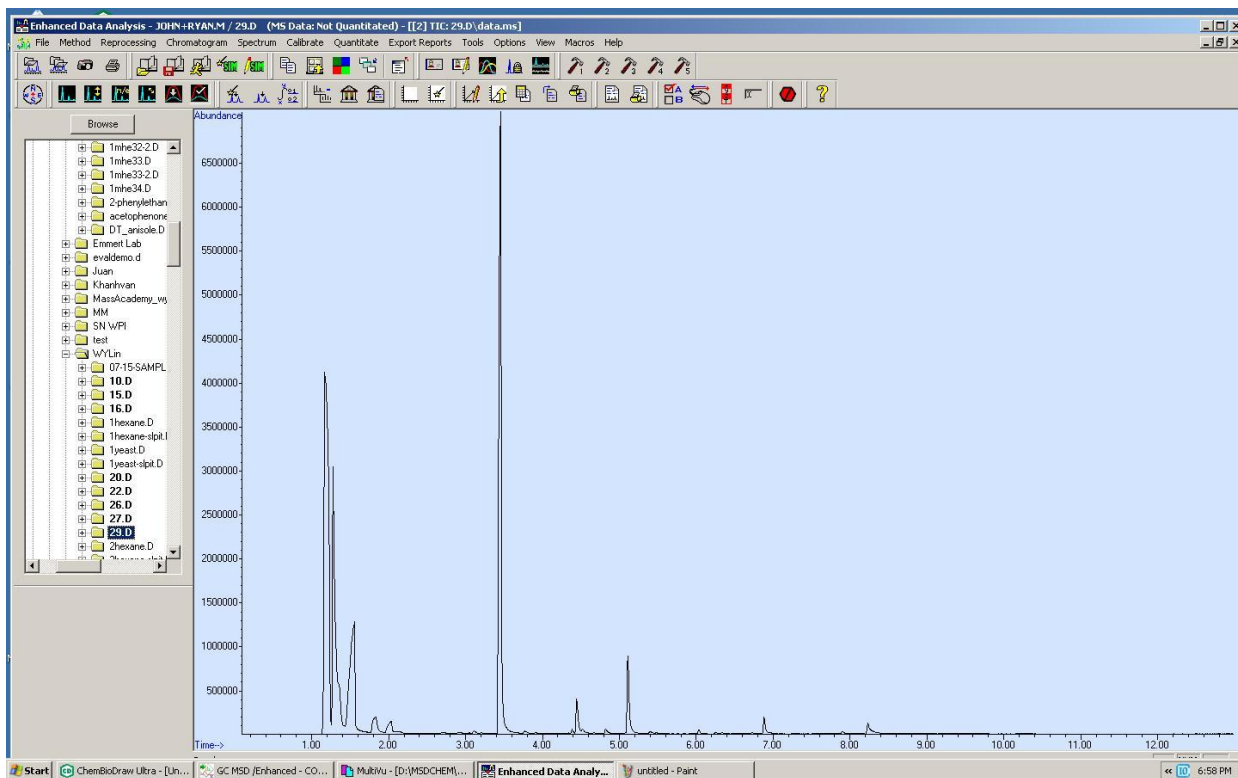
Run 20: Hydroxides and Phosphomolybdic Acid



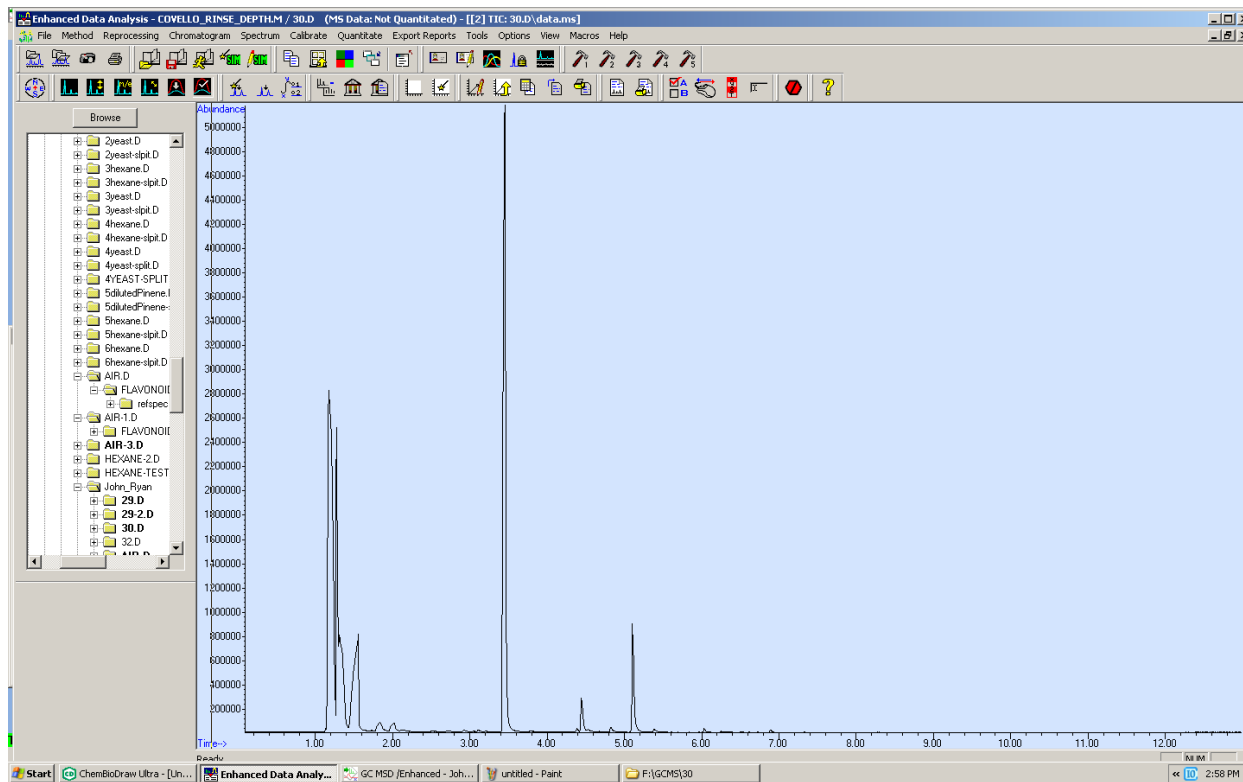
Run 26: Chlorides and Ni(OH)<sub>2</sub>



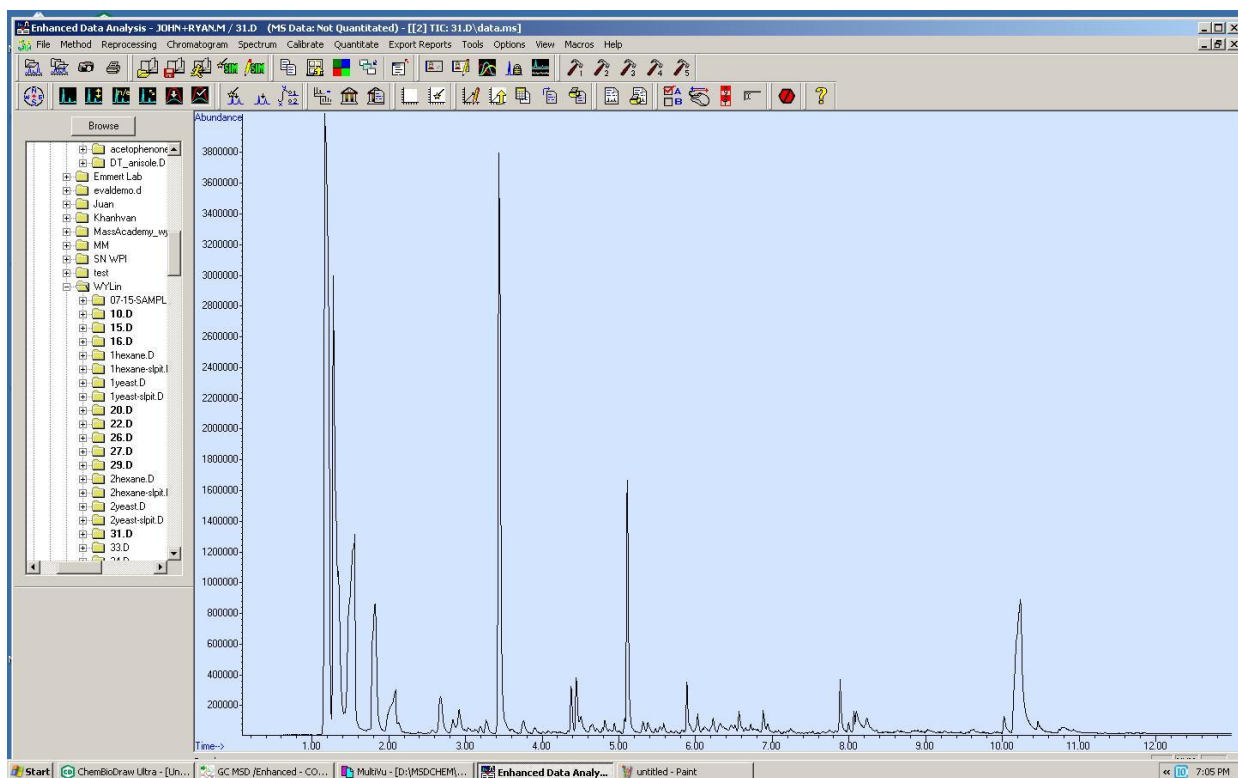
Run 27: Chlorides Na<sub>2</sub>HPO<sub>4</sub>



