Production of Bioliquids from Cellulosic Biomass through Molten Salt Pyrolysis

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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April 25th, 2013

Keywords:

1. Biofuel
2. Molten Salts
3. Pyrolysis
4. Liquid Analysis

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Abstract

Second generation biofuels are fuels that are produced from lignocellulosic biomass, or non-edible plant matter. The ability to utilize such fuels could potentially reduce society's dependence on fossil fuels. Two current techniques that convert lignocellulosic biomass to second-generation biofuels and chemicals include fast pyrolysis and the use of ionic liquids. However, these technologies are uneconomical; therefore, the objective of this study was to develop and optimize a new conversion technique. This method, the pyrolysis of biomass through molten salt media, is a hybrid between fast pyrolysis and ionic liquids. Several experimental parameters were studied over the course of this research including: final reaction temperatures, chloride eutectic compositions, cellulose to eutectic molar ratios, and heating rates of the reaction. All generated samples were analyzed using a gas chromatograph and mass spectrometer. The composition of the ideal molten salt eutectic, as well as the highest liquid yielding reaction parameters, was determined throughout the course of the project.

Acknowledgements

I would sincerely like to thank the WPI faculty and staff that consistently provided me with thorough help and assistance throughout the entirety of this project. The work that was completed would not have been possible without their help, guidance, and enthusiasm. A special thanks to:

- Professors Ravindra Datta and James Dittami, for their consistent feedback, ideas, resources and constructive criticism. The success of this project is due, in large part, to their thorough and sincere help and guidance.
- Andrew Butler for his unceasing willingness to help me analyze 30 different samples with Gateway’s GC/MS. Andy volunteered an amazing amount time and devotion which allowed for the success of this project.
- Corin Galati for the enthusiasm and preparedness to help me conduct a number of the experimental trials throughout the course of this project. His interest in this field of study, as a freshman, was remarkable.
- Jack Ferraro for his ability to always be able to solve the often frequent issues with any of my laboratory equipment. Jack always had the ability to make a large issue, in my eyes, seem small.
- Felicia Vidito for her willingness and ability to always be able to order any chemicals or pieces of equipment as fast as possible. Many important deadlines were kept thanks to Felicia’s help.
- Professor William Clark for graciously allowing me access to his neighboring laboratory in order to use his high accuracy scale.

- Professor Fisktik and Patrick O’Malley for welcoming me into their laboratory with open arms and their acceptance of the loud noises I would often make.
- Drew Martino for helping me to identify several useful eutectics that were highly integrated into this project. Drew was able to make several significant suggestions of chloride eutectics that yielded very good results.
- Goddard Facilities Staff for their ability to always help me maintain a clean and safe laboratory environment.

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1. Introduction

Since the dawn of man, energy has been required in order to conduct everyday tasks. During the prehistoric era, energy was produced through metabolic measures; eating food and performing physical labor. From there, fire, wind, and water began to be used to be utilized in order to produce industrialized energy. Wind and water mills were the main producer of energy that helped civilizations industrialize themselves. Not until the late eighteenth century, when the steam engine was invented, was there a high demand for combustible fuels. Once the use of the steam engine was implemented throughout industrialized countries, the demand for such fuels skyrocketed; thus, humans began the first form of fossil fuel utilization. Coal fed steam engines, allowed an increasing number of nations to become industrialized. In 1859, oil was discovered in Pennsylvania which began the start of the modern petroleum era. Since this time, humans have come to rely more heavily on fossil fuels than any other energy source.

1.1 Fossil Fuels

Currently, 80% of the energy produced globally is derived from fossil fuels, whether it is coal, natural gas, or oil (Naik, et al. 2010). The growth rate of fossil fuel energy production between the years 1800 and 2010 can be seen below in Figure 1. The remarkable growth rate seen in the twentieth century shows how strongly global energy production now relies on fossil fuels. However, due to the fact that fossil fuels are a limited commodity, this growth rate that has taken place since the early twentieth century is expected to cease between the years 2040 and 2050 (Naik, et al. 2010). This is where the peak fossil fuel energy production is thought to take place. It is important to note, however, that energy consumption and demand will not peak during this time. The global population is on the rise, which will be the case for centuries to come. Due to this, energy consumption will continue to grow. The demand of energy production on fossil fuels, therefore, must shift to sustainable energy sources.

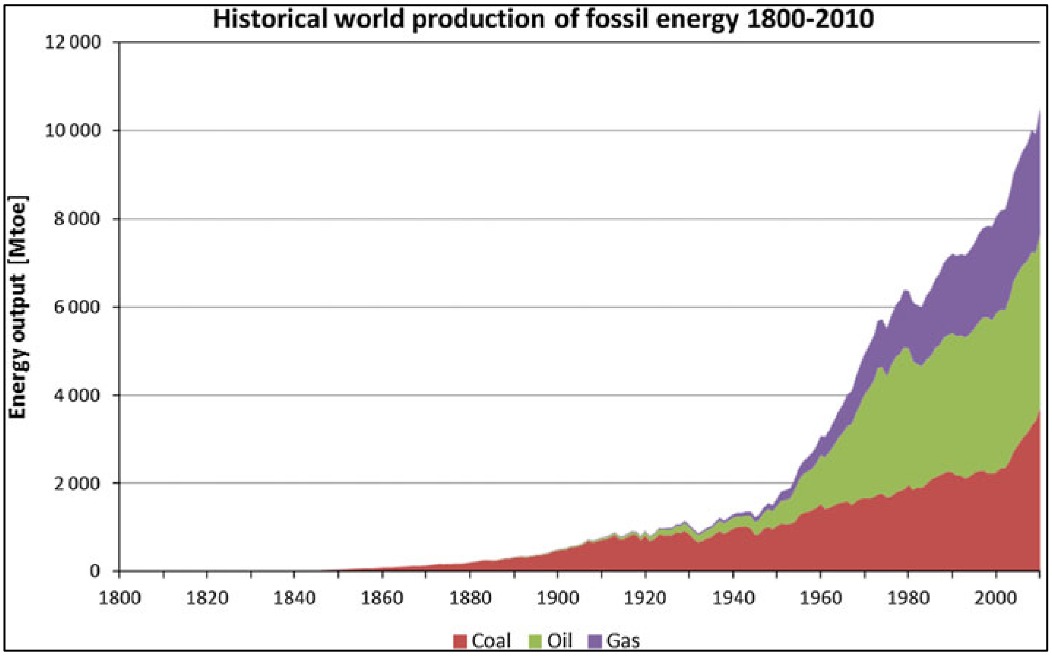

Figure 1: Illustration of the sharp increase of fossil fuels in the twentieth century (Naik, et al. 2010)

The negativities of fossil fuels do not end with the fact that they are a finite energy source. There are also other negative consequences for the use of fossil fuels. For example, fossil fuel power plants emit a large number of air pollutants such as sulfur dioxide, nitrogen oxides, and toxic chemical (Selin 2013). Also, vehicles that are powered by fossil fuels emit carbon monoxide and other particulates (Selin 2013). In addition to these air pollutants, the combustion of fossil fuels also releases carbon dioxide into the atmosphere, which is known to be a major cause of global warming. Therefore, due to the facts that fossil fuels are both finite and harmful to the human population and the environmental, it is imperative that the dependency on them is lessened.

1.2 Renewable Energy Sources

With the likely ending of the oil boom in the near future, the role of renewable energy resources will continue to annually increase. The major renewable energy contributors are currently solar, wind, and hydropower sources. In the United States, there has been an enormous influx of federal tax credits for renewable energy producers. With such tax incentives, and with the need to alleviate the burden on fossil fuels, it is likely that such renewables will play a crucial role in the future.

1.2.1 Wind, Solar and Hydro-power

The necessity of increasing the use of renewable energy sources has been realized. Wind power has become one of the fastest growing contributors in the increase of renewable energy. In fact, between the years 2008 and 2009, wind capacity increased from 24,651 megawatts to 34,296 megawatts, respectively (Peterson 2012). In addition to wind power, solar power has also been on the rise. In the year 2009, the U.S. solar industry grew by over 67% from the previous year (Peterson 2012). Most solar power is generated through photovoltaic systems installed on private lands (Peterson 2012). Wind and solar power have been major contributors in the renewable energy sector; however, hydropower has been the main contributor to electricity production of all renewable resources (Guerro-Lemus and Martinez-Duart 2013). In 2009, 83% of electricity generation from renewable resources came from hydropower (Guerro-Lemus and Martinez-Duart 2013). Hydropower is likely to play a major role in helping undeveloped countries become civilized nations (Guerro-Lemus and Martinez-Duart 2013).

The positive consequences of the implementation of wind, solar, and hydropower are evident. There are no harmful pollutants that are emitted from these sources. Also, there are no carbon dioxide emissions either. These resources will be crucial in shifting the burden of global energy production away from fossil fuels.

1.2.2 Bio-Energy

There is now renowned interest in using plant matter and organic waste to create a new type of fuel that can be integrated into society. One major advantage to the use of biofuels is the belief that they will mitigate global warming (Naik, et al. 2010). This belief is present due to a simple fact; the amount of CO_2 released during the burning of plant biomass is equal to the amount of CO_2 present in the plant matter. Or, to put it in different terms, the burning of organic plant matter does not increase the net CO_2 present in the atmosphere (Naik, et al. 2010).

Currently, there are two different types of biofuels being researched and used. They are first-generation biofuels and second-generation biofuels. First-generation biofuels are obtained from agricultural crops which are grown using similar techniques to food crops. First-generation biofuels are obtained through the use of the plants' sugars (Naik, et al. 2010). Second-generation biofuels are obtained from lignocellulosic materials such as grass, roots, woods, etc. (Naik, et al. 2010). There are many advantages in using second-generation biofuels instead of first-generation, which will be discussed later in this paper. The focus of this paper will be concerning second-generation biofuels, due to the fact that first-generation biofuels are deemed as unsustainable. The goal of this project was to determine a new, effective, and efficient way to implement the use of second-generation biofuels into society in order to alleviate society's dependency of fossil fuels.

1.3 Objective

The main focus of this project was to integrate existing technology that is still in its infancy, into a new way to produce second-generation biofuels and bio-chemicals. An immense amount of research is being conducted towards understanding the reaction mechanisms that turn biomass into fuels and feedstock chemicals. This research has been gathered, in an effort to understand these reactions, in order to determine a more efficient way in which to produce bioliquids from biomass. The major goal of the research conducted, and explained throughout this paper, was to determine the most efficient and highest yielding tactic that turns cellulose into bio-liquid. The technology under review includes the mixing of molten salts with cellulose, or other biomass, in attempt to yield a highly selective and high yielding bio-liquid. The objective was to find the proper technique, reaction conditions, and salt composition.

1.4 General Procedure

In order to fulfill the objectives of this project, a large number of steps were taken. The first step was to determine the molar ratio (cellulose to molten salt) that yields the highest amount of bio-oil. This was done by varying the molar ratio until the highest yield was found. Next, the contents of the molten salt mixture were varied in order to determine the ideal combination. Liquid yield, cost, and selectivity are the parameters that were used to determine which salt mixture was the most suitable. The heating rate of the reaction was also analyzed in order to determine the most efficient way to heat the reaction. This was done by varying the rate at which the molten salt/cellulose mixture was heated and by analyzing the results. All of these procedures will be explained in detail throughout the rest of this paper.

1.5 Overview

There are several succeeding chapters in the rest of this report. Chapter 1, Introduction, will be followed by Chapter 2, Literature Review, which analyzes the current technology that is being implemented towards the production of second-generation biofuels. Following Chapter 2, Literature Review, the Methodology, Chapter 3, will highlight the exact procedures that were implemented. After that, the Results, Chapter 4, of the experimentations will be discussed in length, which will be followed by the Discussion, Chapter 5. Finally, the paper will conclude with the Recommendation, Chapter 6, which will highlight the next steps that should be taken.

2. Literature Review

2.1 Advantages of Biomass

Due to environmental concerns over the high use of fossil fuels, the demand for cleaner and more sustainable fuels has grown over the past years. Biomass is comprised of carbon, hydrogen, oxygen and nitrogen, which is similar to the composition of fossil fuels, which have carbon and hydrogen (Guerrero-Lemus and Martinez-Duart 2013). Because of this, many of the products that are made from fossil fuels can also be derived from biomass. Since biomass is referred to as any organic matter that comes from the agricultural or forestry sector on a recurring basis, it is deemed to be a sustainable fuel and chemical source (Guerrero-Lemus and Martinez-Duart 2013). As mentioned above, in the Cellulose section of this text, biomass is considered to be an inexhaustible resource. In this context, fossil fuels are the exact opposite of biomass; they are a resource that will be depleted at some point in time. Fossil fuel sources are not being recreated over time, at least over a reasonable time span, and it is known that this energy source will someday be gone.

In addition to the sustainability of biomass, another major advantage of the use of biomass is the fact that it yields no net CO_2 emissions (Guerrero-Lemus and Martinez-Duart 2013). Unlike fossil fuels which emit a large amount of pollutants and carbon emissions into the atmosphere, biomass does not. The amount of carbon dioxide that is released through the burning of biomass is equal to the amount of carbon dioxide that the plant matter absorbs throughout its life. For example, carbon dioxide is collected in a plant and used in photosynthesis; when the plant matter is burned, this same carbon dioxide is released. Because of this, the net CO_2 contribution to the atmosphere is zero. Fossil fuels, on the other hand, release an immense amount of CO_2, or greenhouse gases, into the atmosphere when they are burned. This CO_2 has been absent from the atmosphere for millions of years. Therefore, when it is reintroduced, there are many adverse effects that take place to the environment (Guerrero-Lemus and Martinez-Duart 2013). It is evident that the use of biomass, rather than nonrenewable fossil fuels, is much more advantageous since it is both sustainable and environmentally friendly.

2.2 Composition of Biomass

The major components that constitute biomass include cellulose, hemicellulose, and lignin (Yaman, Pyrolysis of biomass to produce fuels and chemical feedstocks 2004). Sugars can be produced directly from some forms of biomass, such as saccharose in sugarcane, or semi-directly from hydrolysis of starch, such as in corn. The bio-fuel that is obtained either directly or semi-directly from agricultural crops is referred to as first-generation bio-fuel and is not viewed as sustainable. Alternatively, the glucose molecules found in cellulose present in wood, straw, grass, municipal solid waste, and crop residues can be used for obtaining biofuel. Using the glucose present in lignocellulosic materials to produce fuel is referred second-generation biofuel technology and is considered sustainable. This is true because there is an abundant supply of these materials that is reproduced annually and is not needed as food (Tollefson 2010).

Lignocellulosic materials are complex mixtures of natural polymers, mainly cellulose (35-50%), hemicelluloses (25-30%), and lignin (15-30%) (Yaman 2004). The technology used to transform lignocellulosic materials into biofuels is still in its infancy. Therefore, the first step in understanding the mechanism of turning these materials into fuels is to first start with cellulose, since it is the most abundant component.

2.1 Cellulose

Cellulose is considered to be the sugar present in cell walls (Ahmed 2012). It is advantageous to extract this sugar in order to convert it into fuels and chemical feedstock;

however, it is difficult to do so. Alpha cellulose has the general chemical formula of $(C_6H_{10}O_5)_n$, and its molecular weight can range from 300,00-500,000 grams per mole (Yaman 2004). Cellulose makes up about 50% of the cell wall material of most biomass (Yaman 2004). Figure 2, below, is a picture of the chemical structure of cellulose. Cellulose is the most abundant organic polymer on earth; in fact, 1.5x10^12 tons of cellulose is produced annually throughout the world (Ahmed 2012). Since there is such abundance of this raw material, it is considered to be inexhaustible.

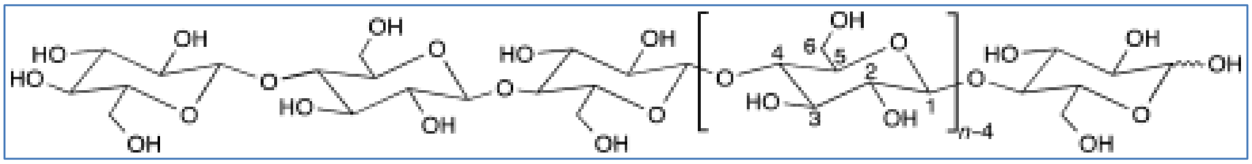

Figure 2: The chemical structure of cellulose (Rinadli and Schuth 2009)

As Figure 2 shows, the molecular structure of cellulose consists of repeating β-D-glucopyranose molecules which are covalently bonded together through interactions between the equatorial OH group of C4 and the C1 carbon atom (Ahmed 2012). The number of β-D-glucopyranose molecules in a given chain of cellulose, varies depending on the origin of the cellulose (Ahmed 2012). For example, cellulose from wood pulp consists of about 300 – 1700 molecules, while cellulose from cotton consists of about 800-10,000 (Ahmed 2012). These chains of β-D-glucopyranose molecules also partake in extensive hydrogen bonding. The OH groups possess high donor reactivity and subsequently form hydrogen bonds with the oxygen molecules resulting in a multitude of crystalline fiber structures. The cellulose chains are densely packed due to the strong hydrogen bonding restrictions (Rinadli and Schuth 2009). This dense packing restricts the accessibility of the hydroxyl groups in the interior features of cellulose's crystalline structure (Rinadli and Schuth 2009). Because of this, reactions that involve fibrous cellulose are only allowed to take place on the surface of the biopolymer (Rinadli and Schuth 2009). The hydrogen bond network makes the dissolution of cellulose very difficult. This can be seen below in Figure 2.

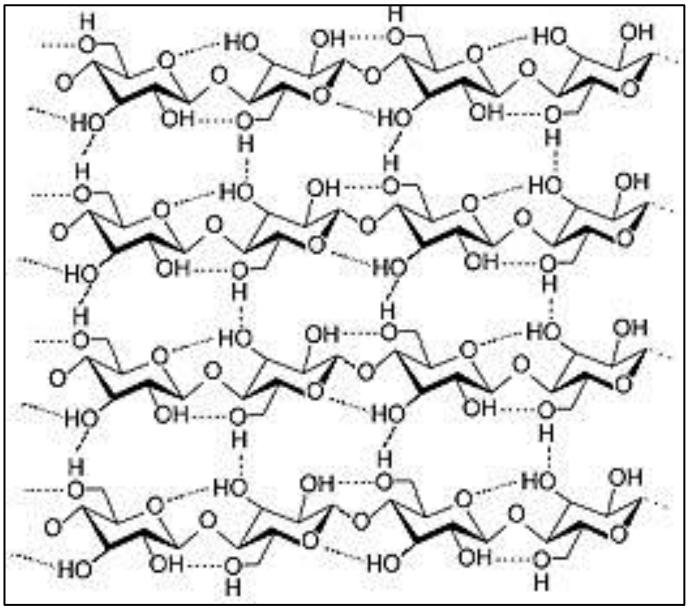

Figure 3: Hydrogen bond networks in cellulose (Rinadli and Schuth 2009)

Due to the high presence of intermolecular bonds, including hydrogen bonds and van der Walls forces, the pretreatment of the lignocellulosic materials is necessary. Pretreatment allows for the breaking of these bonds and for the dissolution of the lignocellulosic material (Rinadli and Schuth 2009). There are several pretreatment tactics that have been implemented thus far. These include "partial chemical degradations, mechanism comminution, activation by swelling, and several other processes, which disrupt partially the structure of cellulose" (Rinadli and Schuth 2009). These techniques are employed in order to improve the reactivity of cellulose and for the extraction of the glucose molecules, within cellulose, to take place (Rinadli and Schuth 2009).

2.3 Second-Generation Biofuels

Second-generation biofuel is produced from lignocellulosic biomass, which is not used for food, and therefore does not compete for agricultural land use (Naik, et al. 2010). Lignocellulosic biomass includes materials such as grass, wood, roots, etc. (Naik, et al. 2010). Since the feedstock for second-generation biofuel does not include crops, it is much more advantageous to implement this type of fuel source, rather than first-generation biofuels. There will be less environmental and economic implications from the use of this type of fuel. The biomass used in this type of fuel is more sustainable, abundant, cheap, and does not compete with food crops (Naik, et al. 2010). Unfortunately, as highlighted above, the appropriate technology is still being research and created for the production of such fuels.

2.3.1 Second-Generation Bioethanol

The components of cellulosic biomass include mainly cellulose and hemicellulose molecules held together by lignin (Naik, et al. 2010). The lignin holds together the cellulose and hemicellulose, making it difficult to extract the sugar molecules (Naik, et al. 2010). Much like first-generation biofuels, there are two different categories to second-generation biofuels; second-generation bioethanol and second-generation biodiesel (Naik, et al. 2010).The current technology used to convert cellulosic biomass into second-generation bioethanol requires five separate steps (Naik, et al. 2010). The first step is to obtain the biomass, either from nonfood crops or organic waste (Naik, et al. 2010). Then the biomass is pretreated in order to separate the organic matter into its basic compounds, cellulose, hemicellulose and lignin (Naik, et al. 2010). The third step requires the hydrolysis of the cellulose and hemicellulose, in order to extract the sugar molecules (Naik, et al. 2010). Once the sugar molecules have been extracted, fermentation is used to produce alcohol from the sugar (Naik, et al. 2010). The final step in this process is to separate the ethanol that is produced during the fermentation process from the other byproducts (Naik, et al. 2010).

2.3.2 Second-Generation Biodiesel

Second-generation biodiesel, or advanced biodiesel, is also a liquid biofuel that is generated from lignocellulosic biomass, however, through a different process (Naik, et al. 2010). The most common process is referred to by the acronym BtL (Biomass-to-Liquids). BtL biodiesel can be produced from any type of organic biomass (Naik, et al. 2010). This process can be broken down into four basic steps. First, the biomass is gasified and vapors are produced. Next, the gas is purified in order to remove carbon particles, tars, and pollutant gases. After, a syngas is obtained. Once the syngas has been produced, a catalytic procedure, called the Fischer-Tropsch process, is implemented in order to turn the syngas into liquid biofuel (Naik, et al. 2010). The hydrogen and carbon monoxide syngas is combined with catalysts under high temperatures and pressures which subsequently yields various types of liquids and gaseous hydrocarbons (Naik, et al. 2010). The biodiesel that is obtained during this process and be blended with diesel from fossil fuels and used in diesel engines (Naik, et al. 2010).

Second-generation biofuels are considered more advantageous than first-generation biofuels due mainly to the fact that this fuel can be produced from any organic plant material, not just food crops (Peterson 2012). In Figure 4, below, is a comparison of petroleum, first-generation, and second-generation fuels. Since agricultural land is not required for second-generation fuel, there are much less environmental and economic implications. There are no food-versus-fuel concerns, and the price of crops would not be affected. However, the production of this type of fuel is not cost effective due to technological obstacles that still need to be overcome (Peterson 2012). Currently, second-generation biofuels are non-commercial.

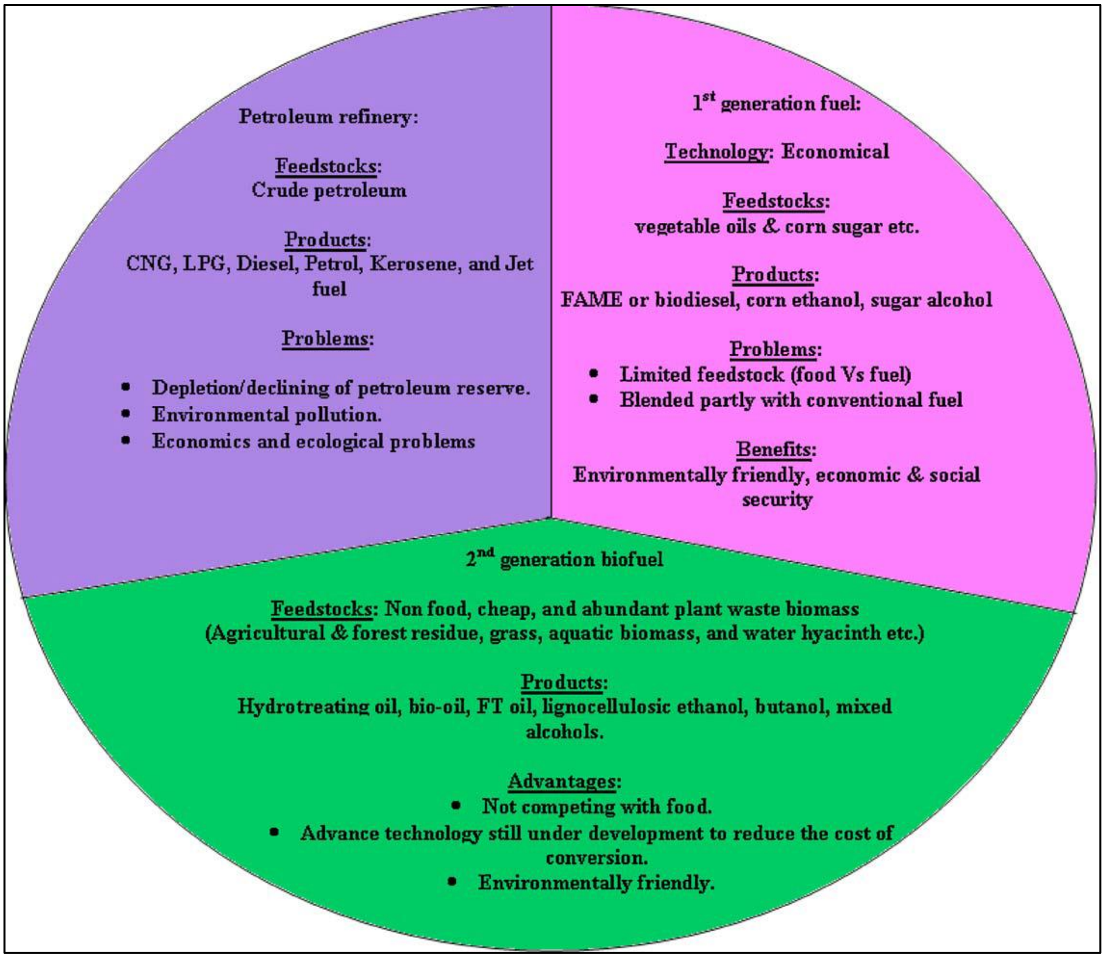

Figure 4: Comparison of first and second generation biofuel and petroleum fuel (Naik, et al. 2010)

2.3.3 Feedstock for Second-Generation Biofuels

The advantage of developing the proper technology to use second-generation biofuels, stems from the fact that a large number of different types of biomass is able to be used. With second-generation biofuels, as highlighted above, crops that are required for human and animal consumption are not required. The different types of biomass that can be used for this type of fuel seem endless. Biomass from trees, forest residues, grasses, and plants are important renewable resources that can be used for both the fuel and chemical industries (Naik, et al. 2010). In all types of biomass, plants convert carbon dioxide and water attained from the atmosphere and, through photosynthesis, into primary and secondary metabolic biochemical

(Naik, et al. 2010). Primary metabolic bio-chemicals include sugar, cellulose, hemicellulose, starch and lignin. Secondary metabolic bio-chemicals include gums, resins, rubber, steroids, plant acid and etc. (Naik, et al. 2010). The primary bio-chemicals are the major components in biomass. Figure 5, below, shows the vast amount of different types of biomass that can be used in second-generation biofuel technology.

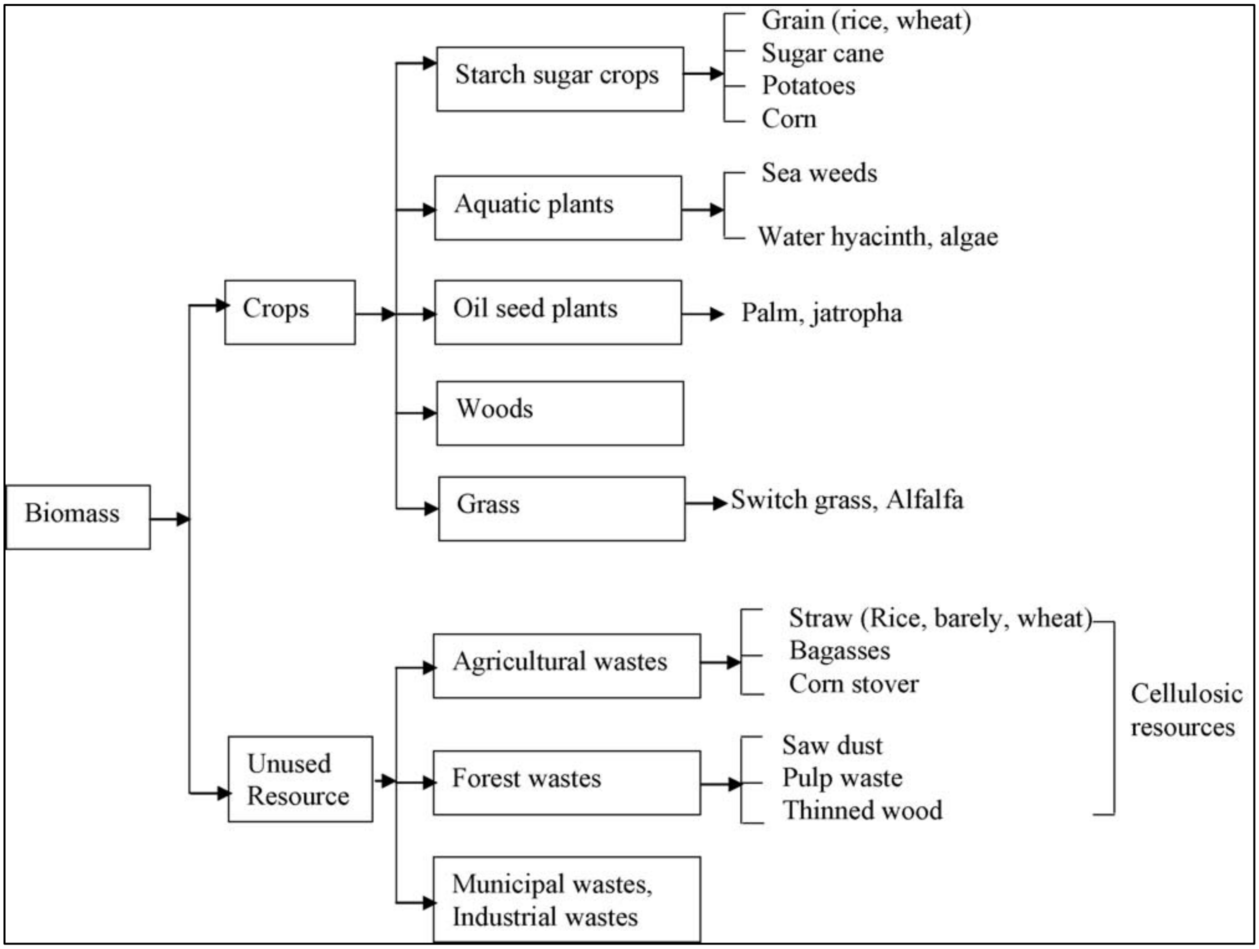

Figure 5: Different types of biomass that can be used with second-generation biofuel technology (Naik, et al. 2010)

There are two major hurdles with the implementation of second-generation biofuels into high use in society. The first problem that must be overcome is developing the proper technology that produces and utilizes bio-based products (Naik, et al. 2010). The second hurdle is finding a suitable way to gradually reduce society's dependence on fossil fuels and place a higher burden on biofuels for the production of chemicals and fuels (Naik, et al. 2010). On the technological side of the matter, there have already been large strives in developing the suitable technology for this task. For example, as Naik et. al. explains:

> *"For future biorefineries separation processes like extractive distillation with ionic liquids and hyperbranched polymers, adsorption with molecular sieve and biobased adsorbents, nanofiltration, extractive-fermentation, membrance pervaporation in bioreactors, and vaccum membrame distillation (VMD) hold significant potential and great promise for further investigations, development and application"* (Naik, et al. 2010).

It is still unknown how or when society will begin to gradually reduce the dependence on fossil fuels. It is evident, however, that there must first be suitable technology to implement renewable resources.

2.3.4 Production of Second-Generation Biofuels

Second-generation biofuels allow for the possibility for fuels to be produced that are carbon neutral; for example, the amount of carbon dioxide concentrations in the atmosphere do not rise because of second-generation biofuels (Naik, et al. 2010). Because of this fact, and because the feedstock for second-generation biofuels is completely renewable, it is beneficial to utilize this resource. However, it is still not cost effective to produce second-generation biofuels due to lack of technological advancements (Naik, et al. 2010). Plant biomass consists mainly of cell walls, or about 75% polysaccharides (Naik, et al. 2010). There is a large amount of sugar present in these polysaccharides; however, it is difficult to extract the energy stored in these sugars. It could be said that second-generation biofuels were the first fuel of man, the burning of wood for heat. However, as fossil fuels were discovered, this source of power was turned away from. Now, the human population is reaching a time in which lignocellulosic materials must be utilized again.

Two different ways in which lignocellulosic biomass can be converted to liquid biofuels include thermochemical processing and biochemical processing (Naik, et al. 2010). Thermochemical processing is essentially heating biomass to higher temperatures using different types of techniques and reaction parameters (Naik, et al. 2010). Biochemical processing uses a variety of different chemicals in order to convert the biomass into a liquid bio-oil (Naik, et al. 2010). Thermochemical processes tend to produce higher yields compared to biochemical processing, because it has the ability of converting all organic compounds (Naik, et al. 2010). Biochemically processing focuses mainly on converting the polysaccharides of the biomass into bio liquids (Naik, et al. 2010). Figure 6, below, is a representation of the different forms of conversion of second-generation biomass to fuel. These techniques will be discussed in the preceding sections.

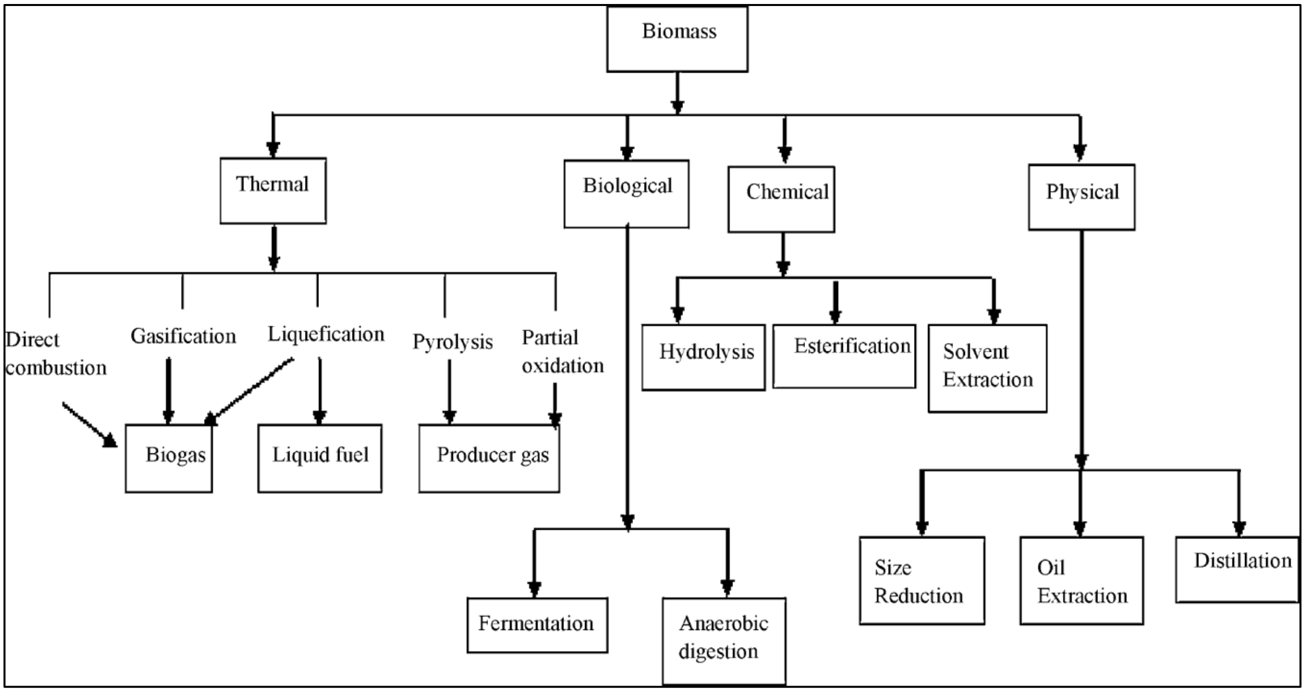

Figure 6: Thermo-chemical conversion processes (Naik, et al. 2010)

2.3.4.2 Hydrolysis of Cellulose

Beginning in the twentieth century, research, aimed to find suitable ways to produce fermentable sugars from cellulose, began (Rinadli and Schuth 2009). However, due to the low cost and high availability of crude oil, this technology was never employed. The process for the hydrolysis of cellulose has remained a fairly costly and highly technical undertaking (Rinadli and Schuth 2009). Several different processes for the acid hydrolysis of biomass are highlighted below.

In the 1920s, the Scholler process was the first technology for the acid hydrolysis of cellulose (Rinadli and Schuth 2009). “In this process, a 0.5 wt% sulfuric acid solution is forced to pass through wood waste, consisting of sawdust compressed in brick-lined percolators” (Rinadli and Schuth 2009). This solution of sulfuric acid and wood waste remained in the percolator for 45 minutes at 170^{o}C under 20 bar. The product of this reaction was a dilute sugar solution that is then fermented. About 50% of the fermentable sugars were yielded with this process.

In a different acid hydrolysis process, called the Bergius process, the hydrolysis is conducted with 40 wt% HCl at room temperature (Rinadli and Schuth 2009). The cellulose and hemicellulose components of the biomass are soluble in the solution; however, the lignin is not. The HCl solution allows for the cellulose to breakdown into oligosaccharides and glucose whereas the hemicellulose produces mannose, xylose, galactose, glucose, and fructose. This solution of HCl and the broken down components of cellulose and hemicellulose is heated at 120^{o}C for a half hour. In this process, a ton of dry wood is converted to about 320 liters of 95% ethanol. The downside of the Bergius process is that HCl is highly corrosive and would require a corrosion-resistant plant to be constructed. Also, it is extremely expensive to recover the HCl.

In a separate process, HCl was used in conjunction with either $CaCl_2$ or LiCl. By utilizing the swelling effects of the salts, yields of up to 85% glucose were claimed (Rinadli and Schuth 2009). The salts were able to swell the cellulosic fibers of the biomass were determined to be the main cause of the high hydrolysis rate (Rinadli and Schuth 2009).

The main drawbacks of acid hydrolysis of lignocellulosic materials include acid recovery, corrosion, and chemical waste produced (Rinadli and Schuth 2009). The recycling of the acid catalyst is typically considered the biggest hurdle in the process (Rinadli and Schuth 2009). For example, in acid hydrolysis processes that utilize H_2SO_4, acid recovery is typically not possible. Since acid recovery is so different and ineffective, it causes the acid hydrolysis process to be economically unfeasible (Rinadli and Schuth 2009).The high costs associated with these drawbacks contribute to the fact that they are not currently being used to produce biofuels from lignocellulosic materials.

2.3.4.1 Pyrolysis of Cellulose

Pyrolysis is the process of heating biomass in the absence of oxygen, resulting in the thermal degradation of the biomass (Naik, et al. 2010). This process results in three main products which are classified as charcoal (solid), bio-oil (liquid), and gas products (Naik, et al. 2010). The char portion of the products contains ash from the thermal decomposition of the organic components (Yaman 2004). The liquid products contain a wide variety of different organic components and water (Yaman 2004). Some of the common liquid products of pyrolysis include acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives and phenolic compounds (Yaman 2004). The gas that is produced during the pyrolysis process typically contained CO_2, CO, CH_4, H_2, C_2H_6, and C_2H_4 (Yaman 2004).

Currently, there are three different types of pyrolysis that can be used to convert biomass into these products; they include conventional pyrolysis, fast pyrolysis, and flash pyrolysis (Naik, et al. 2010). Conventional pyrolysis is the process described above with a very slow heating rate (Yaman 2004). This slow heating rate is typically in the range of 0.1-1 degree kelvin per second (Naik, et al. 2010). There are three stages of conventional pyrolysis. The first stage, pre-pyrolysis, is the thermal decomposition of the biomass between 550 and 950K. During pre-pyrolysis, water elimination, bond breakage, appearance of free radicals, formation of carbonyl and hydroperoxide groups takes place. In the second stage of conventional pyrolysis, is when the main pyrolysis process occurs and when the majority of the pyrolysis products are formed (Naik, et al. 2010). In the final stage of this process, the char that is formed in the second stage, decomposes at a very slow rate, forming carbon rich solid residues (Naik, et al. 2010). This process has been used throughout history for the production of charcoal (Yaman 2004).

Flash pyrolysis of biomass incorporates higher pyrolysis temperatures and heating rates than in conventional and fast pyrolysis (Naik, et al. 2010). It occurs between 1050-1300 Kelvin and with a heating rate in excess of 1000 degrees Kelvin per minute (Naik, et al. 2010). The bio-oil that is produced during this process is typically recycled back into that char that is produced to create a sludge-like mixture called bio-slurry (Naik, et al. 2010). The bio-slurry is then transferred to a gasifier, which is very efficient in creating crude oil. In fact, the conversion rate of biomass to crude oil using this technique is close to 70% conversion. This crude oil produced from biomass can be used directly in engines and turbines; also, its use as a feedstock in refineries is being considered (Naik, et al. 2010).

Fast pyrolysis is the heating of biomass with a very rapid heating rate, typically in the range of 10-200 degrees Kelvin per second (Naik, et al. 2010). The biomass is heated to a temperature of about 850-1250 Kelvin. The liquid that is produced during this process is quickly condensed, so that no secondary conversion of the products can take place (Yaman 2004). During fast pyrolysis, biomass is decomposed to form vapors, aerosol, and char (Naik, et al. 2010). The vapors and aerosol are latter condensed and form a dark brown liquid. Depending on which type of biomass feedstock being used, fast pyrolysis can yield 60-75% bio-oil, 15-25% solid char and 10-20% non-condensed gases (Naik, et al. 2010).

A typical fast pyrolysis process flow is shown below in Figure 7. The major components of a fast pyrolysis process steps include: drying, grinding, reacting, separating, cooling, and collecting (Bridgewater and Peacocke 2000). Most biomass is required to be dried before being used in fast pyrolysis. Since biomass naturally contains water, it is beneficial to remove this moisture before the process begins. This is due to the fact that all of the initial water present in the biomass at the beginning of the reaction will subsequently be present in the bio-oil. Therefore, it is more economical and easier to remove most of the water content before the reaction, rather than after (Bridgewater and Peacocke 2000). In order for the highest heating rates to be employed, the biomass particles must be reduced to a small size. The small particle size not only helps with increasing the heating rate, but it also contributes to high liquid yields (Bridgewater and Peacocke 2000). The biomass particles must be reduced to less than 2 mm for fluidized beds, which can be costly (Bridgewater and Peacocke 2000). A large number of different types of reactors have been investigated for their use in fast pyrolysis and an ideal reactor type has not been determined. However, commercial product of bio-oil from lignocellulosic material is currently being achieved with fluidized bed reactors (Bridgewater and Peacocke 2000). Fluidized bed reactors are advantageous due to the fact that they are relatively easy to use and their size scale be scaled up from a pilot plant to a commercial plant relatively easily (Bridgewater and Peacocke 2000). However, one downside to fluidized bed reactors is the small particle size that is essential for proper liquid yields. Cyclones are typically used in order to separate the vapor and char products of the reaction. Once this separation has taken place, the char can be recycled and burned in order to give off heat to help drive the reaction. The vapor products are subsequently sent to a condenser in which the liquid and gas products are retained. The gas product can be used in the drying process of the biomass. The liquid product, or the bio-oil, is finally collected and can be refined for specific end products (Bridgewater and Peacocke 2000).

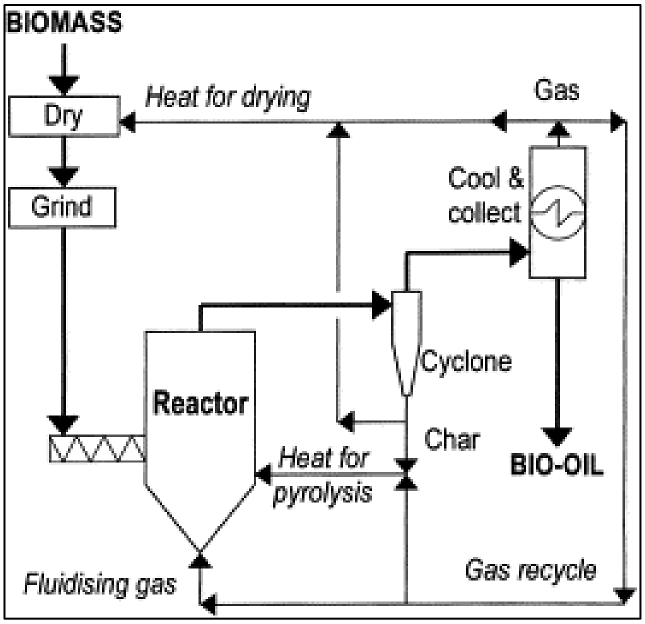

Figure 7: Fast pyrolysis processes for biomass (Bridgewater and Peacocke 2000)

One of the biggest obstacles in optimizing the pyrolysis process is the understanding of exactly how the products are formed. The general biomass pyrolysis process, relative to the biomass, can be seen below in Figure 8. It has been discovered that pyrolysis begins with a network of solid-phase reactions which fractionate and polymerize the biomass (Dauenhauer, et al. 2011). Immediately after the biomass has been fractionated and polymerized, a liquid phase exists for a brief time. During the short liquid phase, a multitude of depolymerization, rearrangement, and dehydration reactions take place until it repolymerizes to form char or volatizes to form vapors (Dauenhauer, et al. 2011). When lower heating rates are used, the vapor components are less likely to be expelled from the biomass; therefore, higher char yields are generated. Utilizing higher heating rates allows for the vapors to be released from the biomass and subsequently condensed to liquids. The vapor products are of most concern since they can be condensed to bio-oil, as described above. However, the reaction mechanism and product distribution of the condensed vapors has not been thoroughly understood, until recently.

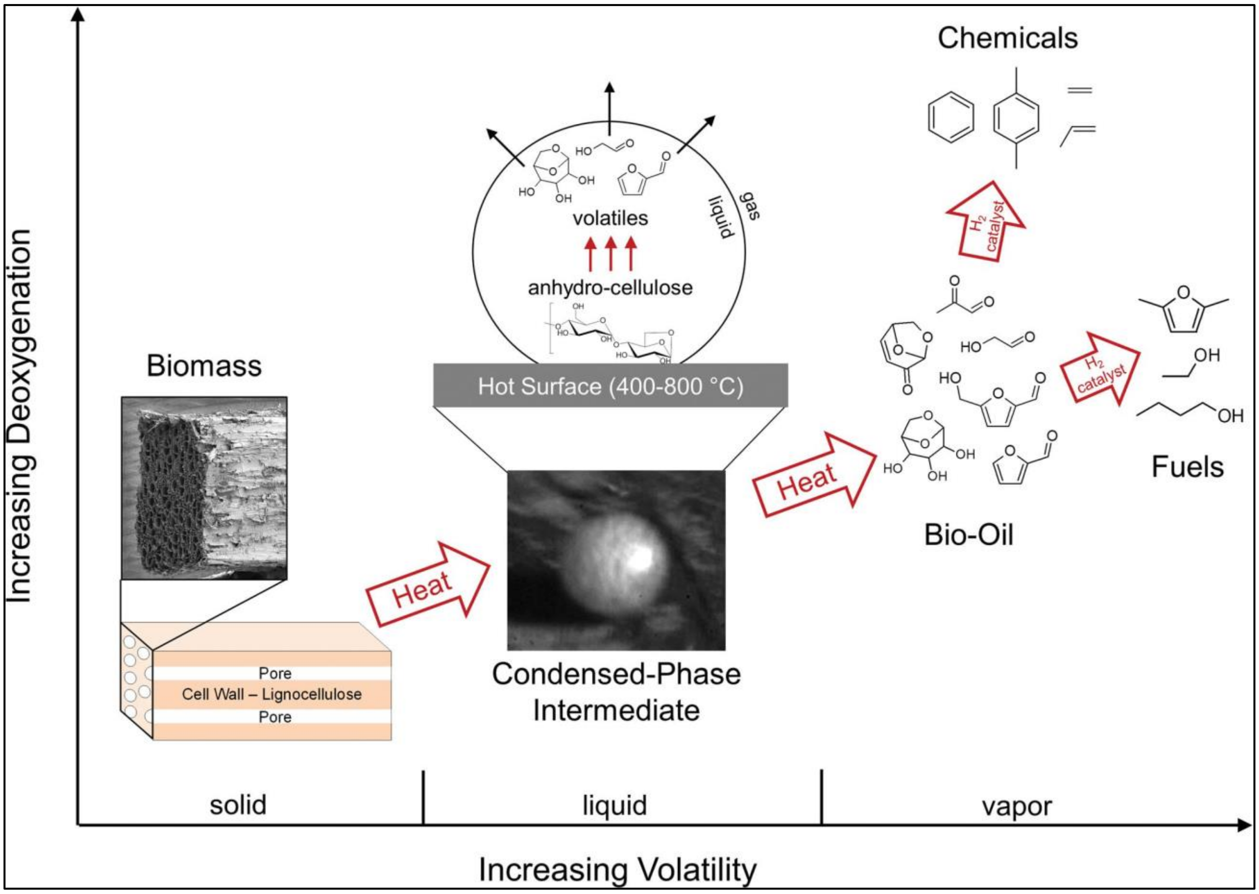

Figure 8: Biomass pyrolysis process (Dauenhauer, et al. 2011)

The understanding of the mechanisms involved in pyrolysis of biomass is hindered for several reasons which include:

> "*the substantial functionality (oxygen-rich) of biomass starting materials, intermediates and products; the temperature sensitivity of many products; the short lifetime (less than*

> *0.1 s) of condensed-phase intermediates; the relatively slow heat transfer which makes isothermal pyrolysis challenging; and the dependence of product yields on the residence time of volatiles within the liquid-phase (which is often controlled by mass transfer"* (Dauenhauer, et al. 2011).

One suitable way of determining the reaction mechanisms of cellulose pyrolysis, is to use computer simulations. However, the wide array of chemical pathways and product distributions does not allow for computer simulations. In fact, it is predicted that is would take years, even with hundreds of computer processors, to compute molecular dynamic simulations of this reaction (Dauenhauer, et al. 2011). In order to overcome these problems, Dauenhauer *et al*, determined that α-cyclodextrin could be used in CPMD simulations to illustrate the major volatile product mechanisms of cellulose pyrolysis (Dauenhauer, et al. 2011). This first step in the computer modeling of this mechanism was to distinguish a molecule that yields similar product distributions of cellulose pyrolysis. Using thin–film pyrolysis techniques Huebner, *et al*, determined that "condensed-phase chemistry of cellulose is similar to that of α-cyclodextrin over a range of reaction temperatures resulting in nearly identical product distributions" (Huebner 10). Once α-cyclodextrin was determined to be a suitable surrogate for cellulose, CPMD simulations of this molecule could be conducted.