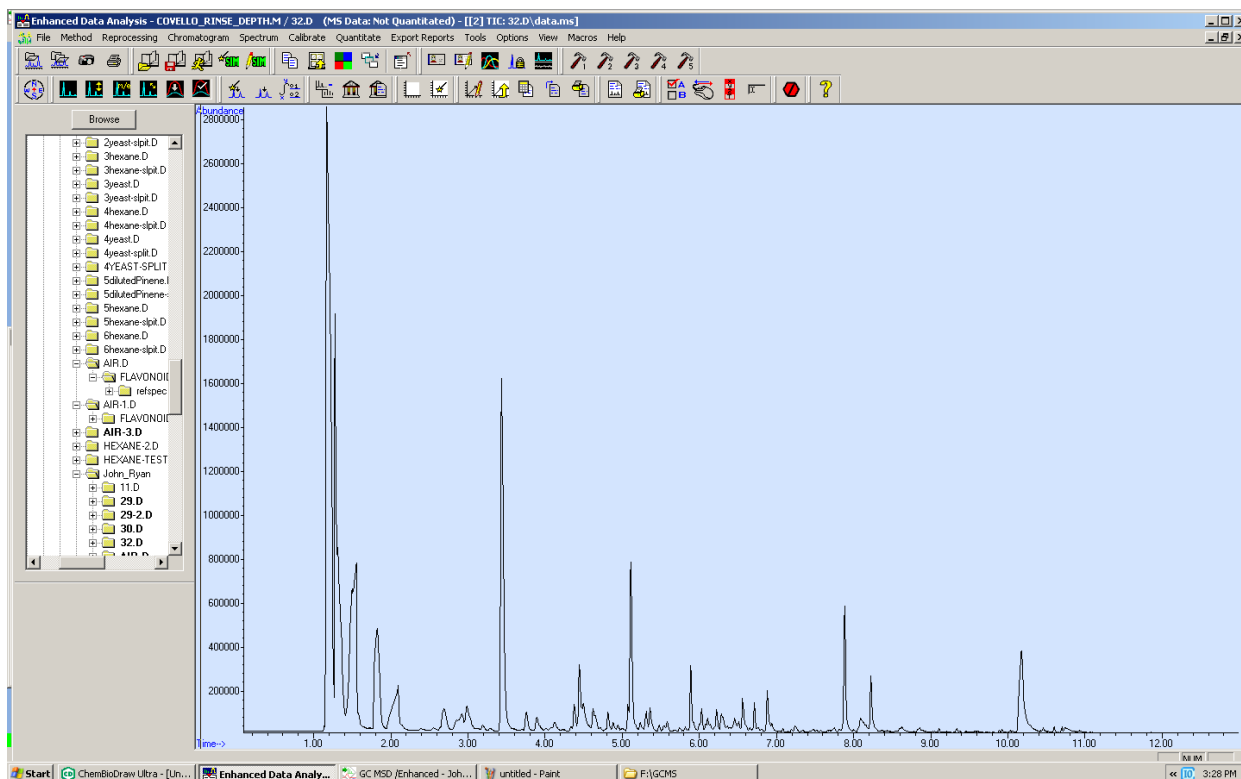
Run 29: Chlorides and ZSM-5



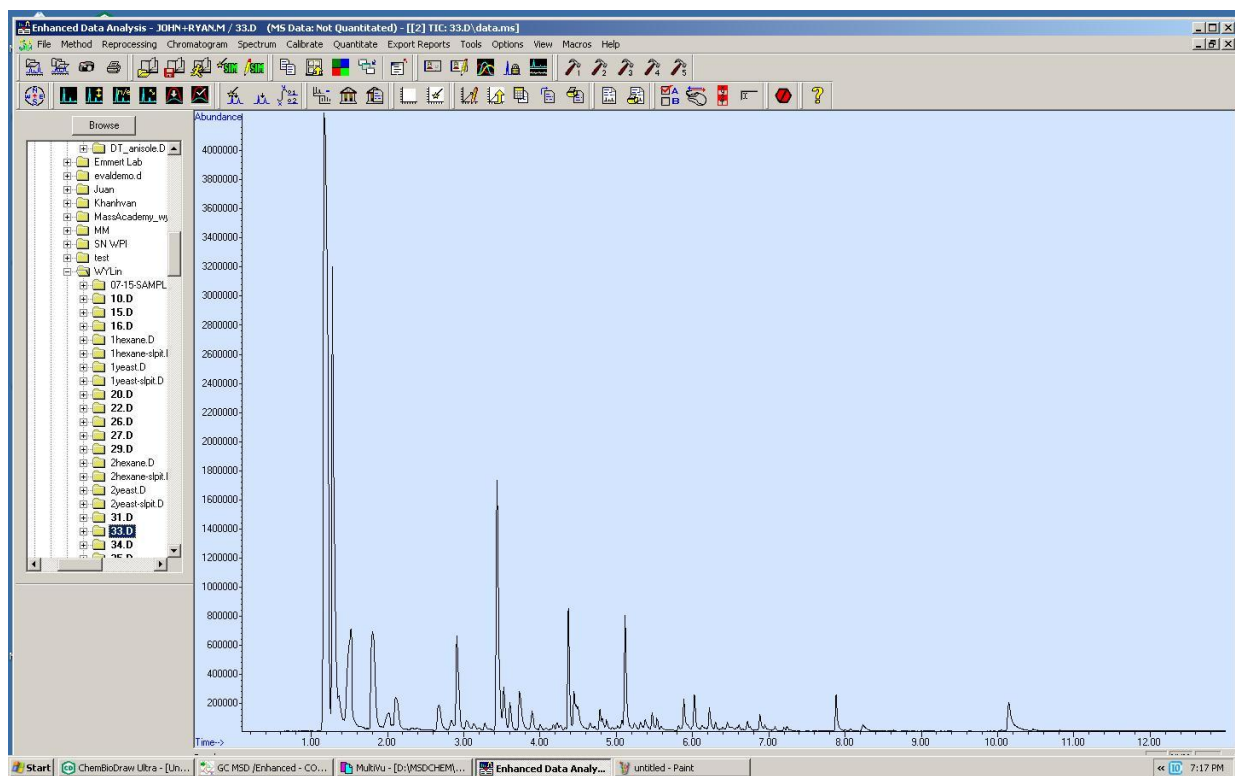
Run 30: Chlorides with No Additional Catalyst