Through the use of α-cyclodextrin, the reaction pathways of cellulose pyrolysis were able to be modeled, some of which can be seen below in Figure 9. These CPMD simulations were used to prove that furans are formed directly from cellulose without any intermediate compounds, such as glucose or levoglucosan. Previously, it was believed that furan and glycoaldehyde formation was initiated by ionic mechanisms; however, these results show that these formations are the results of hemolytic cleavage of the glycosidic bonds (Dauenhauer, et al. 2011). These findings help understand the major condensed-phase pyrolysis pathways; however, further understanding of the various other pathways still remains. Understanding the reaction mechanisms of cellulose pyrolysis is an important step and the findings of (Dauenhauer, et al. 2011), are substantial. Eventually, once more of these pathways have been discovered and understood, they can be used to help design and optimize second-generation biofuels and chemicals.

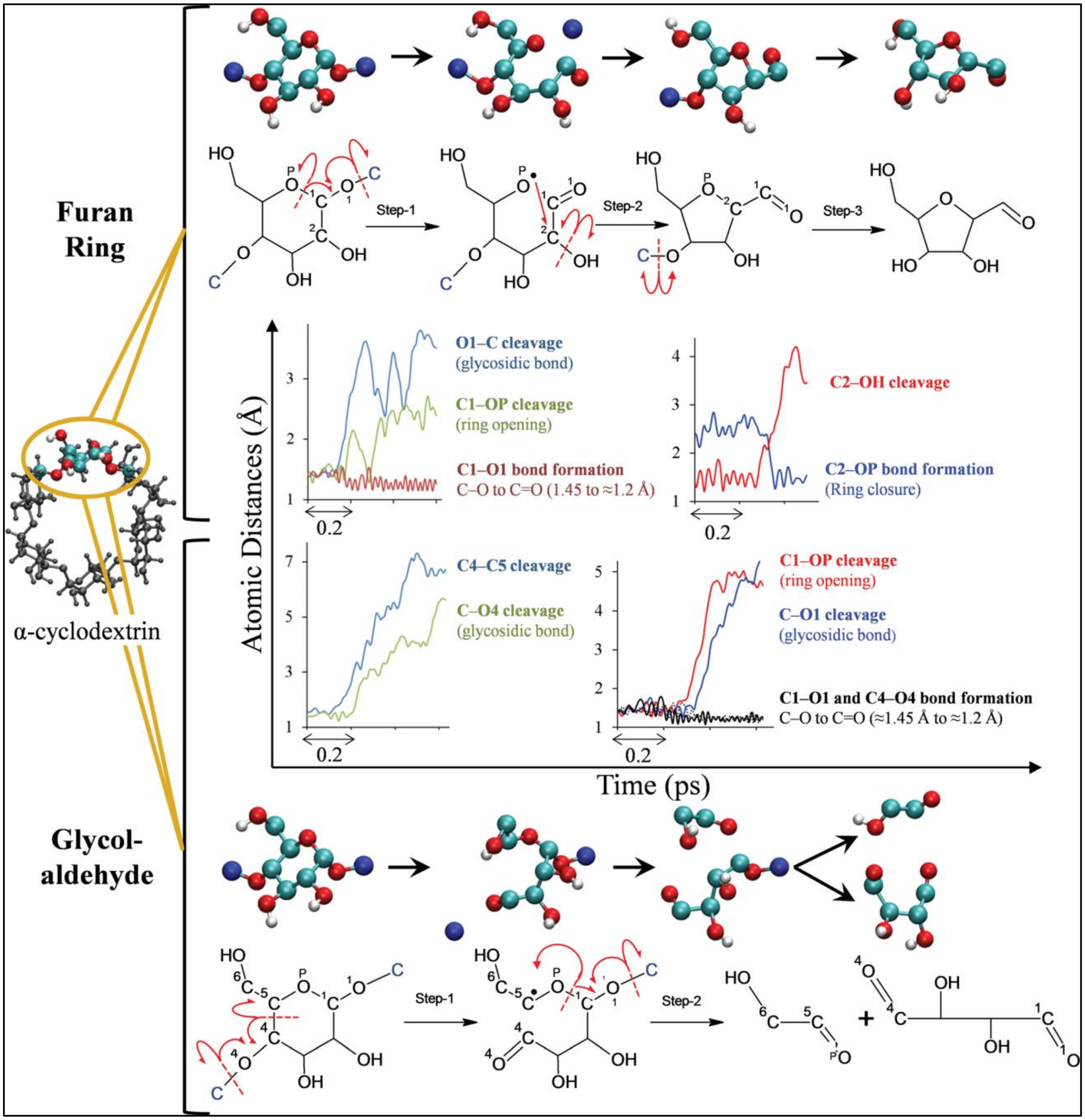

Figure 9: Reaction pathways of α-cyclodextrin (cellulose) pyrolysis (Dauenhauer, et al. 2011)

2.3 Ionic Liquids

One of the major obstacles that must be overcome before lignocellulosic material can be utilized for the production of biofuels and chemicals is the understanding of the deconstruction of lignocellulose. Currently, the paper industry leads the field in regards to lignocellulose treatment processes (Brandt, et al. 2013). However, the technology used in the paper industry is optimized to produce high cellulose yield and high fiber strength materials (Brandt, et al. 2013). This does not align with the needs of a biorefinery due to the fact that high quality fermented sugar solutions are desired (Brandt, et al. 2013). Because of this, the current treatment technologies cannot be employed for the production of biofuels and chemicals from lignocellulosic materials. In order to obtain fermentable sugars from lignocellulose, the structural and chemical obstacles that obstruct the release of carbohydrates must be overcome. Since cellulose is the main constituent of lignocellulose, the deconstruction of cellulose has been the major focus of research over the past years.

Ionic liquids are salts that are liquid and stable at or below 100^{o}C (Brandt, et al. 2013). Since their discovery in the 1990s, ionic liquids have been highly researched; however, in recent years, this research has been focused on their potential role in chemical synthesis, catalysis, and biocatalysis (Brandt, et al. 2013). Through this research, it has been discovered that ionic liquids may be a suitable solvent for the processing of biomass.

Modern ionic liquids contain organic cations. Examples of cations that are used in ionic liquids are highlighted below in Figure 10. In the past, it was believed that the anion played the only role in the dissolution of cellulose (Brandt, et al. 2013). However, recent studies have determined that the organic cations play a more influential role than previously thought. There are three distinct characteristics of cations that play a significant role. The first characteristic is the length of the alkyl, or glycol, chains on the cation. It has been determined that the lengthening of this chain progressively reduces cellulose solubility (Brandt, et al. 2013). Also, the presence of hydroxyl groups in the alkyl chains reduces the solubility of cellulose in ionic liquids (Brandt, et al. 2013). This due to the fact that when hydroxyl groups are present on the alkyl chain, the hydrogen bonding activity within the ionic liquid's cation and anion increase. This increase in molecular bonding reduces the bonding between the anion of the ionic liquid and the hydroxyl groups of the cellulose, therefore reducing the solubility. The final characteristic of cations that plays a significant role is the presence of a protic cation. The presence of a protic cation can entirely prevent the cellulose of being soluble in ionic liquids. Similar to the second characterization, this is due to the fact that the cation and anion are more strongly bonded together (Brandt, et al. 2013).

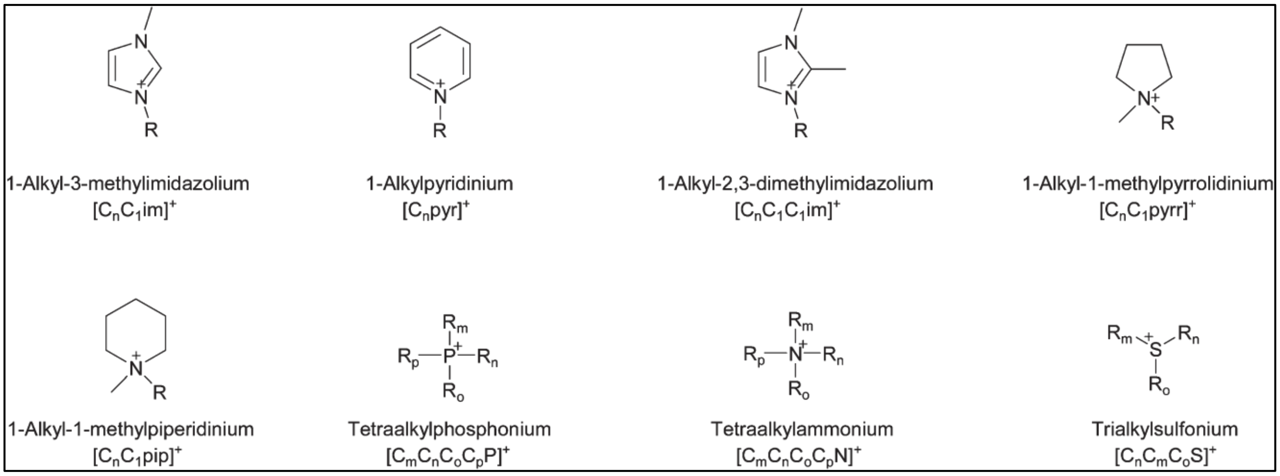

Figure 10: Common cations used in modern ionic liquids (Brandt, et al. 2013)

Although the characteristics of an ionic liquid's cation are important, the characteristics of the anion are more crucial [20]. Ionic liquids that possess anions that can form strong hydrogen bonds with the hydroxyl groups of cellulose are the most suitable for dissolving cellulose [20]. Examples of such anions are shown below in Figure 11 and include, chloride, carboxylates (acetate, formate, propionate, lactate), dialkyl phosphates, diakyl and trialkylphosphonates and amino acids (Brandt, et al. 2013). It is believed that the anion of an ionic liquid interacts with the equatorial hydroxyl groups on the cellulose through hydrogen bonding (Brandt, et al. 2013). Also, it is believed that the size and geometry of the anion is important towards whether or not cellulose is soluble in an ionic liquid (Brandt, et al. 2013).

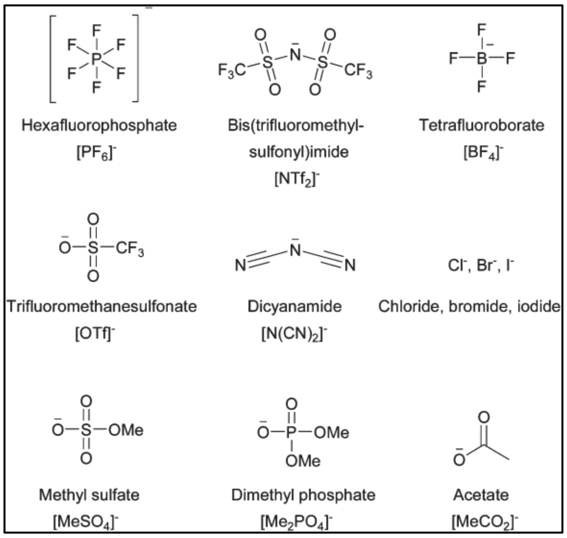

Figure 11: Selection of anions used in modern ionic liquids (Brandt, et al. 2013)

The growing interest in the use of ionic liquids for the production of biofuels and chemicals from lignocellulosic materials is the result of these liquids being able to effectively dissolve cellulose. Because of this, the glucose molecules within the cellulose can more easily be extracted from the lignocellulosic material. Once the glucose has been extracted, it can be hydrolyzed and then fermented into suitable fuels. Ionic liquids have the high ability of dissolving the crystalize structure of cellulose in this material, which has proved to be the most difficult part in utilizing such resources. Once the cellulose network has been de-crystallized, the ionic liquid is then able to disrupt both the hemicellulose and lignin portions of the lignocellulosic material (Brandt, et al. 2013). Also, ionic liquids are much less volatile than HCl, which is used in acid hydrolysis of lignocellulose. Because of this, it could be more easily implemented into a biorefinery (Brandt, et al. 2013).

There are a number of disadvantageous that coincide with the use of ionic liquids. The major concern is due to the high costs of these materials. With the current technology in the ionic liquid field, they are still not economically feasible. The cost of ionic liquids is much too high in relation to the biomass that is processed by them. It has been predicted that for ionic liquids to be economically feasible, they must cost less than $2.50 per kilogram (Brandt, et al. 2013). Another downside to the use of ionic liquids is their recycling throughout a given process. Current technologies do not allow for proper recycling of these materials and, because of their high costs, this is detrimental. Finally, some ionic liquids that are the most suitable for the dissolution of cellulose are harmful to the environment (Brandt, et al. 2013). Because of this, ionic liquids that are more environmentally friendly must be utilized.

2.5 Molten Salts

Molten salts are salts that must be heated to over 100^{o}C in order to reach a liquid state. Molten salts are different than ionic liquids due to the fact that ionic liquids are salts that are liquid at or below 100^{o}C. When most people think of salts, they usually think of common salts such a sodium chloride; most common salts fall under the molten salt category (if not being heated over 100^{o}C). The idea of using molten salts in order to produce bio-oil is a fusion of the current technologies that are currently employed. For example, acid hydrolysis of cellulose uses acids in order to extract the glucose from the cellulose. Also, pyrolysis uses fast heating rates and high temperatures in order to produce bio-oils. Finally, ionic liquids can be used to dissolve cellulose, thus making it easier to refine. The use of molten salts combines all three of these through the use of acids, high heating rates and temperatures, and solubilizing cellulose through ionic interactions.

2.5.1 Previous Research at WPI

In the years 2009, 2010, and 2011, the use of molten salts for producing bio-oils was researched. In the 2009 study, an MQP group researched the gasification of biomass using molten salt media. Various compositions of molten salt eutectics of carbonates and hydroxides were analyzed in order to determine is mixture with a low melting point that could be used to react with biomass. In 2010, another MQP group studied the gas products obtained through the reactions with various types of biomass and molten salts. This group studied several types of reactions including gasification, pyrolysis, thermal depolymerization, and transesterification. Finally, in 2011, another MQP group tested various molten salt combinations, including hydroxide, carbonate, bicarbonate, and chloride eutectics for the use of reacting with biomass. In addition, this group also analyzed several acid base compounds and their effect on this reaction. The product distribution of the products produced was analyzed, and the highest liquid yielding combination was determined. This group determined that chloride eutectics, in conjunction with a catalyst called ZSM-5, yielded the highest weight percent bio-oil. The hydroxides and carbonates produced substantially lower liquid yields. Because of this, the focus of this paper and research was on chloride eutectic molten salts.

2.5.2 Eutectics

A eutectic compound is a mixture of different substances that melts at a lower temperature than at which the different substances melt on their own. For this research, chloride eutectics were employed. The different substances that were used include zinc chloride, sodium chloride, potassium chloride and lithium chloride. A table of the different melting points for these salts can be seen below in Table 1.

Even though all of these chloride salts have very high melting points, when they are mixed together is certain quantities, the melting point of the mixture is significantly lower. It was important to utilize eutectics in these experiments due their low melting points. Since less heat is needed to bring the eutectic to the molten state, much less energy is required for the reaction.

Table 1: Chloride salts used and their melting points

Salt	Melting Point
Zinc Chloride	318 C
Sodium Chloride	801 C
Potassium Chloride	770 C
Lithium Chloride	605 C

In order to find a suitable composition of a eutectic that will melt at a given temperature, phase diagrams can be used, such as in Figure 12. In this image, three salts are presented including zinc chloride, potassium chloride, and sodium chloride. This diagram can be used to find a desired temperature and adjust the mole percent composition of each material. The mole percent is read on the side of the diagram for each substance. The phase lines are followed to the intersecting points where the temperature is displayed based upon the given mole percentages.

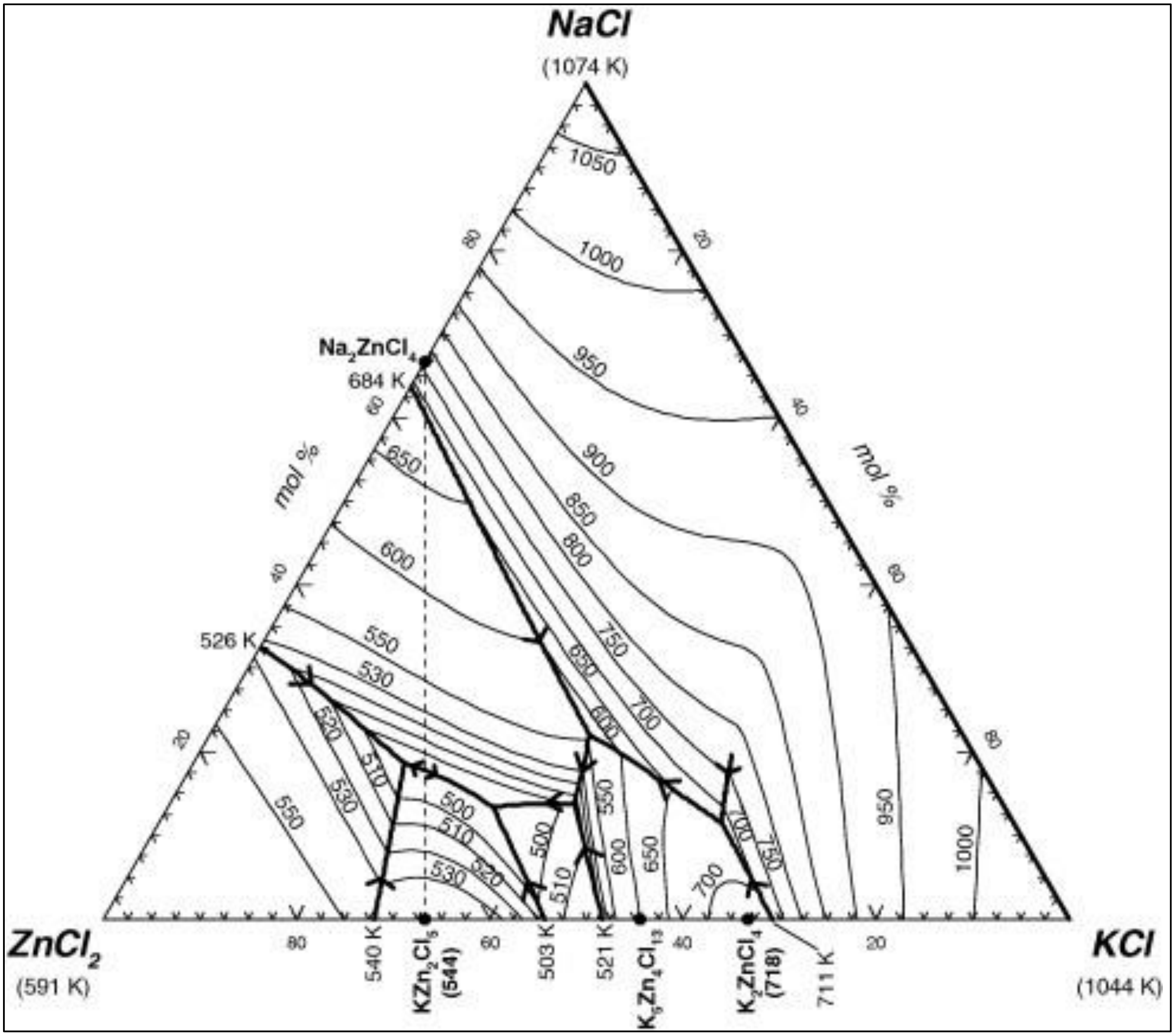

Figure 12: Ternary eutectic phase diagram (Nitta, et al. 2009)

3. Methodology

3.1 Objectives

The objectives of this study included:

- Determining a suitable chloride eutectic to be used as a molten salt in the pyrolysis reaction of cellulose in order to obtain liquid products. Salt under consideration included:
    - Zinc Chloride ($ZnCl_2$)
    - Sodium Chloride ($NaCl$)
    - Potassium Chloride (KCl)
    - Lithium Chloride ($LiCl$)
- Determining the highest liquid product yielding cellulose to molten salt molar ratio for this reaction
- Determining the optimal reaction temperature for the pyrolysis reaction of cellulose
- Determining the highest liquid product yielding combination of the chloride eutectic using the salt listed above.
- Determining the heating rate that produces the highest yielding liquid product
- Analyzing whether or not the addition of basic catalysts would result in higher liquid product yields or higher selectivity of products. Catalysts that were considered included:
    - Zeolite Socony Mobil – 5 (ZSM-5)
    - Nickel (II) Hydroxide ($NiOH_2$)

3.2 Chloride Eutectic Selection

As stated previously, it had been determined by the MQP group in 2012 that the highest liquid product yielding molten salts were chlorides. Because of this, and other supporting research found in the literature, it was determined that the use of a chloride eutectic would be most beneficial. Therefore, it became important to determine a chloride eutectic with a relatively low melting point. Drew Martino, a PhD candidate at WPI, was consulted for this. Drew has done extensive research into bromide eutectics, which have very similar properties to chloride eutectics. He suggested that a eutectic comprised of 40 mole percent $ZnCl_2$, 20 mole percent KCl, and 40 mole percent LiCl be used. (These mole percentages are based on the molecular weight of the metal anion.) Through Drew's research, he has determined that this three compound eutectic has a melting point around 240^{o}C, which is the lowest observed melting point of a $ZnCl_2$, KCl, and LiCl mixture. He has also determined that the use of 40 mole percent of $ZnCl_2$ results in dramatically lower melting points. It was suggested that testing a variety of varying mole percent eutectic mixtures, with these chemicals, should be conducted. In addition to $ZnCl_2$, KCl, and LiCl, sodium chloride was also used in these tests. Since NaCl is very inexpensive, it was important to determine if it could be used instead of the costlier KCl or LiCl.

Therefore, the first step in this research was to conduct bench top trials in order to validate and observe the low melting points of varying chloride eutectics. These trials were used in order to gain further understanding of chloride eutectic mixtures. First, the chloride eutectics were prepared based upon appropriate mole percentages and the salts molecular weights. To prepare the eutectics, $ZnCl_2$, KCl, LiCl were massed with a scale. The three separate salts were combined using a mortar and pestle. Once the salts had been thorough mixing, they were then transferred to a ceramic crucial. Next, the crucial and salts were placed on a heating pad. The temperature was slowly increased using the settings of the heating pad. In Figure 13, below, a mixture of this eutectic can be seen being heated on the heating pad. The temperatures at which the eutectic began to show signs of melting and when it had completed melted were observed with a thermocouple. The chloride eutectics that were tested are presented in Table 2, below.

Figure 13: Chloride eutectic bench top tests

Table 2: Chloride eutectics used in bench top tests

Zinc Chloride Mole %	Sodium Chloride Mole %	Potassium Chloride Mole%	Lithium Chloride Mole %
40	0	20	40
40	30	0	30
40	40	0	20
40	40	20	0
50	30	0	20
50	50	0	0
60	20	20	0
60	30	10	0
60	40	0	0
60	30	0	10
60	20	0	20
70	30	0	0
80	20	0	0
100	0	0	0

3.3 Flow Reactor Setup

3.3.1 Reactor Flow Layout

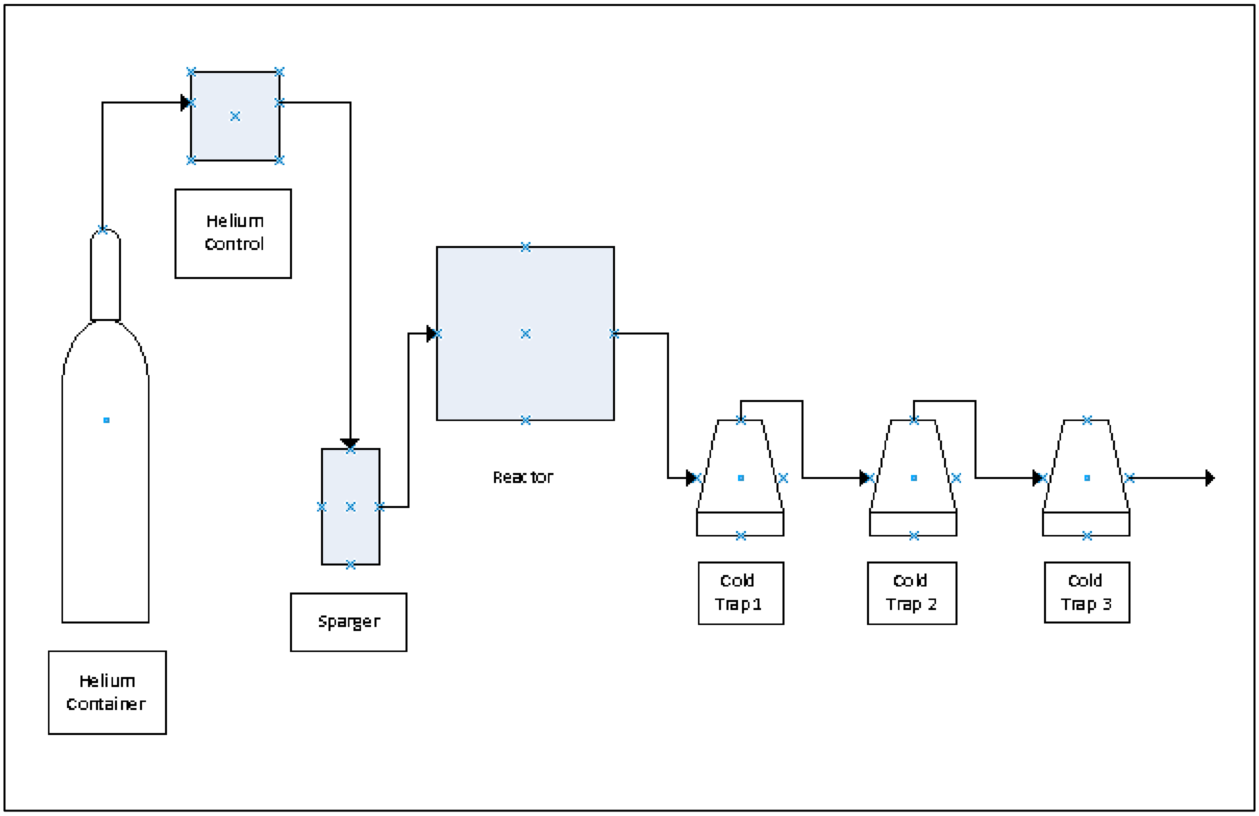

Figure 14: Flow reactor setup

The above system, seen in Figure 14, was the reactor system that was used for all of the molten salt and cellulose pyrolysis reactions. Helium, which was used as the carrier gas for the reaction due to its unreactive properties, was provided to the system by a compressed helium tank. A gas flow meter, manufactured by MKS Instruments, was used to propel the helium through the system. From the helium controller, the gas was sent to a sparger, which was used to purge any impurities in the reactor inlet line. From the sparger, the helium was sent to the reactor tube placed inside the tube furnace. From the furnace, the helium carrier gas transported all volatile components and gases produced in the reaction to the three consecutive cold traps. The cold traps were immersed in an ice bath so that the volatile components could condense and be collected. Figure 15, below is a picture of the flow reactor that was used.

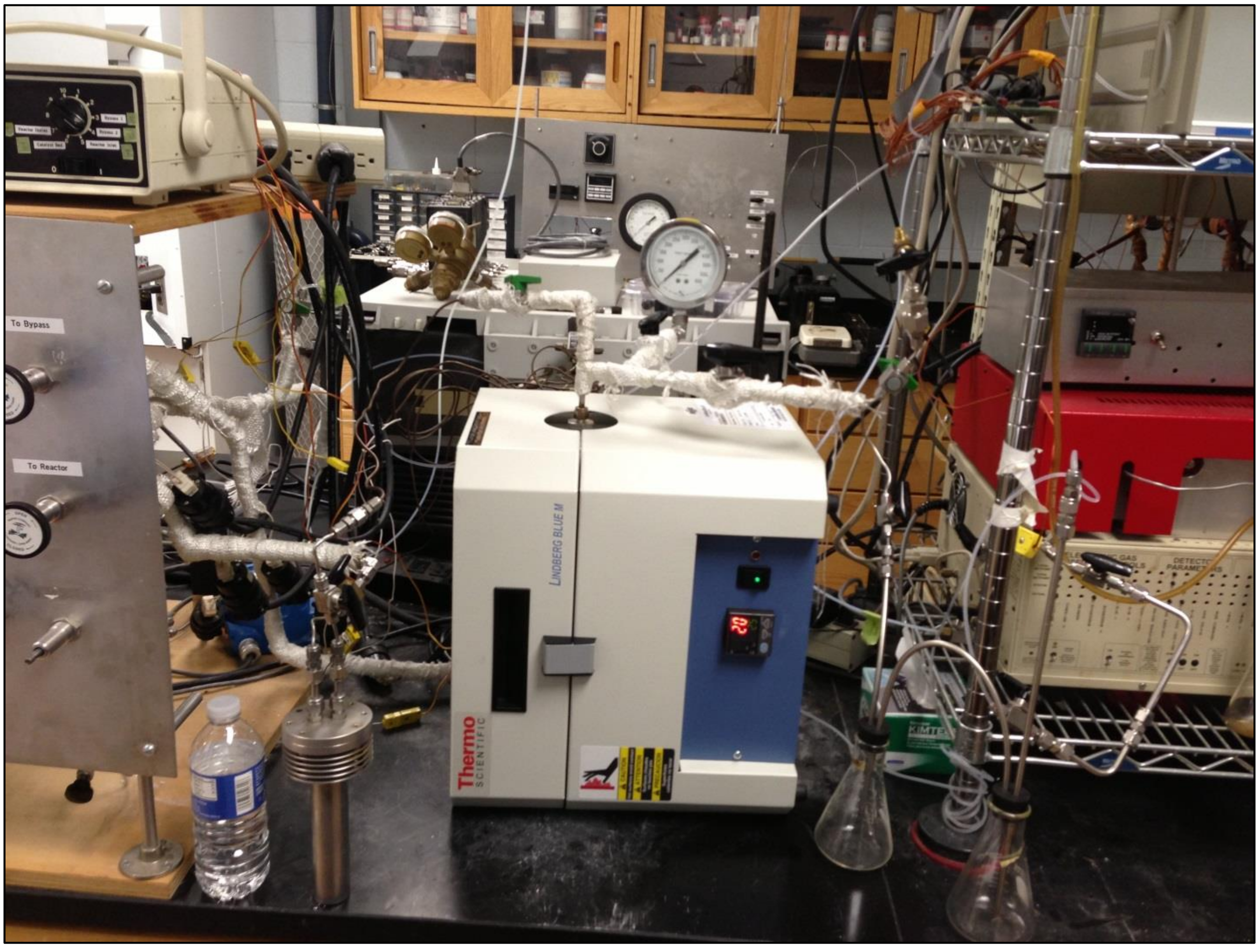

Figure 15: Reactor setup

3.3.2 Design Specifications of the Reactor Tube

The cellulose and molten salt combination was charged in a reactor tube which can be seen below in Figure 16. The reactor tube was a ¾ inch stainless steel tube which measured 14 inches in length. The top of the reactor tube was sealed by a Swagelok ¾ to ¼ inch reducing union. The bottom of the reactor tube was sealed by a Swagelok ¾ inch ferrule cap. These specifications are highlighted below in Figure 16.

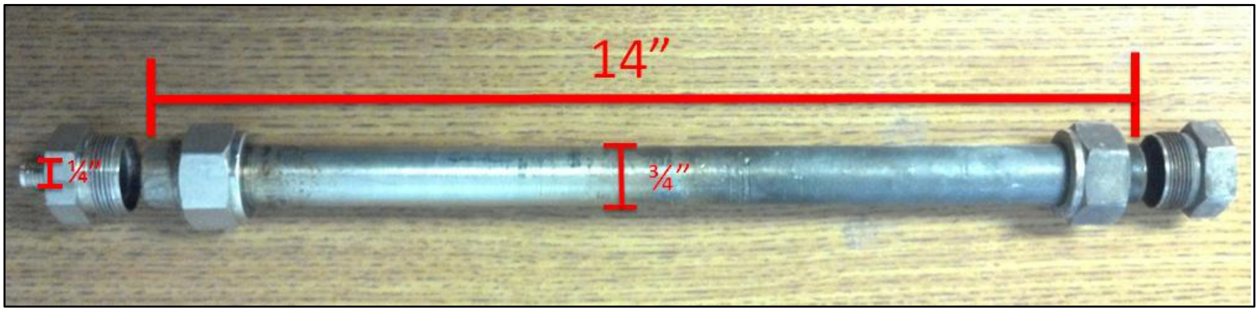

Figure 16: Reactor tube

The helium inlet line, which delivered helium to the bottom of the reactor tube, can be seen below in Figure 17. This inlet line protruded eight inches into the reactor tube from the reducing union in order to ensure that the gases and vaporized material would be carried out of the reactor tube.

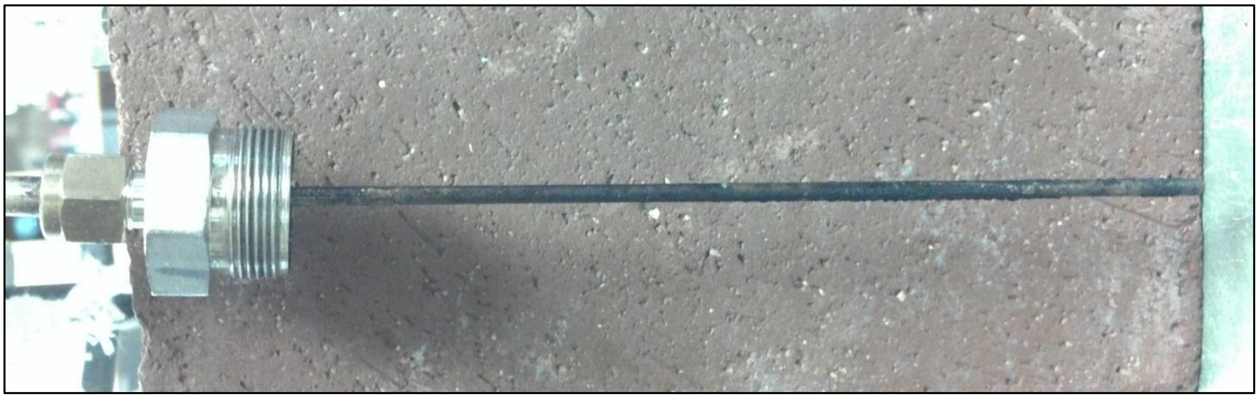

Figure 17: Helium gas inlet line

3.3.3 Furnace

The heat of the reaction was delivered by a Linberg/Blue Mini-Miite TF55030A Tube Furnace, which can be seen above in Figure 15. This furnace had the capability of reaching temperatures up to 1100^{o}C, with quick heat-up and cool-down rates. The furnace had an electronic display on its facade which displayed the set point temperature and the actual temperature. The electronic feature allowed for specific heating programs to be entered. This feature was utilized during the heating rate portion of this experiment. The furnace could be orientated either horizontally or vertically; it was utilized vertically for these experiments. The inside of the furnace contains insulation so that the fear of losing heat to the environment is reduced.

3.4 Flow Reaction Procedure

There were a multitude of steps in in order to complete any given flow reaction experiment; these steps are highlighted below.

1. The desired eutectic mixture was first determined. The necessary salts and the cellulose were massed on a scale in Goddard Hall 221, to the nearest thousandth of a gram.
2. The salts and cellulose were then combined in a mortar and pestle. The mixture was thoroughly mixed and grinded for several minutes in order to ensure even composition throughout. The amount of salt and cellulose used will be presented later in this chapter.
3. Next, the mixture was added to the reactor tube and the tube was sealed through the use of a wrench.
4. The flow system was then sealed completely. The helium gas canister was opened and the system was flushed with helium for 10 minutes. This ensured that no oxygen was present during the pyrolysis reaction.
5. Once the system had been flushed, the furnace was turned on and set to the desired temperature, typically 400°C for most trails. The reaction was then allowed to proceed for, at minimum, one hour, or until liquid ceased to be produced. If temperatures lower than 400°C were used, liquid product collection usually exceeded the one hour time period.

6. Once liquid product collection was over and the reaction had ended, the liquid products were extracted from the condensing flasks. The liquid was then massed and placed into 1-dram vials.
7. Once the system had cooled for about a half hour, the reactor tube was removed from the furnace. The reactor tube was then weighed, in order to determine the mass of the char. The char was then examined and the reactor tube was thoroughly cleaned.
8. Then the reactor lines and cooling flasks were all thorough cleaned to ensure that not liquid or char residue was left behind. Finally, the reactor flow was reassembled and readied for the next experiment

3.5 Liquid Product Retrieval

In the above pyrolysis reaction, volatile components were vaporized in the reactor tube and then condensed in Erlenmeyer flasks. Before and after each experimental trial, the flasks were massed in order to determine the liquid product yield of the reaction. Once the mass of the liquids had been determined, the liquid products were retrieved from the flasks, using a 1 mL graduate pipette was, which can be seen below in Figure 18. The liquids were transferred from the flasks to 1-dram vials. Before and after this transfer, the vials were massed in order to determine the mass of the attainable liquid. This was done because some of the liquid that was produced was very thick, which made liquid product retrieval very difficult. When the liquid was thick, it typically stuck to the flasks. Therefore, the difference between the mass of liquid retrieved and the mass of the attainable liquid is an indication of the viscosity of the liquid product.

Figure 18: Graduate pipette

Once all of the samples had been collected, it was imperative to analyze them using a GC/Mass Spec. However, before this could be done, they samples had to be filtered to ensure that no char, or other non-liquid substances were present. This was done through the use of 2mL mass spectrometer filter vials. These vials were then able to be placed directly into the GC/Mass Spec for analysis. The GC/MS procedure will be discussed later in this chapter.

3.3 Types of Experiments Conducted

In order to fulfill the objectives that were presented at the beginning of this chapter in 3.1 Objectives, it was necessary to conduct several different types of tests throughout this research. These tests included: cellulose baseline tests, final temperature tests, varying molar ratio tests, varying chloride eutectic tests, heating rate tests, and catalyst tests. All of these will be discussed below in the order in which they were conducted.

3.3.1 Cellulose Baseline Tests

In order to be able to compare the effects of using molten salts and catalysts on the pyrolysis reaction of cellulose, it was necessary to perform baseline cellulose tests. These tests were conducted using no molten salt or catalyst media. Five grams of cellulose was charged in the reactor tube and allowed to undergo pyrolysis. This test was conducted four times with end temperatures of 300^{o}C, 350^{o}C, 400^{o}C, and 450^{o}C. These examples were used only as a baseline and to compare the amount of liquid yielded with and without molten salts and catalysts.

3.3.2 Final Temperature Tests

It was also desirable to determine which final temperature for the pyrolysis reaction yielded the highest amount of liquid products. In order to do this, a 5:1 eutectic to cellulose molar ratio was used over a variety of six different temperatures. This molar ratio was chose for the final temperature tests due to the fact that this ratio allowed for near identical masses of both the eutectic and the cellulose. Since this test was one of the first, the ideal molar ratio between the eutectic and the cellulose was not yet known. The temperature range over which these tests were conducted was between 300^{o}C and 550^{o}C. Six trials were conducted at 50^{o}C increments starting at 300^{o}C and ending at 550^{o}C. Temperatures lower than 300^{o}C were not considered due to the fact that the chloride eutectic was not expected to melt completely below this temperature. Temperatures greater than 550^{o}C were not examined due to the fact that temperatures in excess of 550^{o}C would not be economically feasible to use in commercial production.

3.3.3 Varying Chloride Eutectic Tests

In almost all processes, it is extremely important to reduce the operating costs. One of the major operating costs associated with this process is the cost of the molten salts. Certain salts are less expensive than others; therefore, it was important to see if the more expensive salts, such as KCl and LiCl, could be substituted with a less expensive salt, such as NaCl. In order to determine if this was possible, the molten salt pyrolysis of cellulose was conducted using different combinations of $ZnCl_2$, KCl, LiCl, and NaCl. The list of the different combinations can be seen above in Table 1 of Chapter 3.2 Chloride Eutectic Selection. The liquid yield, product distribution, and salt costs were used in determining which eutectics were the most desirable.

3.3.4 Varying Molar Ratio Tests

It was also crucial to determine how much molten salt should be used in relation to the amount of cellulose. For example, should the cellulose only have minimal interaction with the molten salt, or should it be completely immersed in this media? In order to determine the answer to this, varying molar ratio tests were conducted. A wide range of these tests were examined using the eutectic mixture of 40 mole percent $ZnCl_2$, 40 mole percent LiCl, and 20 mole percent KCl. The molar ratios were based on the molecular weight of a monomer of cellulose (162.14 grams per mole) and the eutectic (36.75 grams per mole). The molecular weight and molar compositions of the eutectic are both based upon the metal element of the salt. For example, the molecular weight of $ZnCl_2$, for the mole ratio purposes, was assumed to be the molecular mass of zinc, 65.38g/mol. The tests began with a 1:10 molar ratio of cellulose to eutectic and ended with a final ratio of 20:1. The molar ratios that were used throughout these tests included the following:

- 1:10 mole ratio of cellulose to eutectic
- 3:10 mole ratio of cellulose to eutectic
- 1:2 mole ratio of cellulose to eutectic
- 7:10 mole ratio of cellulose to eutectic
- 9:10 mole ratio of cellulose to eutectic
- 1:1 mole ratio of cellulose to eutectic
- 10:9 mole ratio of cellulose to eutectic
- 10:7 mole ratio of cellulose to eutectic
- 10:5 mole ratio of cellulose to eutectic
- 10:3 mole ratio of cellulose to eutectic

- 10:1 mole ratio of cellulose to eutectic
- 20:1 mole ratio of cellulose to eutectic

After the completion of these tests, the highest liquid yielding ratio was considered as the most favorable.

3.3.5 Heating Rate Tests

In addition to determining the most desirable final temperature set-point, it was just important to determine the influence of the heating rate of the reaction. Once the ideal final temperature, molar ratio, and eutectic composition had been determined, these parameters were used to conduct the heating rate tests. Using the program feature of the electric furnace, several heating rate tests were completed. The furnace was programmed so that the reaction would be heated, started at 20^{o}C, by 5, 10, 20, 30, 40 and 60^{o}C per minute. 60^{o}C per minute represents that fasting heat time that could be achieving using the given furnace; this heating rate is referred to as rapid heating. 3.6 Catalyst Tests

Based upon the research conducted by the previous MQP group in 2012, the use of a catalyst seemed to be relevant in regards to liquid product yield and product distribution. Last year, however, a different eutectic chloride was used. Therefore, it was important to determine if the use of a catalyst had the same effect on the eutectic employed in this study. Two different catalysts were used in order to determine this. The two catalysts that were employed included ZSM-5 and Ni(II)OH_2. Unfortunately, due to time constraints, more than two catalysts could not be analyzed.

3.4 Sample Calculations

There were two certain calculations that were conducted after the completion of each experiment. These calculations included the total percent liquid yield and the total amount of char produced from the biomass. In order to calculate the percent liquid yield, the beaker that collects the condensing volatile components were weighed before the trail began and the masses were recorded. Then, after the reaction had completed, the beaker would be dried of all moisture on the outside of the beaker, and then reweighed with all of the produced liquid inside. Therefore the difference between the two masses of the beaker represented the total amount of liquid produced. This total liquid mass was then divided by the total mass of cellulose charged in the reactor and multiplied by 100 in order to produce a percent yield. The equation that was used for this calculation can be seen below in Equation 1.

$$\frac{Mass\ of\ beaker\ before - Mass\ of\ Beaker\ after}{Mass\ of\ cellulose\ charged} \times 100\% = Percent\ liquid\ yield$$

Equation 1: Calculation for percent liquid yield

In order to determine percent cellulose based char yield produced in the reactions, Equation 2 was used.

$$[(Mass\ of\ reactor\ after - Mass\ of\ reactor\ empty) - Mass\ of\ salt\ used] \times 100$$
$$= Percent\ char\ yield$$

Equation 2: Calculation of percent cellulose based char yield

Non-routine calculations will described in the Appendix of this report.

3.4 GC/MS Procedure and Product Analysis

In order to determine the composition of the samples that were produced, a Gas Chromatography and Mass Specification instrument a was used, located at Gateway Park and is picture below in Figure 19. The exact names of the instruments are:

- Agilent 7890 GC with Agilent HP-5MS 30m x 0.25mm x 0.25um column and Agilent 5183-4647 (870uL) split inlet liner

- Agilent 5975C VL MSD with Triple Axis Detector and Inert EI source
- Agilent G453A auto-sampler tower with Agilent G4514A 150 sample try

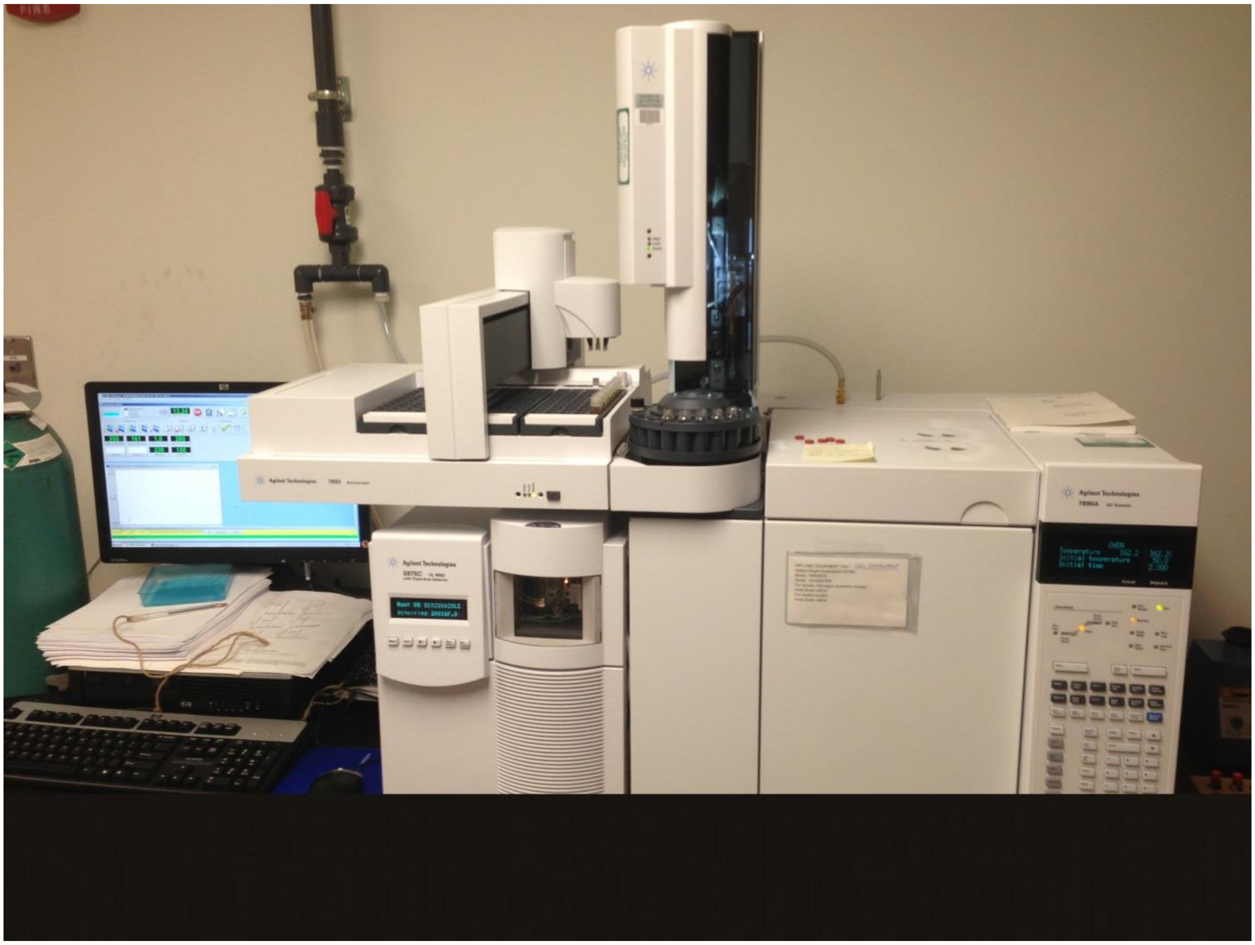

Figure 19: Agilent Technology 7890 Gas Chromatograph

About 450 µL of the samples were first filtered through Thompson 35540 filter vials in order to ensure no carbon residue was present in the samples. All of the vials were then placed in the auto-sampler trays. Once the analysis began, one µL of sample was injected into the GC with a 50:1 split. 54mL per minute of helium was used as the carrier gas. The column oven was first heated to 50^{o}C and held at this temperature for 10 minutes. The temperature was then increased to 180^{o}C at a ramp rate of 5^{o}C per minute. Then, the temperature was increase to 300^{o}C at a ramp rate of 15°C per minute. Finally, the column oven temperature was held at 300°C. The inlet temperature of the mass spectrometer was 280°C. The MS source was held constant at 230°C, and the MS quad was held constant at 150°C. There was no solvent delay for this analysis. The scan mode for the MS was m/z 5-550 (2 samples, 2.69 scans per second). The total run time for one sample was about 49 minutes. This was repeated for all of the samples. The samples that were analyzed included:

Table 3: Samples analyzed using GC/MS

Experiment Number	Zinc Chloride	Sodium Chloride	Potassium Chloride	Lithium Chloride
#	Mole %	Mole %	Mole %	Mole %
1	40	0	20	40
2	40	0	20	40
3	40	0	20	40
9	40	0	20	40
13	40	0	20	40
14	60	20	20	0
15	60	30	10	0
16	60	40	0	0
17	70	30	0	0
18	80	20	0	0
19	50	50	0	0
20	40	40	20	0
21	100	0	0	0
23	70	30	0	0
24	70	30	0	0
25	70	30	0	0
26	70	30	0	0
27	60	20	0	20
28	60	30	0	10
30	40	30	0	30
31	40	40	0	20
35	40	0	20	40
36	70	30	0	0
37	70	30	0	0
38	70	30	0	0
40	40	0	20	40
41	40	0	20	40
42	40	0	20	40

Almost all of the liquid samples that were produced were analyzed using the GC/MS; however, not all of them were. There were several reasons why certain samples were omitted. First, if there were samples that were produced under the same operating conditions and molten salt composition, they were not analyzed. Also, some of the samples produced a very thick and dense bio-oil with minimal amounts of yield. Because of this, it was difficult to extract the liquid from the cold traps and there was an insignificant amount of bio-oil captured to analyze. Finally, there were two samples that were lost during the transfer of the liquid from the original vials to the filter vials.

The results of the GC/MS analysis were used to determine the percent area of each compound in each sample. This was done by integrating the area of each peak on the mass spectrum. The area was calculated using computer software and a percent area was generated. The percent area is not the same at the percent mass. In order to convert the percent area to percent mass, a calibration curve would have had to been generated during the analysis process. However, a calibration curve was never generated and the product distribution of the samples is represented by the percent area of the mass spectrum. It would be advantageous in the future to reanalyze the data and perform a calibration curve.

3.5 Safety Procedures

Throughout the experimental portion of this study, many dangerous and hazardous situations were presented. Due to such situations, it was imperative to maintain a proper safety protocol throughout the entirety of this study. One major hazard of this research was the immense use of high heating temperatures for the reaction. The furnace was often in excess of 400^{o}C; therefore, heat resistant gloves had to be used if handling any components that had been heated by the furnace. Also, many of the chemicals that were utilized in this study are corrosive and/or harmful to the environment. When such chemicals were handled, latex gloves were worn at all times. In addition, the flow reactor was setup underneath a fume hood, so that no harmful fumes were emitted into the laboratory. Finally, all waste that was generated throughout this research was carefully sorted into municipal and hazardous waste. Sincere care was taken around all equipment used throughout Goddard Hall, specifically GH 222 and 221, and Gateway Park.

4. Results and Discussion

4.1 Pyrolysis versus Molten Salt Pyrolysis

The first stage of the experimentations was to conduct normal pyrolysis on cellulose alone, or a cellulose baseline test. This was done with the same procedures that were used throughout the entirety of this project; however, without any molten salts or catalysts. The results of these experiments can be seen below in Figure 20.

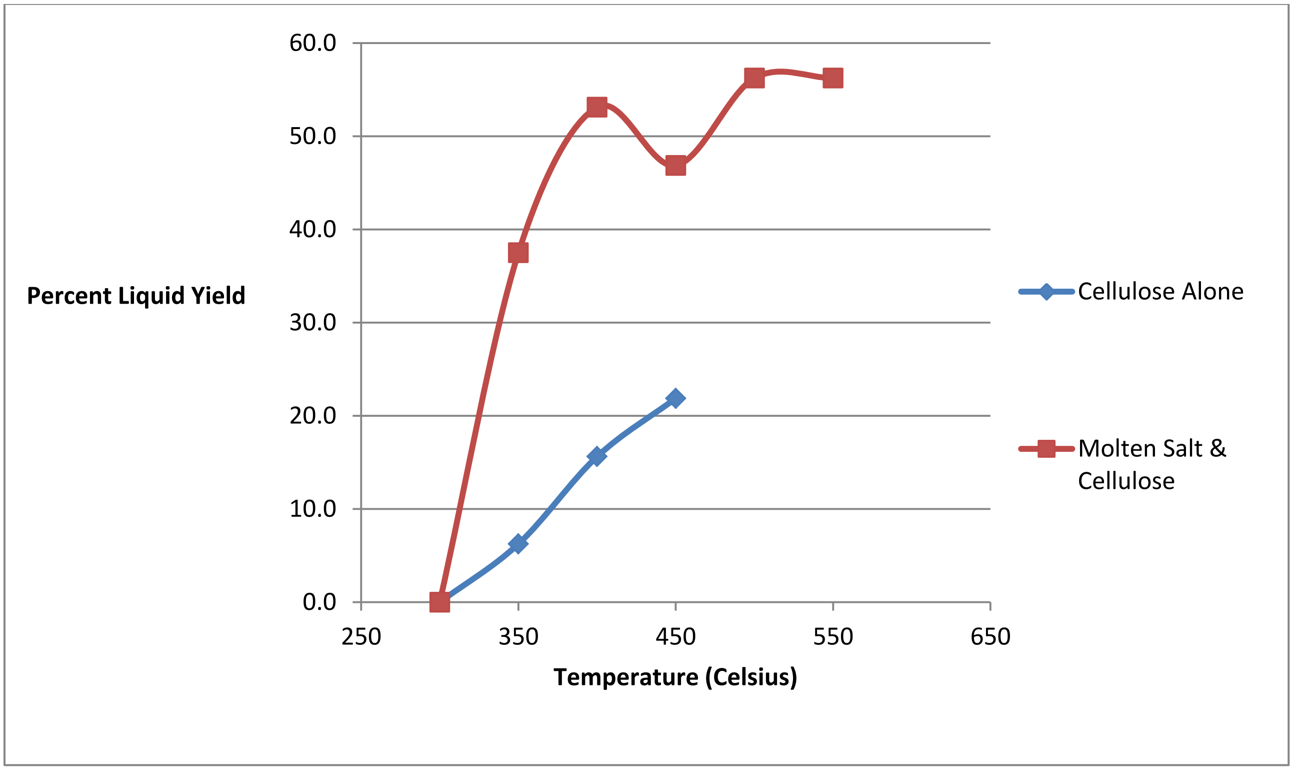

Figure 20: Pyrolysis versus molten salt pyrolysis

In Figure 20, there are two sets of data that are being presented. The first set, indicated in red, is the percent liquid yield through the use of molten salt pyrolysis. For these experiments, a 1 to 5 moles cellulose to moles eutectic ratio was used at the varying temperatures The second set, indicated in blue, is the percent liquid yield through the use of cellulose alone. The only experimental parameter that is different between the two sets of data is the presence of a 1 to 5 moles ratio in the data represented with the red data points. The highest percent liquid yield that was attained through the use of molten salt pyrolysis during the baseline test of cellulose was 56.3%at 550^{o}C. The highest percent liquid yield that was gathered through using cellulose alone was only 21.9% at 450^{o}C. Comparatively, the percent of liquid that was generated at 450^{o}C using molten salts was 46.9%. This clearly indicated that the amount of liquid that was produced was much higher using molten salts, rather than cellulose alone.

4.2 Final Temperature Tests

The experiment was conducted over a range of temperatures in order to determine which final temperature was the most ideal for this reaction. The range of temperatures that was used was 300^{o}C – 550^{o}C, at 50^{o}C increments. All of these experiments were conducted through the use of a 1 to 5 mole cellulose to moles eutectic molar ratio. The results of these experiments are shown below in Figure 21.

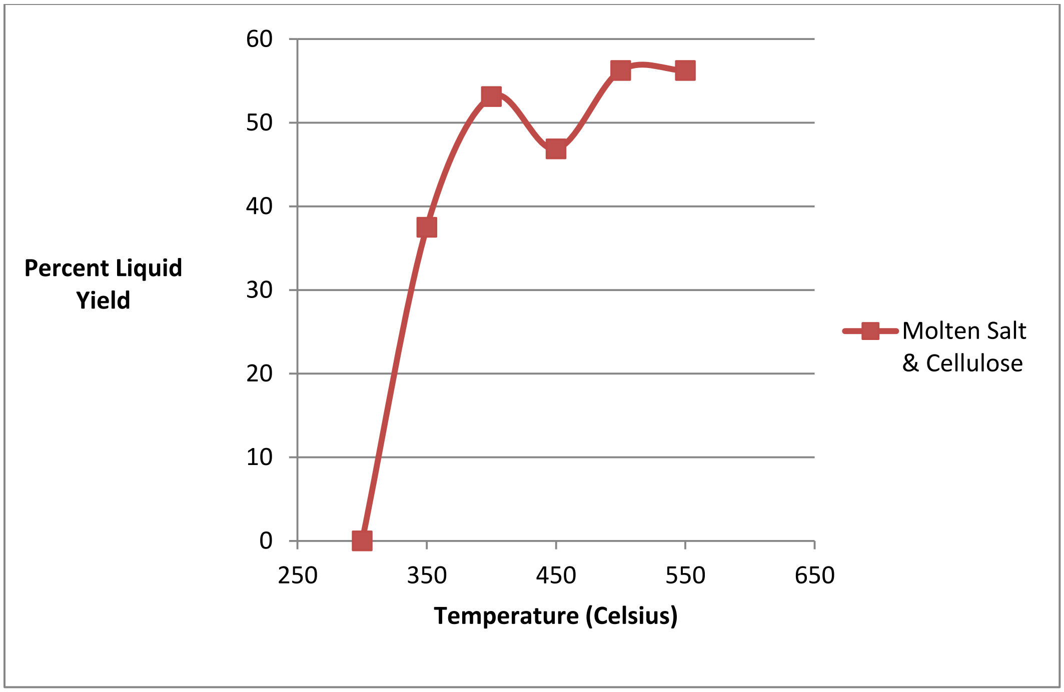

Figure 21: Final reaction temperature tests

This is the same data set that was used to compare the benefits of using molten salts to cellulose alone. There was zero percent liquid yield at the temperature of 300°C. The yield then increased to 37.5% when a final temperature of 350°C was used. There was another increase in percent liquid yield at 400°C; there was 53.1% liquid yield at this temperature. At 450°C, a decrease in percent liquid yield was observed. It is believed that this decrease can be attributed to slight experimental error. However, at both 500°C and 550°C, the percent liquid yield increased back up to expected levels at 56.3% for both temperatures. Since the yields at 400°C, 550°C, and 550°C were within 3.2% liquid yield, it was determined that the amount of liquid produced began to level off around 400°C. Also, since there is only a difference of 3.2% liquid yield between 400°C and 550°C, it was determined that 400°C is the ideal final reaction temperature for this reaction. An increase of 150°C, and the energy costs associated with this increase, does not justify using the higher temperature due to the little difference in the amount of liquid produced.

4.3 Varying Chloride Eutectic Tests

Once the ideal reaction temperature was determined to be 400°C, the next step was to determine which eutectic chloride produces the highest percent liquid yield. In addition to determining which mixtures yield the most liquid, it was also beneficial to determine if more expensive salts, such as lithium chloride and potassium chloride, could be substituted with a less expensive salt, sodium chloride. For example the cost of potassium chloride with greater than or equal to purity of 99.0%, is $60.20 per kilogram. The cost of lithium chloride with greater than or equal to purity of 99.0% is $187.80 per kilogram. However, the cost of sodium chloride with greater than or equal to purity of 99.0% is only $36.90 per kilogram. Because of this, if a chloride mixture using less expensive salts could produce high liquid yields, it would be beneficial continue research in such mixtures. The results of the varying chloride eutectic tests can be seen below in Table 4.

Table 4: Varying chloride eutectic results

Experiment Number	ZnCl2	NaCl	KCl	LiCl	Liquid Yield
#	Mol %	Mol %	Mol %	Mol %	%
13	0.4	0	0.2	0.4	67.7
17	0.7	0.3	0	0	61.1
16	0.6	0.4	0	0	61
30	0.4	0.3	0	0.3	59.2
21	1	0	0	0	57.4

15	0.6	0.3	0.1	0	55.6
14	0.6	0.2	0.2	0	55.3
18	0.8	0.2	0	0	53.8
26	0.7	0.3	0	0	53.8
19	0.5	0.5	0	0	53.6
25	0.7	0.3	0	0	53.5
29	0.5	0.3	0	0.2	51.9
28	0.6	0.3	0	0.1	50.3
27	0.6	0.2	0	0.2	47.3
23	0.7	0.3	0	0	46.1
24	0.7	0.3	0	0	45.9
31	0.4	0.4	0	0.2	41.6
22	0.7	0.3	0	0	41.1
20	0.4	0.4	0.2	0	40.8

All of these experiments were conducted using the same reactions conductions. For example, the final temperature for all of these experiments was 400^{o}C and the mole ratios were 1 to 20 mole cellulose to moles eutectic. Table 4, is organized with the higher liquid yielding eutectic composition at the top. This is followed by the compositions yielding less liquid in decreasing order. As it is indicated above, the chloride eutectic composition of 40 molar percent zinc chloride, 40 molar percent lithium chloride, and 20 molar percent potassium chloride, was able to attain the highest percent liquid yield at 67.7%. The composition of 70 molar percent zinc chloride and 30 molar percent sodium chloride was able to generate the second largest percent liquid yield at 61.1%. Since the liquid percent yield was the highest using 40 molar percent zinc chloride, 40 molar percent lithium chloride, and 20 molar percent potassium chloride, this composition was determined to be the ideal chloride eutectic composition. Therefore, this composition was used throughout the remainder of the experiments.

4.4 Varying Molar Ratio Tests

Once the ideal eutectic composition was determined, it was important to figure out the best cellulose to eutectic molar ratio. For example, it seemed likely that the use of more eutectic, in relation to cellulose, would yield a higher percent liquid yield. In order to determine if there was an ideal ratio, a wide range of ratios were tested. These ratios included: 10 to 1, 10 to 3, 10 to 5, 10 to 7, 10 to 9, 1 to 1, 9 to 10, 7 to 10, 5 to 10, 3 to 10, 1 to 10 and 1 to 20 moles cellulose to moles eutectic. The results of these experiments can be seen below in Figure 22: Varying mole ratio test results.

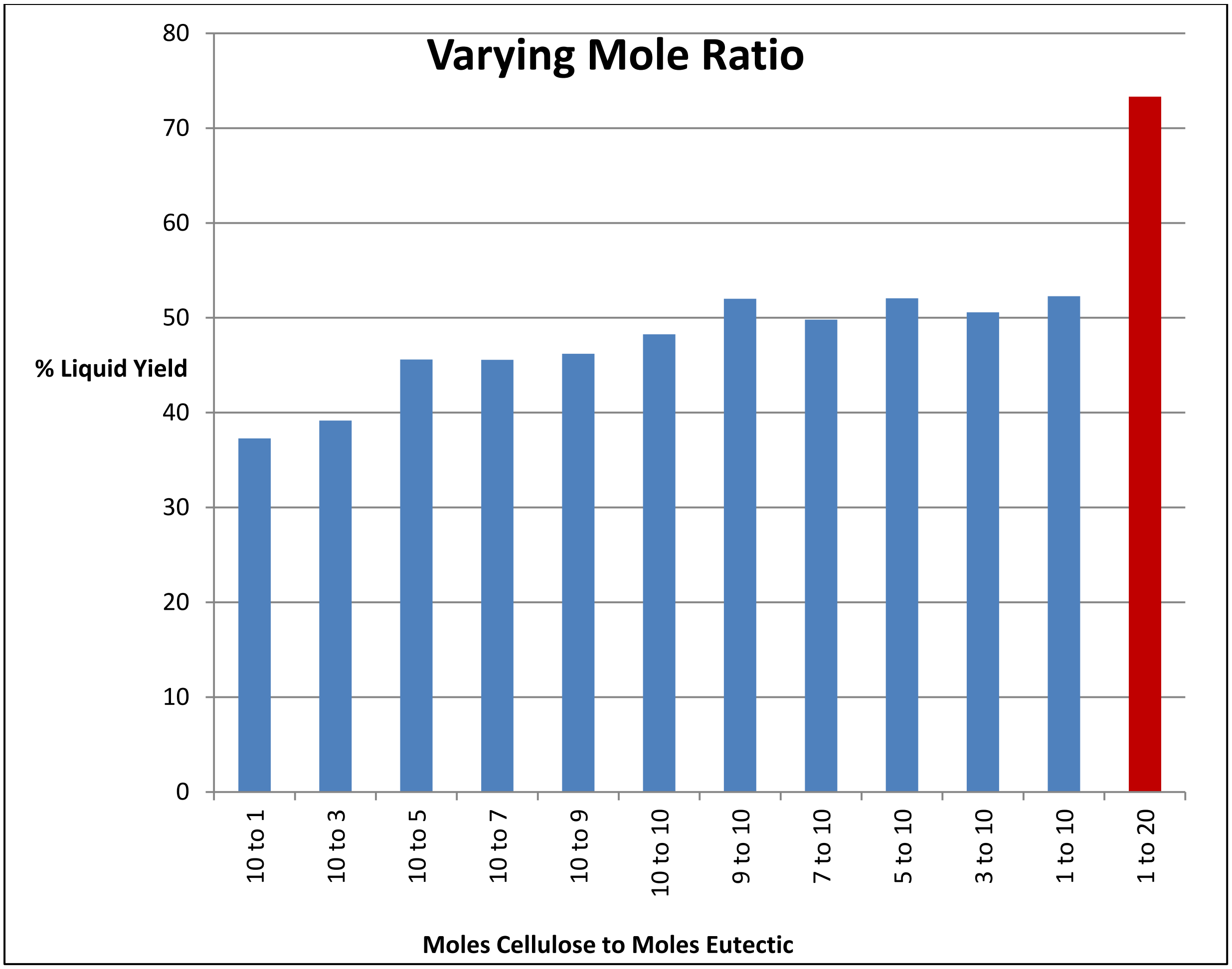

Figure 22: Varying mole ratio test results

The first test that was conducted was the mole ratio of 10 to 1 moles cellulose to moles eutectic. This ratio produced the lowest percent liquid yield, which was expected due to it is most similar to the experiments conducted with cellulose alone. As the mole ratio of moles cellulose to moles eutectic was increased, the percent liquid yield increased. After it was determined that a mole ratio of 1 to 10 moles cellulose to moles eutectic yielded 52.3% liquid yield, it seemed likely that this percent liquid yield would continue to increase with an increase of the moles of eutectic used. Therefore, a mole ratio of 1 to 20 moles cellulose to moles eutectic was tested. This mole ratio was able to yield the highest amount of liquid that was observed throughout the experimentations, 73.3% liquid yield. A higher mole ratio would have been beneficial to see if this percent yield would continue to increase. However, the size of the reactor limited the amount of substances that could be placed inside the reactor. Because of this, a mole ratio higher than 1 to 20 was not tested. It is believed that if a substantially high mole ratio, such as 1 to 100 could be tested, the percent liquid yield would likely near 100%. This is due to the fact that the cellulose would be completely submerged in molten salt, allowing for a higher percent liquid yield. Since a mole ratio of 1 to 20 moles cellulose to moles eutectic was the highest liquid yielding ratio observed, this ratio was used for the remainder of the experiments and determined to be the ideal ratio.

4.5 Heating Rate Tests

The final experimental parameter that was tested was the heating rate of the reaction. In order to test what the ideal heating rate is for this reaction, programs were setup within the furnace using the programmable controls. The heating rates that were tested include 10, 20, 30, 40 and 60°C per minute. The results of these experiments can be seen below in Figure 23.

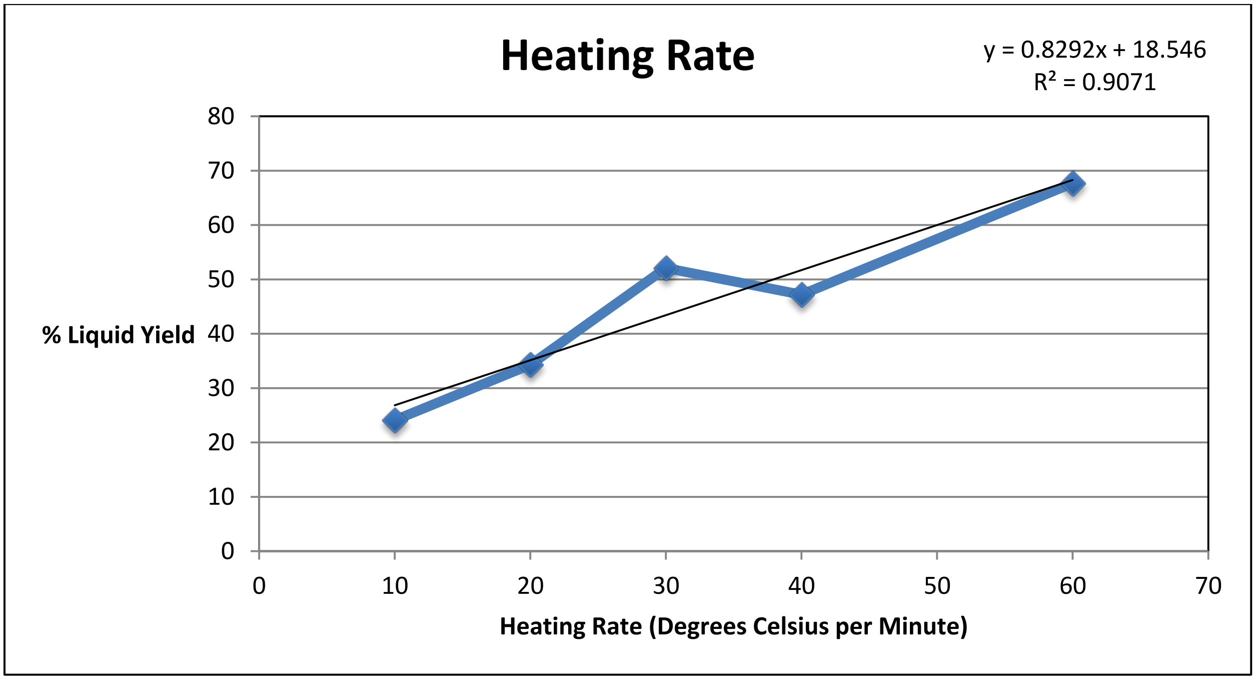

Figure 23: Heating rate test results

In these experiments, 60°C per minute was the highest attainable heating rate and is therefore referred to as rapid heating. The furnace that was used during these experiments did not allow for a heating rate faster than this. Rapid heating was employed by placing the reactor within the furnace, setting the desired end temperature (400°C), and allowing the furnace to heat as fast as possible. The lowest percent liquid yield that was attained during these trails was 24.1% liquid yield at 10°C per minute. The highest percent liquid yield was generated using rapid heating conditions.

The likely reason that a low heating rate correlates to a low liquid yield is because this is a pyrolysis reaction. As mentioned above in the literature section of this paper, there are several types of pyrolysis reactions. Conventional pyrolysis employs low heating rates and thus yields a higher char product. Fast pyrolysis uses a high heating rate and therefore yields a higher liquid yield. This indicates that in these experiments, it is expected that higher heating rates yield greater amounts of liquid products. It would be beneficial to test molten salt pyrolysis with heating rates closer to the ones used in fast pyrolysis, such as 1000 K per minute. However, due to the limitations of the available furnace, a heating rate much lower than this had to be used.

4.6 GC/MS Results

Through analyzing the results with the GC/MS, it was possible to draw a clear picture of the product distribution in the liquid attained. The composition of the molten salts used for each experiment can be seen in below in Table 5.

Table 5: Experiments analyzed using the GC/MS

Experiment Number	Zinc Chloride	Sodium Chloride	Potassium Chloride	Lithium Chloride
#	Mole %	Mole %	Mole %	Mole %
1	40	0	20	40
2	40	0	20	40
3	40	0	20	40
9	40	0	20	40

13	40	0	20	40
14	60	20	20	0
15	60	30	10	0
16	60	40	0	0
17	70	30	0	0
18	80	20	0	0
19	50	50	0	0
20	40	40	20	0
21	100	0	0	0
23	70	30	0	0
24	70	30	0	0
25	70	30	0	0
26	70	30	0	0
27	60	20	0	20
28	60	30	0	10
30	40	30	0	30
31	40	40	0	20
35	40	0	20	40
36	70	30	0	0
37	70	30	0	0
38	70	30	0	0
40	40	0	20	40
41	40	0	20	40
42	40	0	20	40
43	40	0	20	40

4.6.1GC/MS Results - Varying Molar Ratio Tests

As mentioned earlier, not all of the samples were analyzed; however, the majority of them were. The results of the analysis for experiment one can be seen below in Figure 24. This experiment was conducted during the molar ratio tests. A mole ratio of 1 to 10 moles cellulose to moles eutectic was used; therefore, there was much less eutectic than cellulose. It can be seen that there is a wide variety of different products that were formed during this reaction. There were 13 different compounds that were identified and two compounds that were unidentifiable. The major product that was formed was water at 72 percent area. The second highest yielding compound was furfural at 14 % area. The liquid, char, and gas weights for this experiment can be seen below in Table 6.

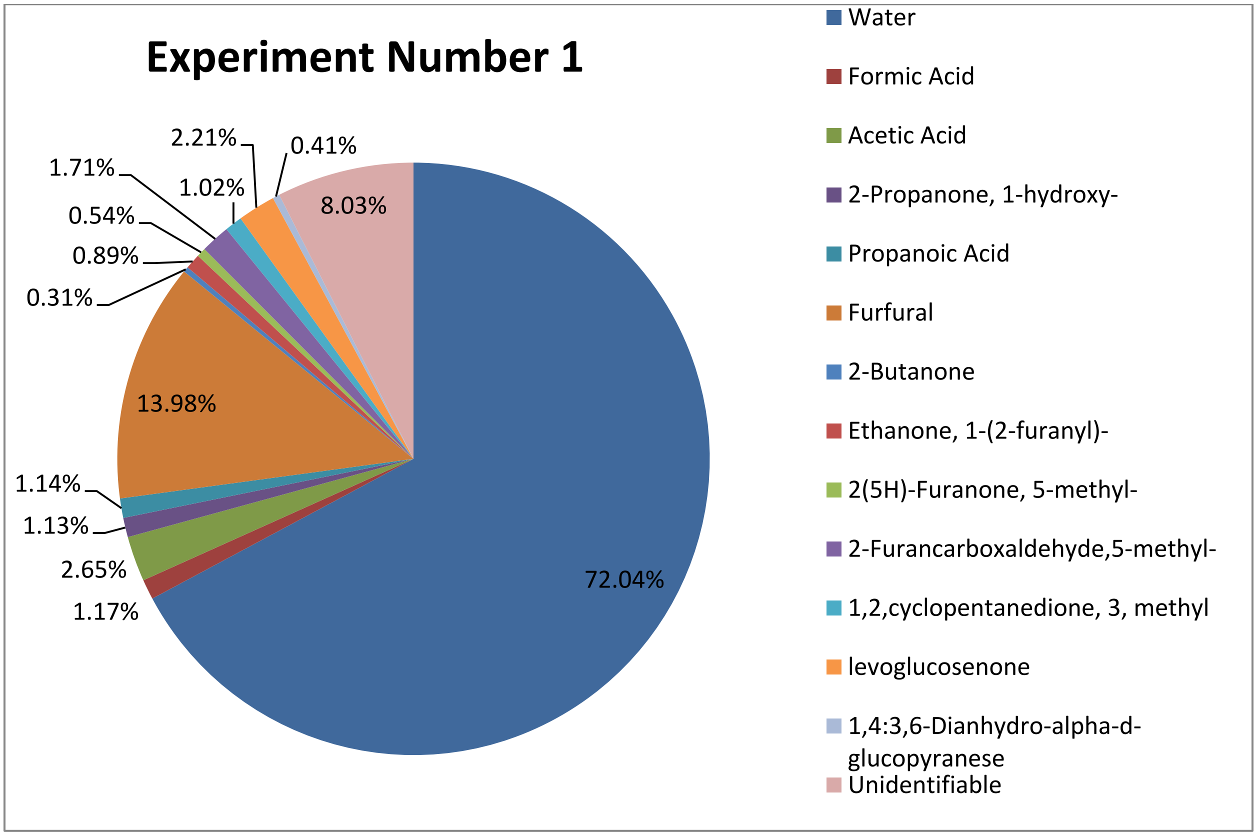

Figure 24: Product distribution of experiment number 1

Table 6: Liquid, char, and gas prodcuts for experiment number 1

10 to 1 Molar Ratio (5g Cellulose)		
	Mass	Yield
Liquid	1.9g	38%
Char	1.4g	28%
Gas	1.7g	34%

The product distribution of experiment 2, seen below in Figure 25, is very similar to the product distribution of experiment 1. The reason for this is that experiment number 2 had a mole ratio of 10 to 3 moles cellulose to moles eutectic. The product distribution for both experiment numbers 1 and 2 are very similar to the product distribution that was be expected for fast pyrolysis. There is a wide variety of different products and only furfural has a high yield.

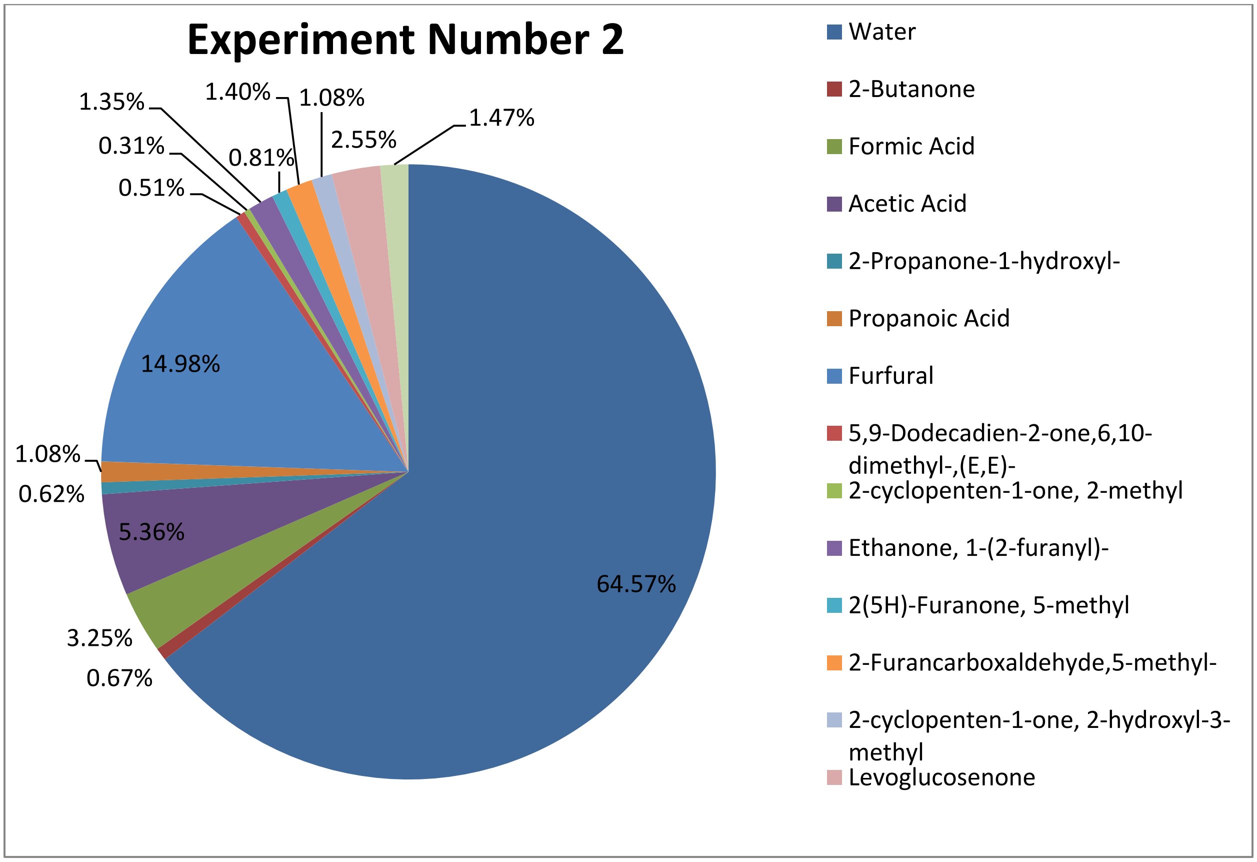

Figure 25: Product distribution of experiment number 2

Table 7: Liquid, char, and gas products for experiment number 2

10 to 3 Molar Ratio (5g Cellulose)		
	Mass	Yield
Liquid	2.0g	40%
Char	1.5g	30%
Gas	1.5g	30%

When the results of experiments 1 and 2 are compared to the GC/MS results of experiment 9, seen below in Figure 26, it is evident that the product distribution is beginning to yield a lower variety of products. Experiment number 9 had a 5 to 10 cellulose to eutectic mole ratio. The amount of molten salt in experiment 9 is higher than in both experiments 1 and 2.

There were only 7 different compounds products during this reaction, compared to the 14 that were produced in the earlier reactions. This indicates that the increasing presence of molten salt decreases the product distribution and allows the reaction to be more selective. This is confirmed in the product distribution of experiment 13 (1:20 cellulose to eutectic mole ratio), seen in Figure 27 which yielded only six different chemical compounds.

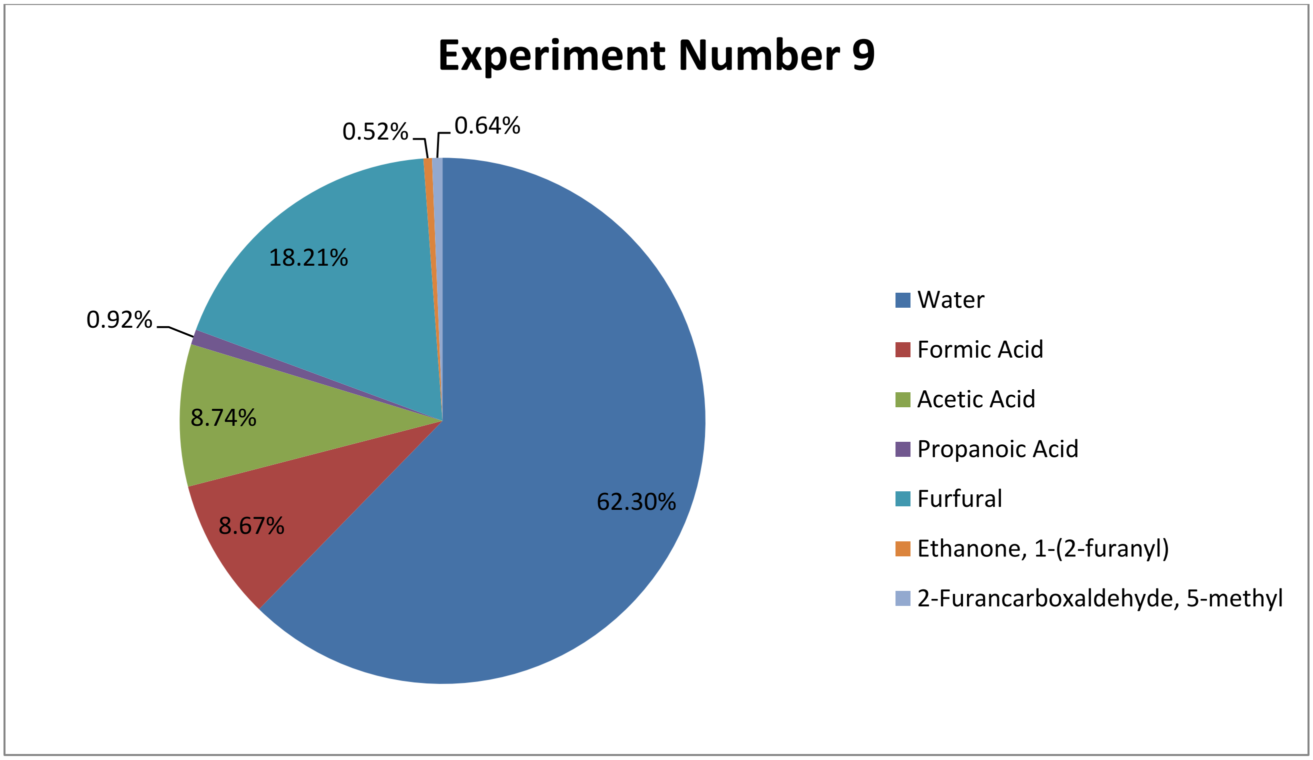

Figure 26: Product distribution of experiment number 9

Table 8: Liquid, char, and gas products for experiment number 9

5 to 10 Molar Ratio (5g Cellulose)		
	Mass	Yield
Liquid	2.6g	52%
Char	1.2g	24%
Gas	1.2g	24%

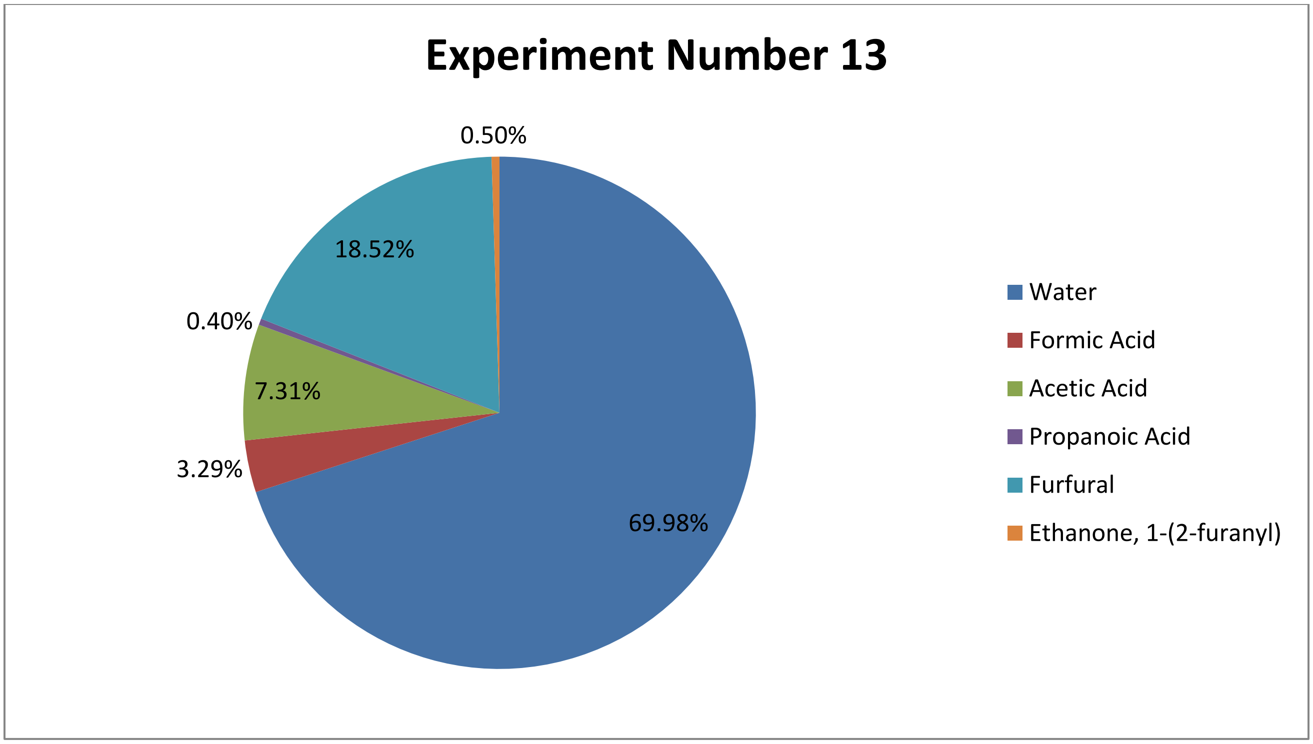

Figure 27: Product distribution of experiment number 13

Table 9: Liquid, char, and gas products for experiment number 13

1 to 20 Molar Ratio (2g Cellulose)		
	Mass	Yield
Liquid	1.35g	67.5%
Char	.03g	1.5%
Gas	.62g	31.0%

As seen in Table 7, Table 8, and Table 9 the percent mass produced relative to the mass of the cellulose used, increased with a higher mole ratio as well. These results have previously been discussed in Chapter 4.4 Varying Molar Ratio Tests. However, it is interesting to note that the mass of the char produced significantly decreased with an increase in the amount of eutectic used.

4.6.2 GC/MS Results – Varying Chloride Eutectic Samples

The product distributions for the remaining experiments with a 1 to 20 cellulose to eutectic mole ratios, yielded similar results. Typically, there were six major products that were formed in the remaining samples. These chemical compounds included water, formic acid, acetic acid, propanoic acid, furfural, and, ethanone 1-(2-furanyll).Experiments 13 through 31 were part of the varying eutectic chloride composition tests, in which different molar percentages of the salt were used. It was evident that the type of salts used clearly effected which types of products would form. For example, when sodium chloride was introduced to the molten salt mixture in experiment 14 (60mol% $ZnCl_2$, 20mol% NaCl and 20mol% LiCl), there was an increase in the percent of water present; from 70% in experiment 13 to 77% in experiment 14. While the water amount increased with the use of sodium chloride, the amount of furfural decreased; from 18.5% in experiment number 13 to 12.6% in experiment number 14.

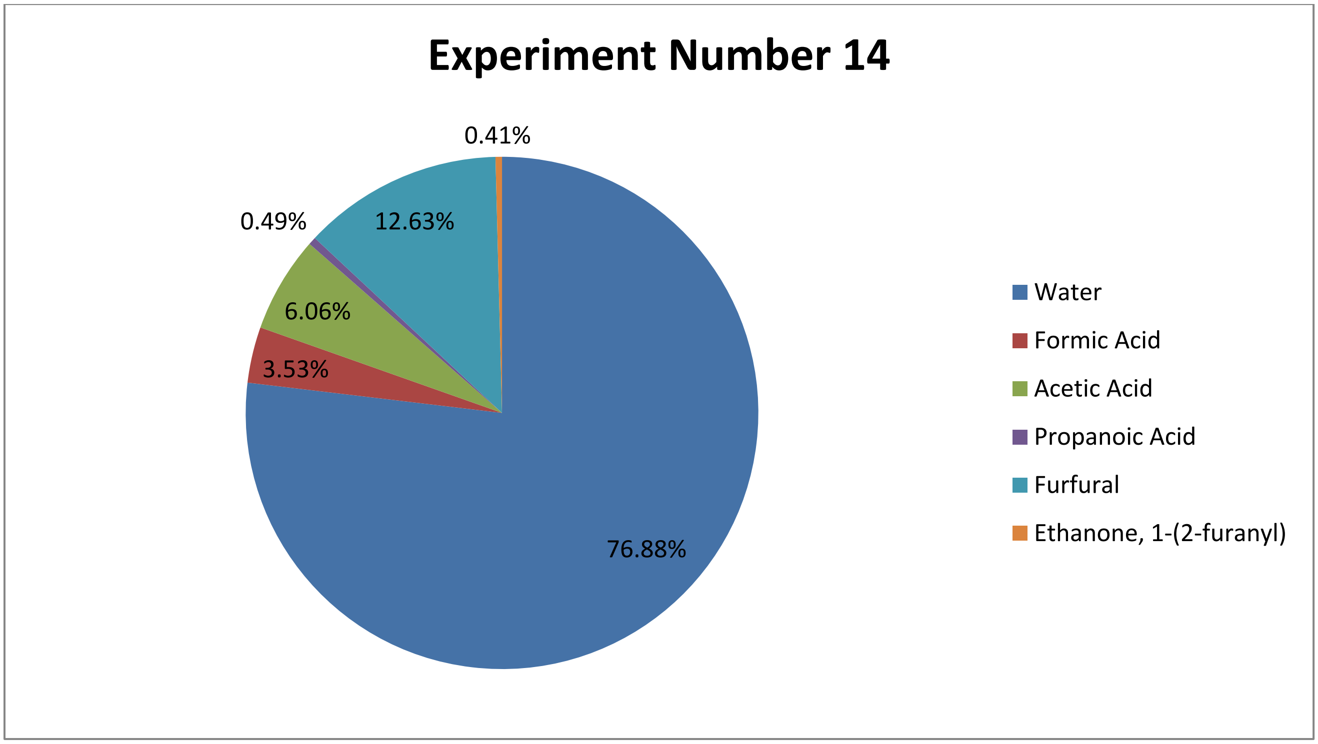

Figure 28: Product distribution for experiment number 14

Table 10: Liquid, char, and gas products of experiment number 14

1 to 20 Molar Ratio (1.3g Cellulose)		
	Mass	Yield
Liquid	0.72g	55.4%
Char	0.12g	9.2%
Gas	0.42g	32.3%

This trend continued in experiment 15 when the molar percent of sodium increased from 20 mol% in experiment 14 to 30 mol%. With this increase of sodium chloride, the percent water produced increased to 80.3% and the percent furfural produced decreased to 11%. This can be seen below in Figure 29. Also, only zinc chloride and sodium chloride salts were used in experiments 16-19. Although the percent mole was slightly different for these experiments, these ones that contained only zinc chloride and sodium chloride produced very similar product distributions. Typically 80% water, 6% furfural, and 8% acetic acid was produced in these experiments. This can be seen below.

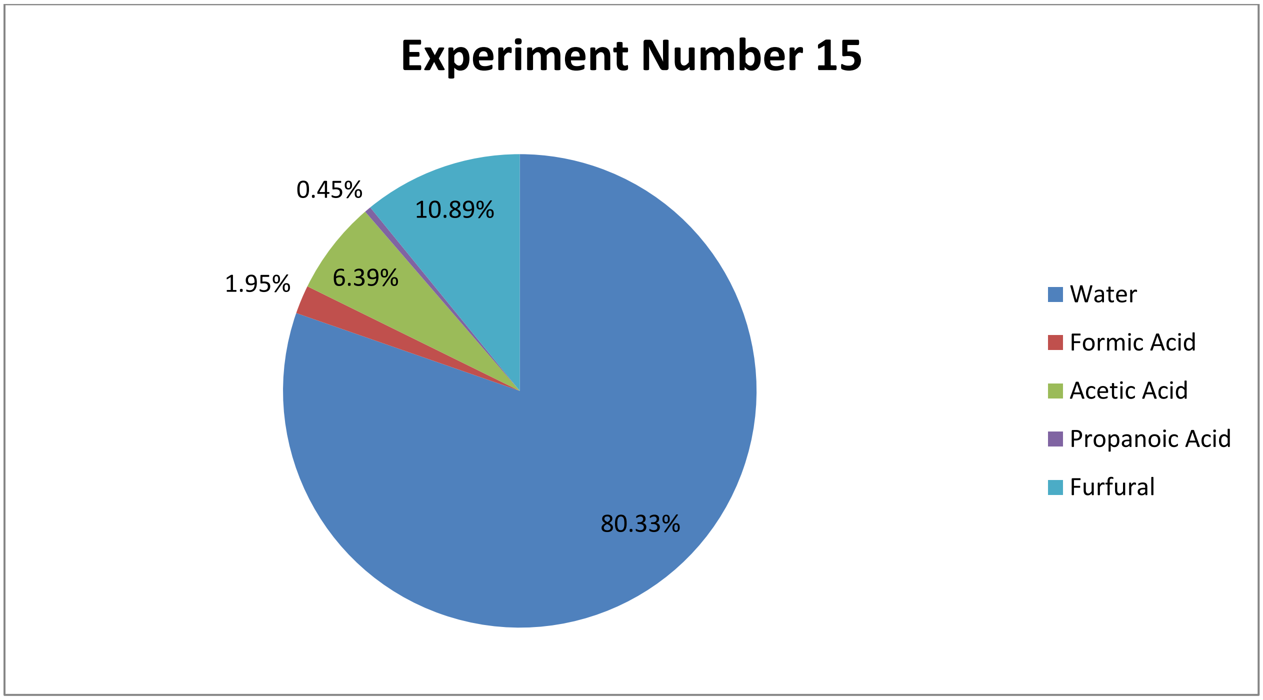

Figure 29: Product distribution for experiment number 15

Table 11: Liquid, char, and gas products for experiment number 15

1 to 20 Molar Ratio (1.3g Cellulose)		
	Mass	Yield
Liquid	0.72g	55.4%
Char	0.28g	21.5%
Gas	0.30g	23.1%

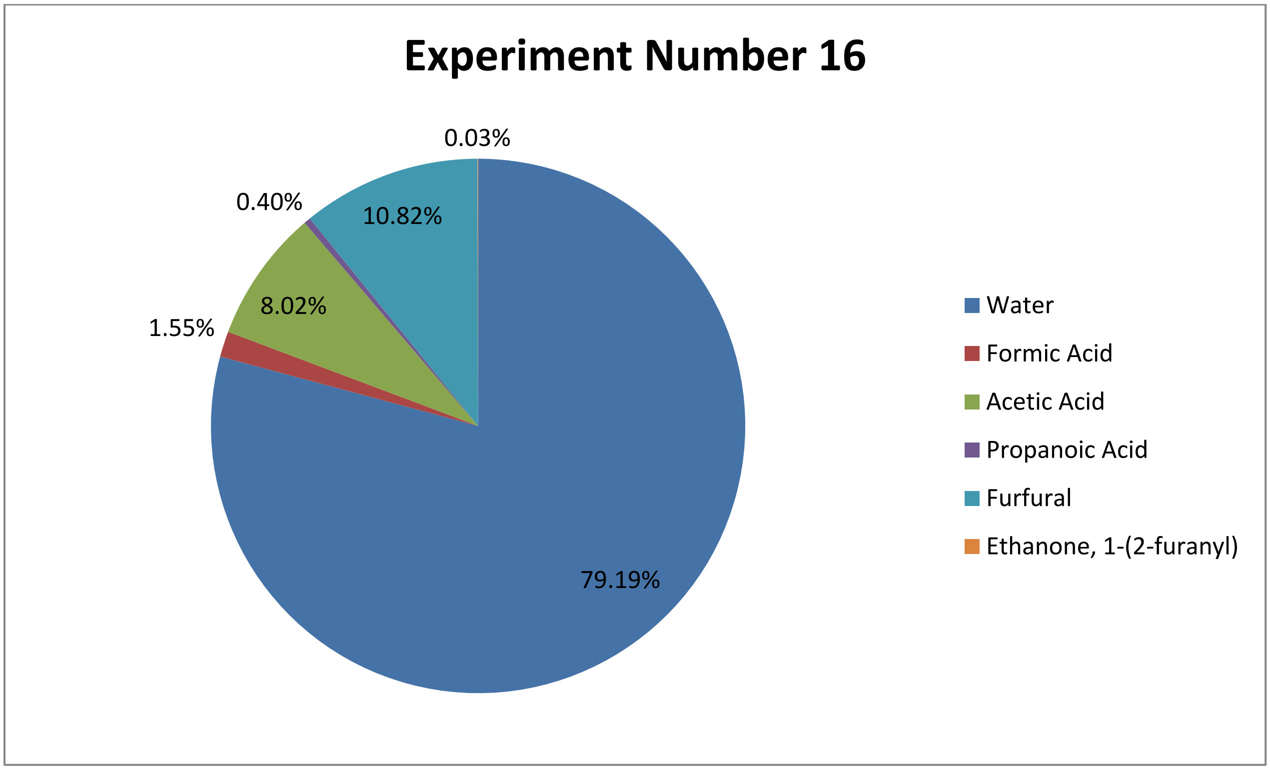

Figure 30: Product distribution of experiment number 16

Table 12: Liquid, char, and gas products for experiment number 16

1 to 20 Molar Ratio (1.3g Cellulose)		
	Mass	Yield
Liquid	0.79g	60.8%
Char	0.33g	25.4%
Gas	0.18g	13.8%

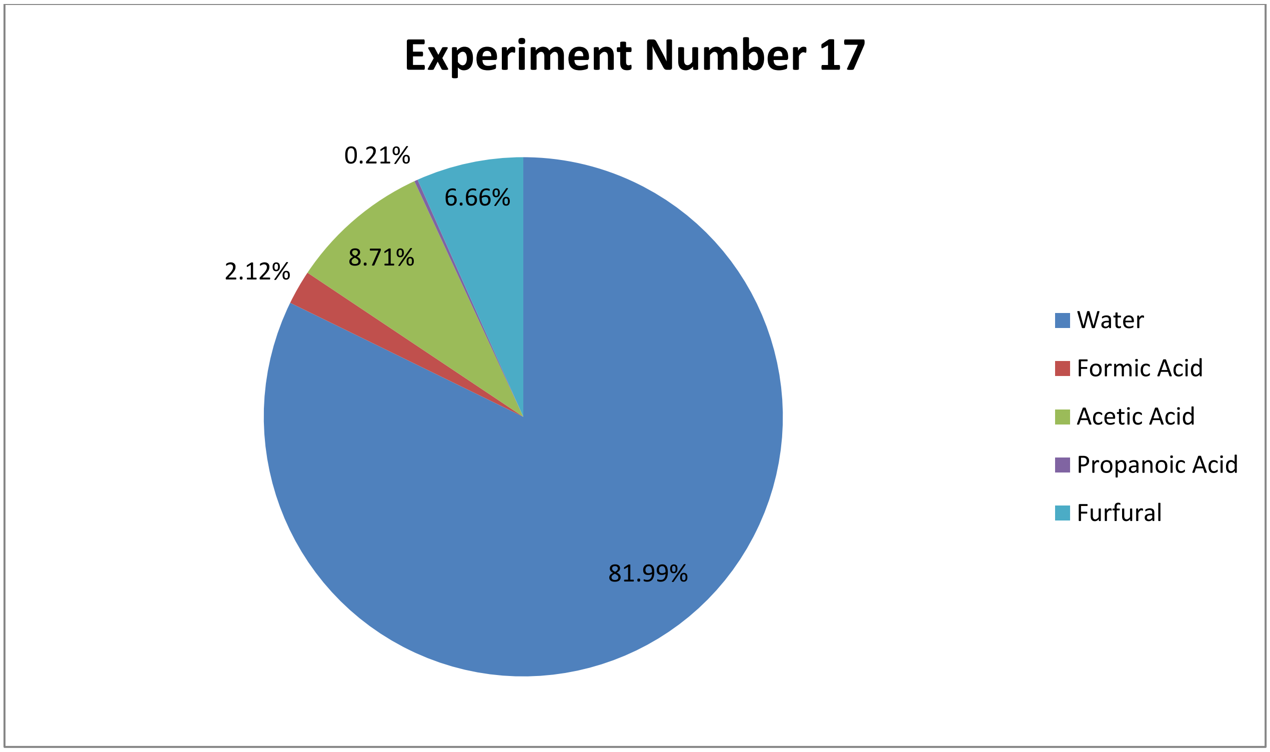

Figure 31: Product distribution of experiment number 17

Table 13: Liquid, char, and gas products of experiment number 17

1 to 20 Molar Ratio (1.3g Cellulose)		
	Mass	Yield
Liquid	0.79g	60.8%
Char	0.06g	4.6%
Gas	0.45g	34.6%