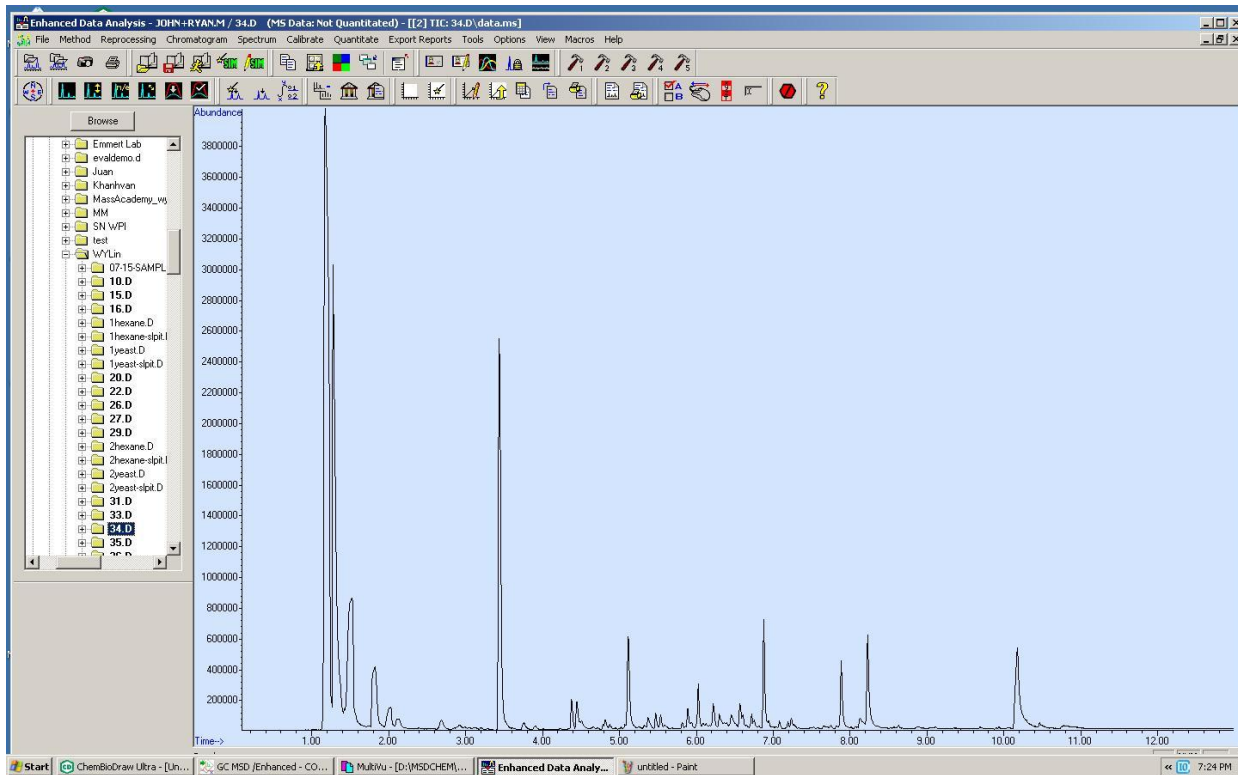
Run 31: Cellulose and ZSM-5 (No Salt)