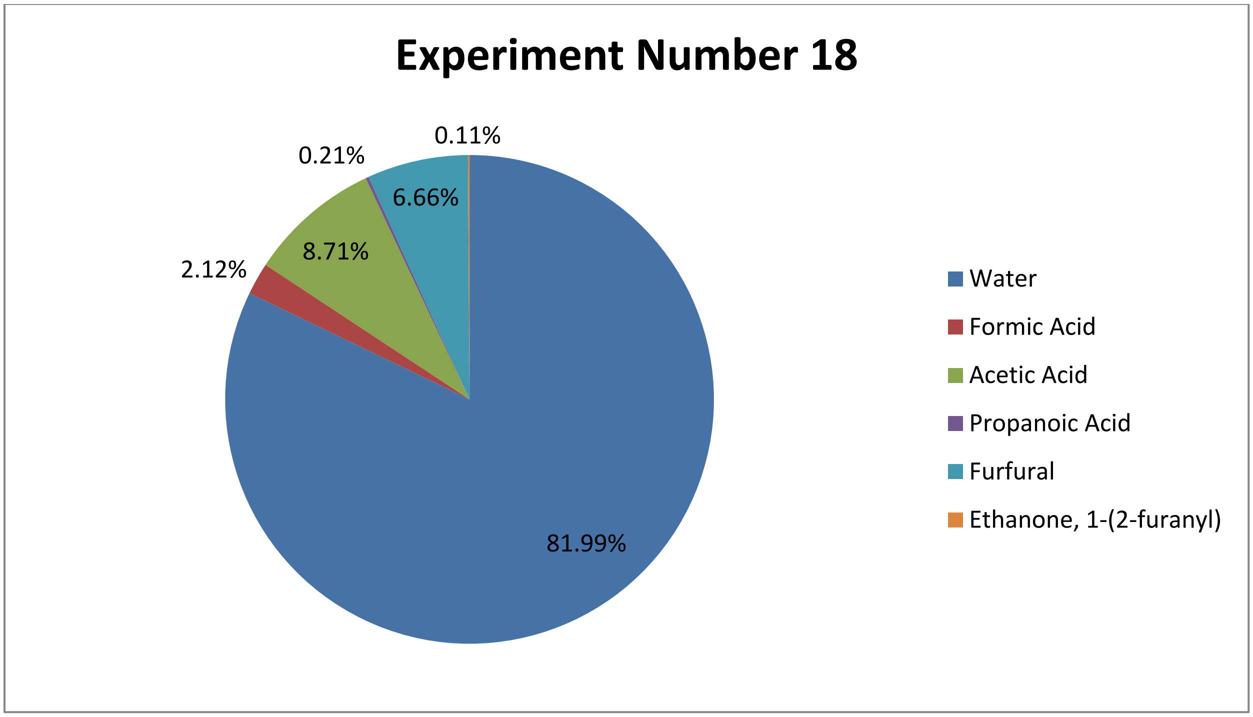

Figure 32: Product distribution of experiment number 18

Table 14: Liquid, char, and gas products of experiment number 18

1 to 20 Molar Ratio (1.3g Cellulose)		
	Mass	Yield
Liquid	0.70g	53.8%
Char	0.18g	13.8%
Gas	0.42g	32.3%

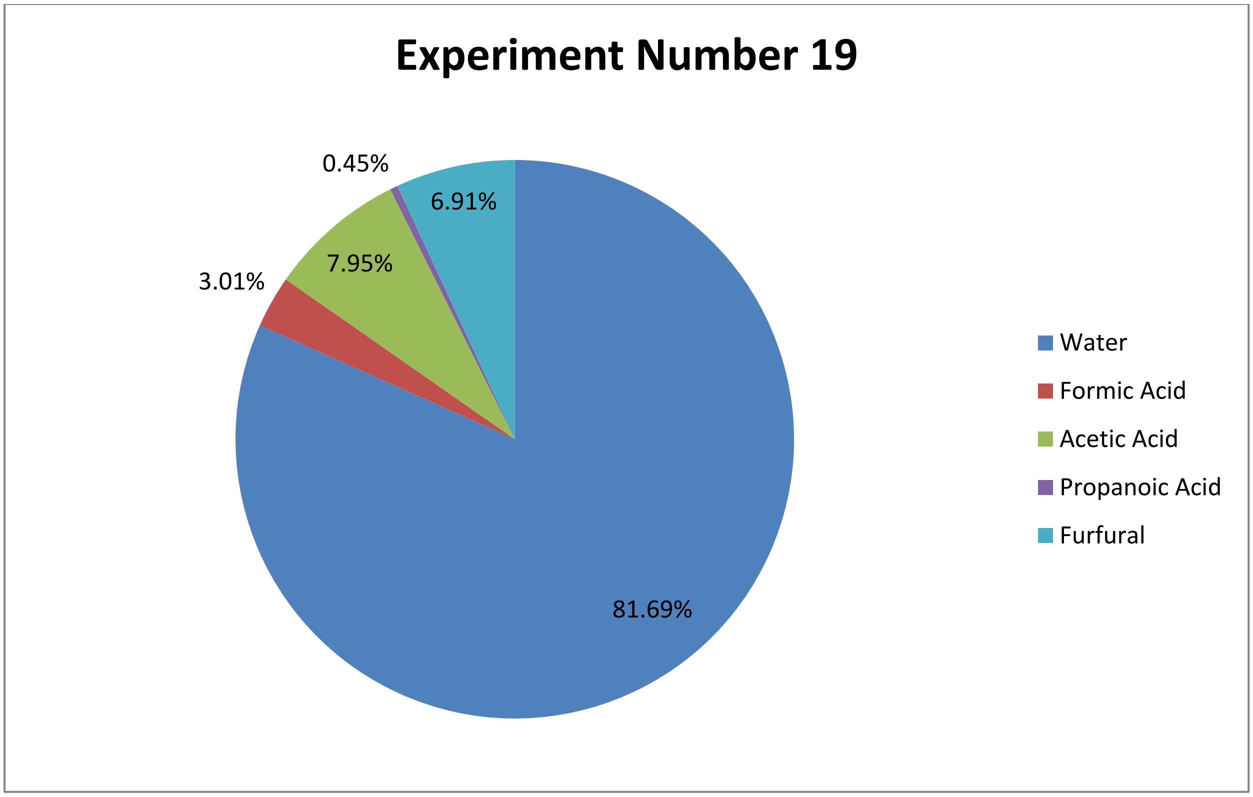

Figure 33: Product distribution of experiment number 19

Table 15: Liquid, char, and gas products for experiment number 19

1 to 20 Molar Ratio (1.3g Cellulose)		
	Mass	Yield
Liquid	0.70g	53.8%
Char	0.41g	31.5%
Gas	0.12g	9.2%

When the composition of the molten salt eutectic returned to not include sodium chloride and a rapid heating rate was employed, the amount of water produced decreased and the amount of furfural increased. This can be seen in experiment number 43 (40mol% $ZnCl_2$, 40mol% LiCl, and 20mol% KCl) in Figure 34. Only 68% water was produced under these ideal reaction temperatures. Also, a high yield of 21.2% furfural was produced. This clearly indicates that when the chloride eutectic that consists of no sodium chloride is used, the amount of water produced is much less, which is a favorable result. Specifically, a chloride eutectic of 40 mol% $ZnCl_2$, 40 mol% LiCl, and 20 mol% KCl produced the highest amount of furfural and the least amount of water.

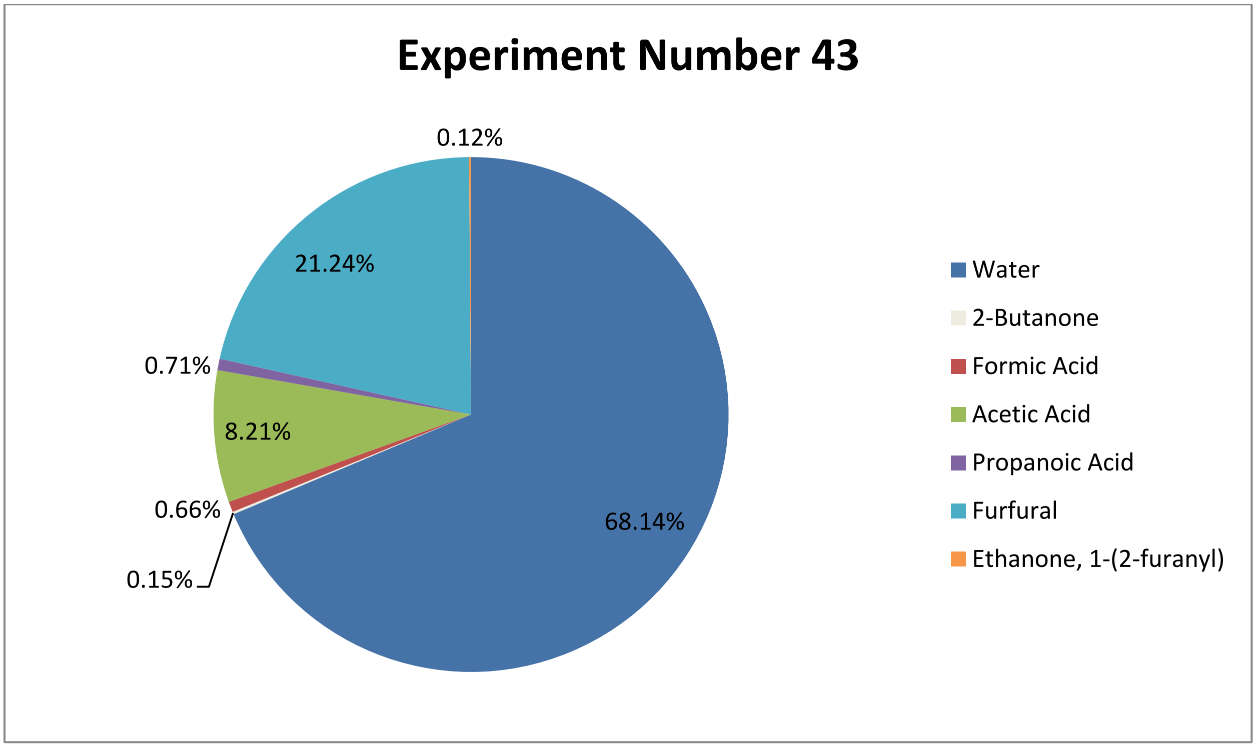

Figure 34: Product distribution of experiment number 43

Table 16: Liquid, char, and gas products for experiment number 43

1 to 20 Molar Ratio (2.5g Cellulose)		
	Mass	Yield
Liquid	1.03g	41.2%
Char	0.60g	24.0%
Gas	0.87g	17.4%

4.6.3 GC/MS Results – Heating Rate Tests

The product distributions of the samples that underwent the heating rate tests were also analyzed. These experiments included numbers 33-44; however, the product distributions of experiments 40-44 were analyzed the most closely, since they employed the use of the ideal eutectic. As seen below in Figure 35, when a heating rate of 10°C per minute was used, there was a very high yield of water at almost 90%. Also, there was an extremely high percent of acetic acid present in this sample at 9.5%. When these results are compared to the product distribution of experiment 41 in Figure 36, with a heating rate of 30°C per minute, it is evident that the percentage of water decreased. The percent water decreased from 89.2% to 81%. What is even more significant is that the percentage of furfural produced increased from only 0.8% to 13.1%. It would have been interesting to seen the product distribution of experiment number 39, with a heating rate of 20°C per minute; however, it is one of the sample that was unfortunately lost in the transfer of vials.

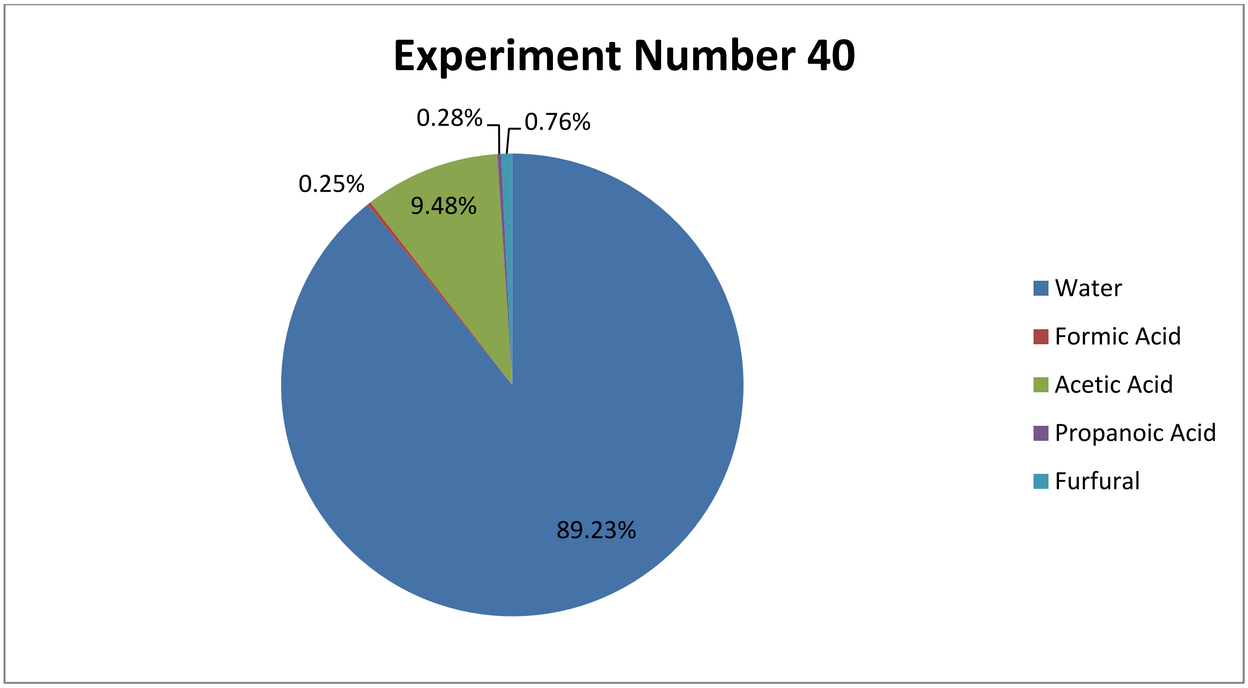

Figure 35: Product distribution of experiment number 40

Table 17: Liquid, char, and gas products for experiment number 40

1 to 20 Molar Ratio (2.5g Cellulose)		
	Mass	Yield
Liquid	0.79g	31.6%
Char	1.00g	40.0%
Gas	0.71g	28.4%

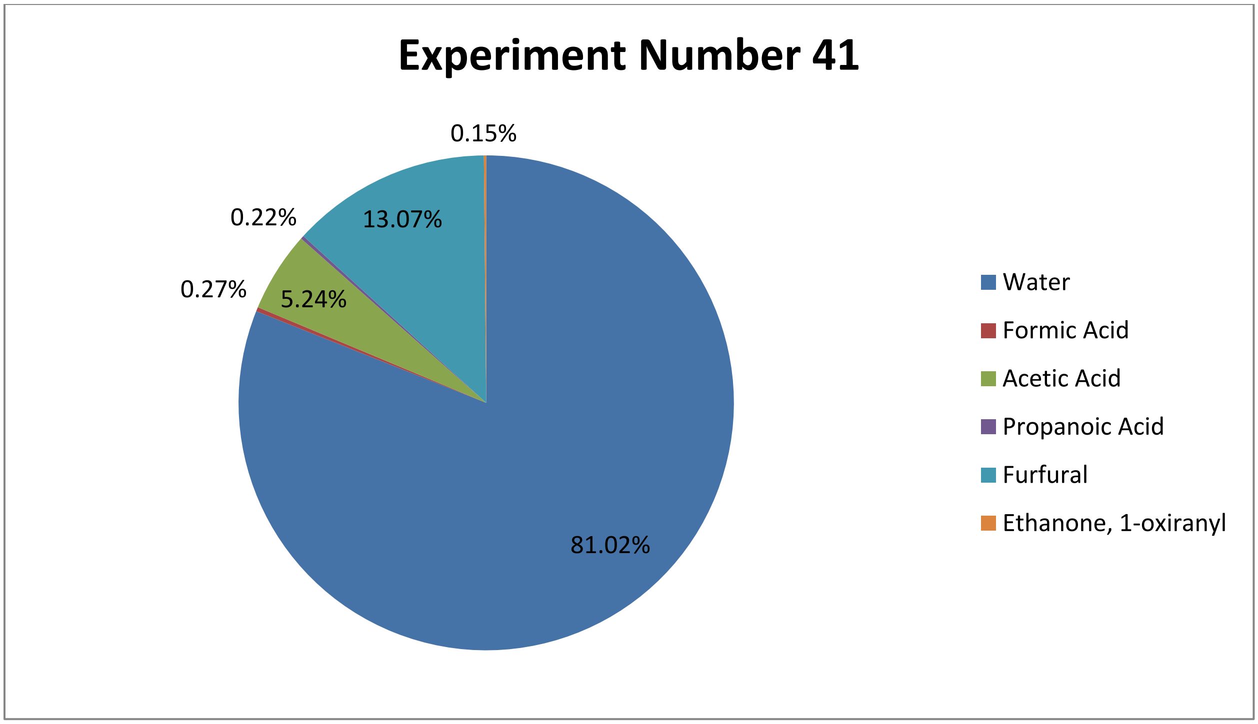

Figure 36: Product distribution of experiment number 41

Table 18: Liquid, char, and gas products for experiment number 41

1 to 20 Molar Ratio (2.5g Cellulose)		
	Mass	Yield
Liquid	1.30g	52.0%
Char	0.50g	20.0%
Gas	0.70g	28.0%

When the heating rate was increased even more to 40^{o}C per minute, the percent of water again decreased and the percentage of furfural increased. This can be seen below in Figure 37. In addition, through the use of rapid heating, there was also a lower percentage of water produced and a higher percentage of furfural produced, which is displayed in Figure 38. Although the percentage of water in experiment 42 is not as low as in experiment 35, it is still significantly lower than with slower heating rates. It is possible that these heating rates were in fact very similar under the experimental conditions. For example, the temperature of cellulose/molten salt mixture inside of the reactor tube is not precisely known. The heating rate is based upon how fast the reactor reached the final temperature, not on how fast the actual material was heated. It would be beneficial to place a temperature probe inside of the reactor in order to determine the precise heating rate that the reaction underwent; however, due to laboratory limitations, this was not possible.

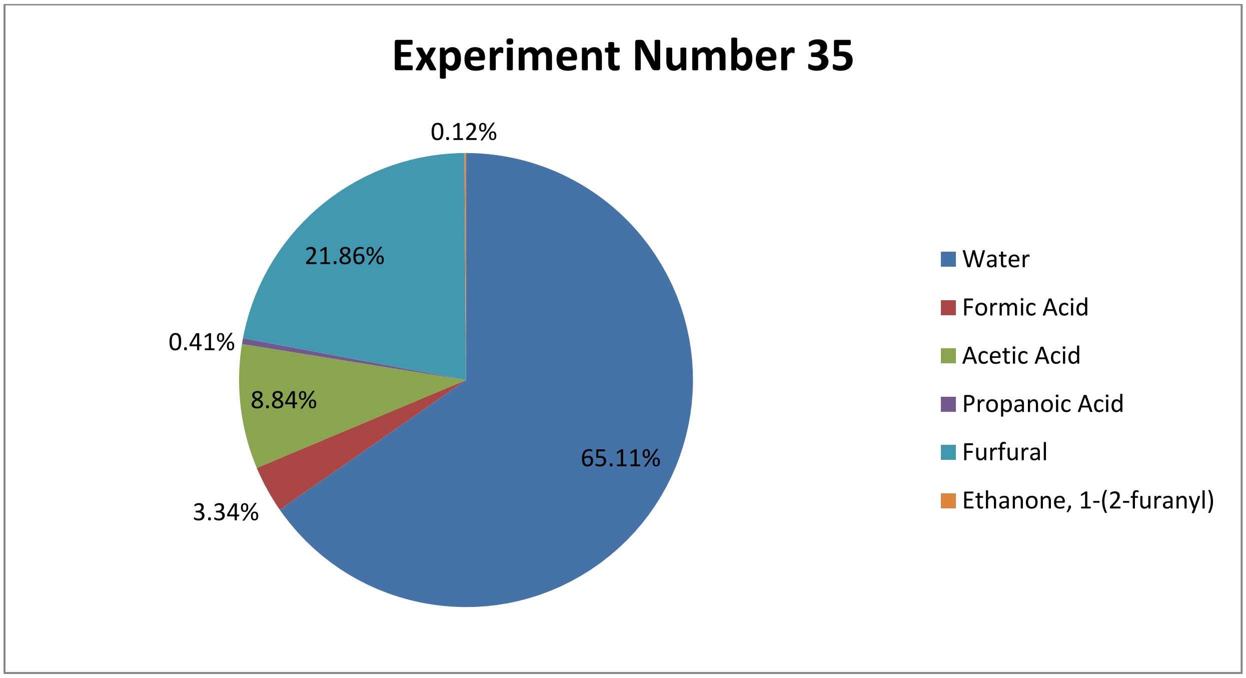

Figure 37: Product distribution of experiment number 35

Table 19: Liquid, char, and gas products of experiment number 35

1 to 20 Molar Ratio (2.5g Cellulose)		
	Mass	Yield
Liquid	1.17g	46.8%
Char	0.50g	20.0%
Gas	0.83g	33.2%

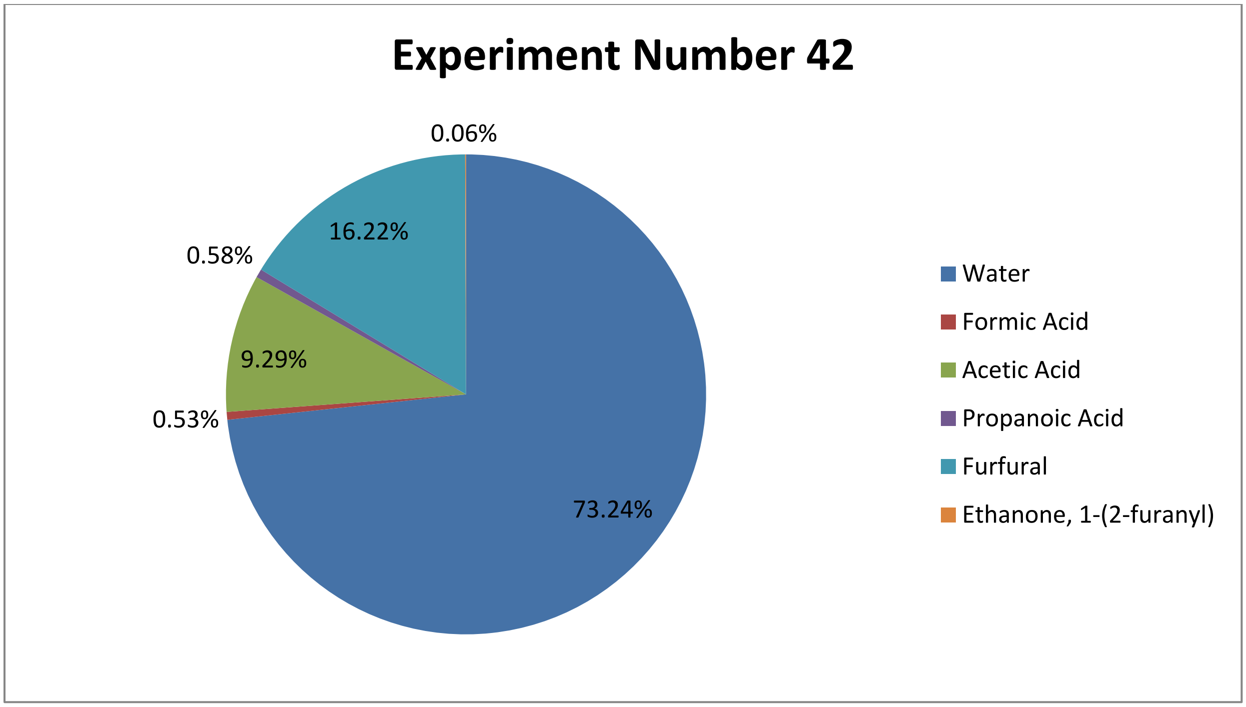

Figure 38: Product distribution of experiment number 42

1 to 20 Molar Ratio (2.5g Cellulose)		
	Mass	Yield
Liquid	1.19g	47.6%
Char	0.90g	36.0%
Gas	0.41g	16.4%

4.7 Mole Balance

In order to determine the accuracy of the equipment and the product distributions, a mole balance was conducted around the experiment that produced the most desirable results, experiment number 13. Using the product distribution of this sample, an accurate mole balance was able to be conducted and can be seen below.

Compound	Percent Total
Water	69.98%
Formic Acid	3.29%
Acetic Acid	7.31%
Propanoic Acid	.40%
Furfural	18.52%
Ethanone, 1-(2-furanyl)	.50%

Initial moles of carbon in the reaction (moles carbon in cellulose):

$$Mass\ cellulose\ \times \frac{Carbon\ Moles\ in\ Cellulose}{Cellulose\ Mol\ Wt} = Initial\ Moles\ Carbon$$

$$2.000g\ \times \frac{6\ mol\ carbon}{162.14\ g/mol} =\ 0.07401\ initial\ moles\ carbon$$

Initial moles of hydrogen in the reaction (moles hydrogen in cellulose):

$$Mass\ cellulose\ \times \frac{Hydrogen\ Moles\ in\ Cellulose}{Cellulose\ Mol\ Wt} = Initial\ Moles\ Hydrogen$$

$$2.000g\ \times \frac{10\ mol\ hydrogen}{162.14\ g/mol} =\ 0.12335\ initial\ moles\ carbon$$

Initial moles of oxygen in the reaction (moles oxygen in cellulose):

$$Mass\ cellulose\ \times \frac{Oxygen\ Moles\ in\ Cellulose}{Cellulose\ Mol\ Wt} = Initial\ Moles\ Oxygen$$

$$2.000g\ \times \frac{5\ mol\ oxygen}{162.14\ g/mol} =\ 0.12335\ initial\ moles\ carbon$$

The amount of carbon, hydrogen, and oxygen present in the liquid and char products was then calculated. For the liquid, the percent of each component was used to determine how much carbon, hydrogen, and oxygen was present. Then, once the amount of each element was known for the liquid product, the percentages of carbon, hydrogen, and oxygen in the char could be calculated. Since the exact composition of the char was unknown, these percentages were used in order to gain an accurate estimation. Char is mainly comprised of carbon, however, it would not be accurate to refer to the molecular weight of char as 12.01 g/mol (the molecular weight of carbon). Therefore, by finding the percentage of carbon, hydrogen, and oxygen in the char, a multiplier was determined, in order to use a more accurate molecular weight. Through this more accurate molecular weight, the carbon, hydrogen, and oxygen moles in the char were than calculated. Finally, the percent close of each element was able to be determined. The gas was ignored in this mole balance. The results of the mole balance for experiment number 13 are below in Table 20. Although the closures are close to 100%, it is important to note that these calculates do not take into account the gaseous products.

Table 20: Mole percent closure for experiment number 13

	Initial Moles	Product Moles	Percent Closure
Carbon	0.07401	0.07172	96.9%
Hydrogen	0.12335	0.12407	100.6%
Oxygen	0.06168	0.06287	101.9%

4.8 Equipment Analysis

For the most part, all of the equipment used was able to suitable perform under the desired conditions. In the preliminary running of the flow reactor, several problems where run into. These problems included smoke escaping from the reactor tube, liquid leaking from the lines, and the furnace blowing a fuse. However, since most of these issues were encountered early, it was possible to mediate and fix the situations. Two new reactor tubes were constructed and new end caps for the tubes were ordered. Also, all of the lines of the flow reactor were disassembled and replaced. Once this was completed, there were no other significant problems that were not able to be dealt with.

The only unreliable piece of equipment that had to be utilized was the scale located in GH 222. This scale had to be used to mass the reactor tube, due to the high weight of the tube. The accuracy of this scale was only to the 0.1g. There was more accurate scale that was used for massing all of the salts, cellulose, beakers, and vials; however, the maximum weight of this scale did not permit the reactor tube. Because of this, the char results have a much higher experimental error than any of the other data. Since the accuracy of the char was in question, it was difficult to perform a precise and accurate material mass balance.

5. Conclusion

Through the analysis of the various experimental parameters that were studied, several conclusions can be made for the ideal reaction temperature of the molten salt pyrolysis of biomass into furanic liquids. First, the ideal final temperature of the reaction should be 400^{o}C. Also, this temperature should be reached using rapid heating rates. It was determined that a heating rate of 60^{o}C per minute was the ideal rate for these experiments; however, it is likely that an even higher heating rate would produce a higher liquid yield. Also, the ideal eutectic mixture that yielded both the highest percent liquid yield and the highest percent non-water products was a combination of 40 molar percent zinc chloride, 40 molar percent lithium chloride, and 20 molar percent potassium chloride. All of these molar percentages are based off the mass of the metal component. In addition to this, it was determine that a cellulose to eutectic mole ratio of 1 to 20 yielded that highest percentage of liquid products. Also, this mole ratio also allowed for a small yield in different products, which was typically around 6 or 7 compounds. This is compared to the 14 different compounds that were found using a 10 to 1 cellulose to eutectic mole ratio. Therefore, the ideal reaction conditions for the molten salt pyrolysis of biomass are as followed:

- Eutectic composition: 40 mol% ZnCl, 40 mol% LiCl, 20 mol% KCL
- Final Temperature: 400^{o}C
- Heating Rate: 60^{o}C per minute
- Cellulose to Eutectic mole ratio: 1 to 20

If these conditions are utilized, one can expect to produce nearly 70% liquid yield that is comprised of about 70 % water and 20% furfural. Therefore, about 0.7g of furfural can be produced from 5.0g of cellulose.

Another significant conclusion is that the presence of NaCl in the chloride eutectic significantly hinders the production of furfural. Instead of furfural being produced, when NaCl is present, the reaction tends to produce very high yields of water. Since water is an undesirable product, it can be concluded that it should not be a substitute for either LiCl or KCl.

6. Recommendations

Due to the fact that promising results were generated throughout the entirety of the report, it would be beneficial to continue to conduct further research. The molten salt pyrolysis of biomass has been proved to be a successful way to convert cellulose to bio-liquid. Several experimental parameters were analyzed in the context of this report in order to optimize the functionality of this technique; however, there are other further steps that can be taken.

6.1 The Effect of the Addition of Catalysts

Due largely to time constraint issues and to the fact that this project was completed by one person, there was not enough time to investigate the effect of different catalysts of the liquid product yield and distribution. Therefore, it would be important to add catalysts to the reaction. It is likely that proton donating catalysts would allow the product distribution to be different than what was generated in this report. Two possible catalysts that should be analyzed are ZSM-5 and $Ni(II)OH_2$.

6.2 Gas and Char Analysis

In previous MQPs, the gas composition of the reaction were analyzed through gas chromatography. However, there were no satisfactory results that were generated. Because of this, it would be interesting to device a proper technique for the capturing and analyzing of he gas. It is unknown what the gas flow rate is throughout the reaction. It would be beneficial to find the volume of the gas as well as the composition so that an accurate molar balance could be performed.

In addition to the analysis of the gas produced, analyzing the components of the char would also be advantageous. Knowing the chemical components of the char would add in the completion of a successful mass balance around the reaction. Perhaps more importantly than the composition, is devising a way in which to extract the spent salts from the char. If a proper technique could be developed to successfully extract the eutectic chlorides from the char, they could be potentially reused, which would result in significant cost savings. One possible idea to solve this problem, is finding a suitable solution that was dissolve the salts out of the char. The salt/solvent solution could then be heated and the salt could be collected. The cost reduction of second-generation bio-oil production techniques is paramount. Knowing the composition of the gas would perhaps help devise a way to recycle this gas into the process, which would save money. Also, the ability to recycle the chloride eutectic would have positive economic impacts.

6.3 Variation of Feedstock Materials

Although cellulose is the major component of lignocellulosic material, it only constitutes about half of all biomass. Therefore, the results of this project are promising; however, further analysis of hemicellulose and lignin must also be conducted. Different feedstock materials should begin to be tested, instead of pure cellulose. Materials such as recycled paper, sawdust, grass clippings, leaves, and etc., should be analyzed. In order to make this a commercially feasible way to produce second-generation bio-oil, waste materials, such as these, must be able to be utilized.

The preparation of these materials is likely to be one of the most important aspects of the reaction. For example, during fast pyrolysis, all feed material is heated in order to remove the majority of its moisture content; it is likely that this would be necessary. Also, in fast pyrolysis, the feed material is grinded to very small particles. This allows for the reaction to take place more quickly with higher heating rates. Particle size would be particularly important in the molten salt pyrolysis of biomass due to the needed interaction between the biomass and the molten salt. Reducing the particle size would allow better contact between the two components.

Therefore, when analyzing different feedstock materials, it will be important to keep in mind proper pretreatment methods.

6.3 Pilot Scale Testing

Once all possible experimental parameters have been optimized for this process, it will be essential to increase the size and complexity of the flow reactor. In order for this to be a feasible commercial process, a pilot scale process should be created. Such a process would likely be similar to the ones that are currently being used in fast pyrolysis. Lignocellulosic biomass should be fed to a grinder so that the particles are a suitable size. Then the biomass would be sent to a reactor where it would mix with the molten salt/catalyst mixture. The gases and volatile components would be released overhead. All char material would be separated by a cyclone and the gas and volatiles would then be sent to a condenser. The gas that does not condense would be sent back to the heater to held aid in drying the biomass. The char that is separated in the cyclone could be burned and the heat could be used for driving the reaction. The volatiles would be allowed to condense into liquid product. The most difficult part of this process would be determining a way to separate the char and the molten salt within the reactor. Different reactor types should be analyzed as well as methods for the char removal.

7. Works Cited

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Appendices

Appendix A: GC/MS Results – Zoomed in Spectra

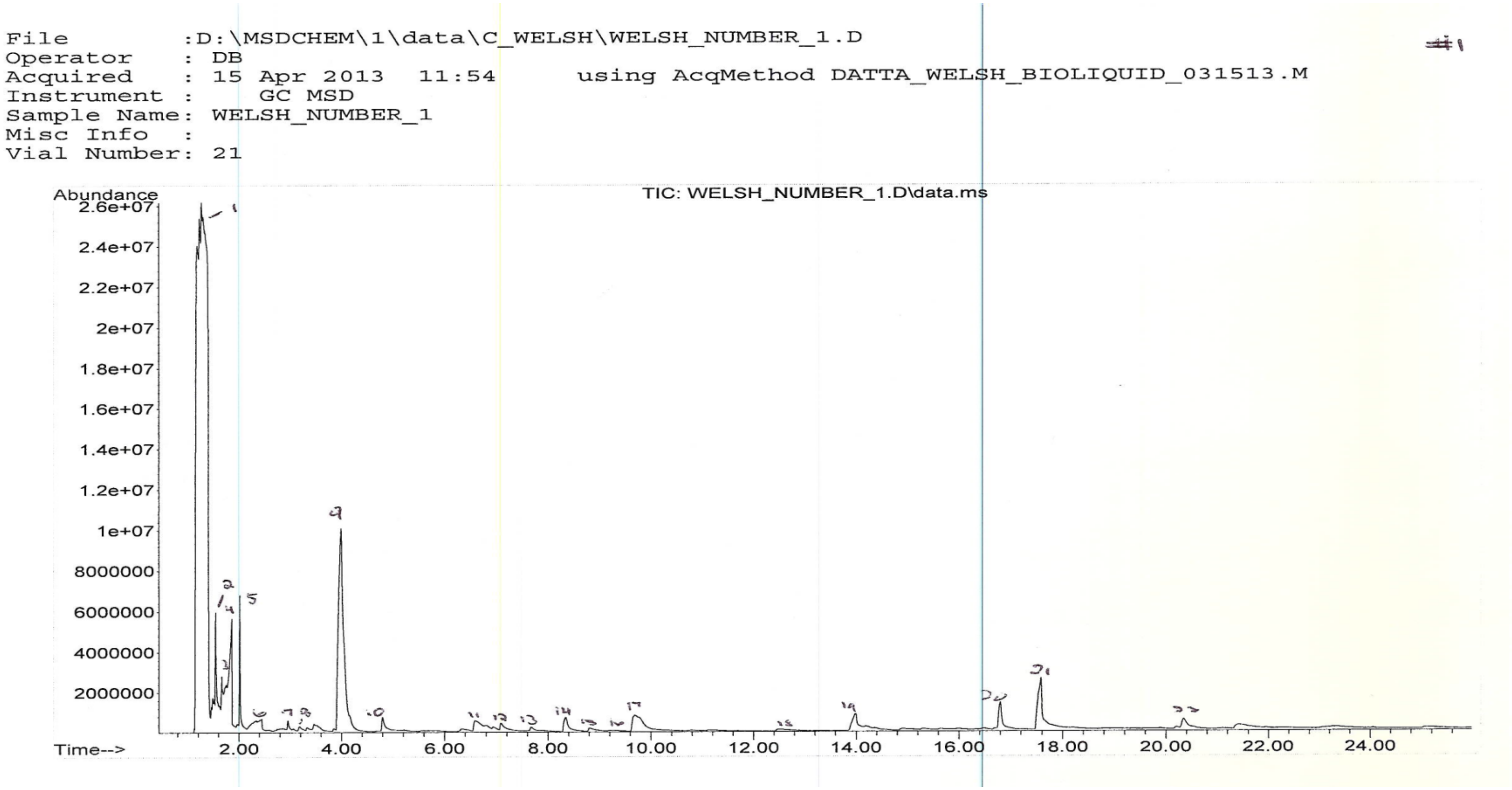

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Figure 39: Zoomed in Spectrum Run 1

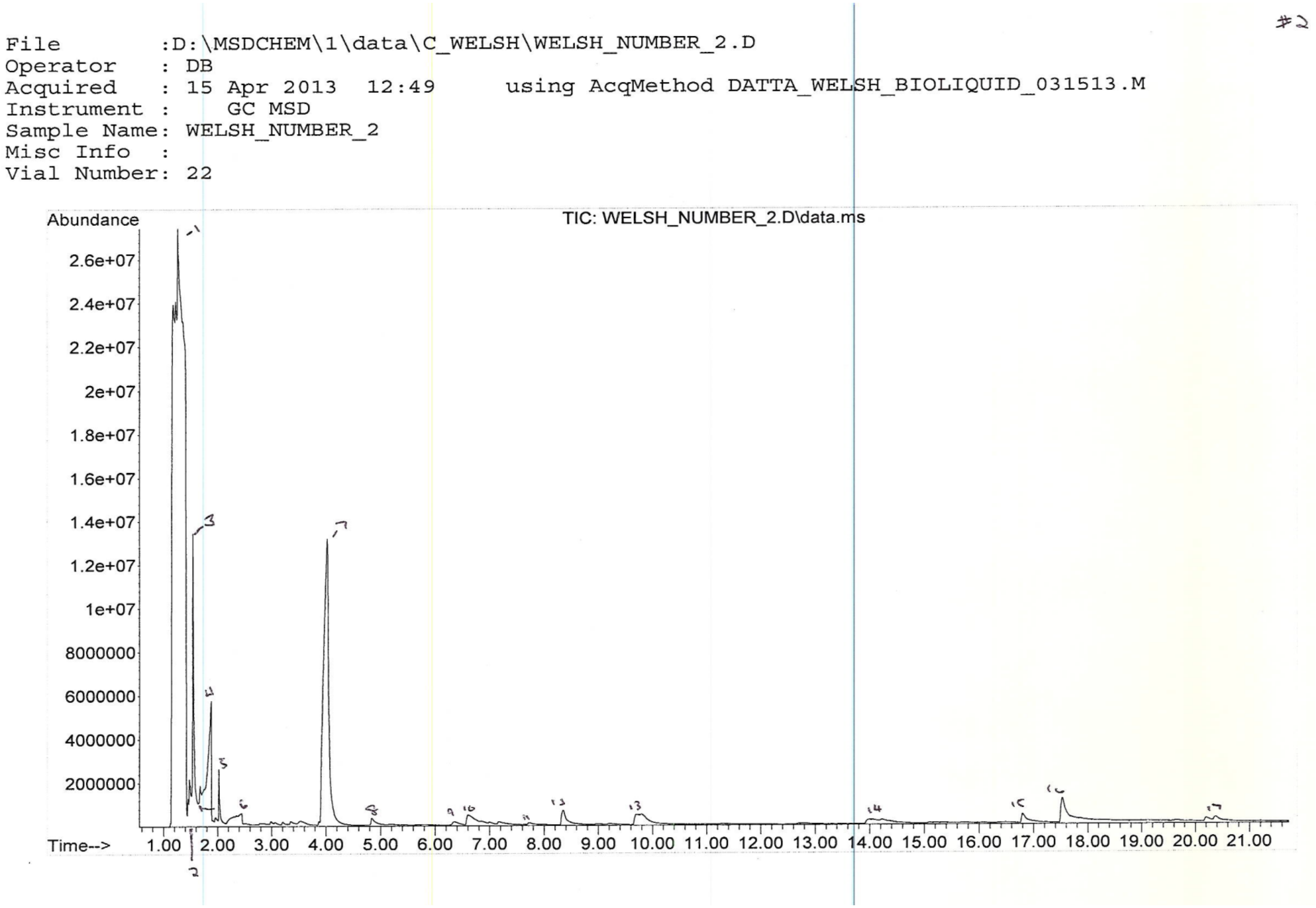

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Figure 40: Zoomed in Spectrum Run 2

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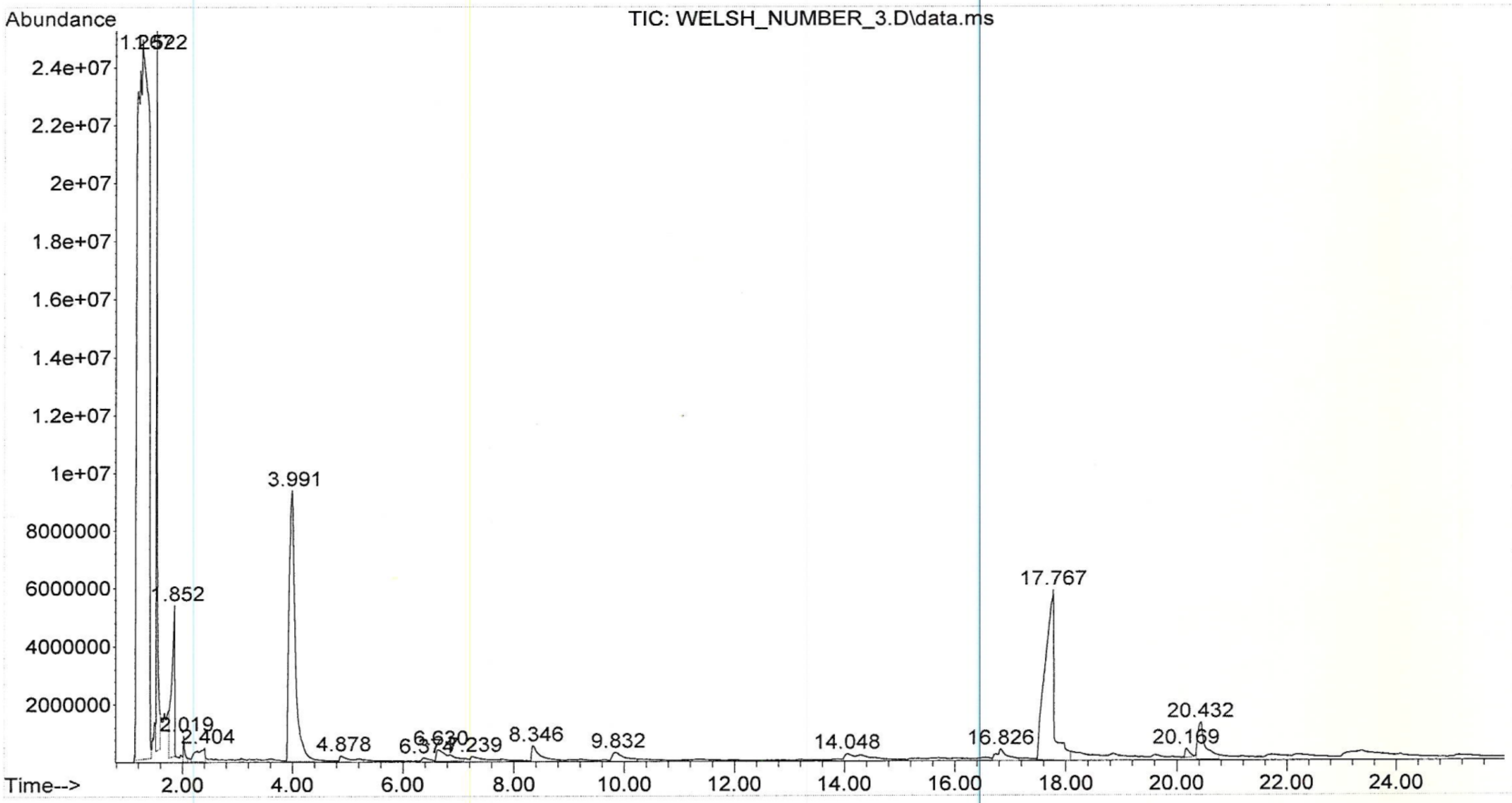

Figure 41: Zoomed in Spectrum Run 3

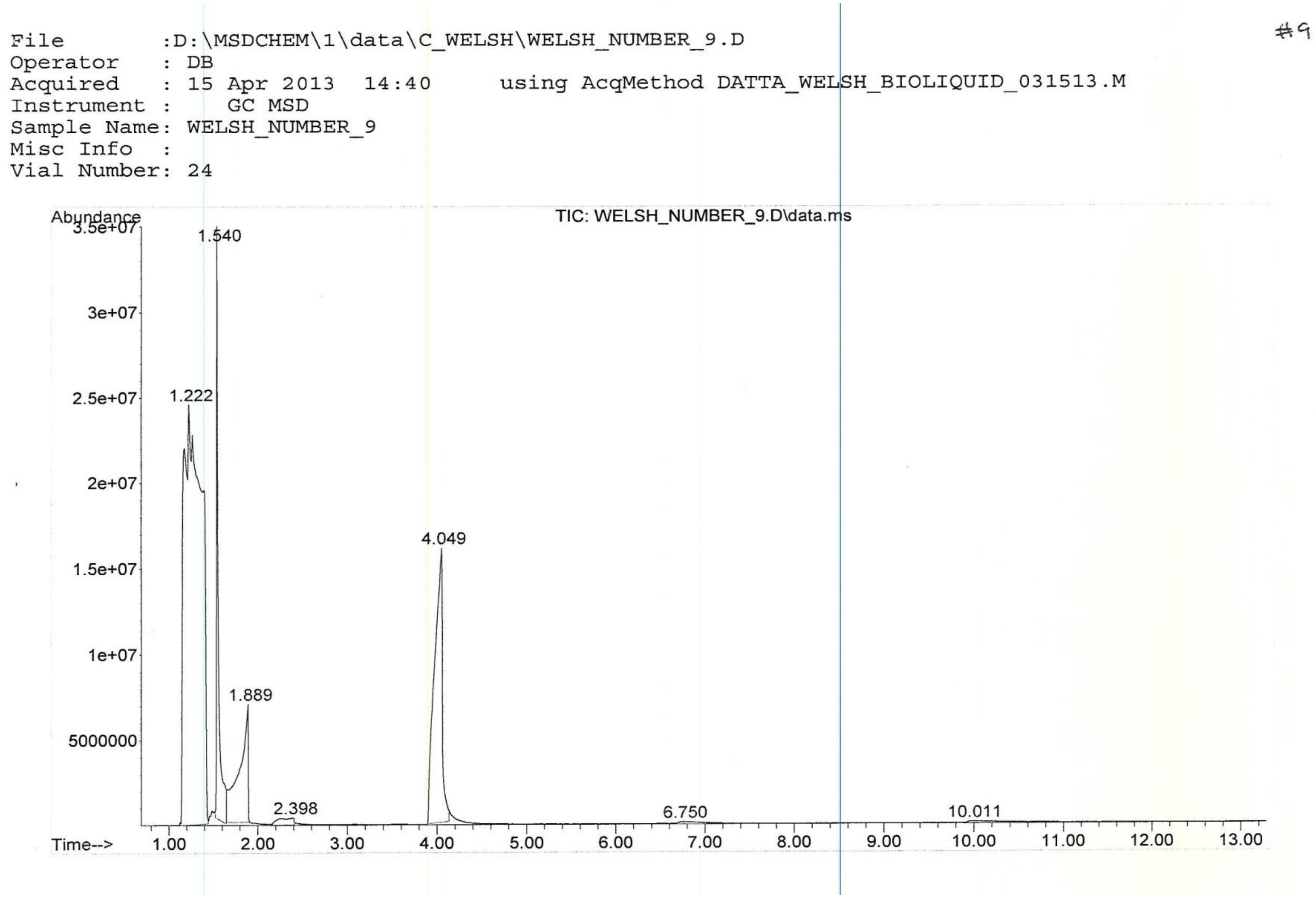

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Figure 42: Zoomed in Spectrum Run 9

#13

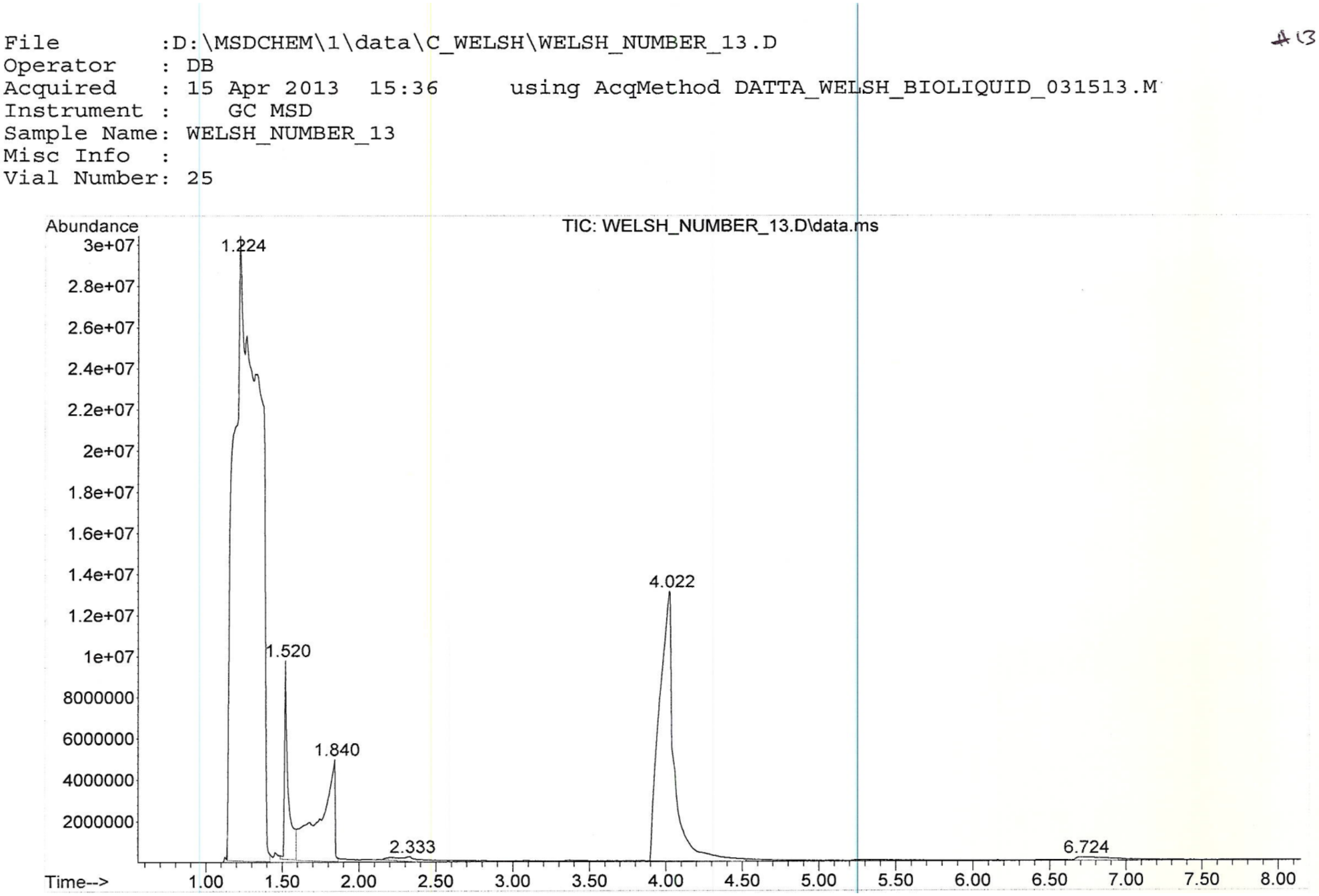

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Figure 43: Zoomed in Spectrum Run 13

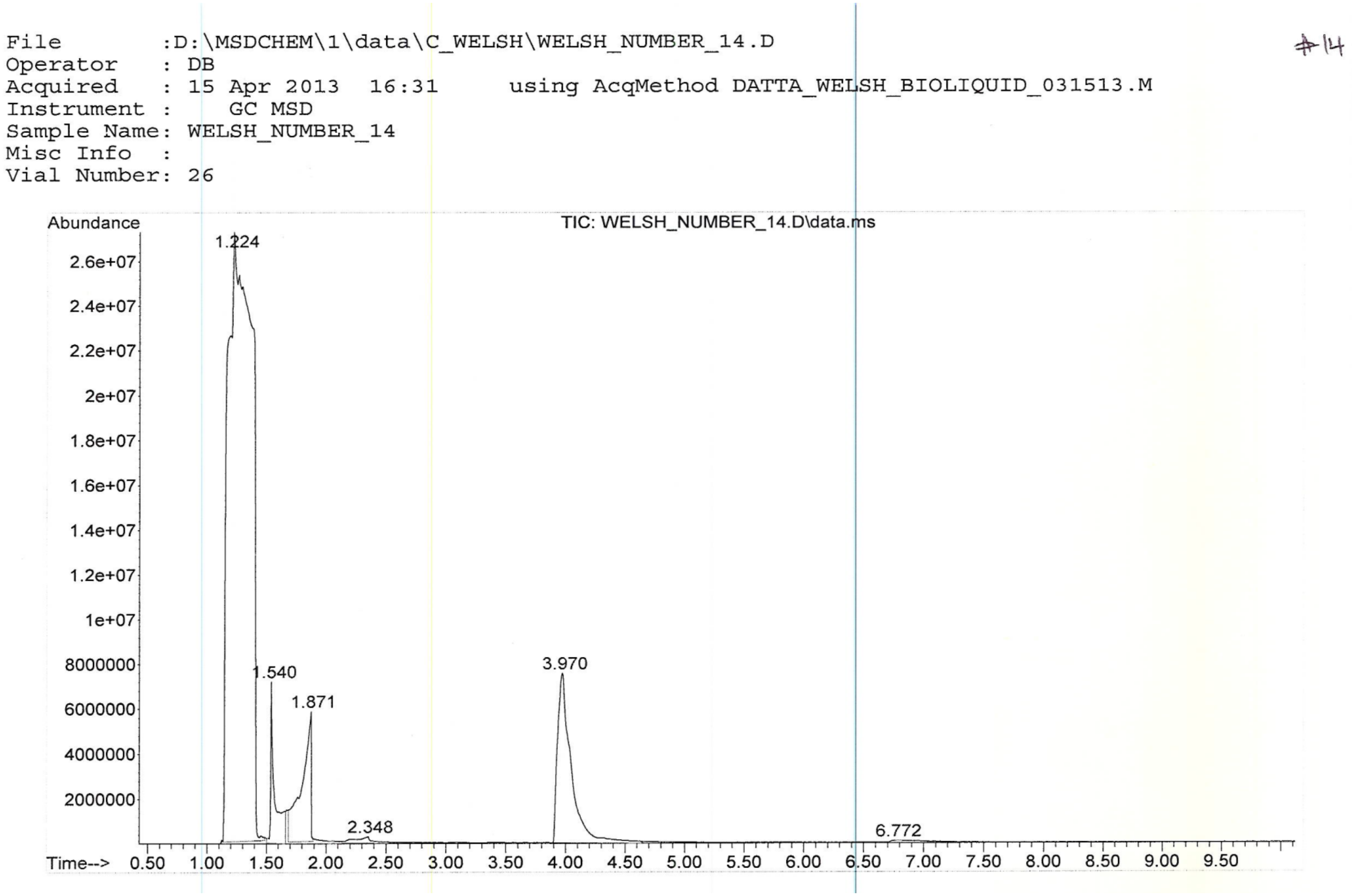

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Figure 44: Zoomed in Spectrum Run 14

#15

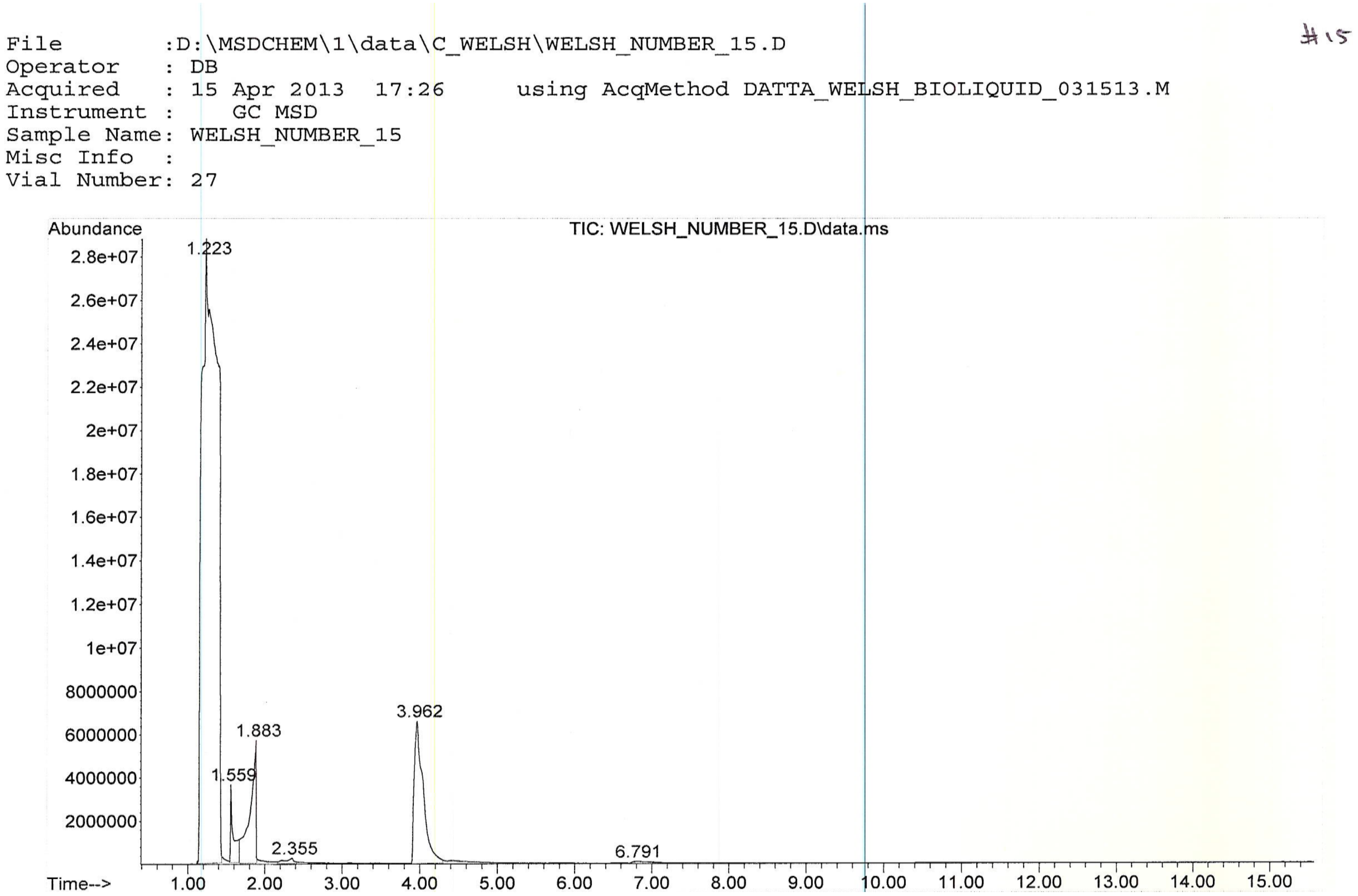

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Figure 45: Zoomed in Spectrum Run 15

#16

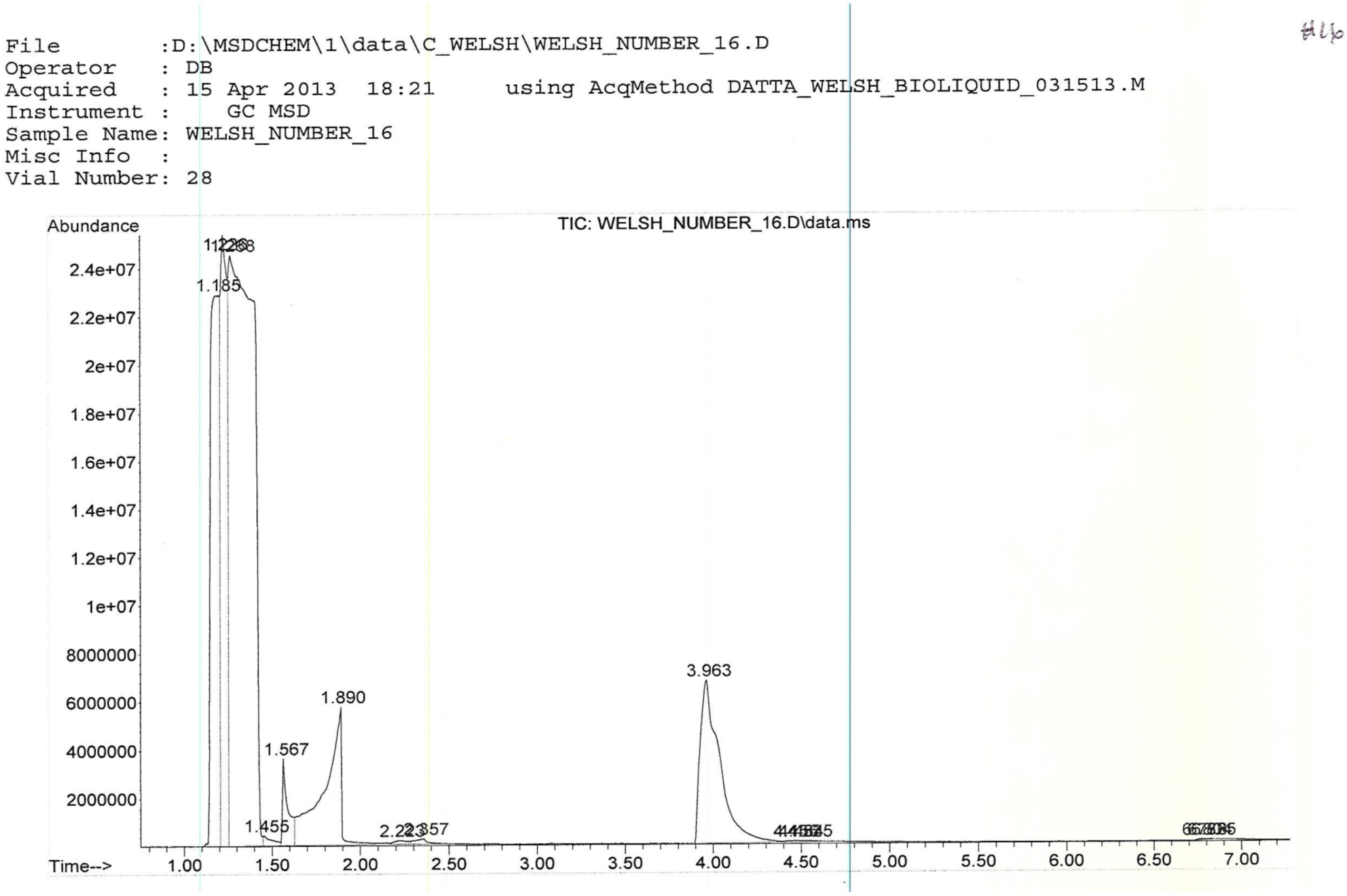

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Figure 46: Zoomed in Spectrum Run 16

#17

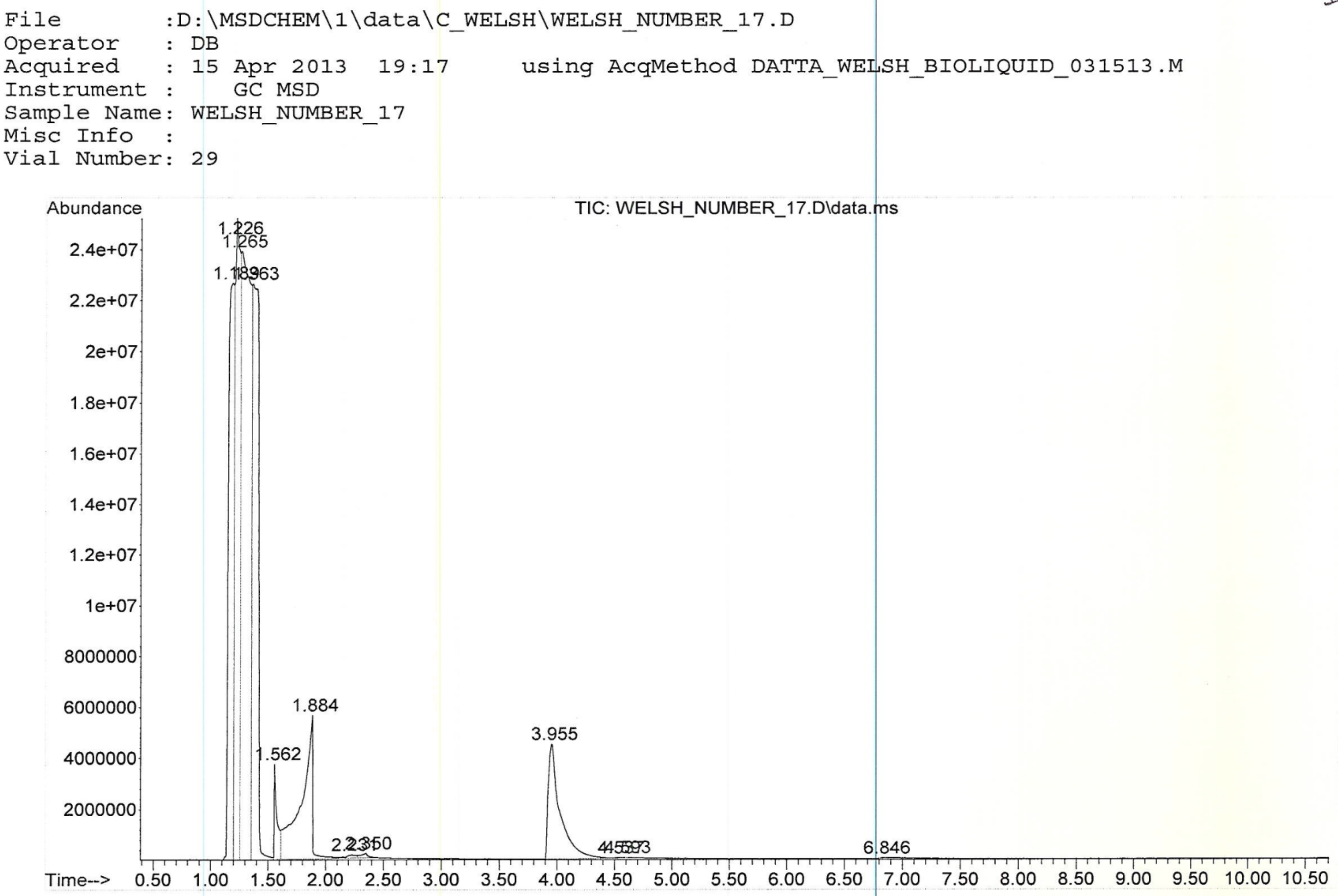

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Figure 47: Zoomed in Spectrum Run 17

#18

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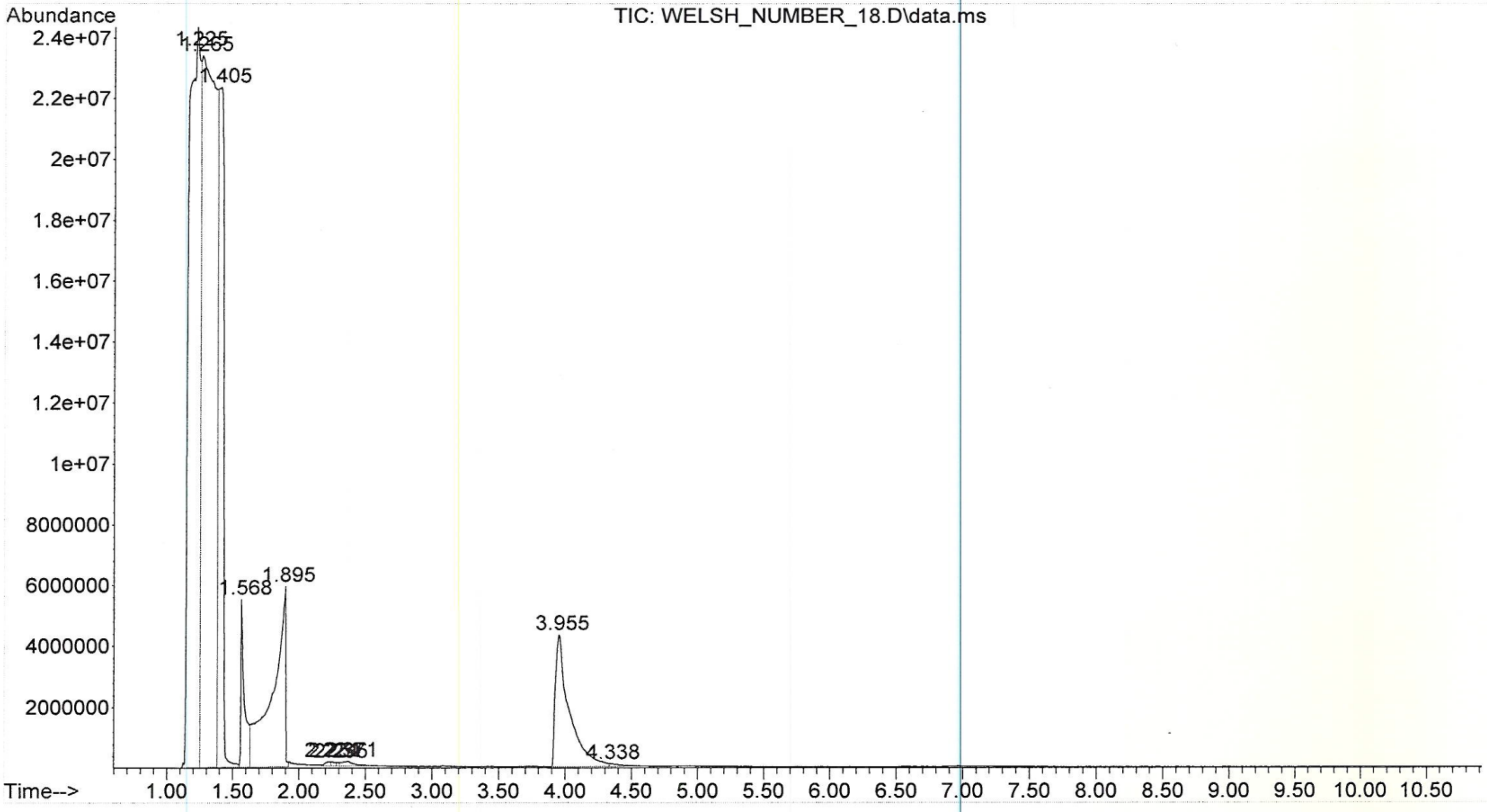

Figure 48: Zoomed in Spectrum Run 18

#19

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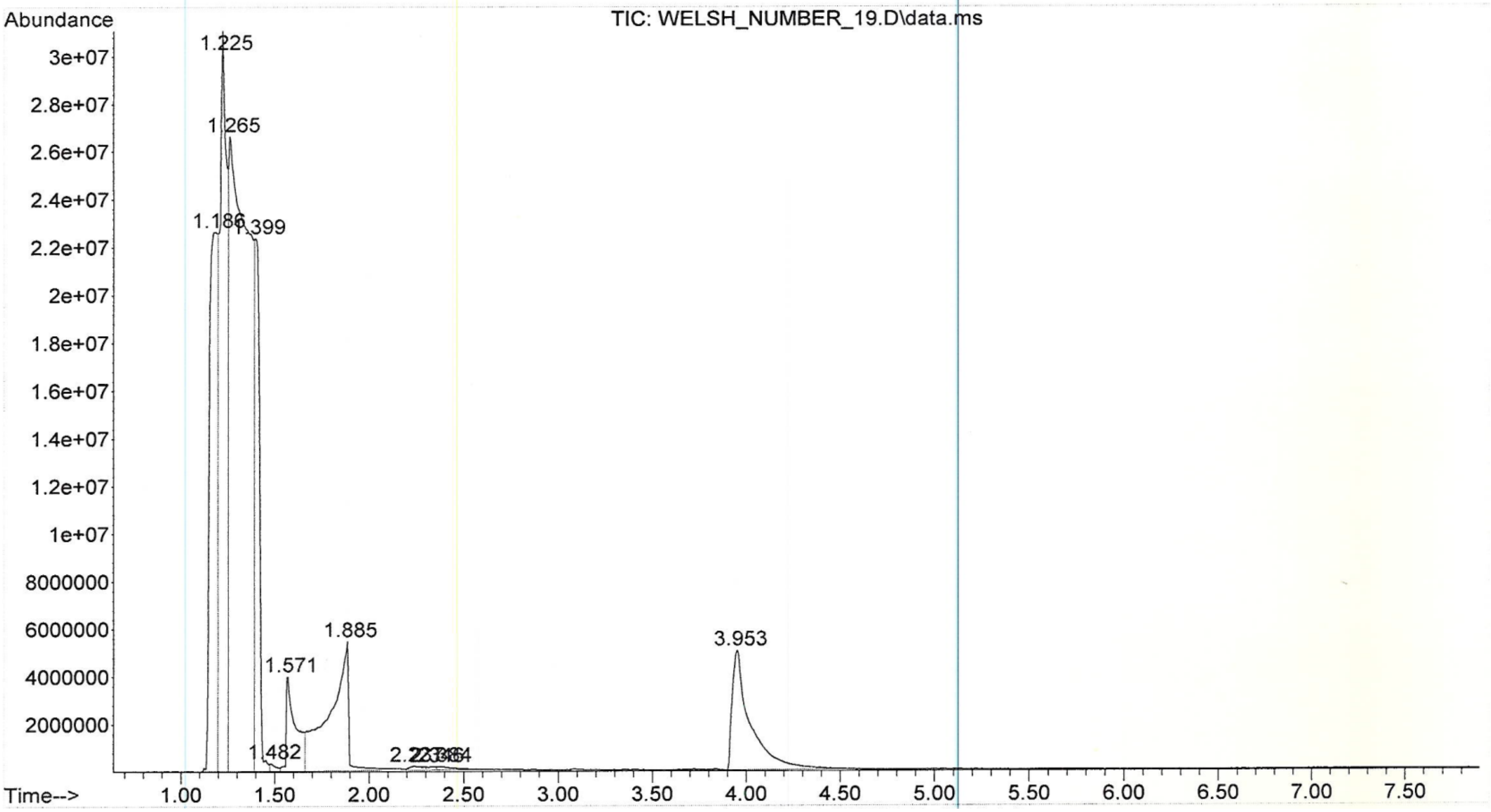

Figure 49: Zoomed in Spectrum Run 18

#20

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File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_20.D
Operator    : DB
Acquired    : 15 Apr 2013   22:03      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_20
Misc Info   :
Vial Number: 32
```

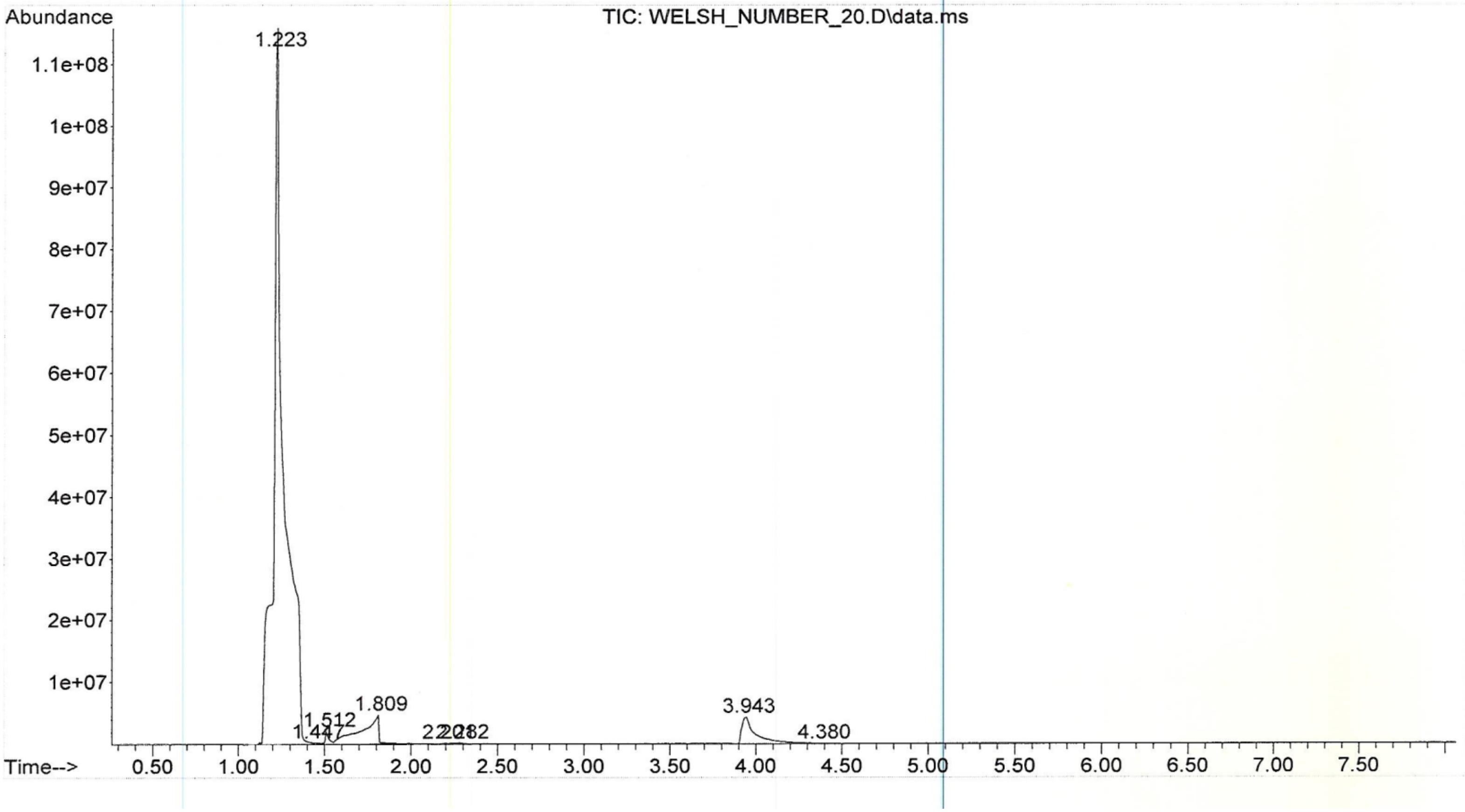
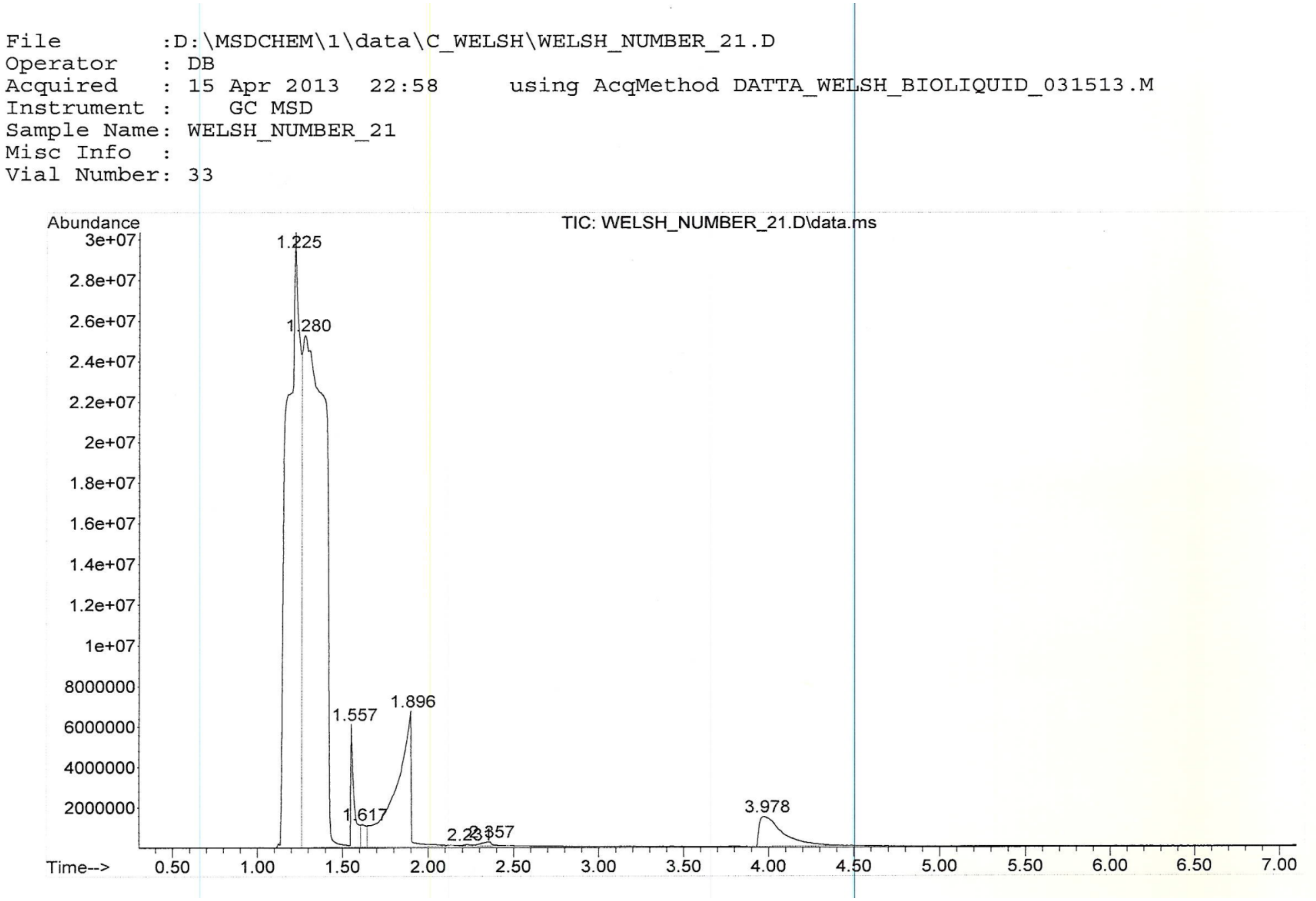


Figure 50: Zoomed in Spectrum Run 20



```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_21.D
Operator    : DB
Acquired    : 15 Apr 2013   22:58      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_21
Misc Info   :
Vial Number: 33
```

Figure 51: Zoomed in Spectrum Run 21

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_23.D
Operator    : DB
Acquired    : 15 Apr 2013  23:53      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_23
Misc Info   :
Vial Number: 34
```

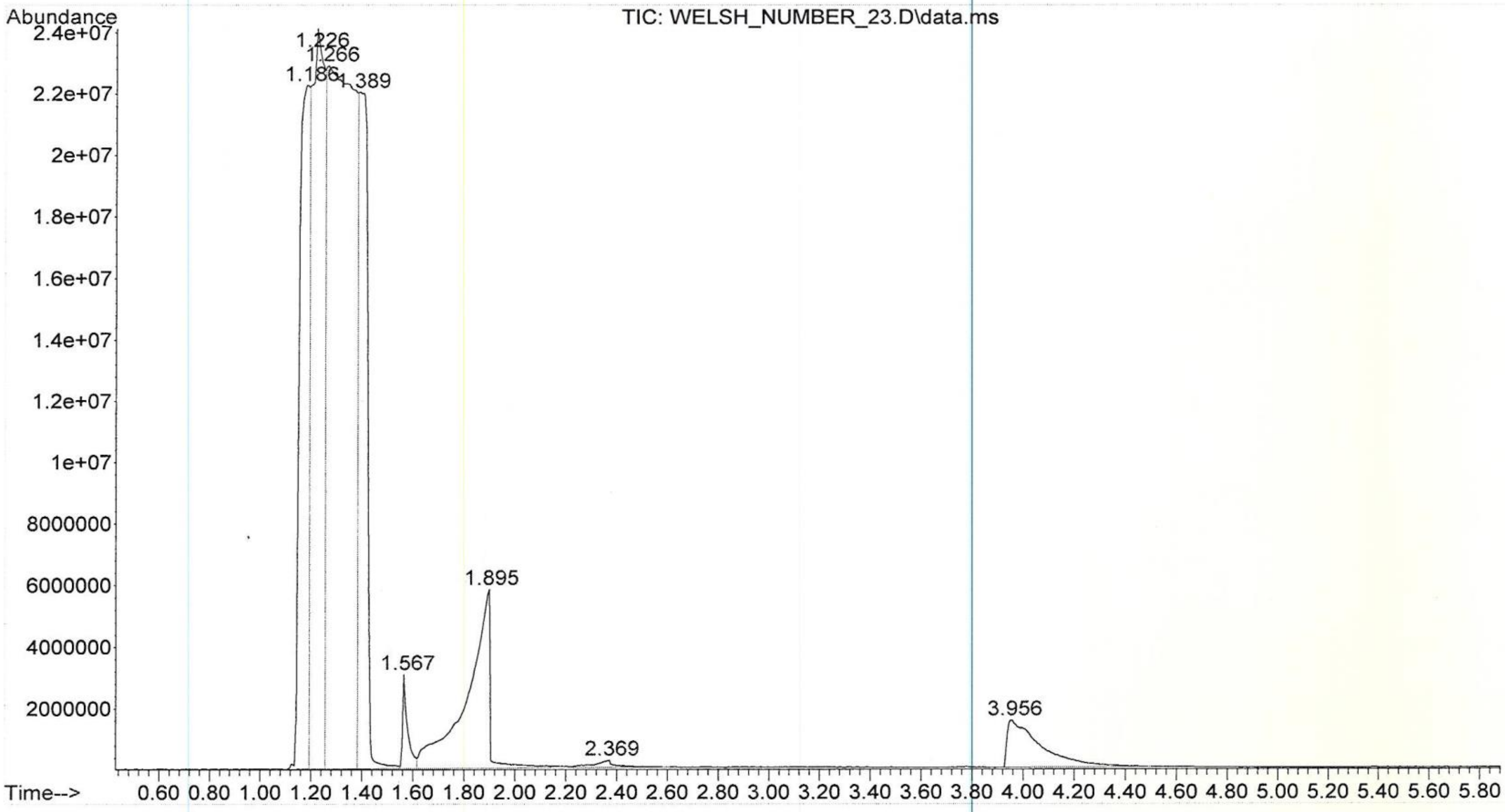


Figure 52: Zoomed in Spectrum Run 22

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_24.D
Operator    : DB
Acquired    : 16 Apr 2013   00:49      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :     GC MSD
Sample Name: WELSH_NUMBER_24
Misc Info   :
Vial Number: 35
```

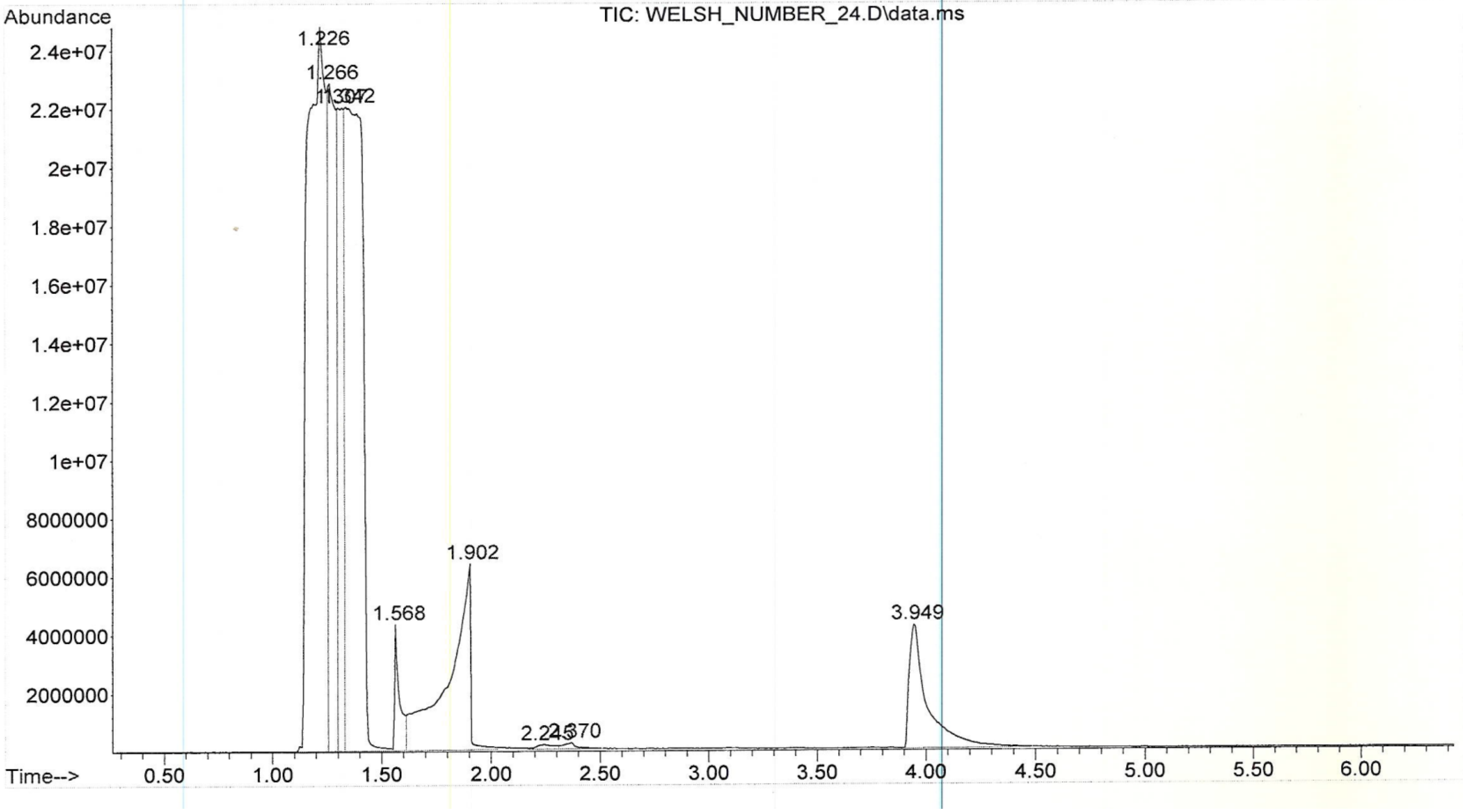
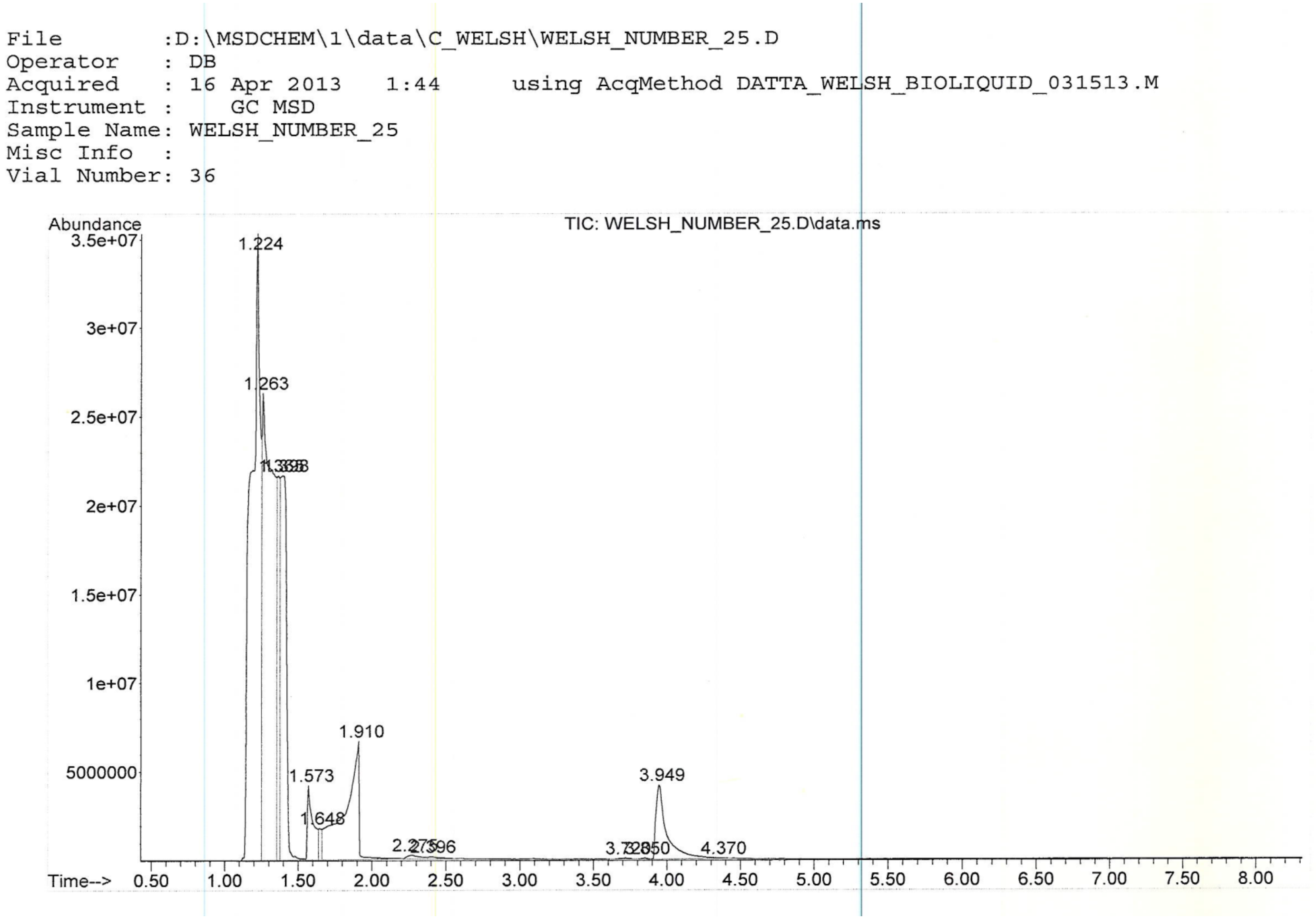


Figure 53: Zoomed in Spectrum Run 24



```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_26b.D
Operator    : DB
Acquired    : 16 Apr 2013   8:21      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_26
Misc Info   :
Vial Number: 37
```

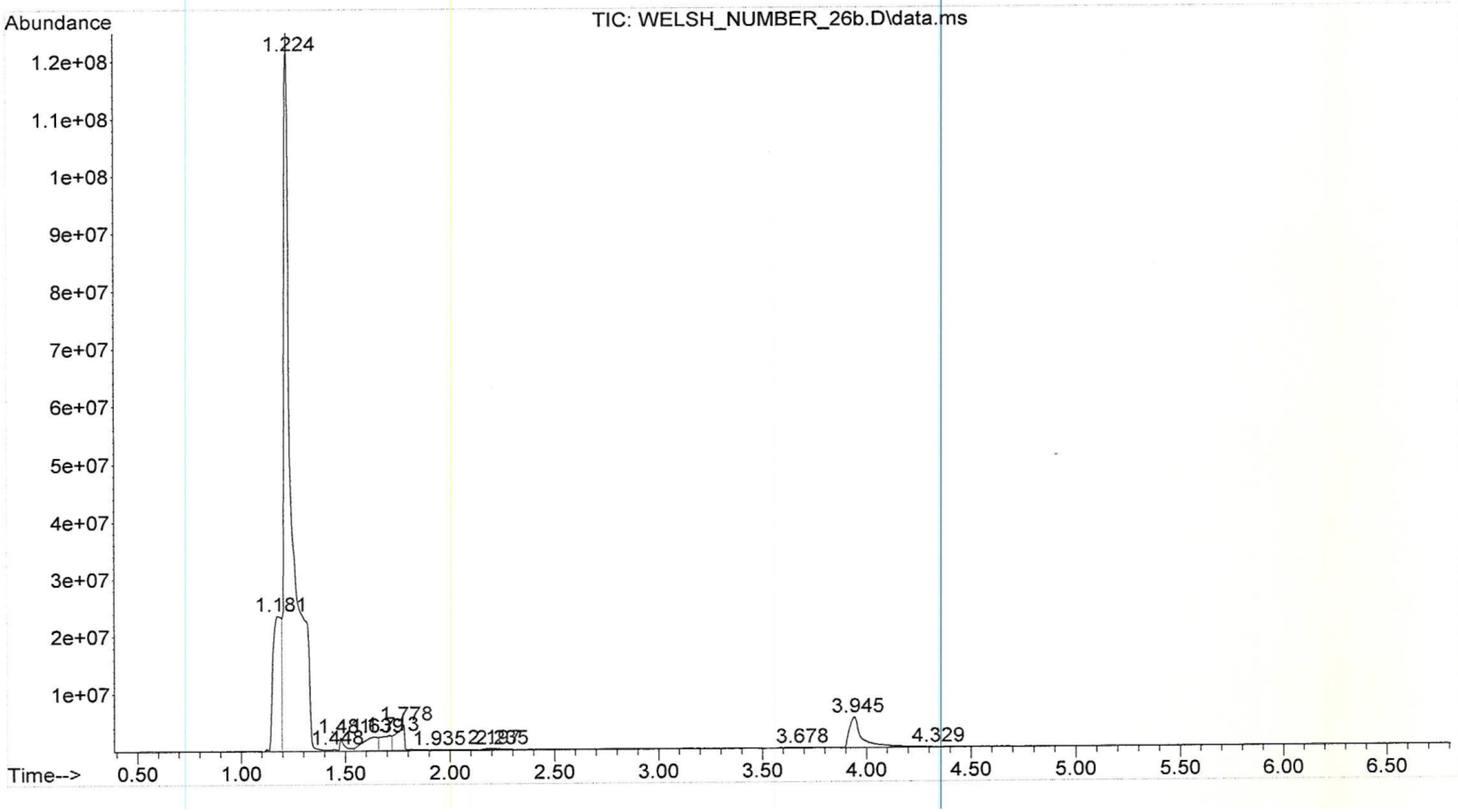


Figure 55: Zoomed in Spectrum Run 26

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_27.D
Operator    : DB
Acquired    : 16 Apr 2013    9:17      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :     GC MSD
Sample Name: WELSH_NUMBER_27
Misc Info   :
Vial Number: 38
```