Run 32: Cellulose with No Salt or Catalyst

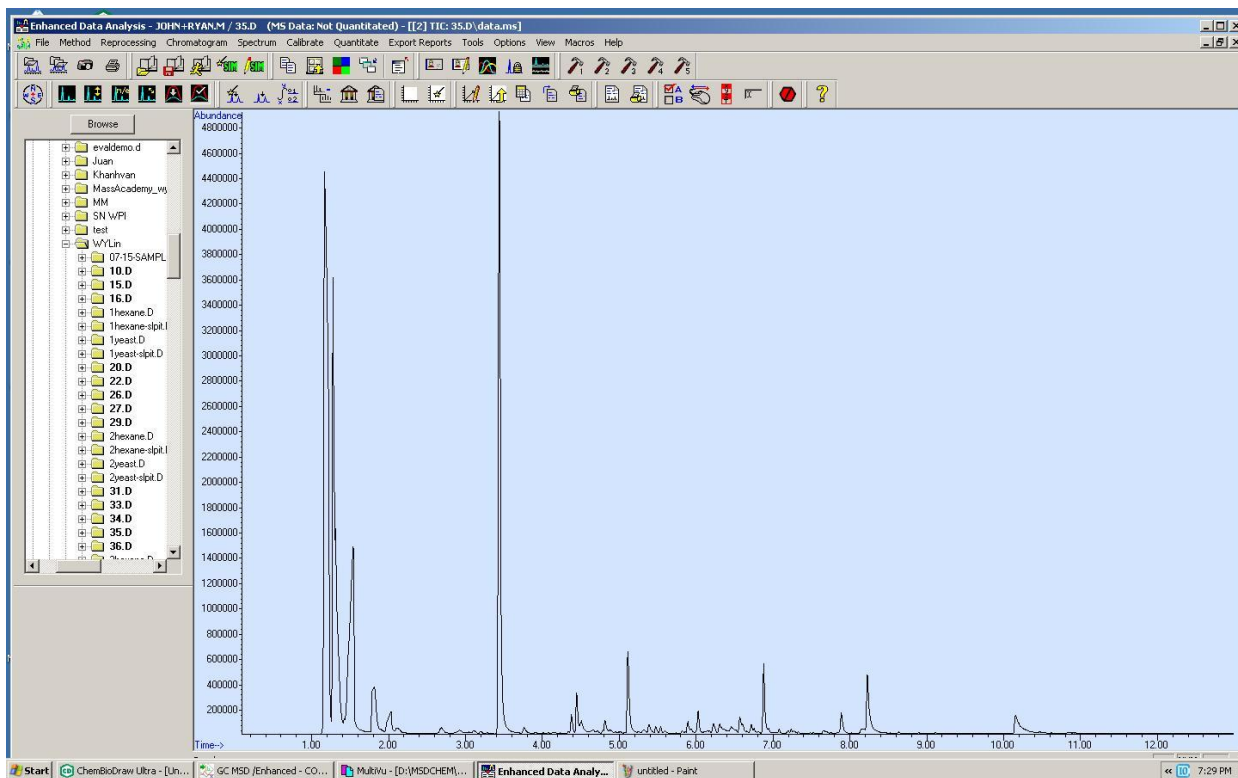


Run 33: Carbonates with No Catalyst

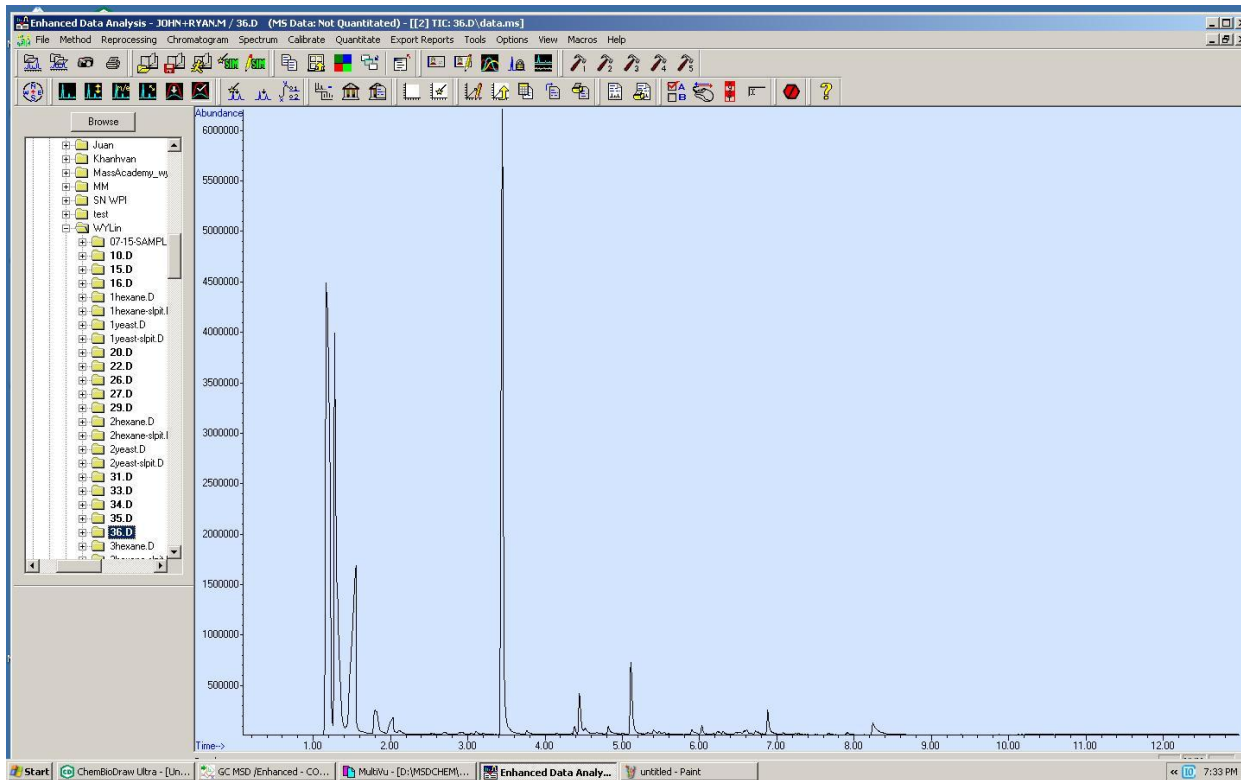


Run 34: Chlorides (3 g) and ZSM-5





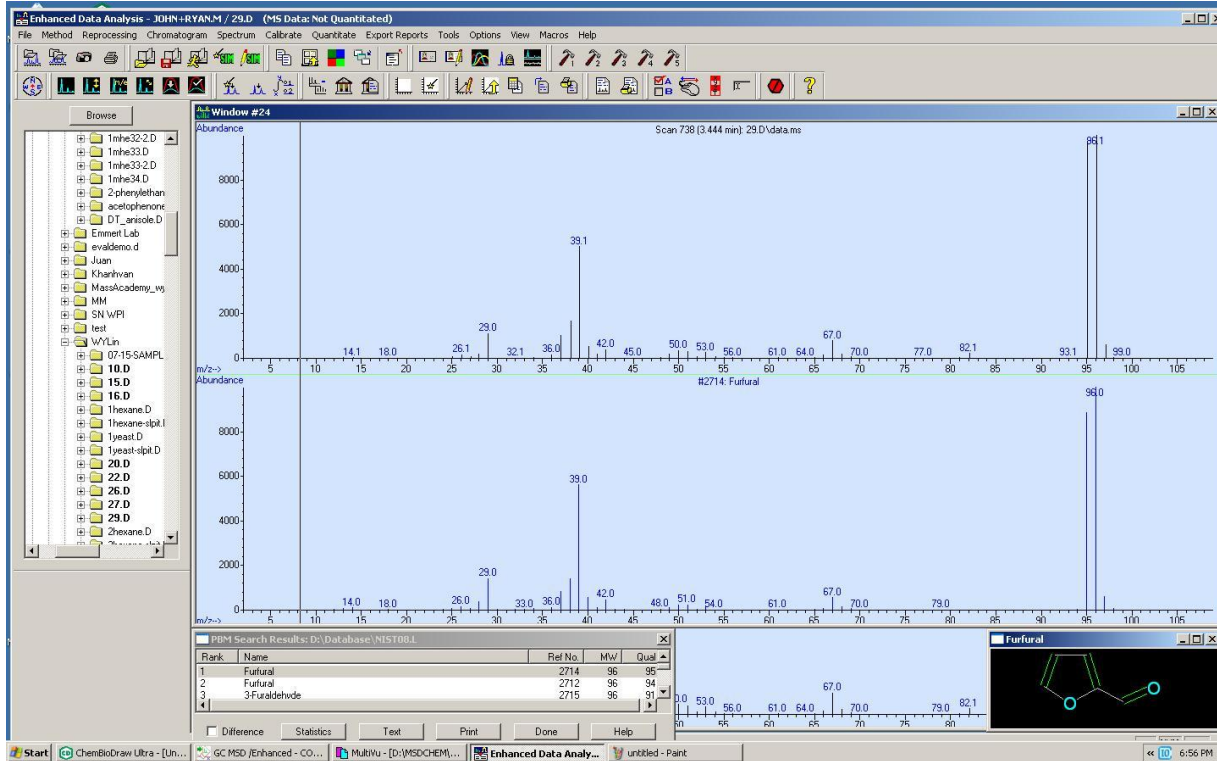
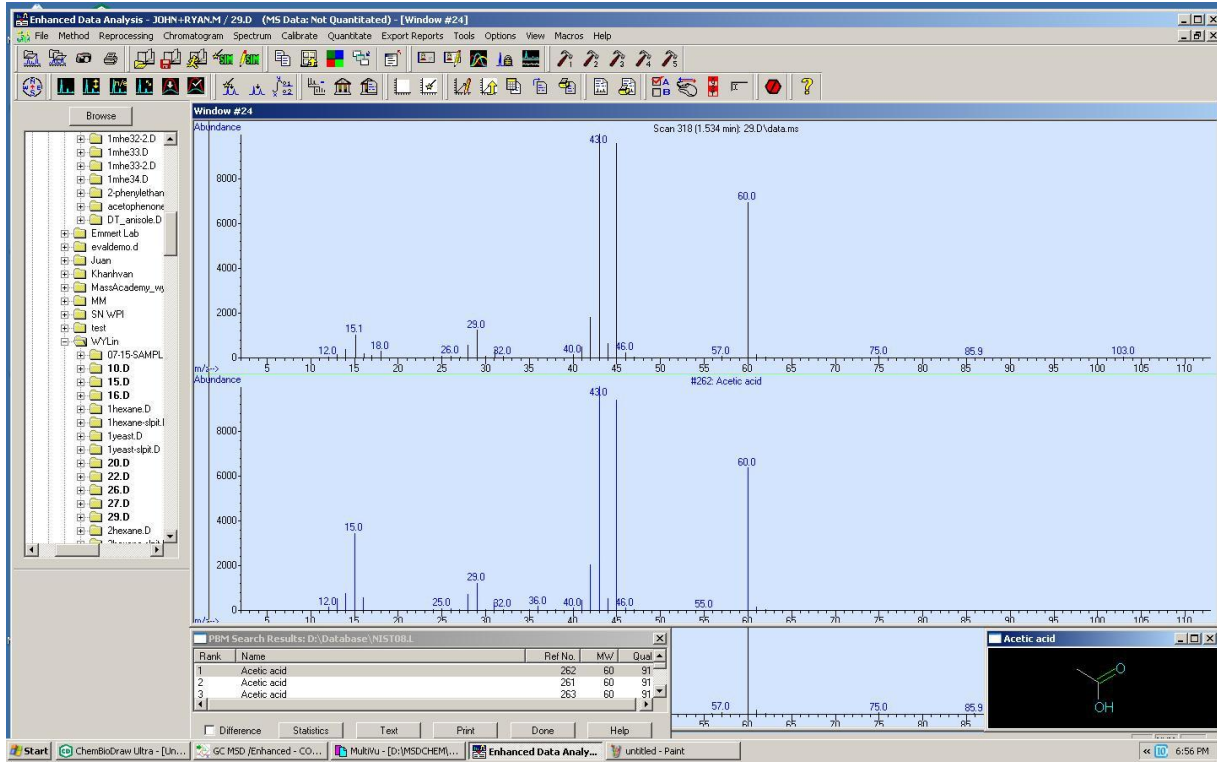
Run 35: Chlorides and ZSM-5 (1 g)