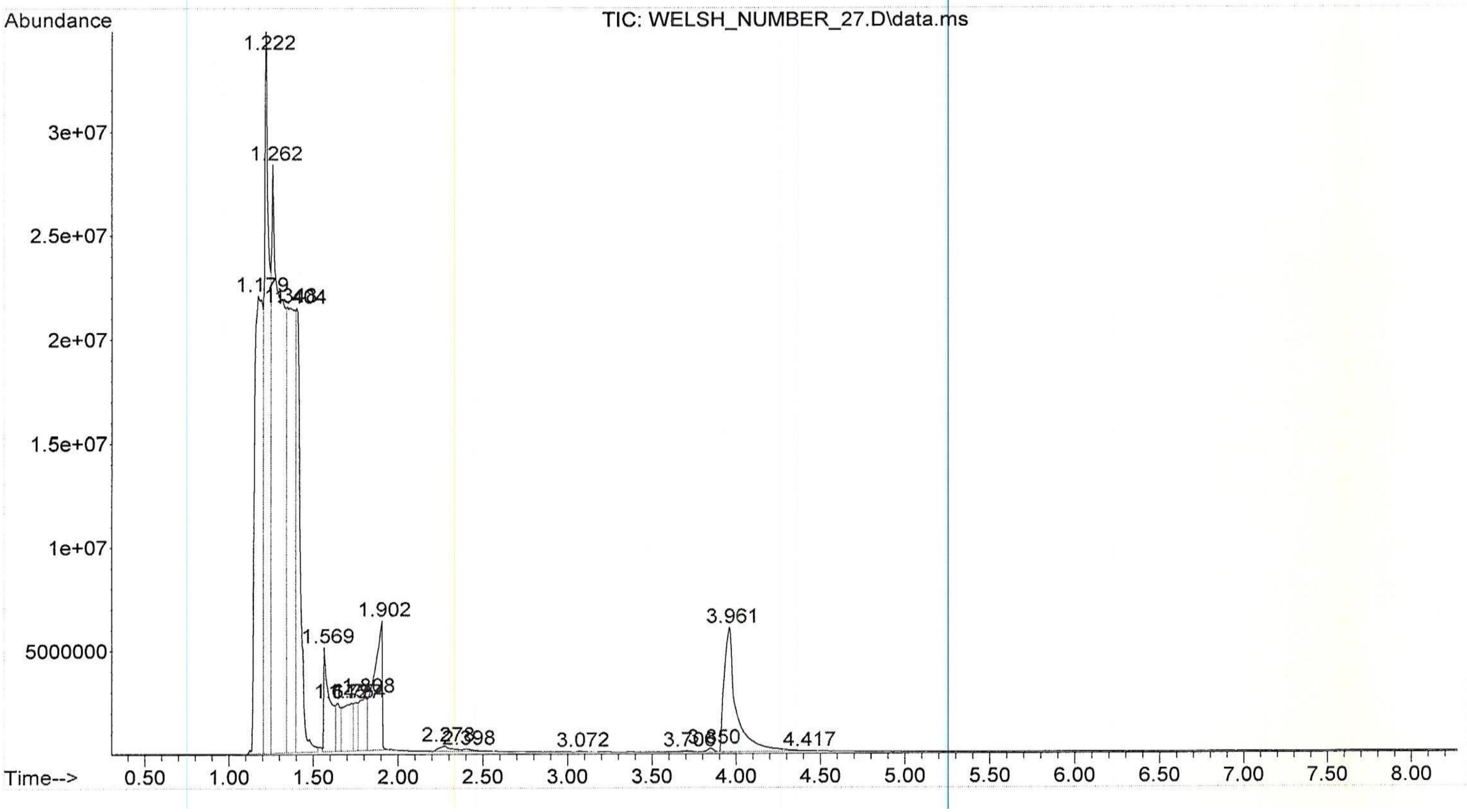


Figure 56: Zoomed in Spectrum Run 27

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_28.D
Operator    : DB
Acquired    : 16 Apr 2013   10:12      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_28
Misc Info   :
Vial Number: 39
```

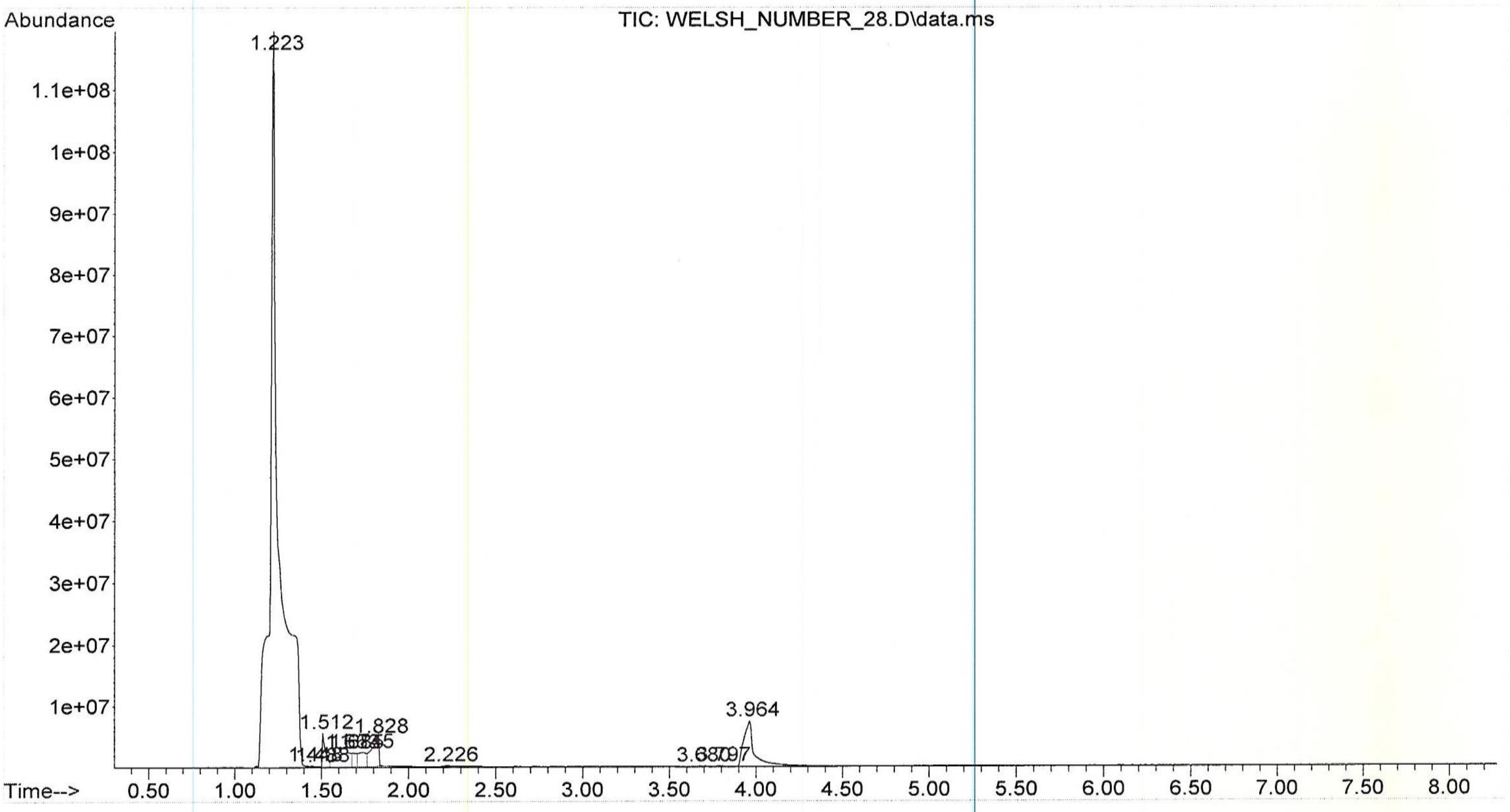


Figure 57: Zoomed in Spectrum Run 28

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_30.D
Operator    : DB
Acquired    : 16 Apr 2013   11:07     using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_30
Misc Info   :
Vial Number: 40
```

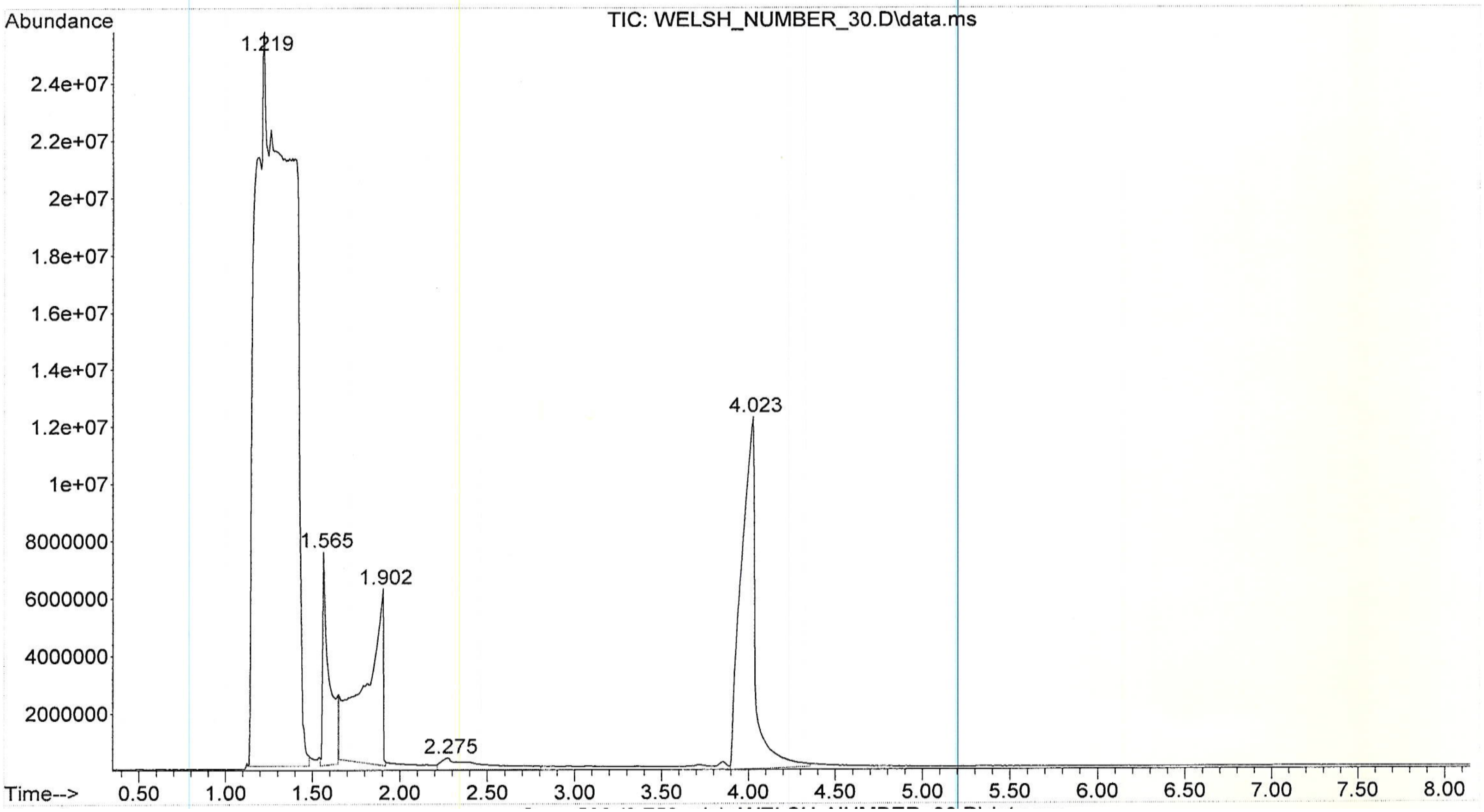
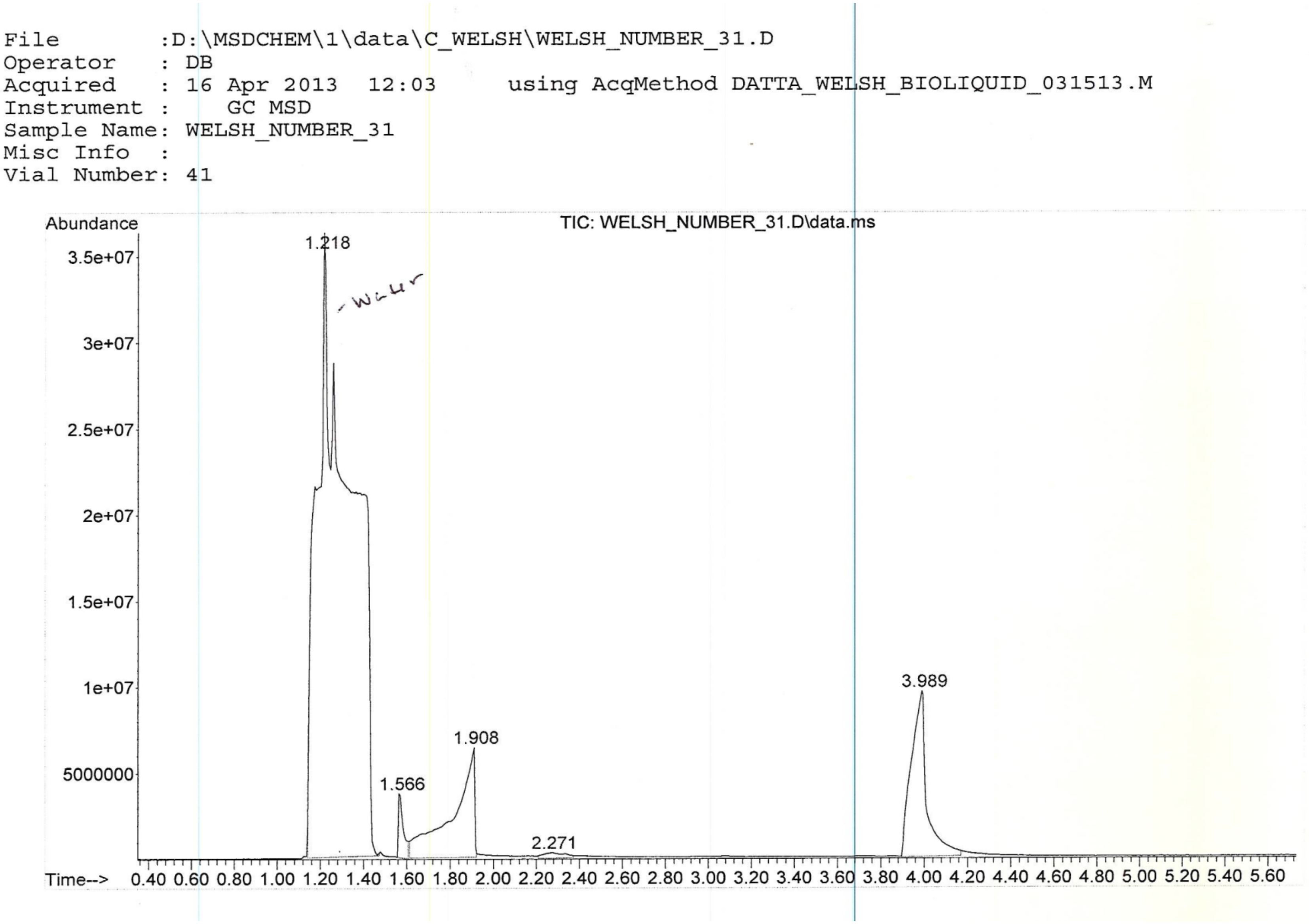


Figure 58: Zoomed in Spectrum Run 30



```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_31.D
Operator    : DB
Acquired    : 16 Apr 2013   12:03      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument :     GC MSD
Sample Name: WELSH_NUMBER_31
Misc Info   :
Vial Number: 41
```

- Water

Figure 59: Zoomed in Spectrum Run 31

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_35.D
Operator    : DB
Acquired    : 16 Apr 2013   13:38      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :     GC MSD
Sample Name: WELSH_NUMBER_35
Misc Info   :
Vial Number: 42
```

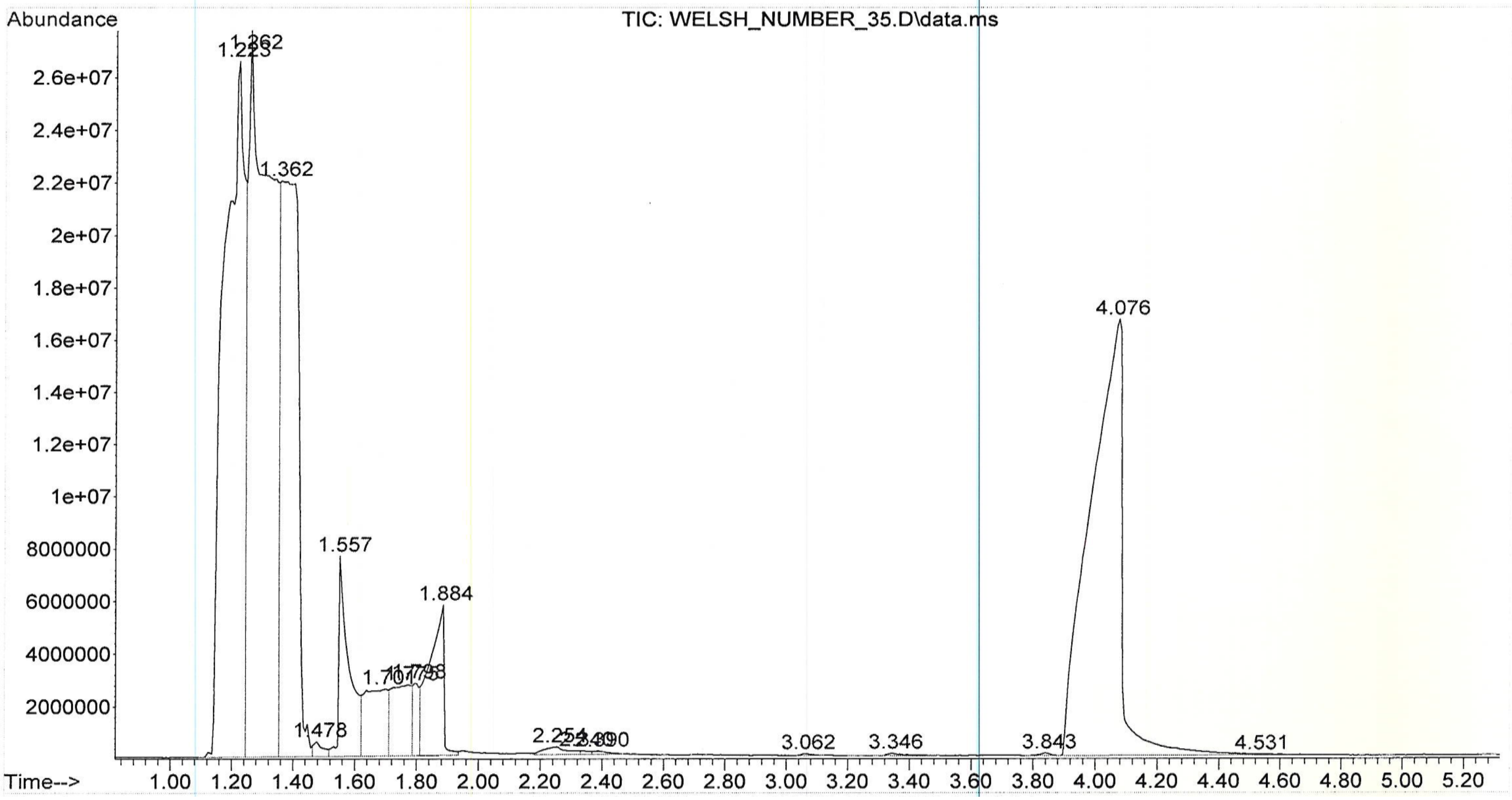


Figure 60: Zoomed in Spectrum Run 35

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_36.D
Operator    : DB
Acquired    : 16 Apr 2013  14:33      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_36
Misc Info   :
Vial Number: 43
```

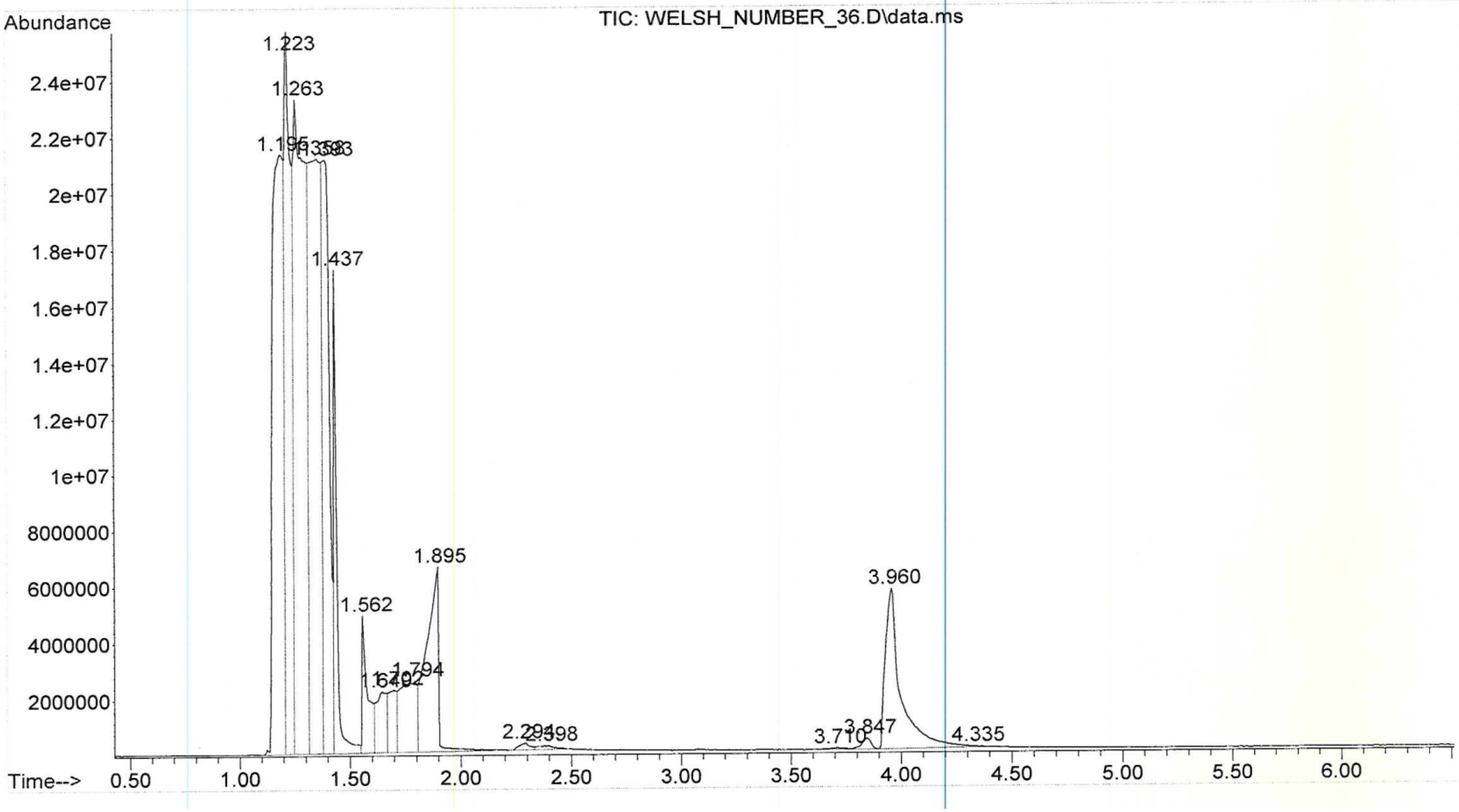
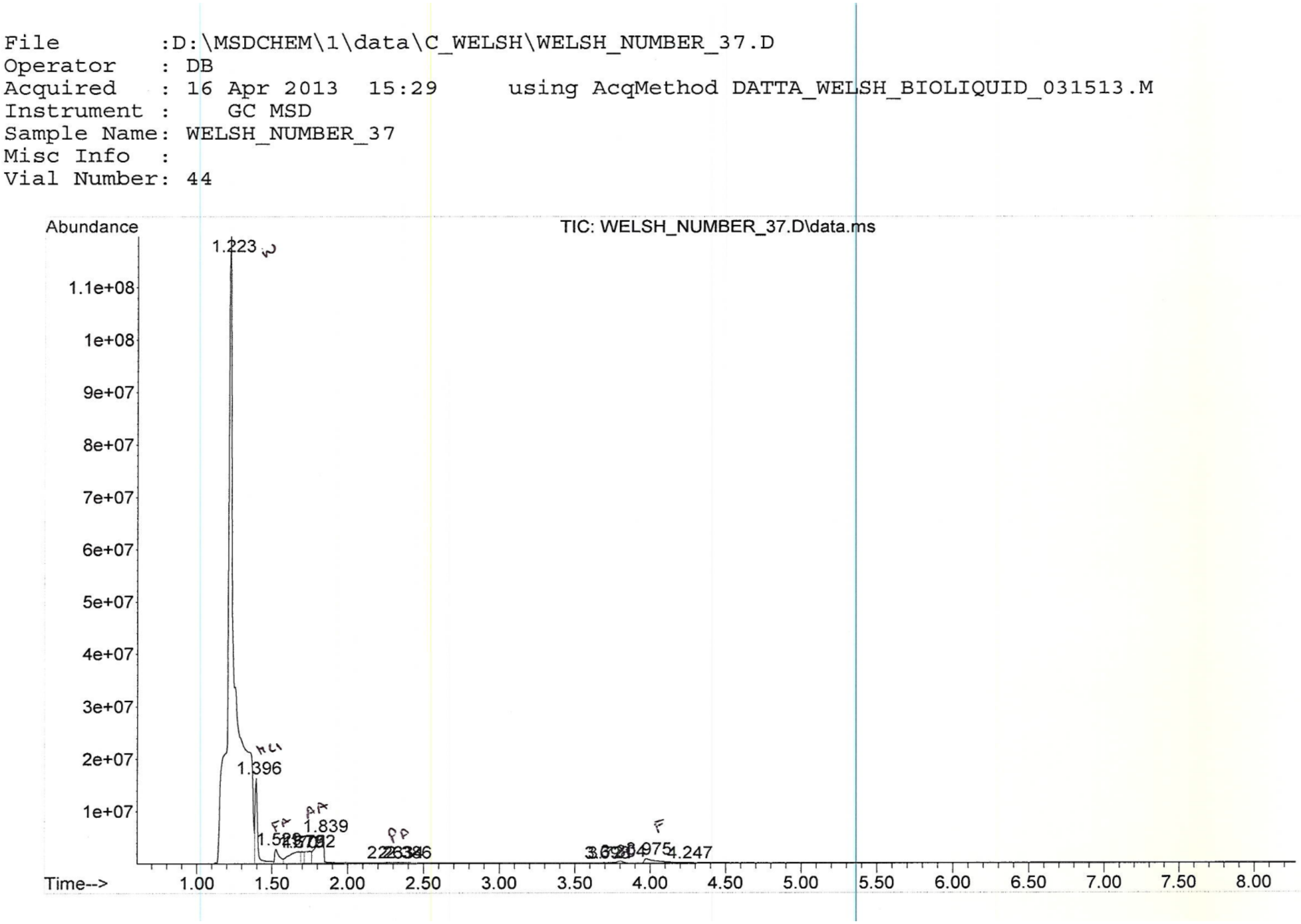


Figure 61: Zoomed in Spectrum Run 36



```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_37.D
Operator    : DB
Acquired    : 16 Apr 2013   15:29      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :     GC MSD
Sample Name: WELSH_NUMBER_37
Misc Info   :
Vial Number: 44
```

Figure 62: Zoomed in Spectrum Run 37

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_38.D
Operator    : DB
Acquired    : 16 Apr 2013   16:24      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_38
Misc Info   :
Vial Number: 45
```

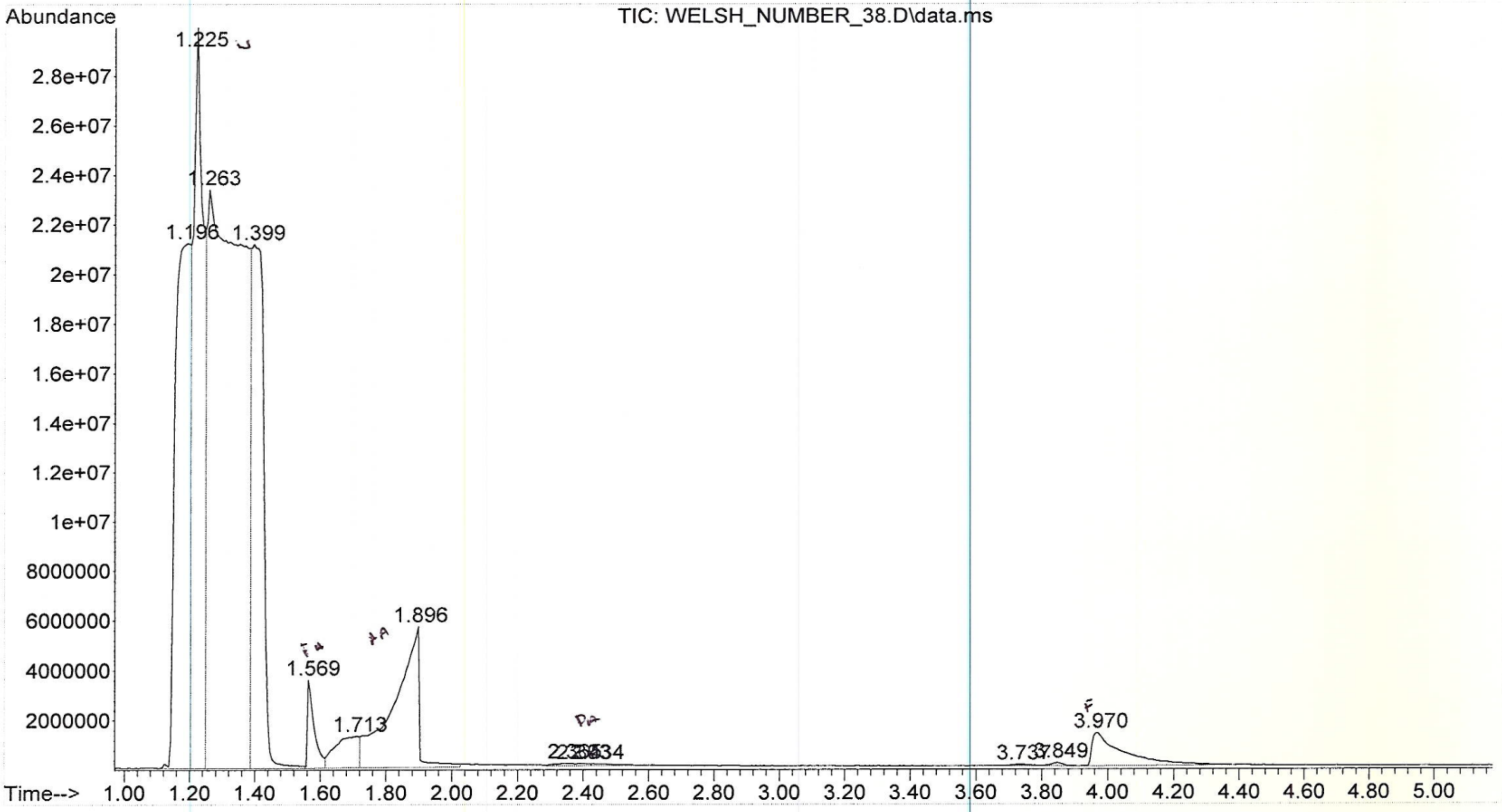


Figure 63: Zoomed in Spectrum Run 38

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_40.D
Operator    : DB
Acquired    : 16 Apr 2013   17:20      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument :     GC MSD
Sample Name: WELSH_NUMBER_40
Misc Info  :
Vial Number: 46
```

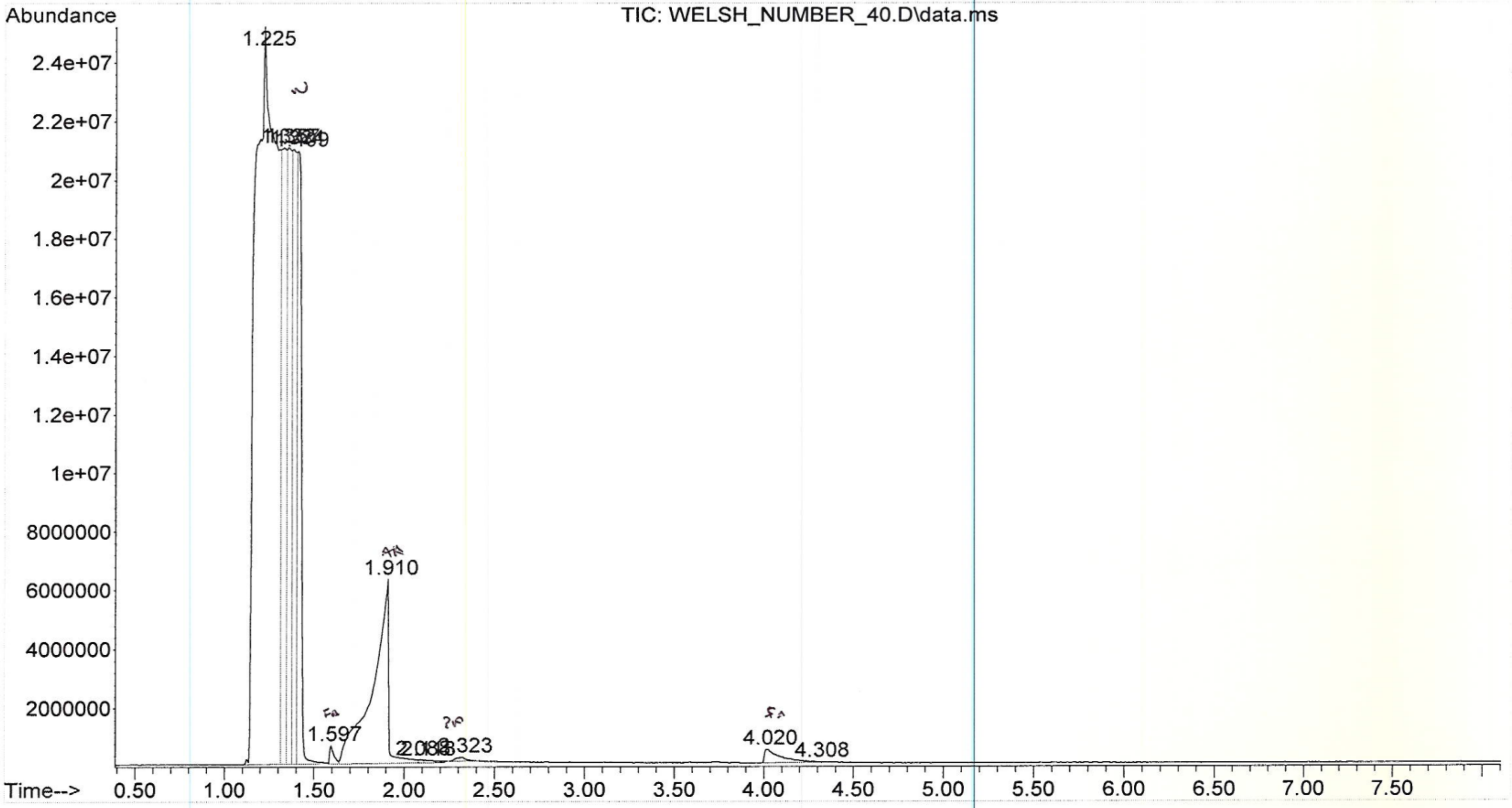


Figure 64: Zoomed in Spectrum Run 40

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_41.D
Operator    : DB
Acquired    : 16 Apr 2013   18:15      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :     GC MSD
Sample Name: WELSH_NUMBER_41
Misc Info   :
Vial Number: 47
```

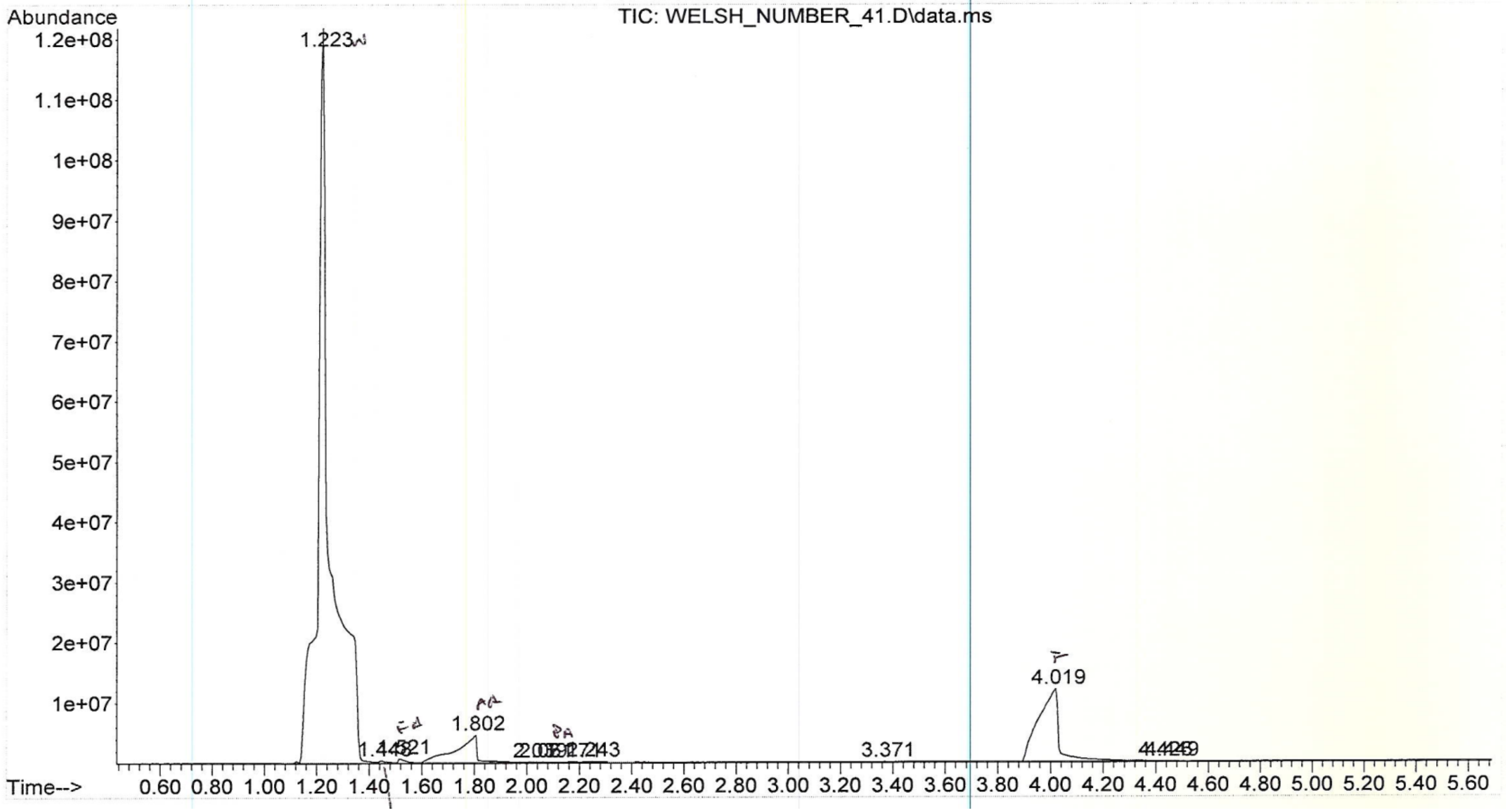


Figure 65: Zoomed in Spectrum Run 41

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_42.D
Operator    : DB
Acquired    : 16 Apr 2013   19:10      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :    GC MSD
Sample Name: WELSH_NUMBER_42
Misc Info   :
Vial Number: 48
```

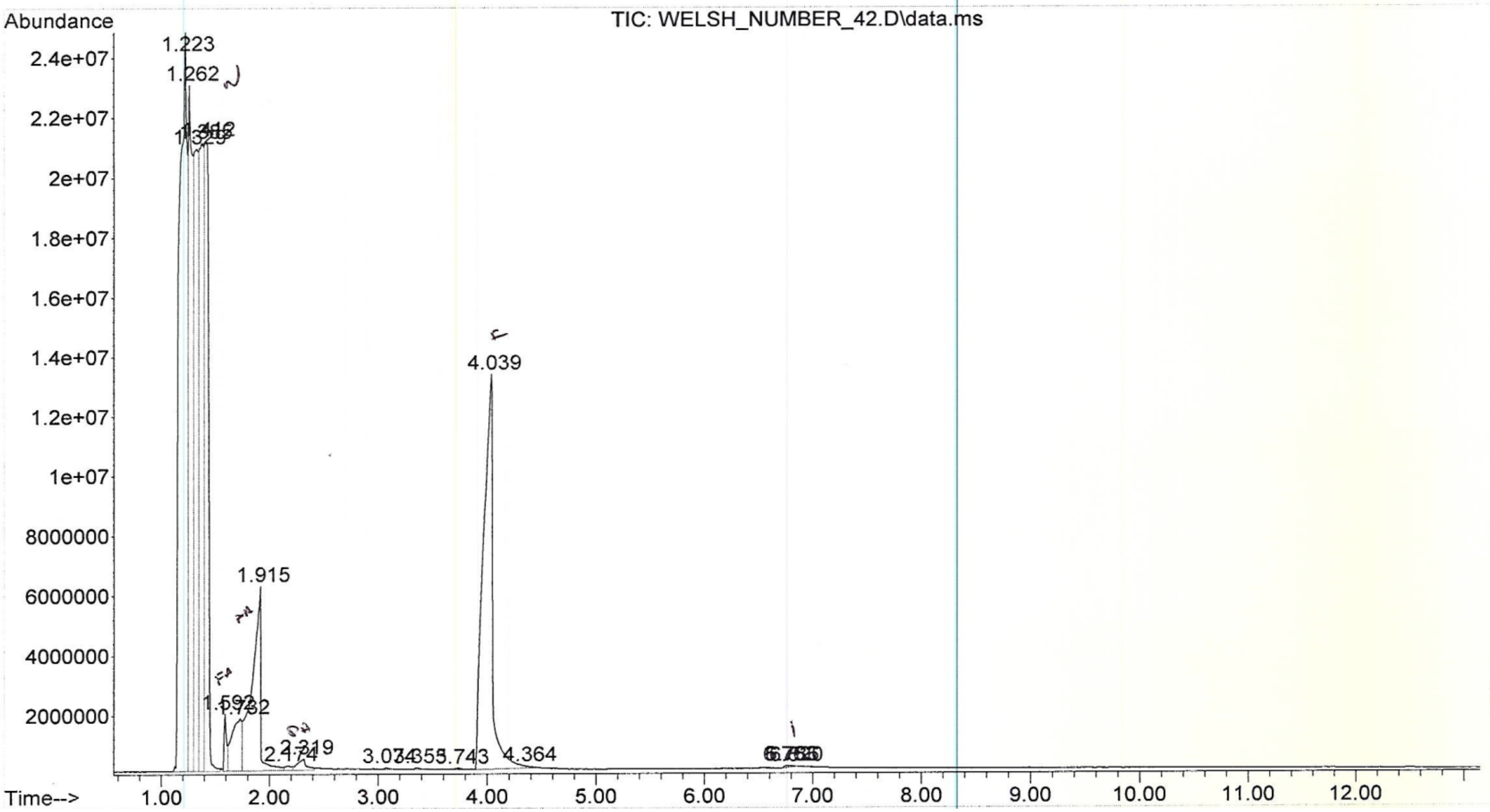


Figure 66: Zoomed in Spectrum Run 42

```
File        :D:\MSDCHEM\1\data\C_WELSH\WELSH_NUMBER_43.D
Operator    : DB
Acquired    : 16 Apr 2013   20:06      using AcqMethod DATTA_WELSH_BIOLIQUID_031513.M
Instrument  :     GC MSD
Sample Name: WELSH_NUMBER_43
Misc Info   :
Vial Number: 49
```

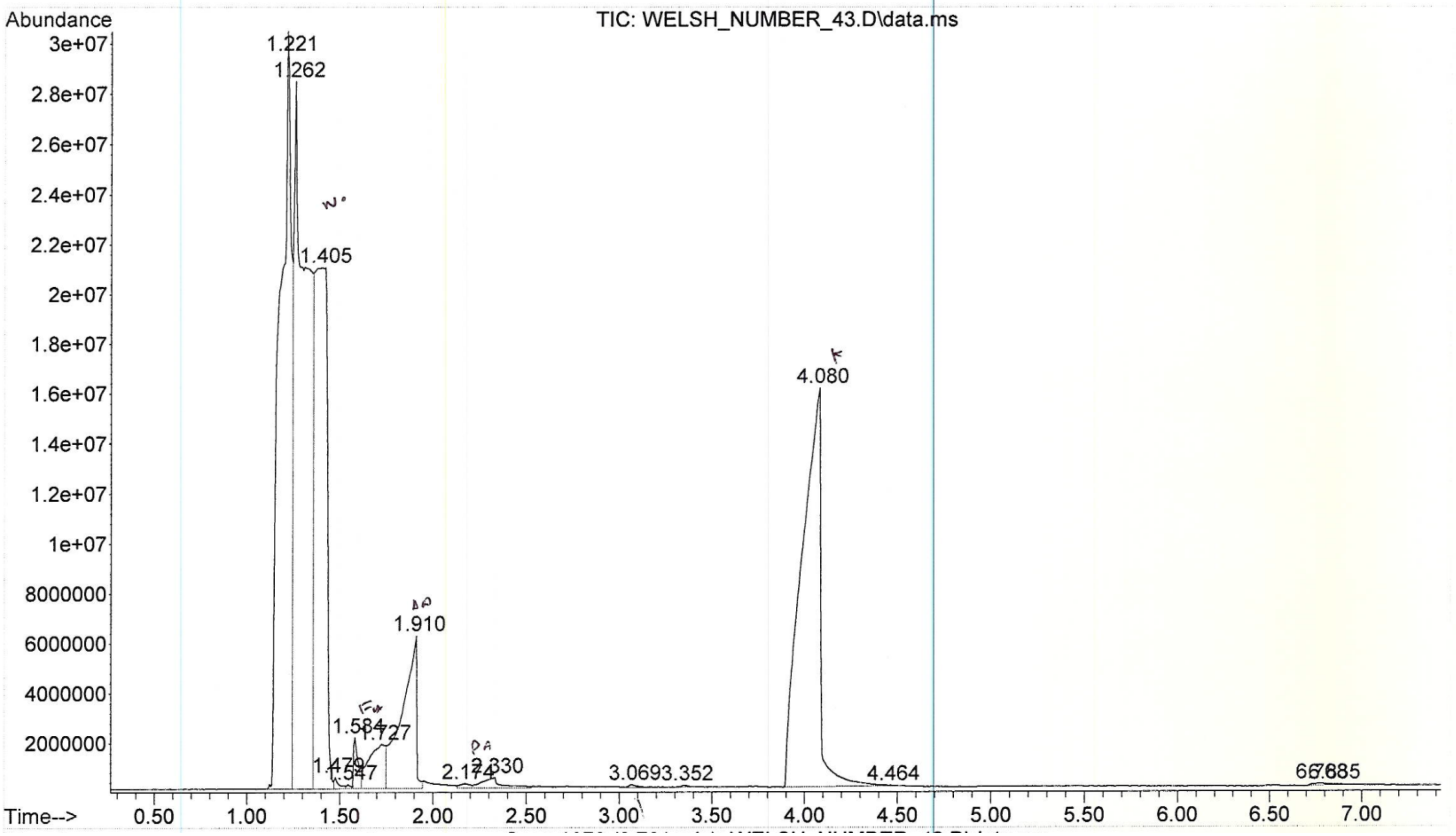
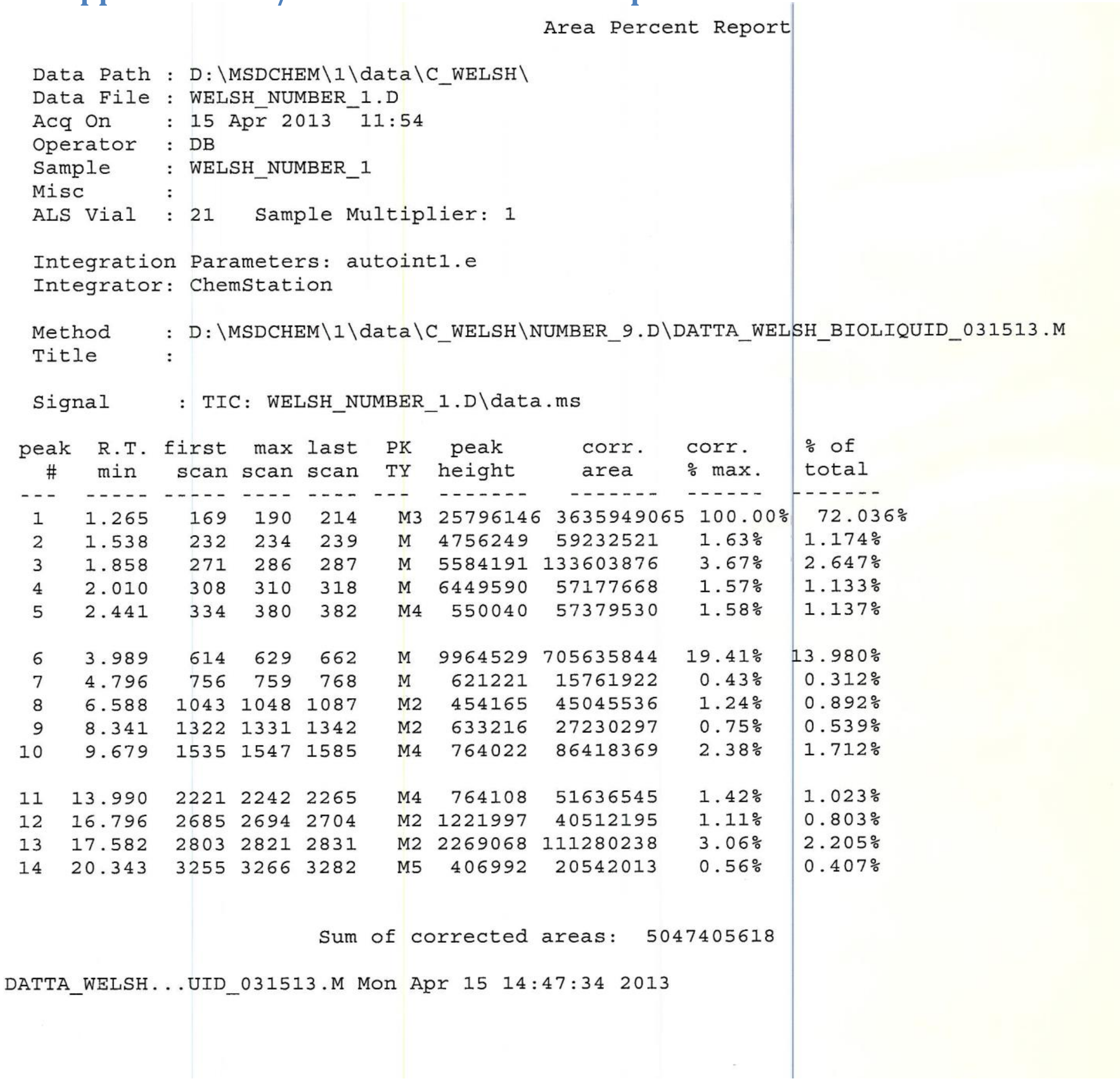


Figure 67: Zoomed in Spectrum Run 43

Appendix B: GC/MS Results – Percent Reports



```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_1.D
  Acq On    : 15 Apr 2013   11:54
  Operator  : DB
  Sample    : WELSH_NUMBER_1
  Misc      :
  ALS Vial  : 21   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_1.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.     corr.    % of
   #   min   scan scan scan  TY  height     area     % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------   ------  -------
  1   1.265   169  190  214   M3 25796146 3635949065 100.00%  72.036%
  2   1.538   232  234  239   M  4756249   59232521   1.63%   1.174%
  3   1.858   271  286  287   M  5584191  133603876   3.67%   2.647%
  4   2.010   308  310  318   M  6449590   57177668   1.57%   1.133%
  5   2.441   334  380  382   M4  550040   57379530   1.58%   1.137%

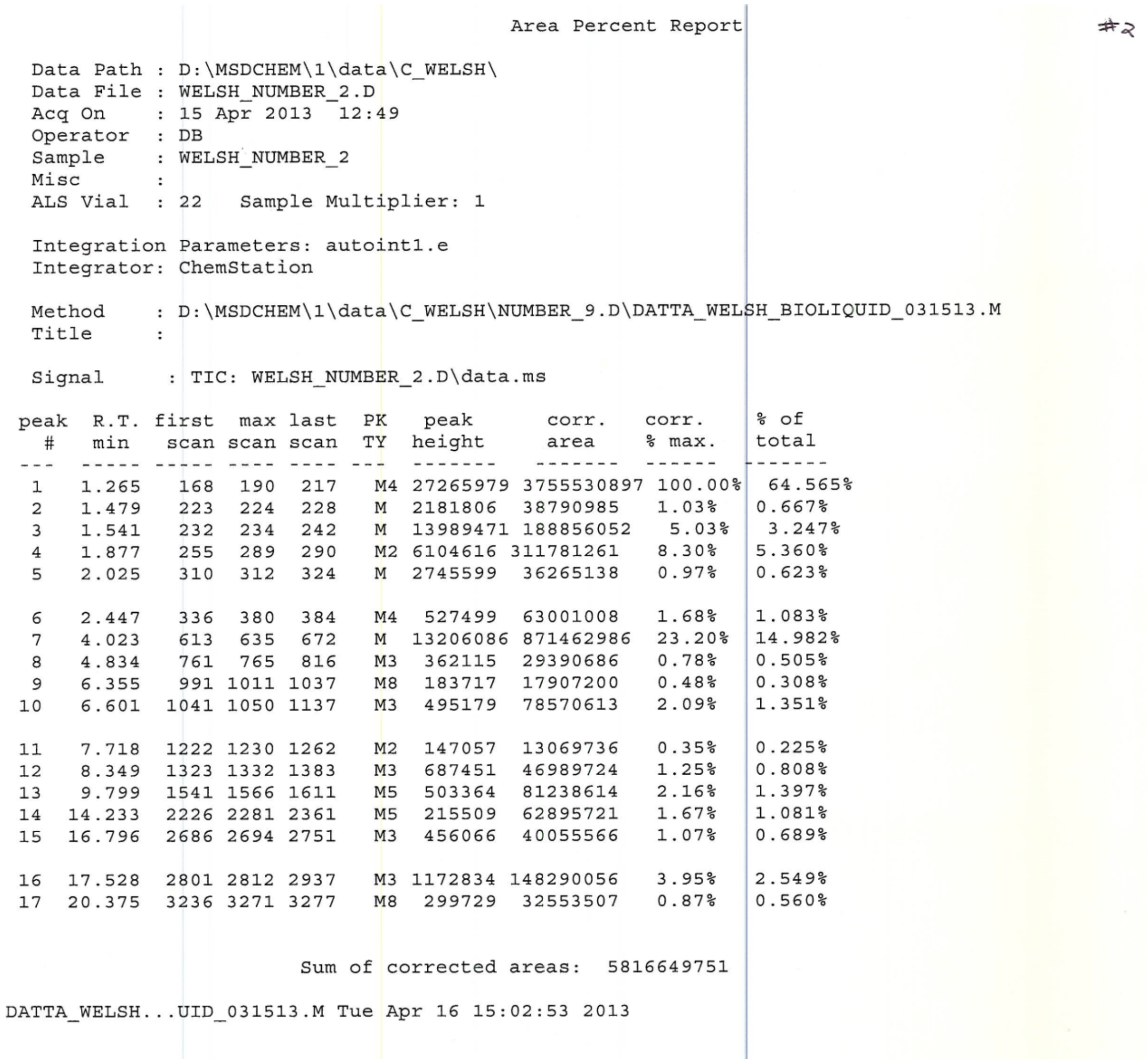
  6   3.989   614  629  662   M  9964529  705635844  19.41%  13.980%
  7   4.796   756  759  768   M   621221   15761922   0.43%   0.312%
  8   6.588  1043 1048 1087   M2  454165   45045536   1.24%   0.892%
  9   8.341  1322 1331 1342   M2  633216   27230297   0.75%   0.539%
 10   9.679  1535 1547 1585   M4  764022   86418369   2.38%   1.712%

 11  13.990  2221 2242 2265   M4  764108   51636545   1.42%   1.023%
 12  16.796  2685 2694 2704   M2 1221997   40512195   1.11%   0.803%
 13  17.582  2803 2821 2831   M2 2269068  111280238   3.06%   2.205%
 14  20.343  3255 3266 3282   M5  406992   20542013   0.56%   0.407%


                         Sum of corrected areas:   5047405618

DATTA_WELSH...UID_031513.M Mon Apr 15 14:47:34 2013
```

Figure 68: Percentage Report Run 1



```
                                   Area Percent Report                         #2

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_2.D
  Acq On    : 15 Apr 2013  12:49
  Operator  : DB
  Sample    : WELSH_NUMBER_2
  Misc      :
  ALS Vial  : 22   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal      : TIC: WELSH_NUMBER_2.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
   #   min   scan scan scan  TY  height     area     % max.   total
 ---  ----- ----- ---- ---- --- -------   -------   ------  -------
  1   1.265   168  190  217  M4 27265979 3755530897 100.00%  64.565%
  2   1.479   223  224  228  M  2181806   38790985   1.03%  0.667%
  3   1.541   232  234  242  M  13989471 188856052   5.03%   3.247%
  4   1.877   255  289  290  M2 6104616 311781261   8.30%  5.360%
  5   2.025   310  312  324  M  2745599   36265138   0.97%  0.623%

  6   2.447   336  380  384  M4  527499   63001008   1.68%  1.083%
  7   4.023   613  635  672  M  13206086 871462986  23.20%  14.982%
  8   4.834   761  765  816  M3  362115   29390686   0.78%  0.505%
  9   6.355   991 1011 1037  M8  183717   17907200   0.48%  0.308%
 10   6.601  1041 1050 1137  M3  495179   78570613   2.09%  1.351%

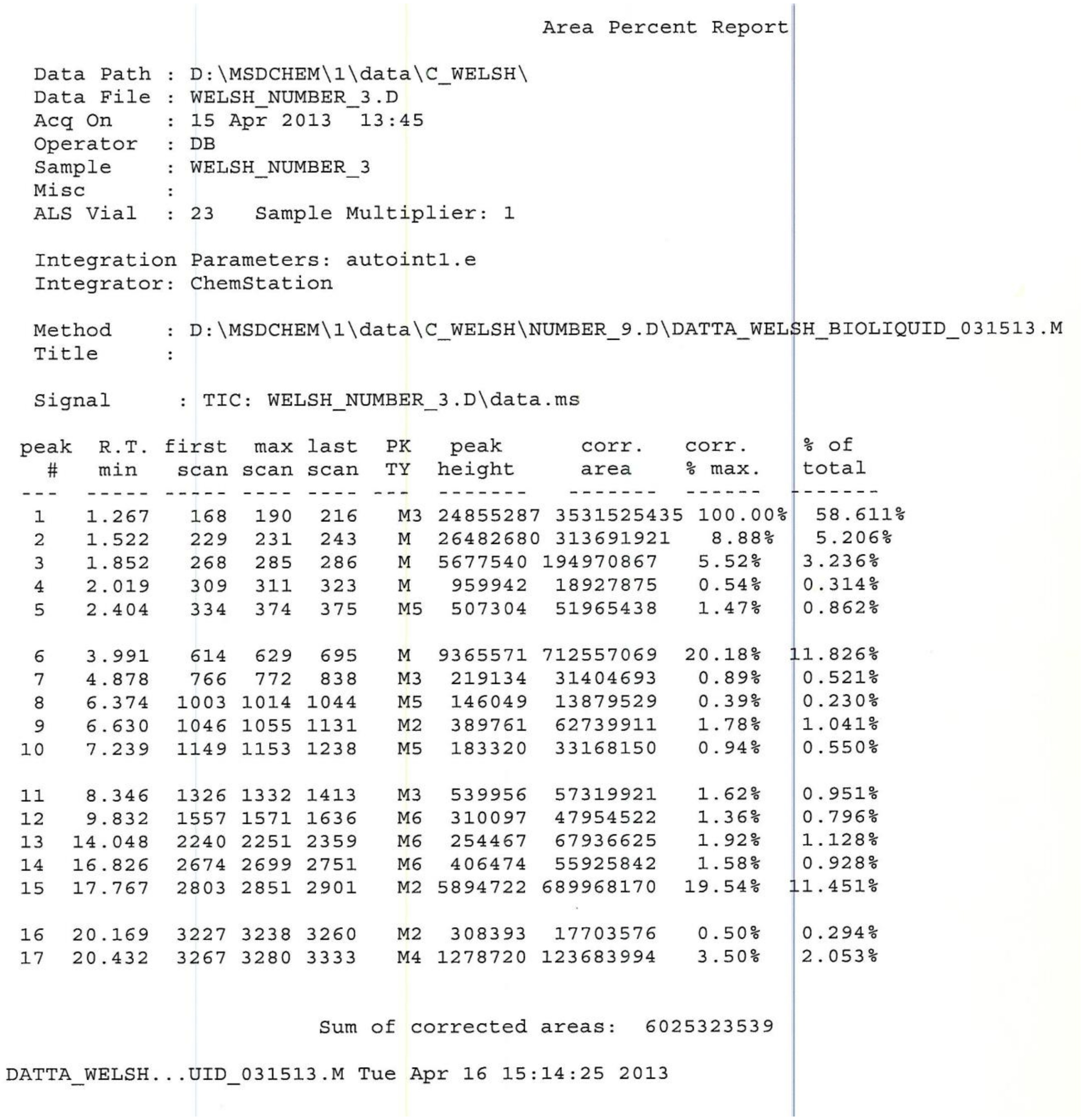
 11   7.718  1222 1230 1262  M2  147057   13069736   0.35%  0.225%
 12   8.349  1323 1332 1383  M3  687451   46989724   1.25%  0.808%
 13   9.799  1541 1566 1611  M5  503364   81238614   2.16%  1.397%
 14  14.233  2226 2281 2361  M5  215509   62895721   1.67%  1.081%
 15  16.796  2686 2694 2751  M3  456066   40055566   1.07%  0.689%

 16  17.528  2801 2812 2937  M3 1172834 148290056   3.95%  2.549%
 17  20.375  3236 3271 3277  M8  299729   32553507   0.87%  0.560%


                        Sum of corrected areas:   5816649751

DATTA_WELSH...UID_031513.M Tue Apr 16 15:02:53 2013
```

Figure 69: Percentage Report Run 2



```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_3.D
  Acq On    : 15 Apr 2013  13:45
  Operator  : DB
  Sample    : WELSH_NUMBER_3
  Misc      :
  ALS Vial  : 23   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_3.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.267   168  190  216   M3 24855287 3531525435 100.00%  58.611%
  2   1.522   229  231  243   M  26482680 313691921   8.88%   5.206%
  3   1.852   268  285  286   M  5677540 194970867   5.52%   3.236%
  4   2.019   309  311  323   M   959942  18927875   0.54%   0.314%
  5   2.404   334  374  375   M5  507304  51965438   1.47%   0.862%

  6   3.991   614  629  695   M  9365571 712557069  20.18%  11.826%
  7   4.878   766  772  838   M3  219134  31404693   0.89%   0.521%
  8   6.374  1003 1014 1044   M5  146049  13879529   0.39%   0.230%
  9   6.630  1046 1055 1131   M2  389761  62739911   1.78%   1.041%
 10   7.239  1149 1153 1238   M5  183320  33168150   0.94%   0.550%

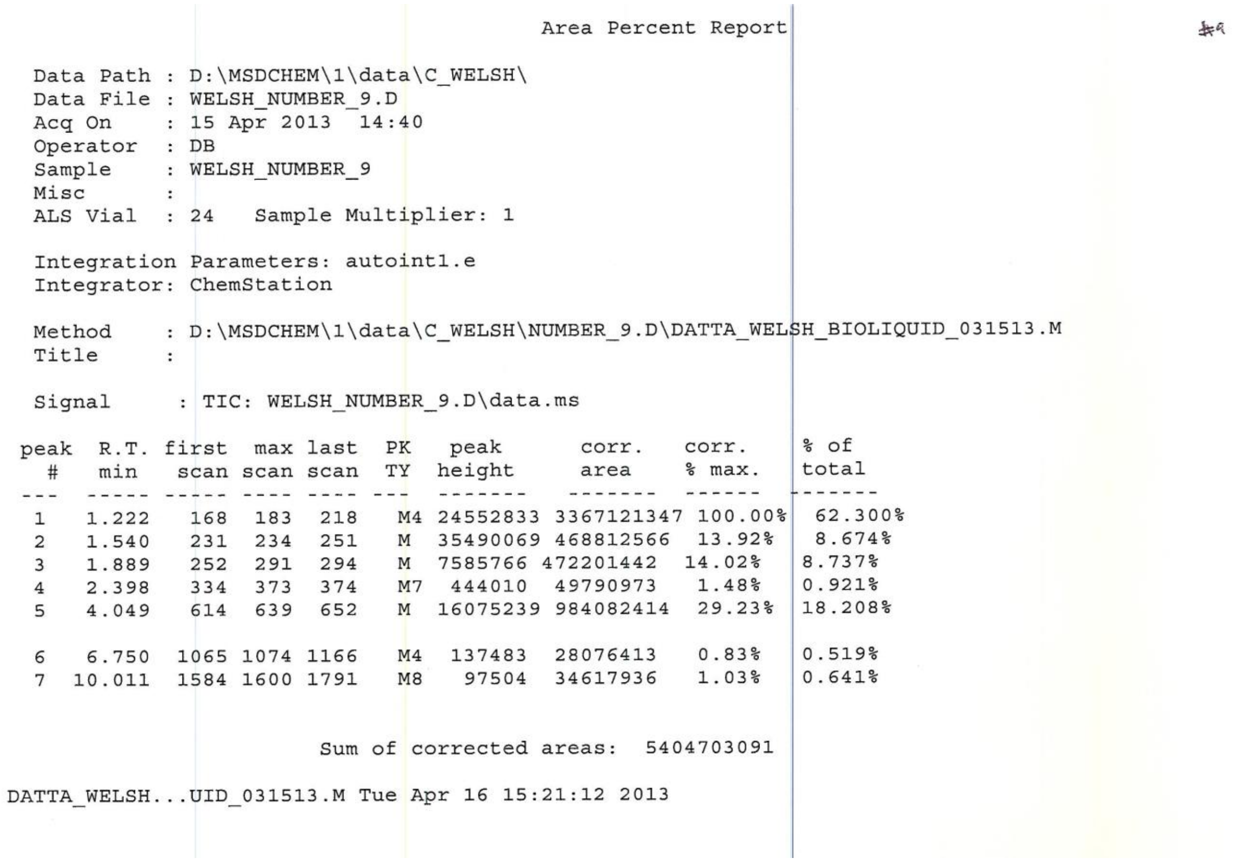
 11   8.346  1326 1332 1413   M3  539956  57319921   1.62%   0.951%
 12   9.832  1557 1571 1636   M6  310097  47954522   1.36%   0.796%
 13  14.048  2240 2251 2359   M6  254467  67936625   1.92%   1.128%
 14  16.826  2674 2699 2751   M6  406474  55925842   1.58%   0.928%
 15  17.767  2803 2851 2901   M2 5894722 689968170  19.54%  11.451%

 16  20.169  3227 3238 3260   M2  308393  17703576   0.50%   0.294%
 17  20.432  3267 3280 3333   M4 1278720 123683994   3.50%   2.053%


                       Sum of corrected areas:   6025323539

DATTA_WELSH...UID_031513.M Tue Apr 16 15:14:25 2013
```

Figure 70: Percentage Report Run 3



#9

```
                                   Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_9.D
  Acq On    : 15 Apr 2013  14:40
  Operator  : DB
  Sample    : WELSH_NUMBER_9
  Misc      :
  ALS Vial  : 24   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_9.D\data.ms

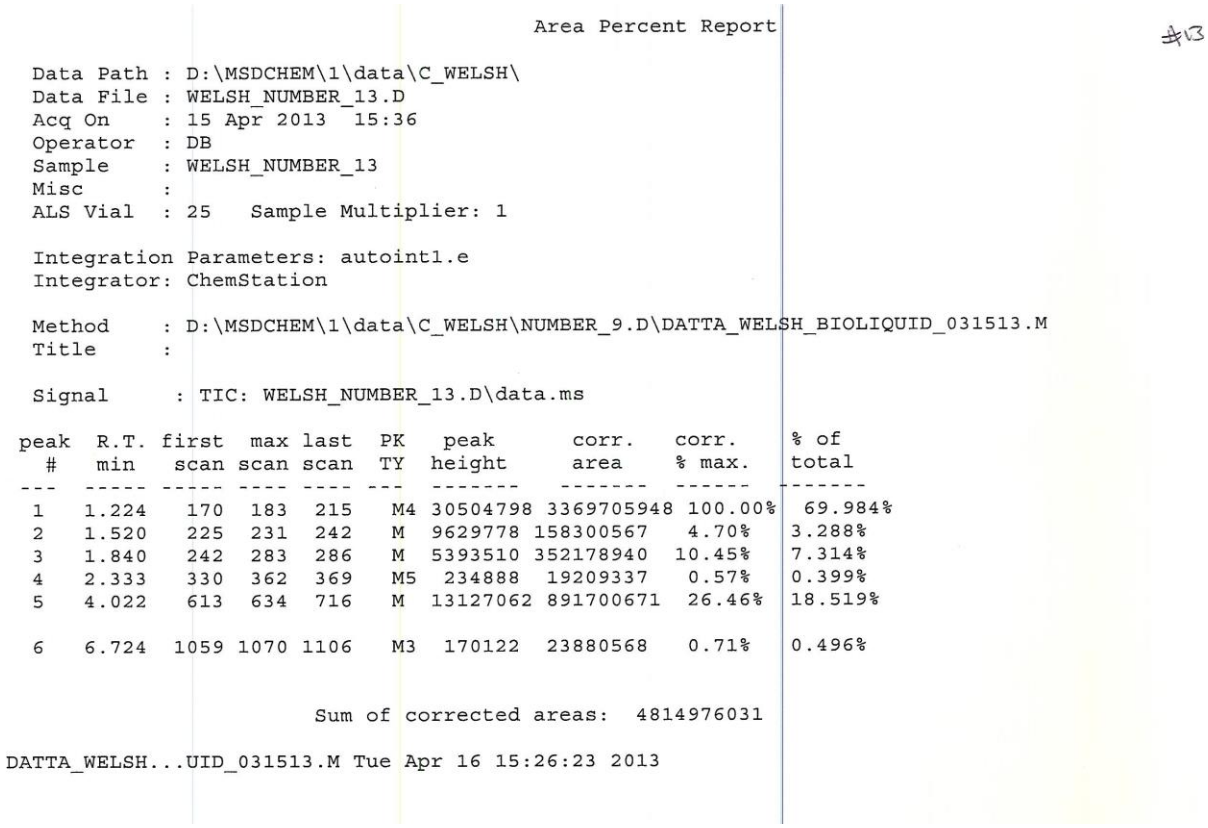
 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.222   168  183  218  M4 24552833 3367121347 100.00%  62.300%
  2   1.540   231  234  251  M  35490069 468812566  13.92%   8.674%
  3   1.889   252  291  294  M  7585766 472201442  14.02%   8.737%
  4   2.398   334  373  374  M7  444010   49790973   1.48%   0.921%
  5   4.049   614  639  652  M  16075239 984082414  29.23%  18.208%

  6   6.750  1065 1074 1166  M4  137483   28076413   0.83%   0.519%
  7  10.011  1584 1600 1791  M8   97504   34617936   1.03%   0.641%


                       Sum of corrected areas:  5404703091

DATTA_WELSH...UID_031513.M Tue Apr 16 15:21:12 2013
```

Figure 71: Percentage Report Run 9



#13

```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_13.D
  Acq On    : 15 Apr 2013  15:36
  Operator  : DB
  Sample    : WELSH_NUMBER_13
  Misc      :
  ALS Vial  : 25   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_13.D\data.ms

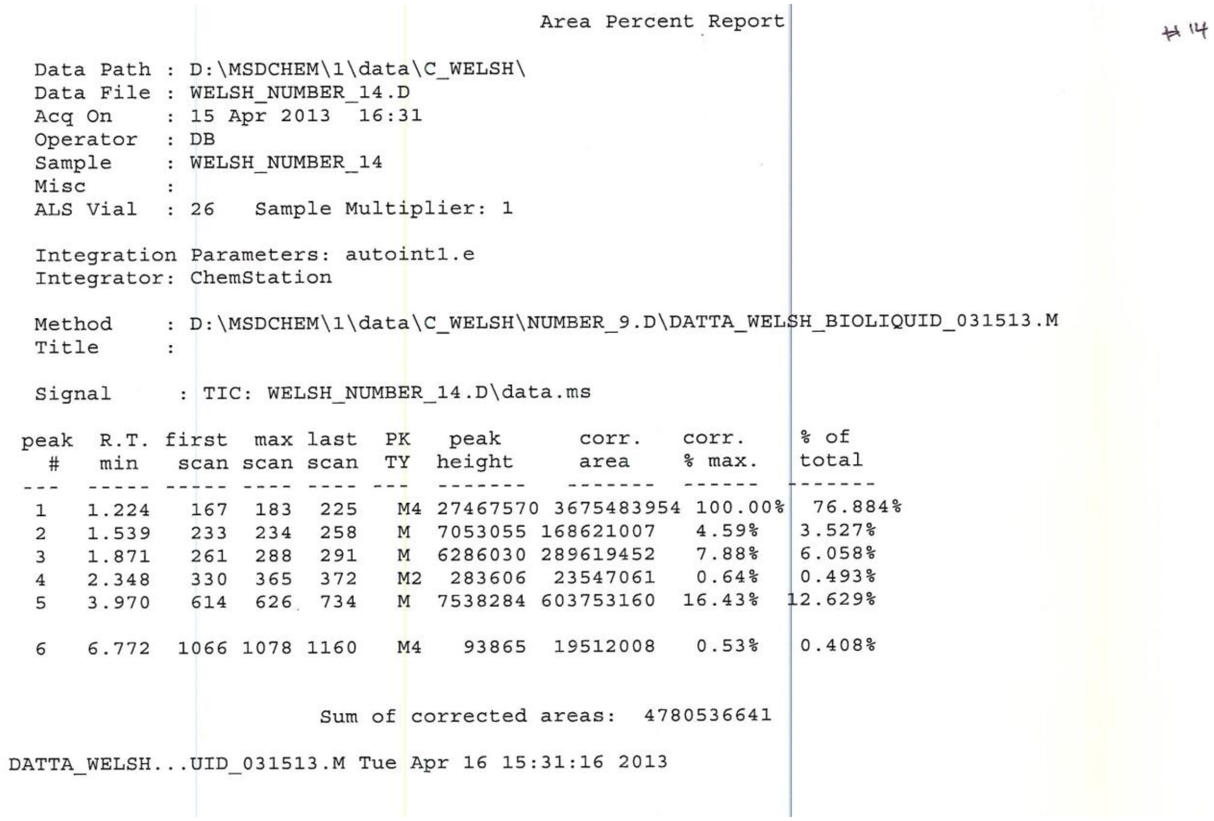
 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.224   170  183  215   M4 30504798 3369705948 100.00%  69.984%
  2   1.520   225  231  242   M  9629778 158300567   4.70%  3.288%
  3   1.840   242  283  286   M  5393510 352178940  10.45%  7.314%
  4   2.333   330  362  369   M5  234888  19209337   0.57%  0.399%
  5   4.022   613  634  716   M  13127062 891700671  26.46%  18.519%

  6   6.724  1059 1070 1106   M3  170122  23880568   0.71%  0.496%


                       Sum of corrected areas:  4814976031

DATTA_WELSH...UID_031513.M Tue Apr 16 15:26:23 2013
```

Figure 72: Percentage Report Run 9



```
                                    Area Percent Report                    #14

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_14.D
  Acq On    : 15 Apr 2013  16:31
  Operator  : DB
  Sample    : WELSH_NUMBER_14
  Misc      :
  ALS Vial  : 26   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_14.D\data.ms

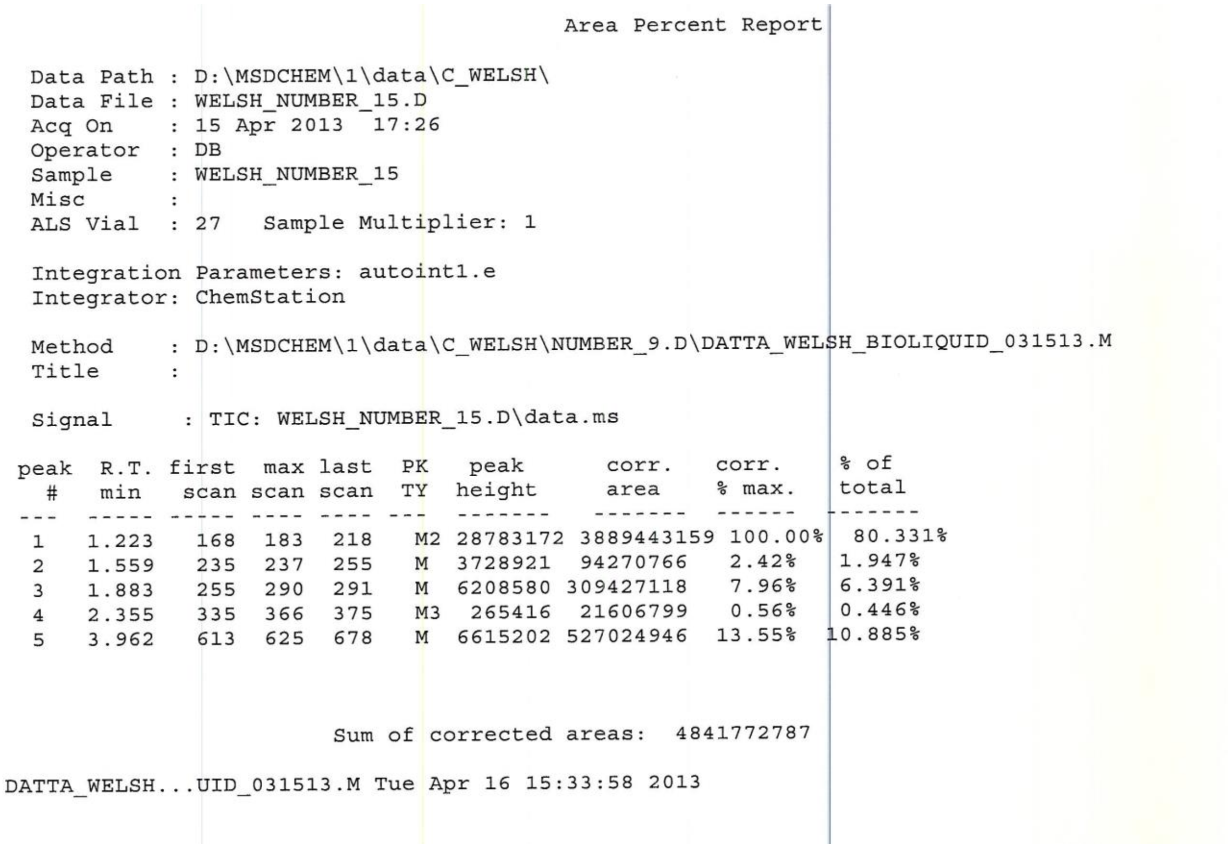
 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.224   167  183  225  M4 27467570 3675483954 100.00%  76.884%
  2   1.539   233  234  258  M  7053055 168621007   4.59%   3.527%
  3   1.871   261  288  291  M  6286030 289619452   7.88%   6.058%
  4   2.348   330  365  372  M2  283606  23547061   0.64%   0.493%
  5   3.970   614  626  734  M  7538284 603753160  16.43%  12.629%

  6   6.772  1066 1078 1160  M4   93865  19512008   0.53%   0.408%


                      Sum of corrected areas:  4780536641

DATTA_WELSH...UID_031513.M Tue Apr 16 15:31:16 2013
```

Figure 73: Percentage Report Run 14



```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_15.D
  Acq On    : 15 Apr 2013  17:26
  Operator  : DB
  Sample    : WELSH_NUMBER_15
  Misc      :
  ALS Vial  : 27   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

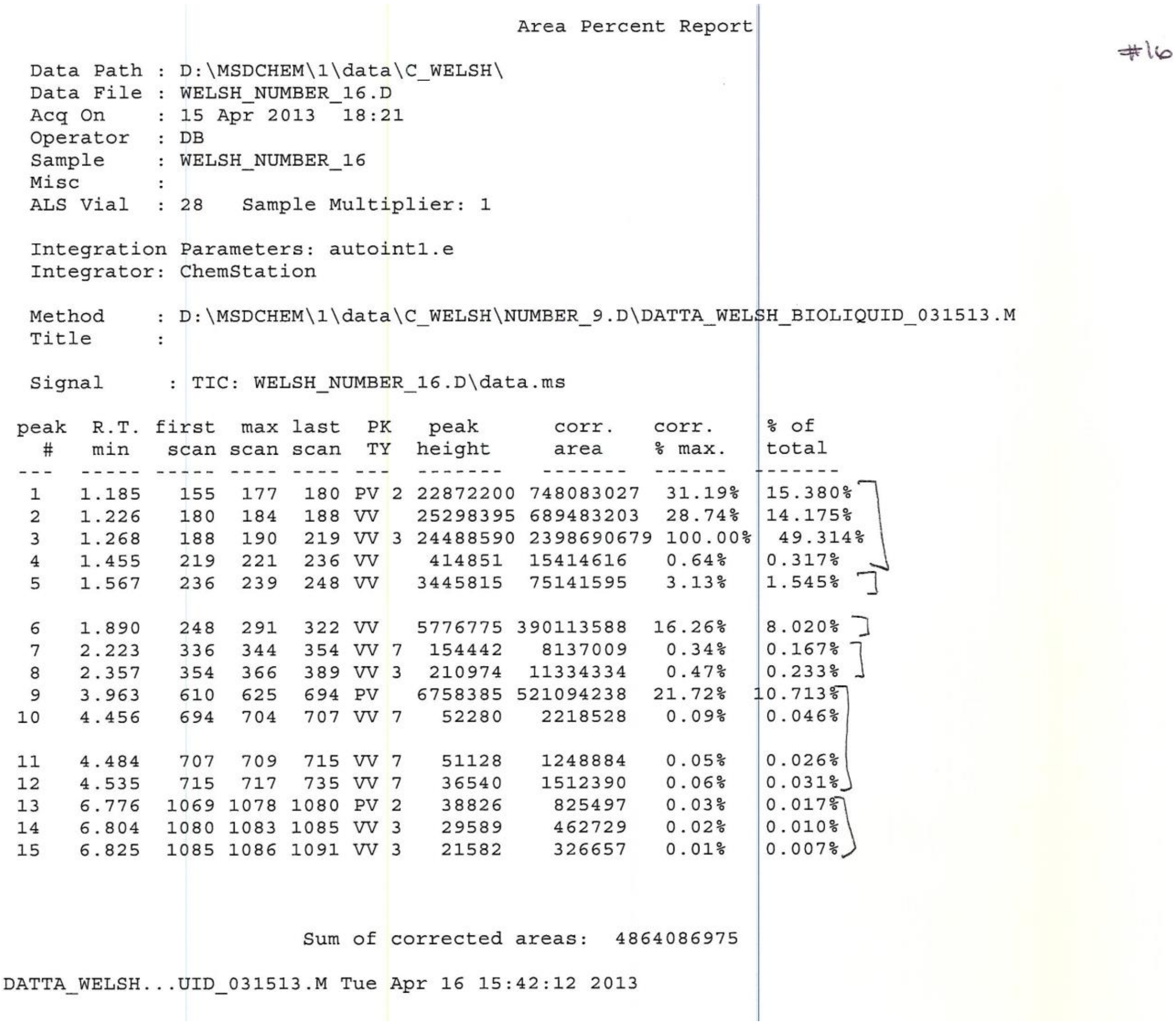
  Signal     : TIC: WELSH_NUMBER_15.D\data.ms

peak  R.T. first  max last  PK   peak      corr.    corr.    % of
  #   min   scan scan scan  TY  height      area    % max.   total
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   1.223   168  183  218  M2 28783172 3889443159 100.00%  80.331%
 2   1.559   235  237  255  M  3728921   94270766   2.42%  1.947%
 3   1.883   255  290  291  M  6208580 309427118   7.96%  6.391%
 4   2.355   335  366  375  M3  265416   21606799   0.56%  0.446%
 5   3.962   613  625  678  M  6615202 527024946  13.55%  10.885%


                        Sum of corrected areas:  4841772787

DATTA_WELSH...UID_031513.M Tue Apr 16 15:33:58 2013
```

Figure 74: Percentage Report Run 15



#16

```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_16.D
  Acq On    : 15 Apr 2013   18:21
  Operator  : DB
  Sample    : WELSH_NUMBER_16
  Misc      :
  ALS Vial  : 28   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_16.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #    min  scan scan scan  TY   height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.185   155  177  180 PV 2 22872200 748083027  31.19%  15.380%
  2   1.226   180  184  188 VV   25298395 689483203  28.74%  14.175%
  3   1.268   188  190  219 VV 3 24488590 2398690679 100.00%  49.314%
  4   1.455   219  221  236 VV     414851  15414616   0.64%  0.317%
  5   1.567   236  239  248 VV    3445815  75141595   3.13%  1.545%

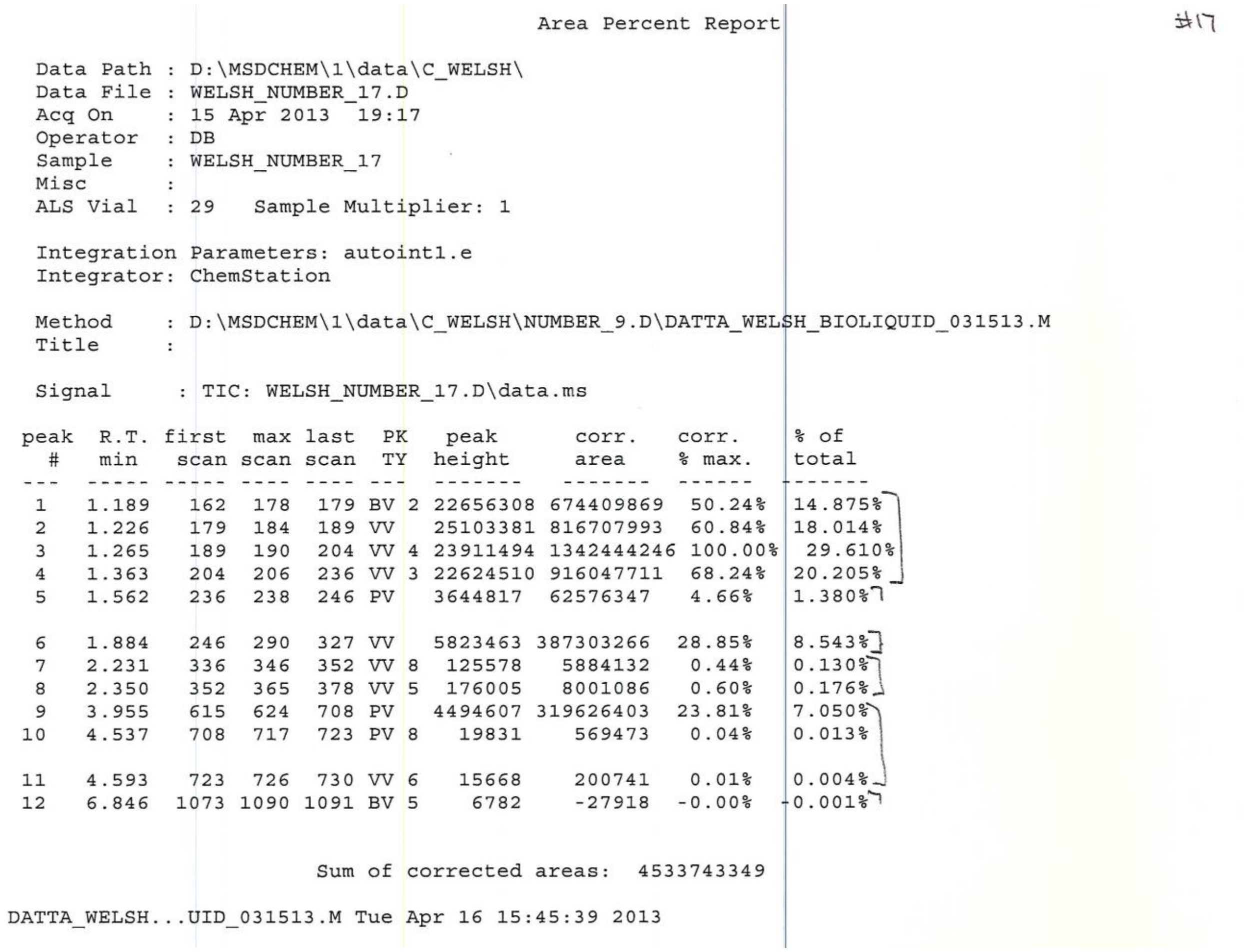
  6   1.890   248  291  322 VV    5776775 390113588  16.26%  8.020%
  7   2.223   336  344  354 VV 7   154442   8137009   0.34%  0.167%
  8   2.357   354  366  389 VV 3   210974  11334334   0.47%  0.233%
  9   3.963   610  625  694 PV    6758385 521094238  21.72% 10.713%
 10   4.456   694  704  707 VV 7    52280   2218528   0.09%  0.046%

 11   4.484   707  709  715 VV 7    51128   1248884   0.05%  0.026%
 12   4.535   715  717  735 VV 7    36540   1512390   0.06%  0.031%
 13   6.776  1069 1078 1080 PV 2    38826    825497   0.03%  0.017%
 14   6.804  1080 1083 1085 VV 3    29589    462729   0.02%  0.010%
 15   6.825  1085 1086 1091 VV 3    21582    326657   0.01%  0.007%


                         Sum of corrected areas:   4864086975

DATTA_WELSH...UID_031513.M Tue Apr 16 15:42:12 2013
```

Figure 75: Percentage Report Run 16



#17

```
                                       Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_17.D
  Acq On    : 15 Apr 2013  19:17
  Operator  : DB
  Sample    : WELSH_NUMBER_17
  Misc      :
  ALS Vial  : 29   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_17.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.   corr.     % of
   #   min   scan scan scan  TY  height     area    % max.    total
 ---  ----- ----- ---- ---- --- -------   -------  ------   ------
  1   1.189   162  178  179 BV 2 22656308 674409869  50.24%  14.875%
  2   1.226   179  184  189 VV   25103381 816707993  60.84%  18.014%
  3   1.265   189  190  204 VV 4 23911494 1342444246 100.00%  29.610%
  4   1.363   204  206  236 VV 3 22624510 916047711  68.24%  20.205%
  5   1.562   236  238  246 PV    3644817  62576347   4.66%   1.380%

  6   1.884   246  290  327 VV    5823463 387303266  28.85%   8.543%
  7   2.231   336  346  352 VV 8  125578    5884132   0.44%   0.130%
  8   2.350   352  365  378 VV 5  176005    8001086   0.60%   0.176%
  9   3.955   615  624  708 PV   4494607 319626403  23.81%   7.050%
 10   4.537   708  717  723 PV 8   19831     569473   0.04%   0.013%

 11   4.593   723  726  730 VV 6   15668     200741   0.01%   0.004%
 12   6.846  1073 1090 1091 BV 5    6782     -27918  -0.00%  -0.001%


                       Sum of corrected areas:   4533743349

DATTA_WELSH...UID_031513.M Tue Apr 16 15:45:39 2013
```

Figure 76: Percentage Report Run 17

#18

```
                                  Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_18.D
  Acq On    : 15 Apr 2013  20:12
  Operator  : DB
  Sample    : WELSH_NUMBER_18
  Misc      :
  ALS Vial  : 30   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_18.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------  -------  ------  -------
  1   1.225   155  183  188 PV 2 24321672 1386046877  78.82%  29.769% } 1
  2   1.265   188  190  208 VV 3 23364327 1758512189 100.00%  37.769% } H2O
  3   1.405   208  212  236 VV 2 22326982 672783159  38.26%  14.450% }
  4   1.568   236  239  249 VV    5295901  98875146   5.62%  2.124% ] 2
  5   1.895   249  292  296 VV    5775155 405705062  23.07%  8.714% ] 3

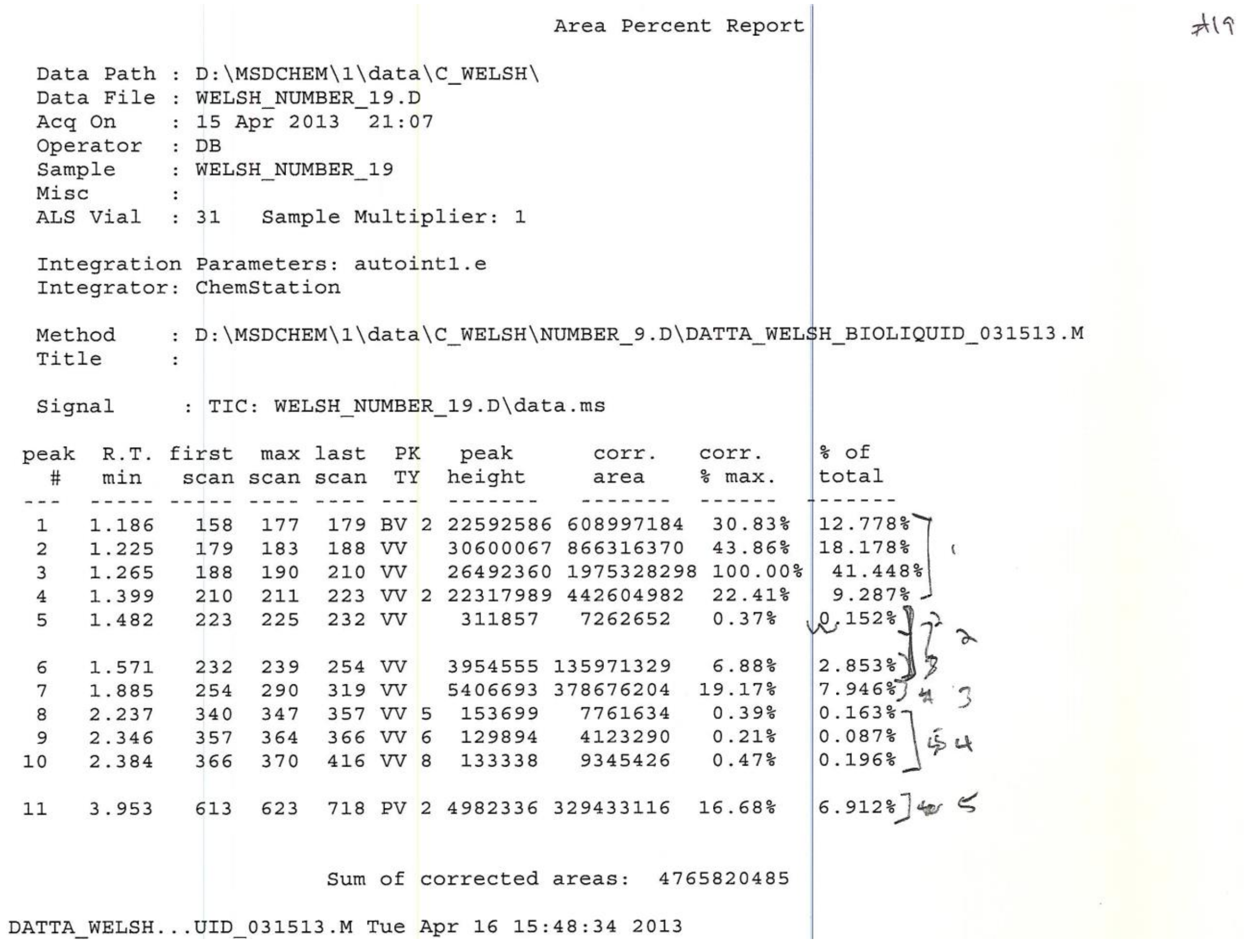
  6   2.224   336  345  348 VV 7  147269   4331455   0.25%  0.093% ]
  7   2.251   348  349  354 VV 5  140721   2958836   0.17%  0.064% ] 4
  8   2.295   354  356  358 VV 3  117123   1644300   0.09%  0.035% ]
  9   2.371   358  368  396 VV 7  152491   9906066   0.56%  0.213% ]
 10   3.955   615  624  684 PV    4291915 310287117  17.64%  6.664% ] 5

 11   4.338   684  685  719 VV 5   91788   4909067   0.28%  0.105% ] 6


                       Sum of corrected areas:   4655959276

DATTA_WELSH...UID_031513.M Tue Apr 16 15:46:43 2013
```

Figure 77: Percentage Report Run 18



```
                                    Area Percent Report                                     #19

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_19.D
  Acq On    : 15 Apr 2013  21:07
  Operator  : DB
  Sample    : WELSH_NUMBER_19
  Misc      :
  ALS Vial  : 31   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_19.D\data.ms

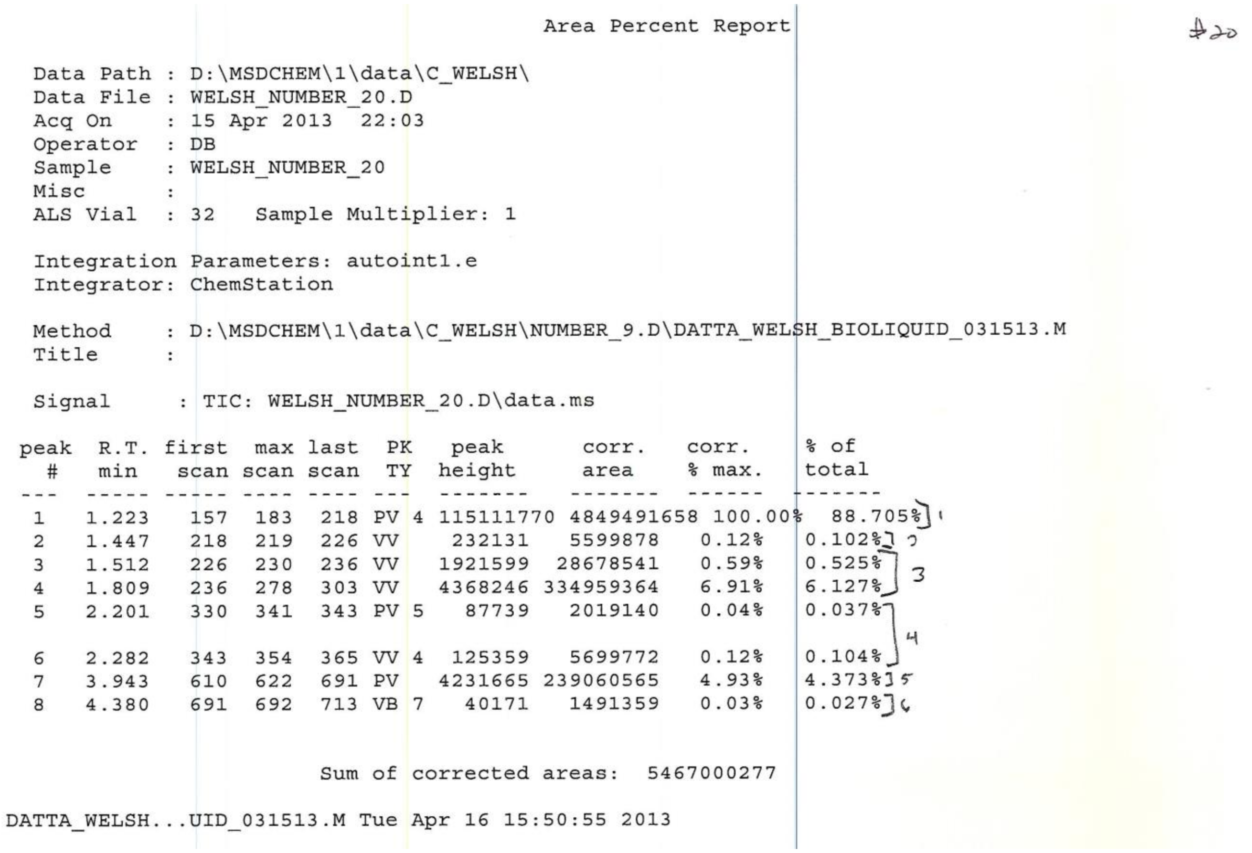
 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
  #    min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.186   158  177  179 BV 2 22592586 608997184  30.83%  12.778%
  2   1.225   179  183  188 VV   30600067 866316370  43.86%  18.178%    1
  3   1.265   188  190  210 VV   26492360 1975328298 100.00%  41.448%
  4   1.399   210  211  223 VV 2 22317989 442604982  22.41%   9.287%
  5   1.482   223  225  232 VV     311857   7262652   0.37%   0.152%
                                                                        2
  6   1.571   232  239  254 VV    3954555 135971329   6.88%   2.853%
  7   1.885   254  290  319 VV    5406693 378676204  19.17%   7.946%    3
  8   2.237   340  347  357 VV 5  153699    7761634   0.39%   0.163%
  9   2.346   357  364  366 VV 6  129894    4123290   0.21%   0.087%    4
 10   2.384   366  370  416 VV 8  133338    9345426   0.47%   0.196%

 11   3.953   613  623  718 PV 2 4982336 329433116  16.68%   6.912%    5


                         Sum of corrected areas:   4765820485

DATTA_WELSH...UID_031513.M Tue Apr 16 15:48:34 2013
```

Figure 78: Percentage Report Run 19



#20

```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_20.D
  Acq On    : 15 Apr 2013  22:03
  Operator  : DB
  Sample    : WELSH_NUMBER_20
  Misc      :
  ALS Vial  : 32   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

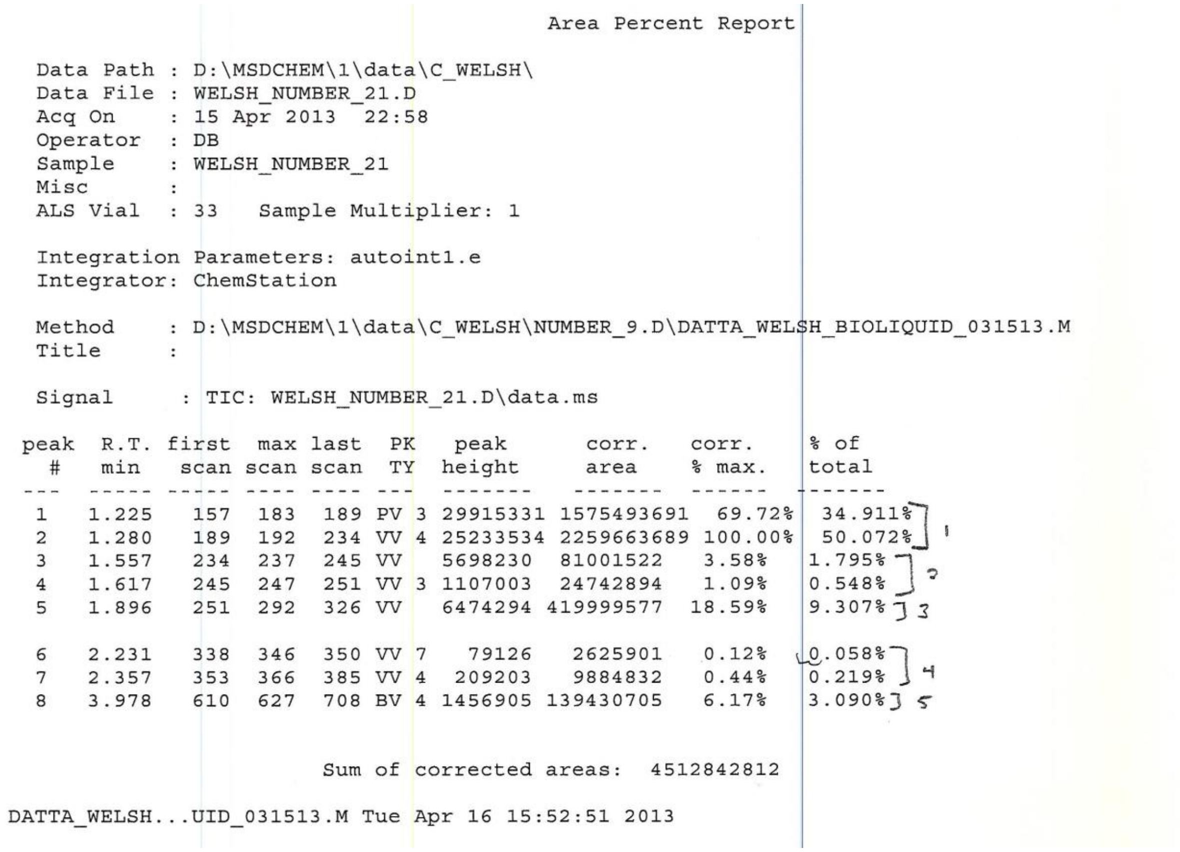
  Signal     : TIC: WELSH_NUMBER_20.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- --- -------   -------  ------   -------
   1  1.223   157  183  218 PV 4 115111770 4849491658 100.00%  88.705% 1
   2  1.447   218  219  226 VV     232131    5599878   0.12%   0.102% 2
   3  1.512   226  230  236 VV    1921599   28678541   0.59%   0.525%
   4  1.809   236  278  303 VV    4368246  334959364   6.91%   6.127%  3
   5  2.201   330  341  343 PV 5     87739    2019140   0.04%   0.037%
                                                                     4
   6  2.282   343  354  365 VV 4   125359    5699772   0.12%   0.104%
   7  3.943   610  622  691 PV    4231665  239060565   4.93%   4.373% 5
   8  4.380   691  692  713 VB 7    40171    1491359   0.03%   0.027% 6


                          Sum of corrected areas:    5467000277

DATTA_WELSH...UID_031513.M Tue Apr 16 15:50:55 2013
```