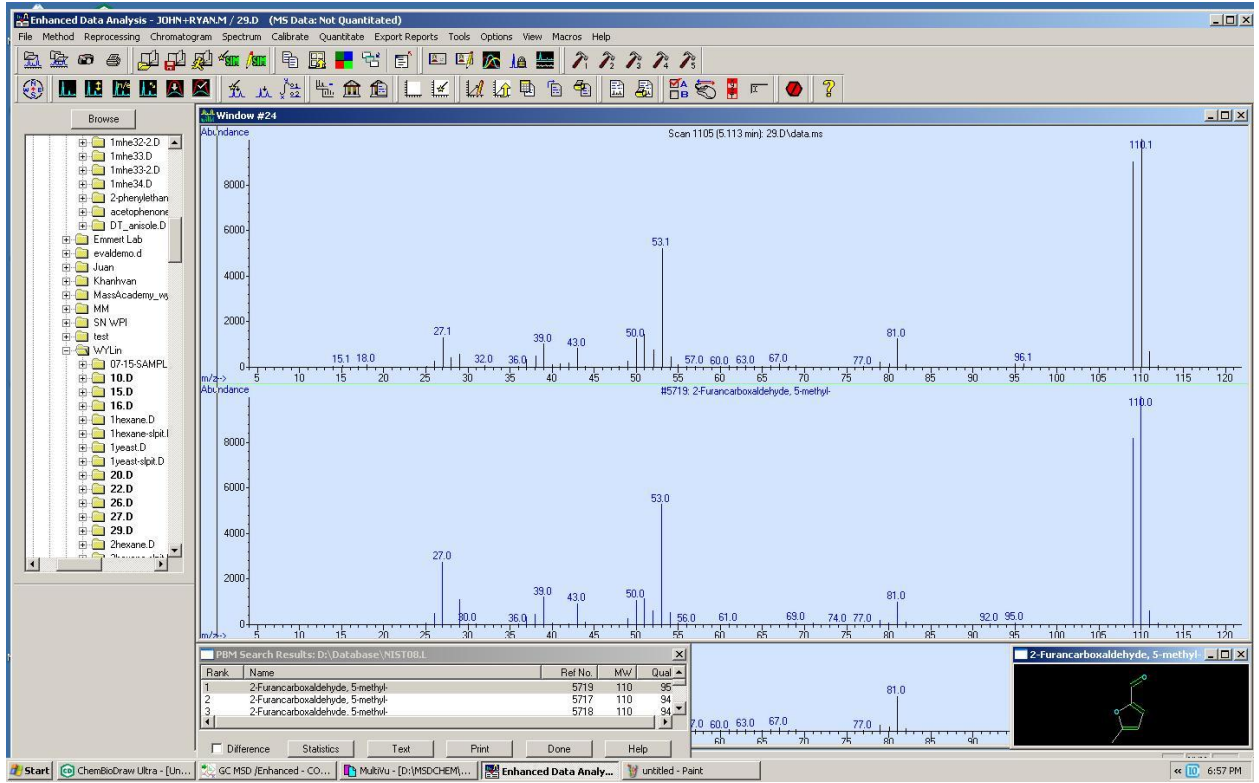
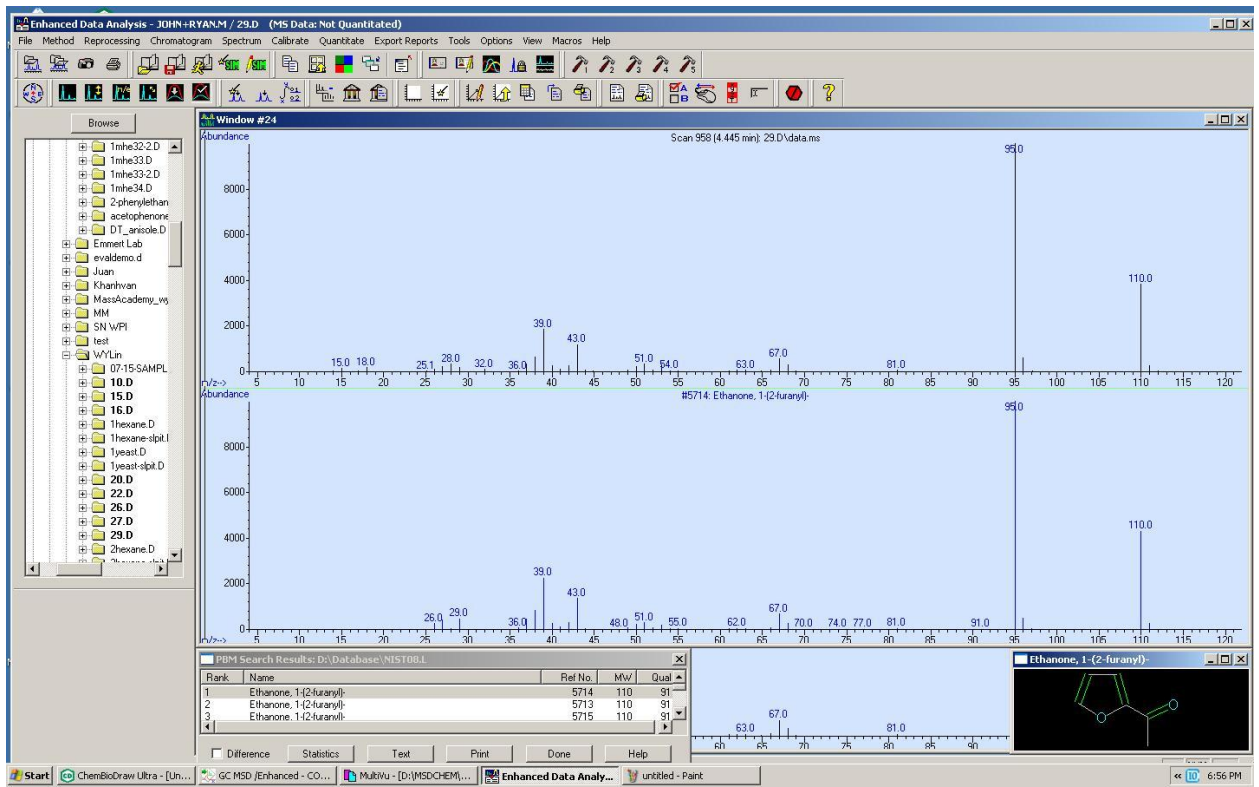


Run 36: Chlorides and ZSM-5 & Ni(OH)<sub>2</sub>

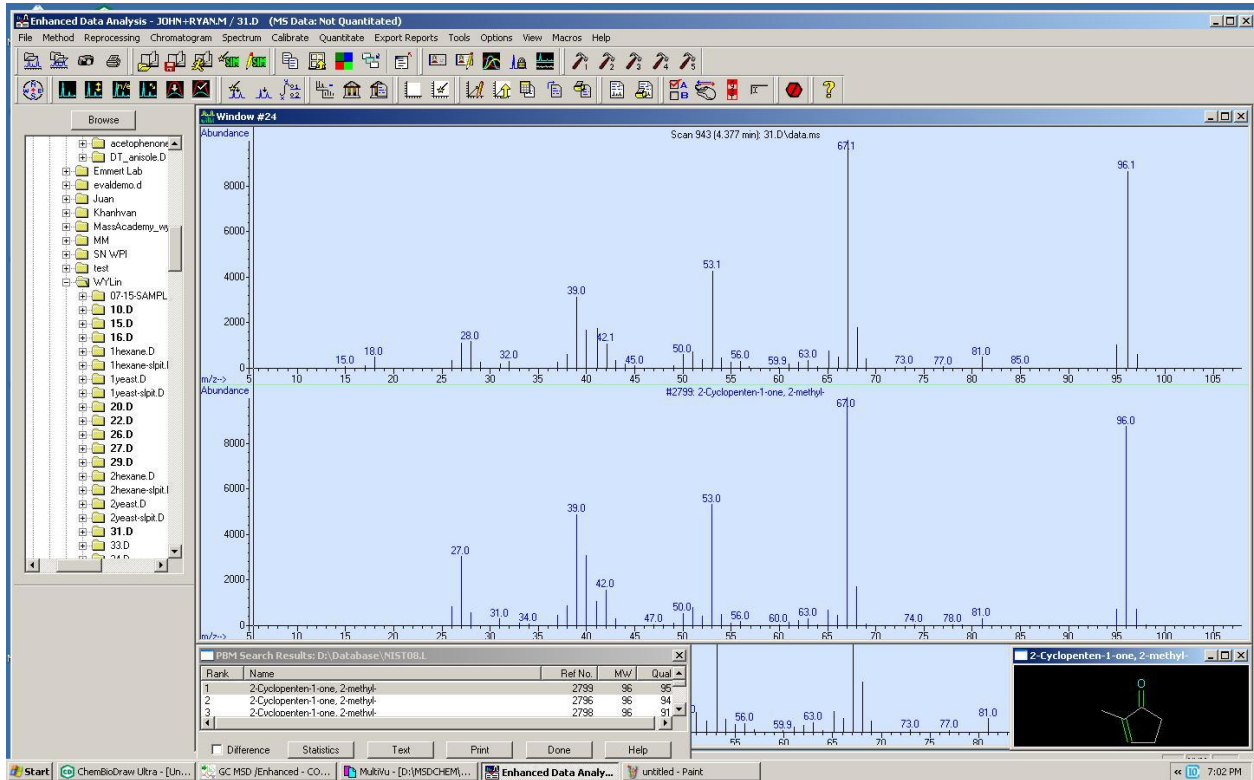
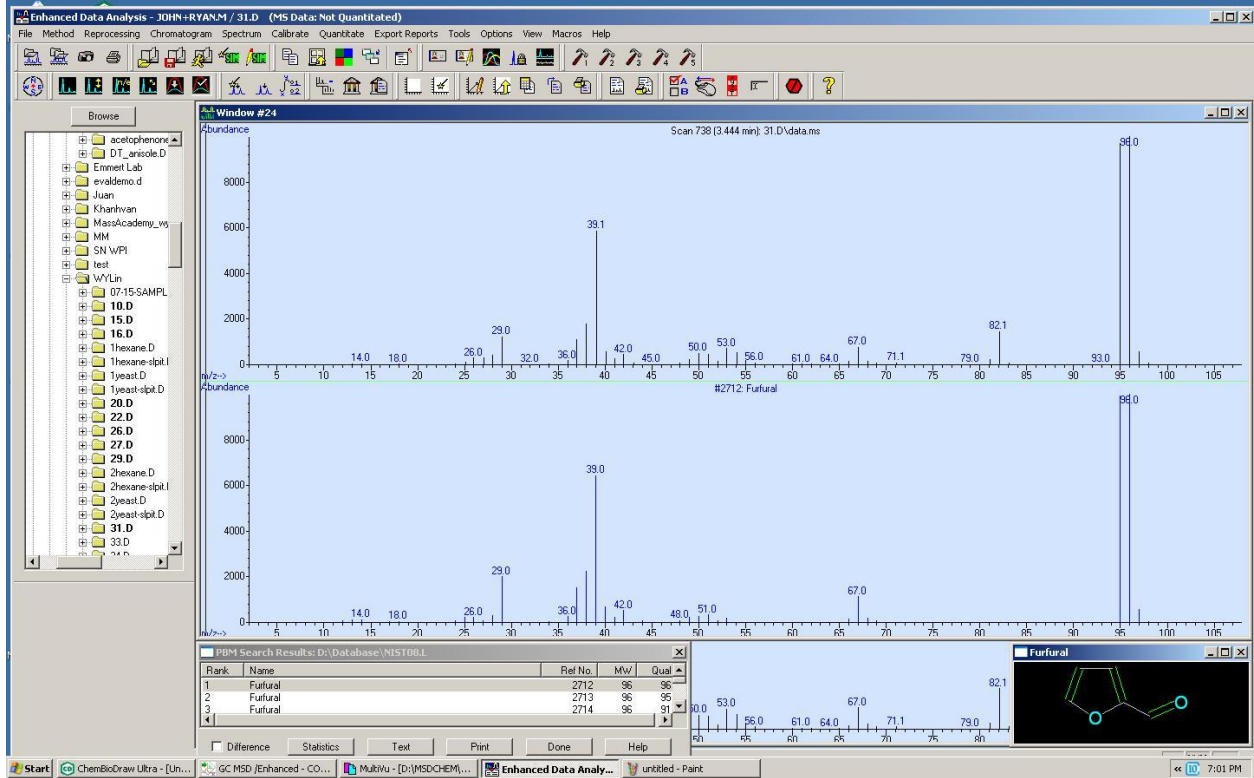
# Appendix C: Sample Raw Mass Spectrometer Data

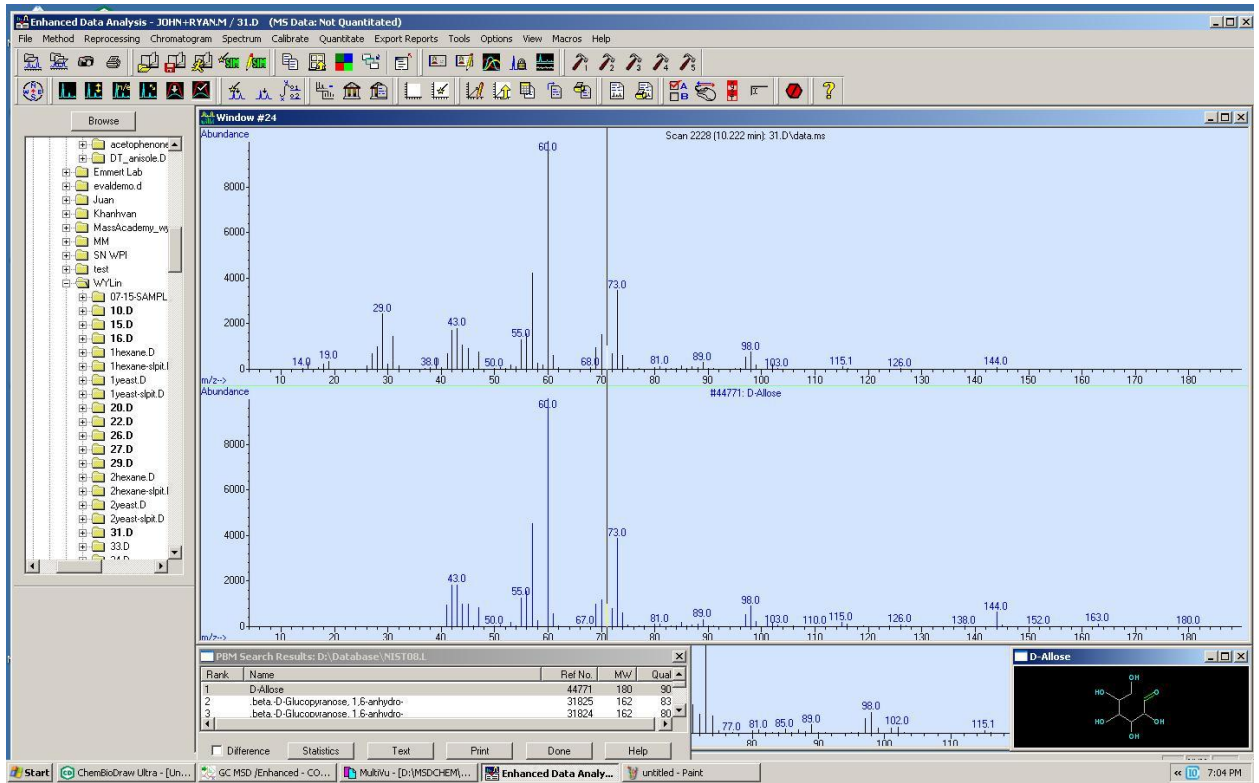
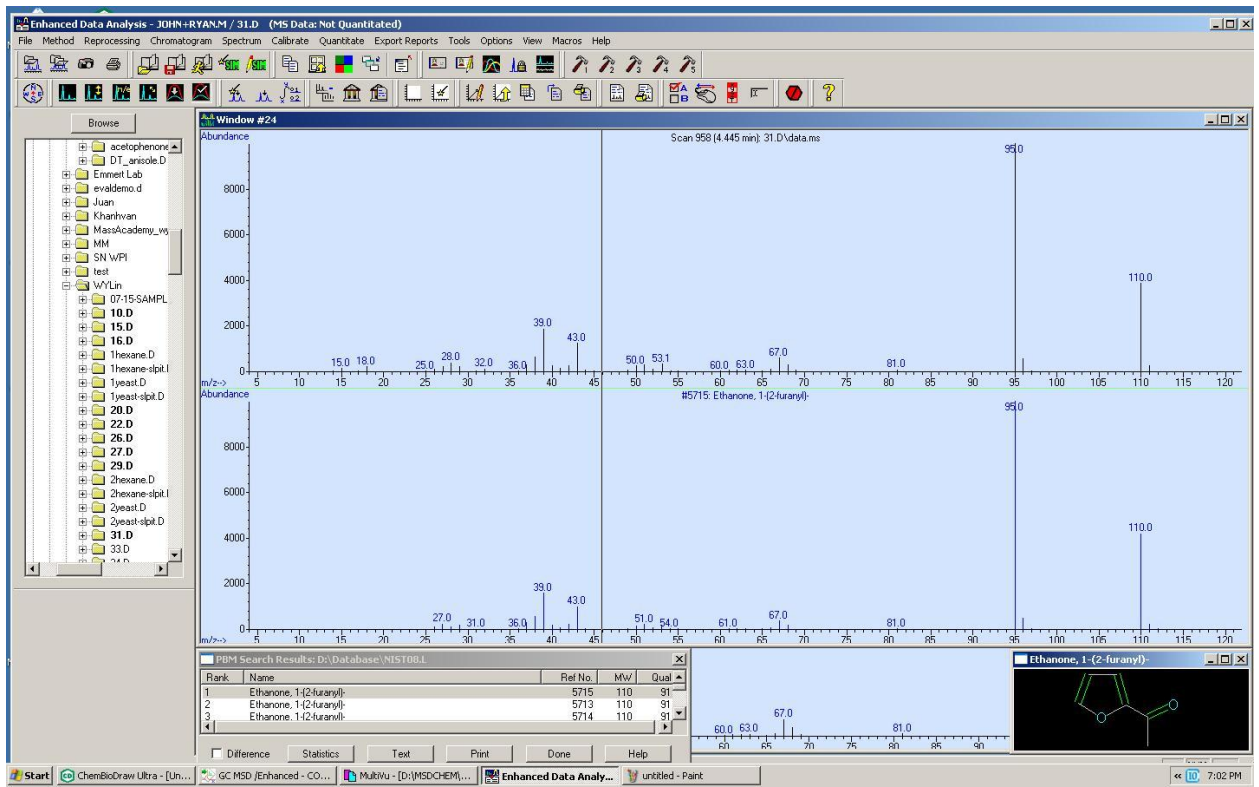
## Run 29 – Chlorides and ZSM-5



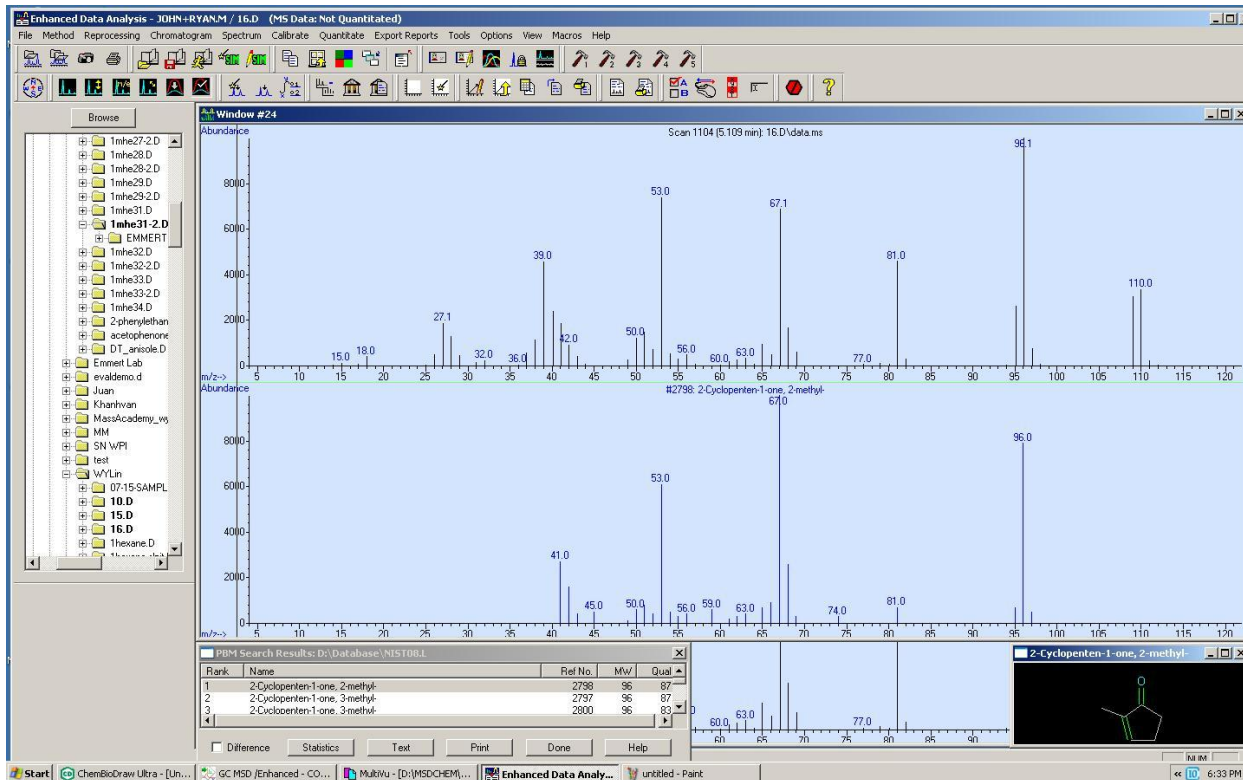
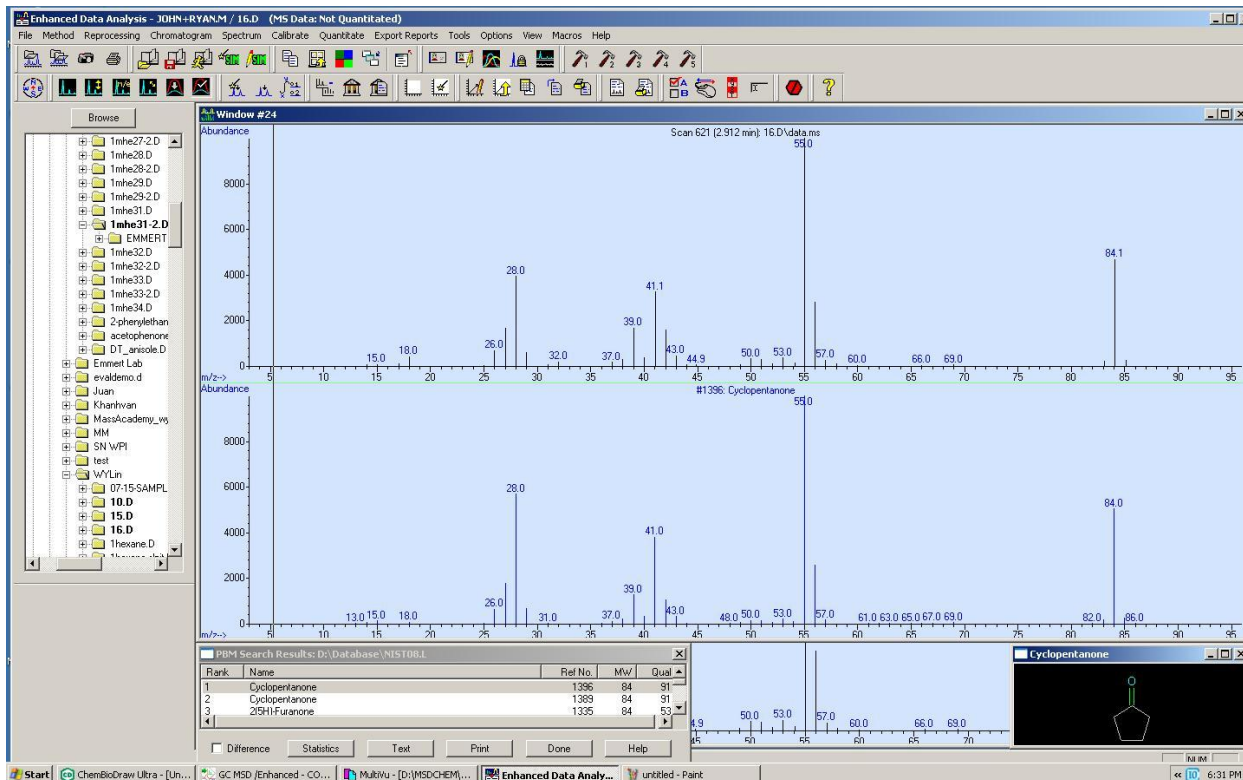


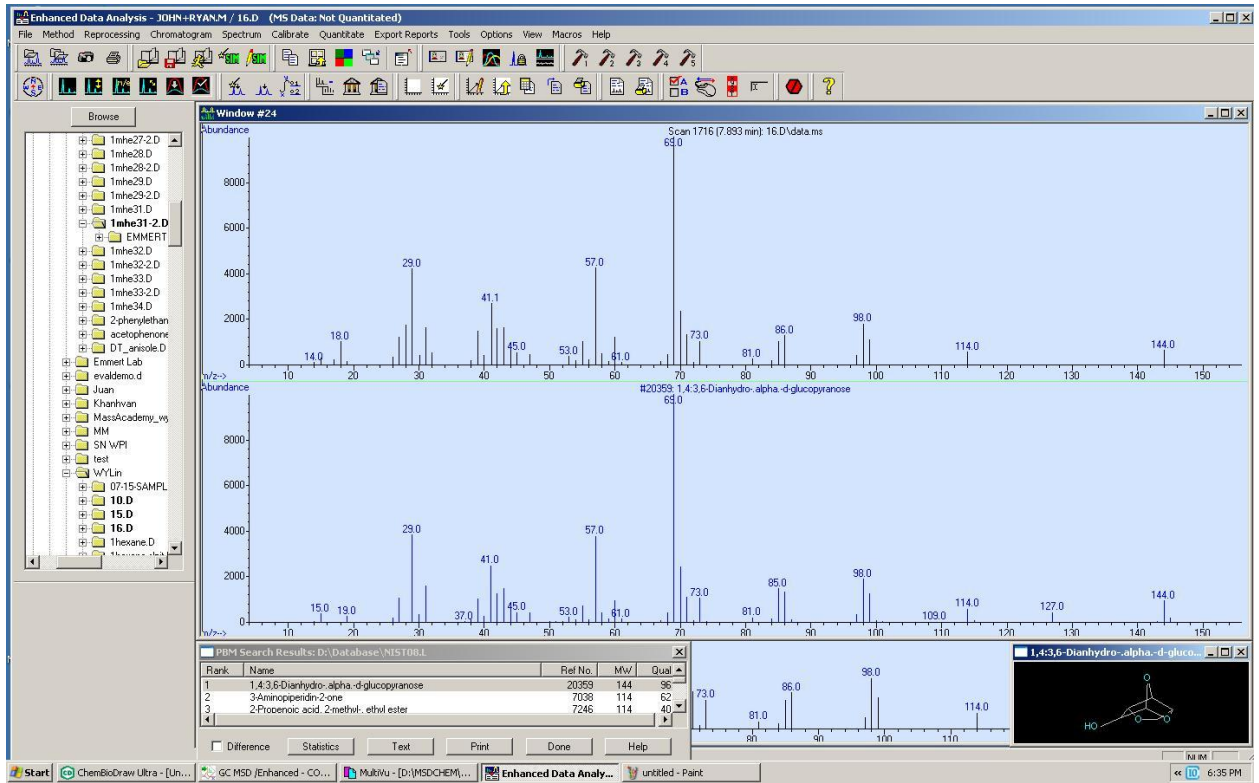
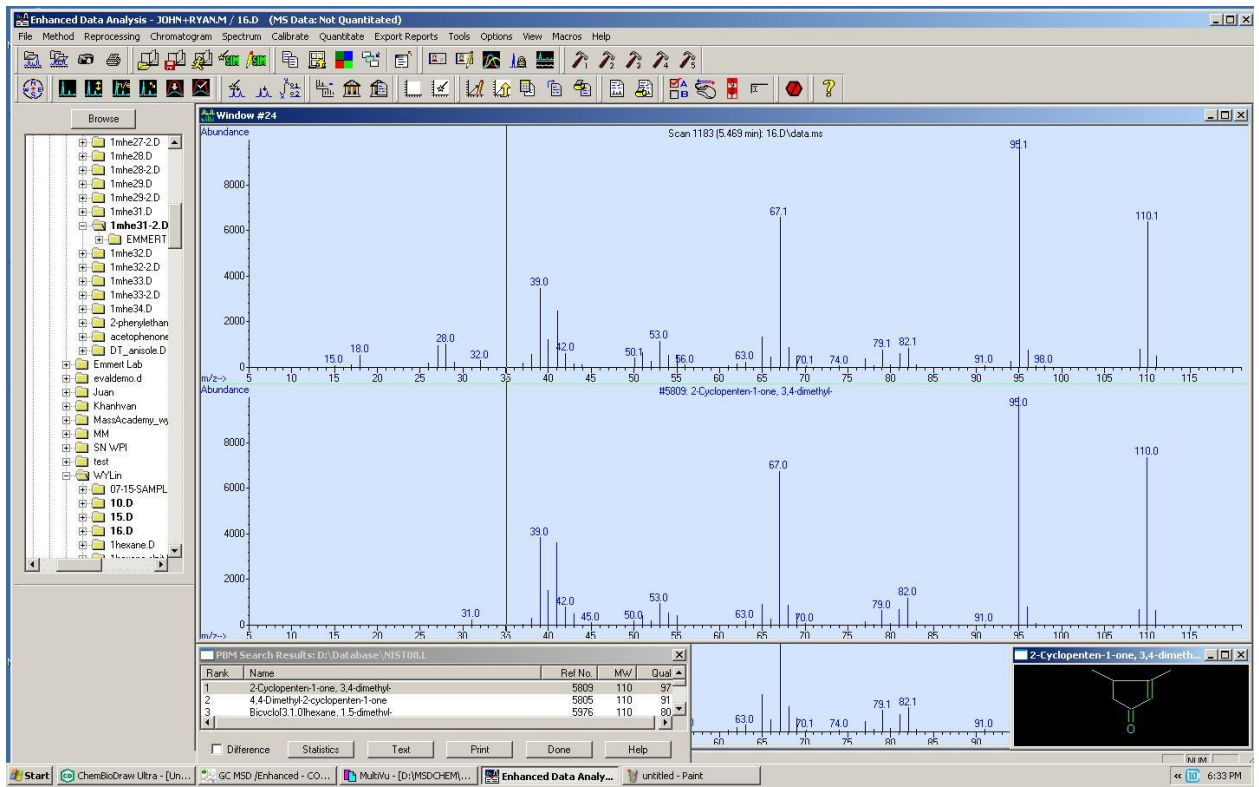
# Run 31 – Cellulose Alone





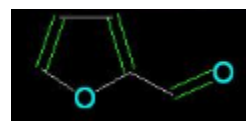
# Run 16 – Carbonates and Ni(OH)<sub>2</sub>



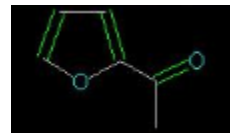


## Appendix D: Product Molecular Structures

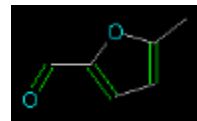
Furfural



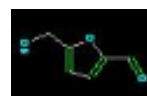
2-Acetylfuran



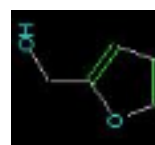
5-methyl-2-Furaldehyde



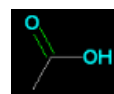
5-hydroxymethyl-2-Furaldehyde



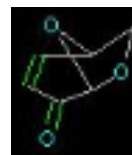
2-Furanmethanol



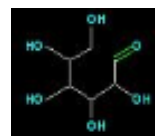
Acetic Acid



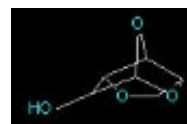
Levoglucosanone



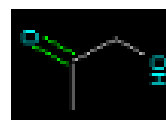
D-Allose



1,4:3,6-dianhydro- $\alpha$ -D-Glucopyranose

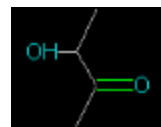


1-hydroxy-2-Propanone

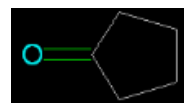




3-hydroxy-2-Butanone



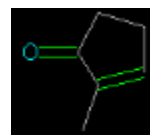
Cyclopentanone



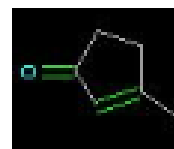
2-Cyclopenten-1-one



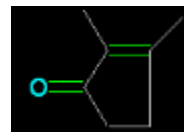
2-methyl-2-Cyclopenten-1-one



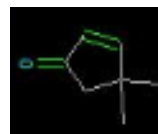
3-methyl-2-Cyclopenten-1-one



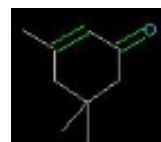
2,3-dimethyl-2-Cyclopenten-1-one



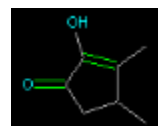
4,4-dimethyl-2-Cyclopenten-1-one



3,5,5-trimethyl-2-Cyclohexen-1-one



2-hydroxy-3,4-dimethyl-2-Cyclopenten-1-one



## Appendix E: Salt and Catalyst Compound Data

Name: Lithium Chloride  
Formula: LiCl  
Molecular Weight: 42.4 g/mol  
Color: White  
Melting Point: 605 °C  
Safety Precautions: N/A

Name: Sodium Chloride  
Formula: NaCl  
Molecular Weight: 58.4 g/mol  
Color: White  
Melting Point: 801 °C  
Safety Precautions: N/A

Name: Potassium Chloride  
Formula: KCl  
Molecular Weight: 74.6 g/mol  
Color: White  
Melting Point: 770 °C  
Safety Precautions: Harmful if ingested in large quantities.

Name: Lithium Hydroxide  
Formula: LiOH  
Molecular Weight: 24.0 g/mol  
Color: White  
Melting Point: 462 °C  
Safety Precautions: N/A

Name: Sodium Hydroxide  
Formula: NaOH  
Molecular Weight: 40.0 g/mol  
Color: White  
Melting Point: 318 °C  
Safety Precautions: Strong base.

Name: Potassium Hydroxide  
Formula: KOH  
Molecular Weight: 56.1 g/mol  
Color: White  
Melting Point: 406 °C  
Safety Precautions: N/A

Name: Lithium Carbonate  
Formula:  $\text{LiCO}_3$   
Molecular Weight: 73.9 g/mol  
Color: White  
Melting Point: 723 °C  
Safety Precautions: N/A

Name: Sodium Carbonate  
Formula:  $\text{NaCO}_3$   
Molecular Weight: 106.0 g/mol  
Color: White  
Melting Point: 851 °C  
Safety Precautions: N/A

Name: Potassium Carbonate  
Formula:  $\text{KCO}_3$   
Molecular Weight: 138.2 g/mol  
Color: White  
Melting Point: 891 °C  
Safety Precautions: N/A

Name: Zinc Chloride  
Formula:  $\text{ZnCl}_2$   
Molecular Weight: 136.3 g/mol  
Color: White  
Melting Point: 292 °C  
Safety Precautions: N/A

Name: Nickel (II) Hydroxide  
Formula:  $\text{Ni(OH)}_2$   
Molecular Weight: 92.7 g/mol  
Color: Green  
Melting Point: 230 °C  
Safety Precautions: N/A

Name: Sodium Hydrogen Phosphate Dibasic  
Formula:  $\text{Na}_2\text{HPO}_4$   
Molecular Weight: 142.0 g/mol  
Color: White  
Melting Point: 250 °C  
Safety Precautions: N/A

Name: Phosphomolybdic Acid

Formula:  $(\text{MoO}_3)_{12}(\text{H}_3\text{PO}_4)$

Molecular Weight: 1825 g/mol

Color: Yellow

Melting Point: °C

Safety Precautions: Do not ingest. Avoid skin contact.

Name: Zeolite Socony Mobil – 5 (ZSM-5)

Formula:  $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \cdot 16\text{H}_2\text{O}$  ( $0 < n < 27$ )

Color: White

Safety Precautions: N/A