Figure 79: Percentage Report Run 20



```
                                                  Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_21.D
  Acq On    : 15 Apr 2013   22:58
  Operator  : DB
  Sample    : WELSH_NUMBER_21
  Misc      :
  ALS Vial  : 33   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_21.D\data.ms

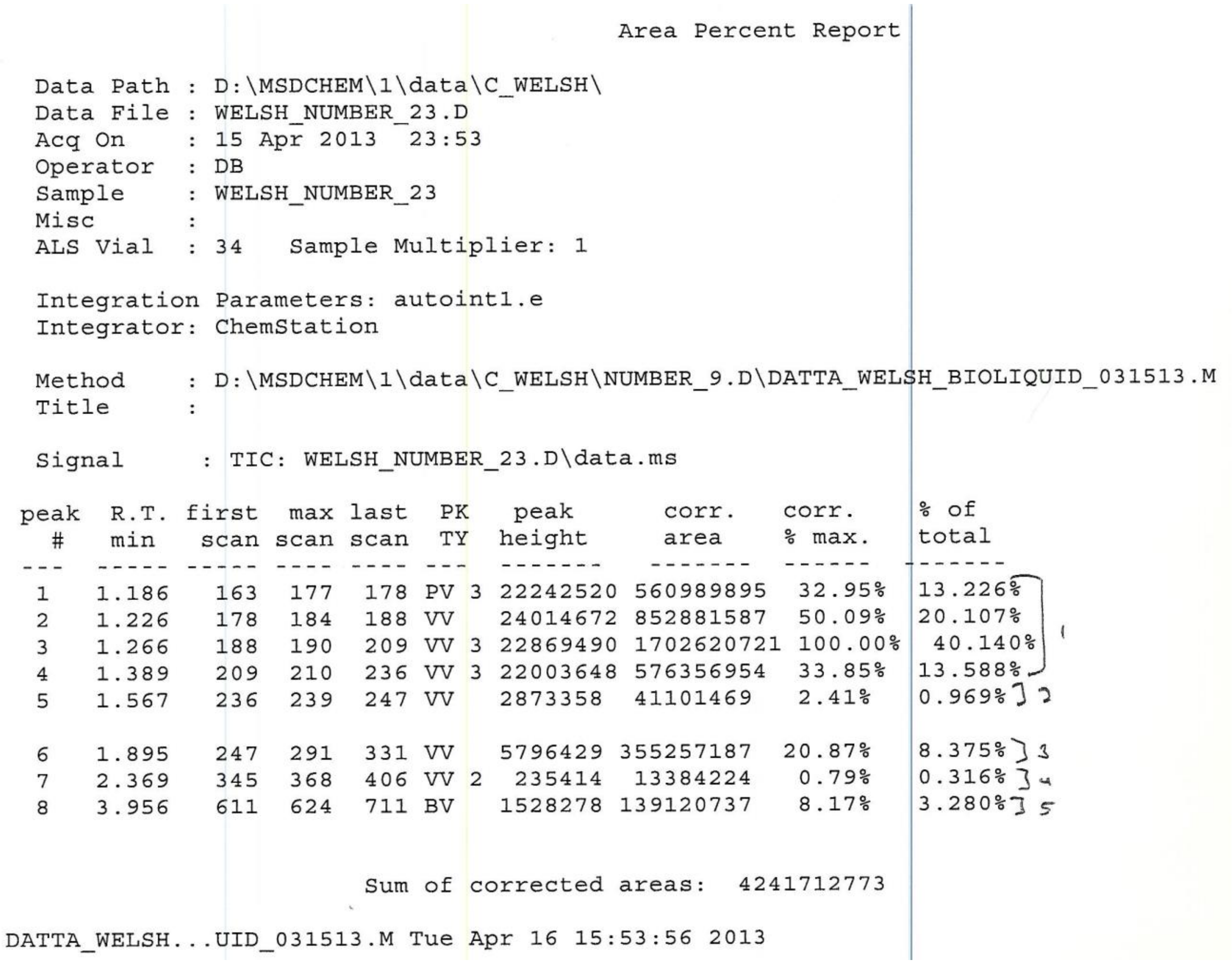
 peak  R.T. first  max last  PK   peak      corr.    corr.     % of
   #   min   scan scan scan  TY  height     area    % max.    total
 ---  ----- ----- ---- ---- --- -------   -------  ------   -------
  1   1.225   157  183  189 PV 3 29915331 1575493691  69.72%  34.911% ]
  2   1.280   189  192  234 VV 4 25233534 2259663689 100.00%  50.072% ] 1
  3   1.557   234  237  245 VV   5698230  81001522   3.58%   1.795% ]
  4   1.617   245  247  251 VV 3 1107003  24742894   1.09%   0.548% ] 2
  5   1.896   251  292  326 VV   6474294 419999577  18.59%   9.307% ] 3

  6   2.231   338  346  350 VV 7   79126   2625901   0.12%   0.058% ]
  7   2.357   353  366  385 VV 4  209203   9884832   0.44%   0.219% ] 4
  8   3.978   610  627  708 BV 4 1456905 139430705   6.17%   3.090% ] 5


                         Sum of corrected areas:  4512842812

DATTA_WELSH...UID_031513.M Tue Apr 16 15:52:51 2013
```

Figure 80: Percentage Report Run 21



```
                                                Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_23.D
  Acq On    : 15 Apr 2013   23:53
  Operator  : DB
  Sample    : WELSH_NUMBER_23
  Misc      :
  ALS Vial  : 34   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_23.D\data.ms

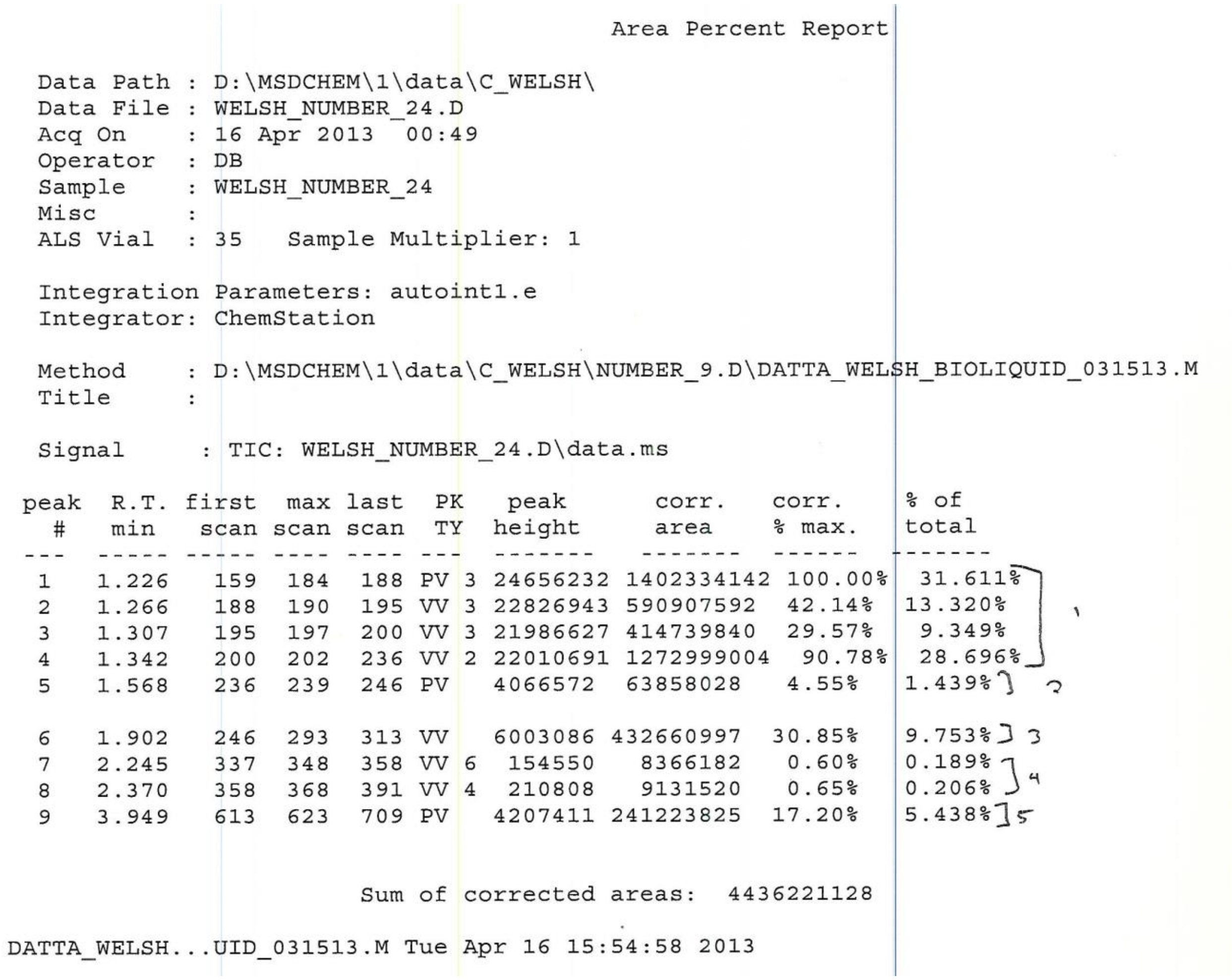
 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
   #   min  scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.186   163  177  178 PV 3 22242520 560989895  32.95%  13.226%
  2   1.226   178  184  188 VV   24014672 852881587  50.09%  20.107%
  3   1.266   188  190  209 VV 3 22869490 1702620721 100.00%  40.140%  1
  4   1.389   209  210  236 VV 3 22003648 576356954  33.85%  13.588%
  5   1.567   236  239  247 VV    2873358  41101469   2.41%   0.969% ] 2

  6   1.895   247  291  331 VV    5796429 355257187  20.87%   8.375% ] 3
  7   2.369   345  368  406 VV 2   235414  13384224   0.79%   0.316% ] 4
  8   3.956   611  624  711 BV    1528278 139120737   8.17%   3.280% ] 5


                     Sum of corrected areas:  4241712773

DATTA_WELSH...UID_031513.M Tue Apr 16 15:53:56 2013
```

Figure 81: Percentage Report Run 22



```
                                         Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_24.D
  Acq On    : 16 Apr 2013  00:49
  Operator  : DB
  Sample    : WELSH_NUMBER_24
  Misc      :
  ALS Vial  : 35   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_24.D\data.ms

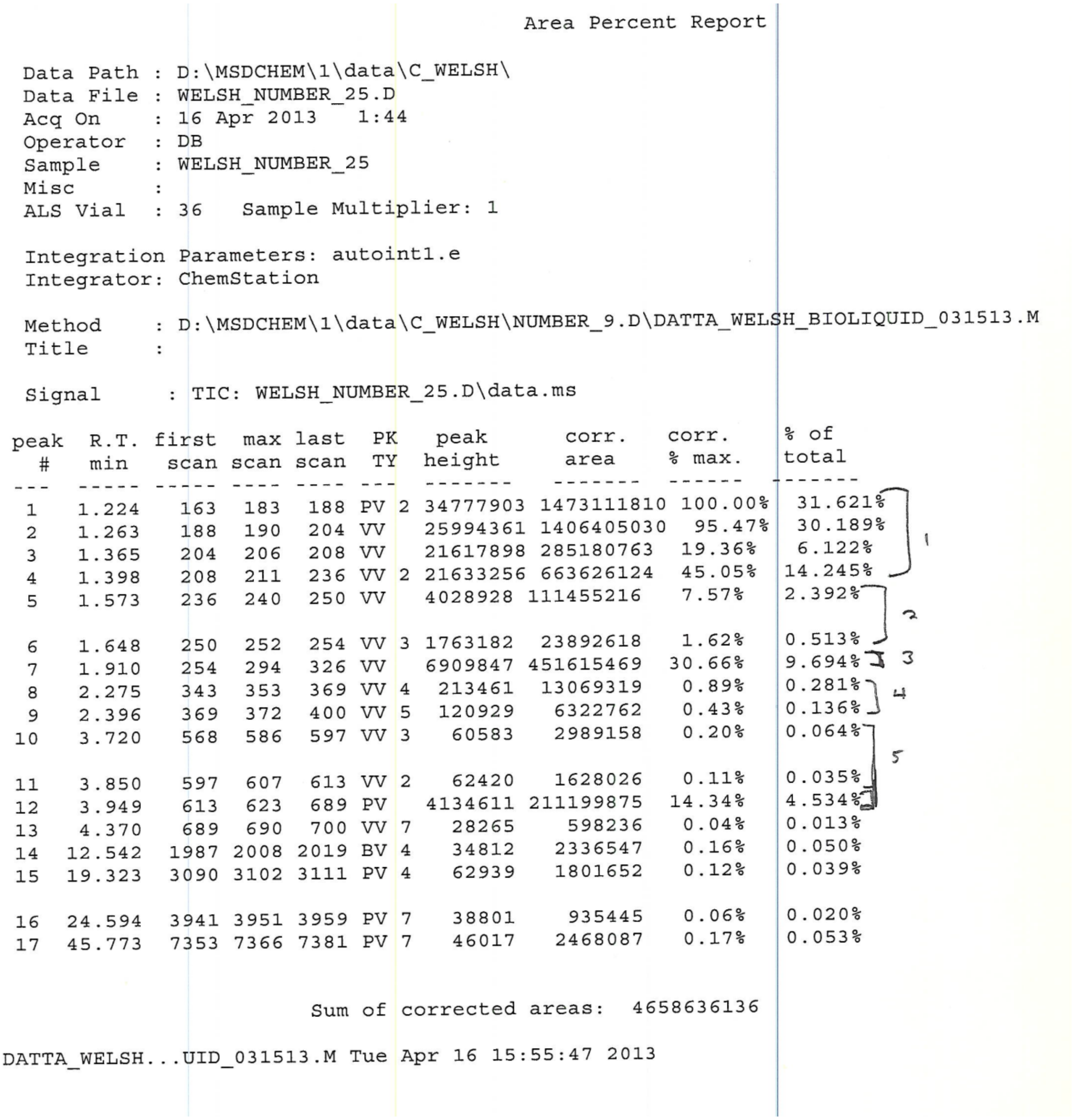
 peak  R.T. first  max last  PK   peak      corr.     corr.    % of
   #   min   scan scan scan  TY  height     area     % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.226   159  184  188 PV 3 24656232 1402334142 100.00%  31.611%
  2   1.266   188  190  195 VV 3 22826943 590907592  42.14% 13.320%     1
  3   1.307   195  197  200 VV 3 21986627 414739840  29.57%   9.349%
  4   1.342   200  202  236 VV 2 22010691 1272999004  90.78%  28.696%
  5   1.568   236  239  246 PV    4066572  63858028   4.55%  1.439%  ]  2

  6   1.902   246  293  313 VV    6003086 432660997  30.85%  9.753%  ] 3
  7   2.245   337  348  358 VV 6   154550   8366182   0.60%  0.189%
  8   2.370   358  368  391 VV 4   210808   9131520   0.65%  0.206%  ] 4
  9   3.949   613  623  709 PV    4207411 241223825  17.20%  5.438%  ] 5


                     Sum of corrected areas:   4436221128

DATTA_WELSH...UID_031513.M Tue Apr 16 15:54:58 2013
```

Figure 82: Percentage Report Run 24



```
                                                 Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_25.D
  Acq On    : 16 Apr 2013   1:44
  Operator  : DB
  Sample    : WELSH_NUMBER_25
  Misc      :
  ALS Vial  : 36   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_25.D\data.ms

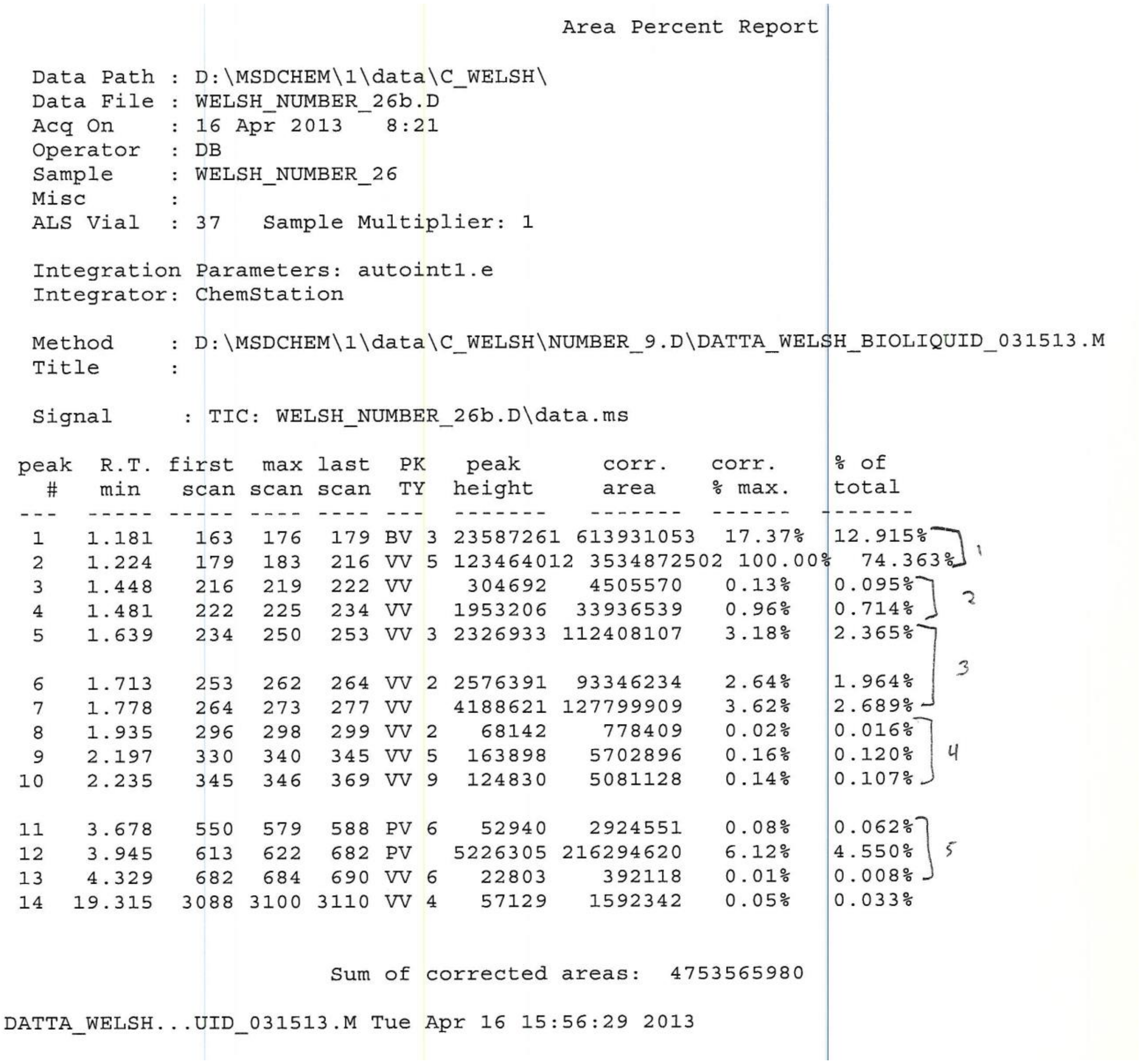
 peak  R.T. first  max last  PK   peak       corr.    corr.    % of
  #    min   scan scan scan  TY  height      area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.224   163  183  188 PV 2 34777903 1473111810 100.00%  31.621%
  2   1.263   188  190  204 VV   25994361 1406405030  95.47%  30.189%
  3   1.365   204  206  208 VV   21617898 285180763  19.36%   6.122%   1
  4   1.398   208  211  236 VV 2 21633256 663626124  45.05%  14.245%
  5   1.573   236  240  250 VV    4028928 111455216   7.57%  2.392%
                                                                      2
  6   1.648   250  252  254 VV 3  1763182  23892618   1.62%  0.513%
  7   1.910   254  294  326 VV    6909847 451615469  30.66%  9.694%   3
  8   2.275   343  353  369 VV 4   213461  13069319   0.89%  0.281%
  9   2.396   369  372  400 VV 5   120929   6322762   0.43%  0.136%   4
 10   3.720   568  586  597 VV 3    60583   2989158   0.20%  0.064%
                                                                      5
 11   3.850   597  607  613 VV 2    62420   1628026   0.11%  0.035%
 12   3.949   613  623  689 PV    4134611 211199875  14.34%  4.534%
 13   4.370   689  690  700 VV 7    28265    598236   0.04%  0.013%
 14  12.542  1987 2008 2019 BV 4    34812   2336547   0.16%  0.050%
 15  19.323  3090 3102 3111 PV 4    62939   1801652   0.12%  0.039%

 16  24.594  3941 3951 3959 PV 7    38801    935445   0.06%  0.020%
 17  45.773  7353 7366 7381 PV 7    46017   2468087   0.17%  0.053%


                       Sum of corrected areas:   4658636136

DATTA_WELSH...UID_031513.M Tue Apr 16 15:55:47 2013
```

Figure 83: Percentage Report Run 25



```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_26b.D
  Acq On    : 16 Apr 2013   8:21
  Operator  : DB
  Sample    : WELSH_NUMBER_26
  Misc      :
  ALS Vial  : 37   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_26b.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
   #   min   scan scan scan  TY  height     area     % max.   total
 ---  ----- ----- ---- ---- --- -------  -------  ------  -------
   1  1.181   163  176  179 BV 3 23587261 613931053  17.37%  12.915%   1
   2  1.224   179  183  216 VV 5 123464012 3534872502 100.00%  74.363%
   3  1.448   216  219  222 VV     304692   4505570   0.13%  0.095%    2
   4  1.481   222  225  234 VV    1953206  33936539   0.96%  0.714%
   5  1.639   234  250  253 VV 3 2326933 112408107   3.18%  2.365%

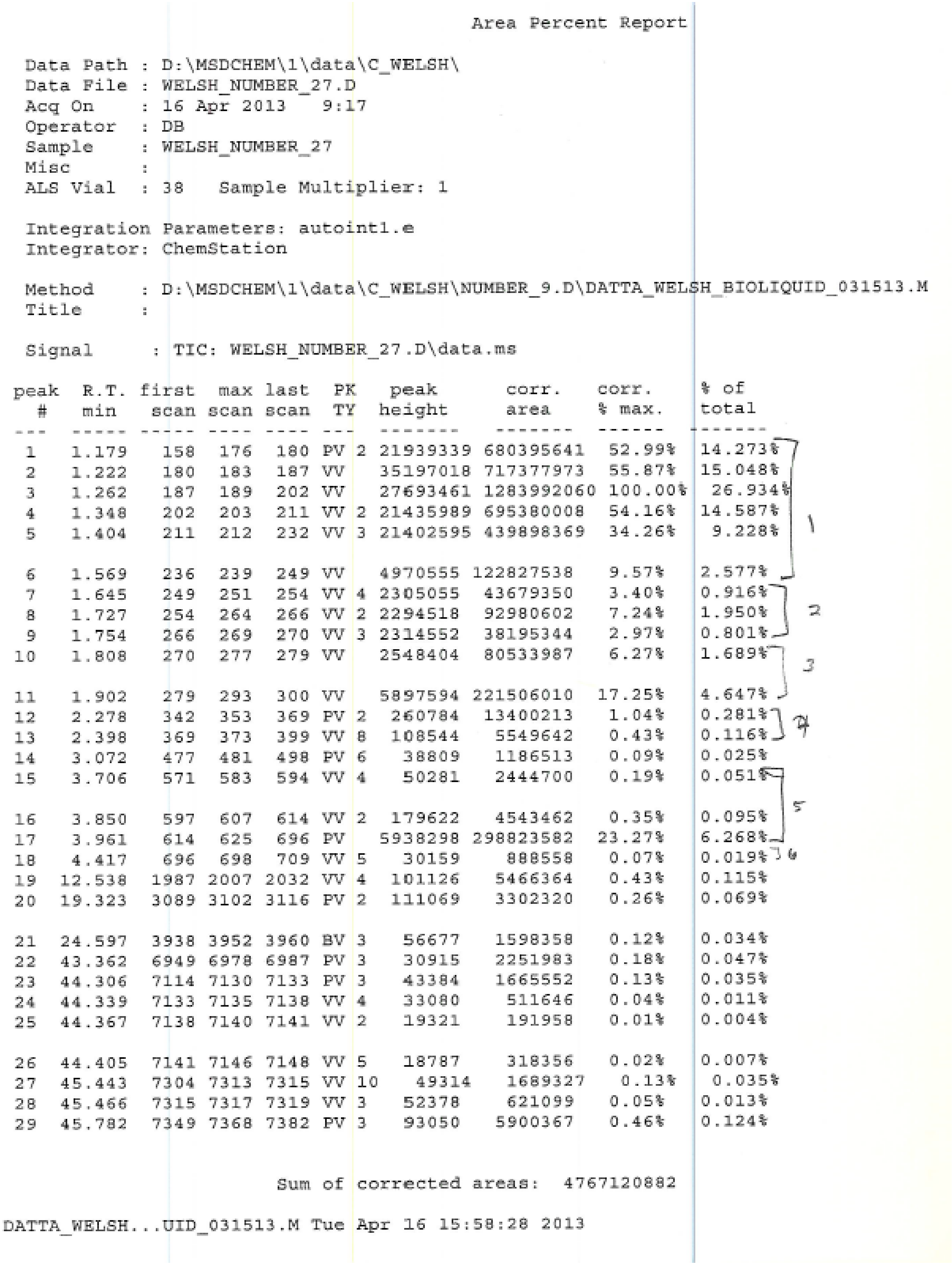
   6  1.713   253  262  264 VV 2 2576391  93346234   2.64%  1.964%    3
   7  1.778   264  273  277 VV   4188621 127799909   3.62%  2.689%
   8  1.935   296  298  299 VV 2   68142    778409   0.02%  0.016%
   9  2.197   330  340  345 VV 5  163898   5702896   0.16%  0.120%    4
  10  2.235   345  346  369 VV 9  124830   5081128   0.14%  0.107%

  11  3.678   550  579  588 PV 6   52940   2924551   0.08%  0.062%
  12  3.945   613  622  682 PV   5226305 216294620   6.12%  4.550%    5
  13  4.329   682  684  690 VV 6   22803    392118   0.01%  0.008%
  14 19.315  3088 3100 3110 VV 4   57129   1592342   0.05%  0.033%


                       Sum of corrected areas:  4753565980

DATTA_WELSH...UID_031513.M Tue Apr 16 15:56:29 2013
```

Figure 84: Percentage Report Run 26



```
                                             Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_27.D
  Acq On    : 16 Apr 2013   9:17
  Operator  : DB
  Sample    : WELSH_NUMBER_27
  Misc      :
  ALS Vial  : 38   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_27.D\data.ms

peak  R.T. first  max last  PK   peak      corr.    corr.    % of
  #   min   scan scan scan  TY  height     area    % max.   total
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   1.179   158  176  180 PV 2 21939339 680395641  52.99%  14.273%
 2   1.222   180  183  187 VV   35197018 717377973  55.87%  15.048%
 3   1.262   187  189  202 VV   27693461 1283992060 100.00%  26.934%
 4   1.348   202  203  211 VV 2 21435989 695380008  54.16%  14.587%
 5   1.404   211  212  232 VV 3 21402595 439898369  34.26%   9.228%   1

 6   1.569   236  239  249 VV    4970555 122827538   9.57%   2.577%
 7   1.645   249  251  254 VV 4  2305055  43679350   3.40%   0.916%
 8   1.727   254  264  266 VV 2  2294518  92980602   7.24%   1.950%   2
 9   1.754   266  269  270 VV 3  2314552  38195344   2.97%   0.801%
10   1.808   270  277  279 VV    2548404  80533987   6.27%   1.689%   3

11   1.902   279  293  300 VV    5897594 221506010  17.25%   4.647%
12   2.278   342  353  369 PV 2   260784  13400213   1.04%   0.281%
13   2.398   369  373  399 VV 8   108544   5549642   0.43%   0.116%   4
14   3.072   477  481  498 PV 6    38809   1186513   0.09%   0.025%
15   3.706   571  583  594 VV 4    50281   2444700   0.19%   0.051%
                                                                     5
16   3.850   597  607  614 VV 2   179622   4543462   0.35%   0.095%
17   3.961   614  625  696 PV    5938298 298823582  23.27%   6.268%
18   4.417   696  698  709 VV 5    30159    888558   0.07%   0.019%   6
19  12.538  1987 2007 2032 VV 4   101126   5466364   0.43%   0.115%
20  19.323  3089 3102 3116 PV 2   111069   3302320   0.26%   0.069%

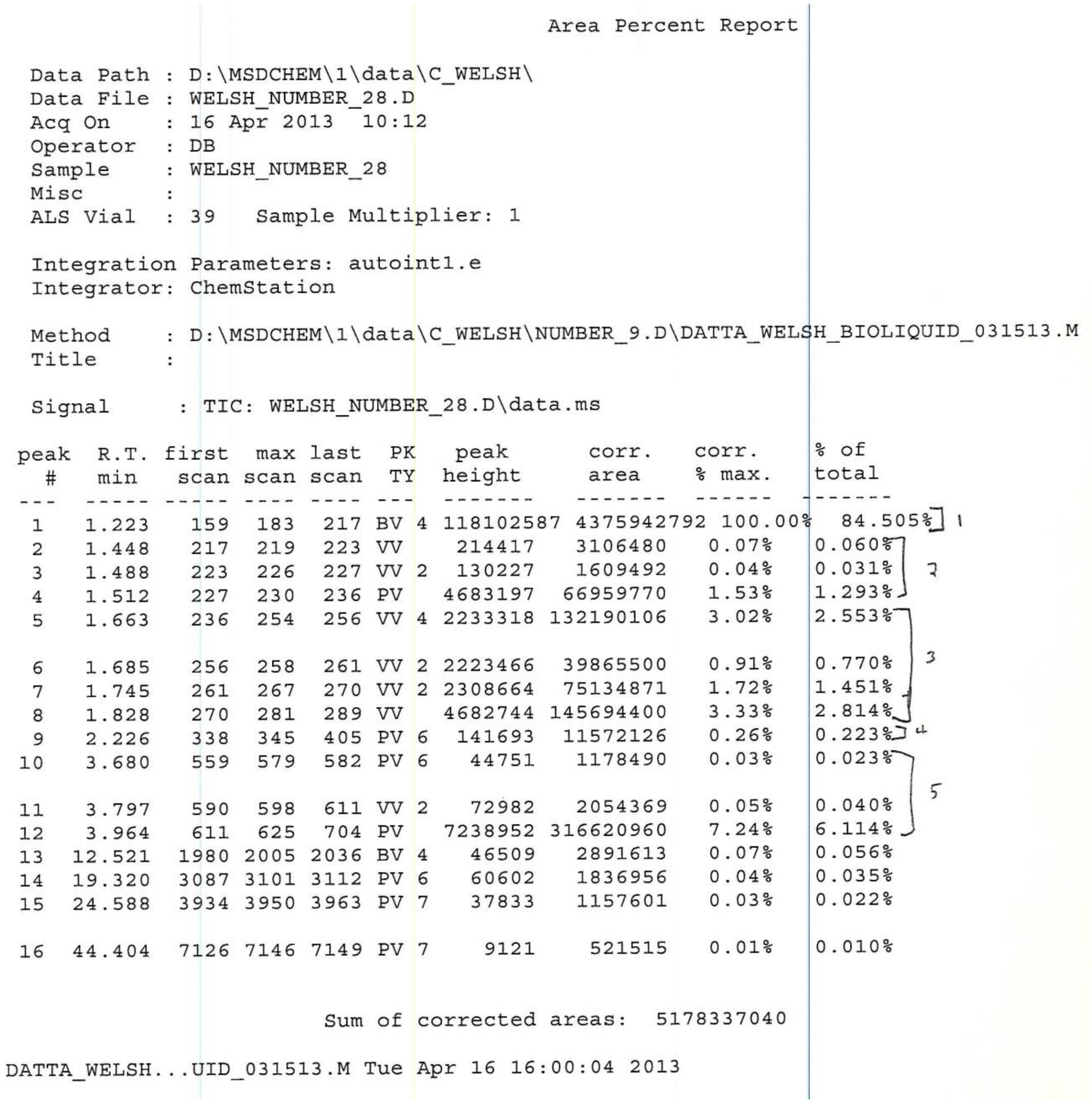
21  24.597  3938 3952 3960 BV 3    56677   1598358   0.12%   0.034%
22  43.362  6949 6978 6987 PV 3    30915   2251983   0.18%   0.047%
23  44.306  7114 7130 7133 PV 3    43384   1665552   0.13%   0.035%
24  44.339  7133 7135 7138 VV 4    33080    511646   0.04%   0.011%
25  44.367  7138 7140 7141 VV 2    19321    191958   0.01%   0.004%

26  44.405  7141 7146 7148 VV 5    18787    318356   0.02%   0.007%
27  45.443  7304 7313 7315 VV 10    49314    1689327   0.13%   0.035%
28  45.466  7315 7317 7319 VV 3    52378    621099   0.05%   0.013%
29  45.782  7349 7368 7382 PV 3    93050   5900367   0.46%   0.124%


                        Sum of corrected areas:   4767120882

DATTA_WELSH...UID_031513.M Tue Apr 16 15:58:28 2013
```

Figure 85: Percentage Report Run 27



```
                                  Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_28.D
  Acq On    : 16 Apr 2013  10:12
  Operator  : DB
  Sample    : WELSH_NUMBER_28
  Misc      :
  ALS Vial  : 39   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_28.D\data.ms

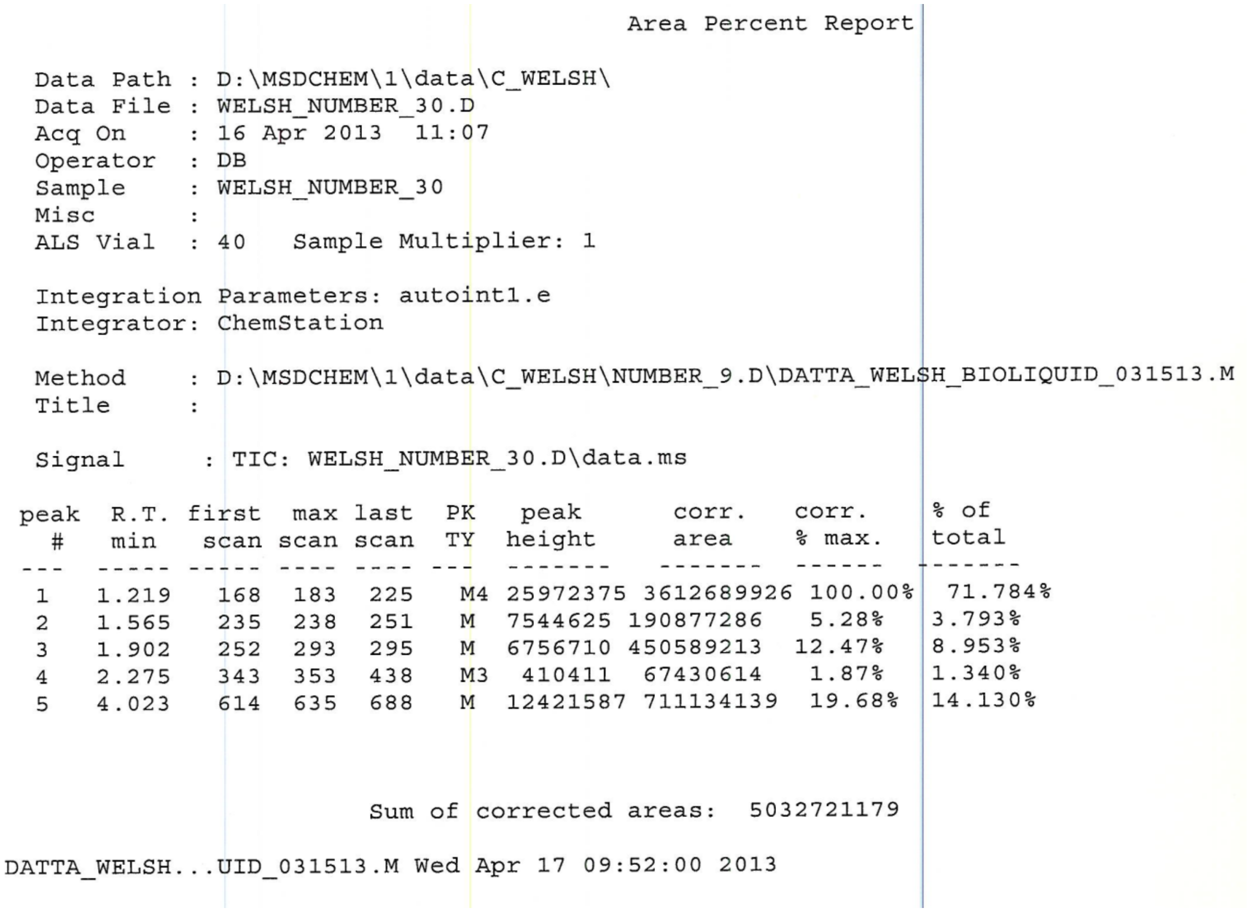
 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- --- -------   -------  ------   -------
  1   1.223   159  183  217 BV 4 118102587 4375942792 100.00%  84.505% ] 1
  2   1.448   217  219  223 VV     214417   3106480   0.07%  0.060% ┐
  3   1.488   223  226  227 VV 2   130227   1609492   0.04%  0.031% │ 2
  4   1.512   227  230  236 PV    4683197  66959770   1.53%  1.293% ┘
  5   1.663   236  254  256 VV 4 2233318 132190106    3.02%  2.553% ┐
                                                                    │
  6   1.685   256  258  261 VV 2 2223466  39865500    0.91%  0.770% │ 3
  7   1.745   261  267  270 VV 2 2308664  75134871    1.72%  1.451% │
  8   1.828   270  281  289 VV   4682744 145694400    3.33%  2.814% ┘
  9   2.226   338  345  405 PV 6  141693  11572126    0.26%  0.223% ] 4
 10   3.680   559  579  582 PV 6   44751   1178490    0.03%  0.023% ┐
                                                                    │ 5
 11   3.797   590  598  611 VV 2   72982   2054369    0.05%  0.040% │
 12   3.964   611  625  704 PV   7238952 316620960    7.24%  6.114% ┘
 13  12.521  1980 2005 2036 BV 4   46509   2891613    0.07%  0.056%
 14  19.320  3087 3101 3112 PV 6   60602   1836956    0.04%  0.035%
 15  24.588  3934 3950 3963 PV 7   37833   1157601    0.03%  0.022%

 16  44.404  7126 7146 7149 PV 7    9121    521515    0.01%  0.010%


                     Sum of corrected areas:   5178337040

DATTA_WELSH...UID_031513.M Tue Apr 16 16:00:04 2013
```

Figure 86: Percentage Report Run 28



```
                                              Area Percent Report

 Data Path : D:\MSDCHEM\1\data\C_WELSH\
 Data File : WELSH_NUMBER_30.D
 Acq On    : 16 Apr 2013  11:07
 Operator  : DB
 Sample    : WELSH_NUMBER_30
 Misc      :
 ALS Vial  : 40   Sample Multiplier: 1

 Integration Parameters: autoint1.e
 Integrator: ChemStation

 Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
 Title     :

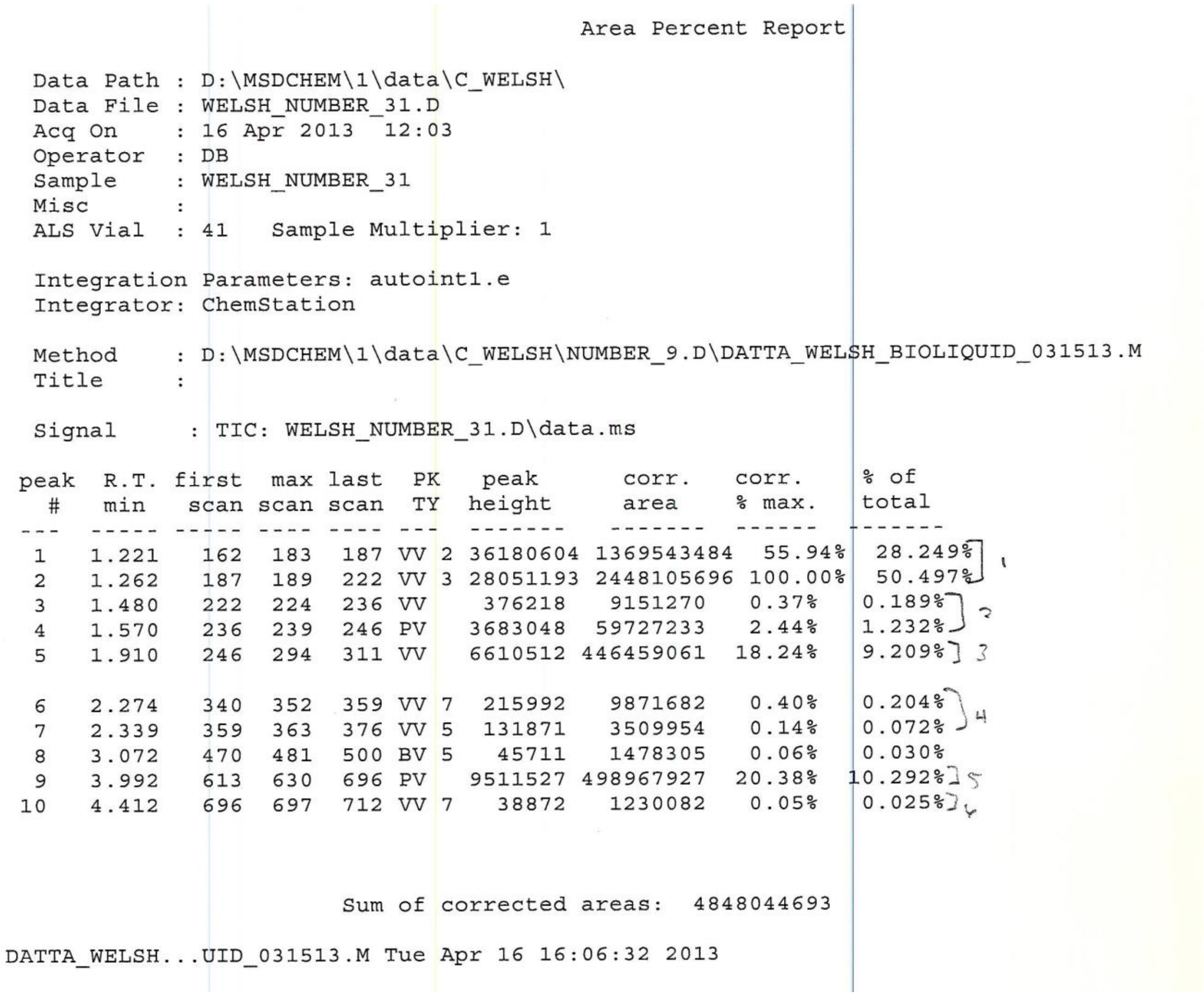
 Signal     : TIC: WELSH_NUMBER_30.D\data.ms

peak  R.T. first  max last  PK   peak      corr.    corr.    % of
  #   min   scan scan scan  TY  height     area    % max.   total
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   1.219   168  183  225  M4 25972375 3612689926 100.00%  71.784%
 2   1.565   235  238  251  M  7544625 190877286   5.28%  3.793%
 3   1.902   252  293  295  M  6756710 450589213  12.47%  8.953%
 4   2.275   343  353  438  M3  410411  67430614   1.87%  1.340%
 5   4.023   614  635  688  M  12421587 711134139  19.68%  14.130%


                        Sum of corrected areas:  5032721179

DATTA_WELSH...UID_031513.M Wed Apr 17 09:52:00 2013
```

Figure 87: Percentage Report Run 30



```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_31.D
  Acq On    : 16 Apr 2013  12:03
  Operator  : DB
  Sample    : WELSH_NUMBER_31
  Misc      :
  ALS Vial  : 41   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_31.D\data.ms

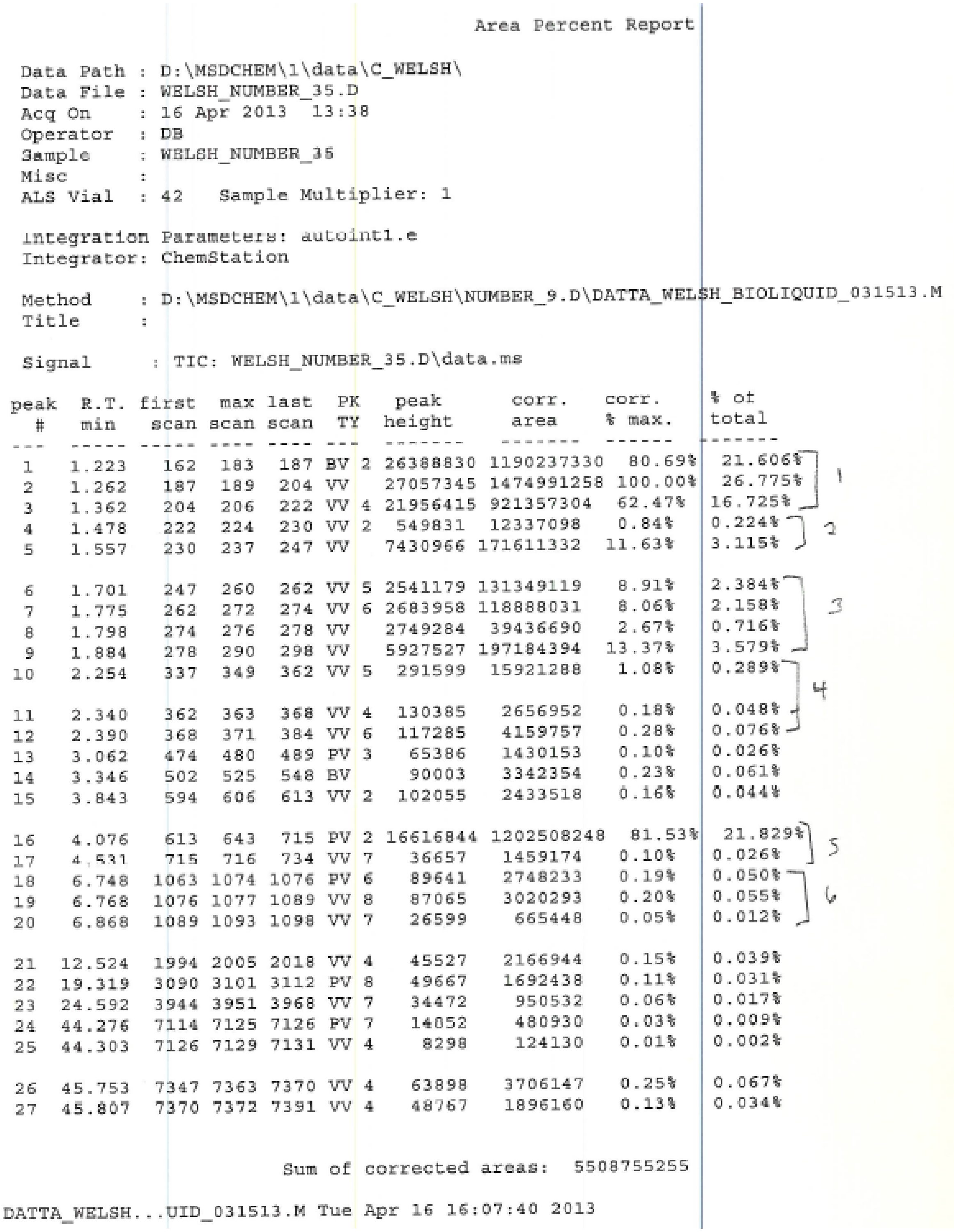
 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
  #    min   scan scan scan  TY  height     area     % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------   -------
  1   1.221   162  183  187 VV 2 36180604 1369543484  55.94%   28.249%] 1
  2   1.262   187  189  222 VV 3 28051193 2448105696 100.00%   50.497%]
  3   1.480   222  224  236 VV     376218    9151270   0.37%   0.189%] 2
  4   1.570   236  239  246 PV    3683048   59727233   2.44%   1.232%]
  5   1.910   246  294  311 VV    6610512  446459061  18.24%   9.209%] 3

  6   2.274   340  352  359 VV 7   215992    9871682   0.40%   0.204%] 4
  7   2.339   359  363  376 VV 5   131871    3509954   0.14%   0.072%]
  8   3.072   470  481  500 BV 5    45711    1478305   0.06%   0.030%
  9   3.992   613  630  696 PV    9511527  498967927  20.38%  10.292%] 5
 10   4.412   696  697  712 VV 7    38872    1230082   0.05%   0.025%] 6


                          Sum of corrected areas:    4848044693

DATTA_WELSH...UID_031513.M Tue Apr 16 16:06:32 2013
```

Figure 88: Percentage Report Run 31



```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_35.D
  Acq On    : 16 Apr 2013   13:38
  Operator  : DB
  Sample    : WELSH_NUMBER_35
  Misc      :
  ALS Vial  : 42   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_35.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.      corr.    % of
   #   min  scan  scan scan  TY  height     area      % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------   ------   -------
  1   1.223   162  183  187 BV 2 26388830 1190237330  80.69%   21.606%
  2   1.262   187  189  204 VV   27057345 1474991258 100.00%   26.775%   1
  3   1.362   204  206  222 VV 4 21956415  921357304  62.47%   16.725%
  4   1.478   222  224  230 VV 2   549831   12337098   0.84%   0.224%    2
  5   1.557   230  237  247 VV    7430966  171611332  11.63%   3.115%

  6   1.701   247  260  262 VV 5  2541179  131349119   8.91%   2.384%
  7   1.775   262  272  274 VV 6  2683958  118888031   8.06%   2.158%    3
  8   1.798   274  276  278 VV    2749284   39436690   2.67%   0.716%
  9   1.884   278  290  298 VV    5927527  197184394  13.37%   3.579%
 10   2.254   337  349  362 VV 5   291599   15921288   1.08%   0.289%
                                                                        4
 11   2.340   362  363  368 VV 4   130385    2656952   0.18%   0.048%
 12   2.390   368  371  384 VV 6   117285    4159757   0.28%   0.076%
 13   3.062   474  480  489 PV 3    65386    1430153   0.10%   0.026%
 14   3.346   502  525  548 BV      90003    3342354   0.23%   0.061%
 15   3.843   594  606  613 VV 2   102055    2433518   0.16%   0.044%

 16   4.076   613  643  715 PV 2 16616844 1202508248  81.53%   21.829%   5
 17   4.531   715  716  734 VV 7    36657    1459174   0.10%   0.026%
 18   6.748  1063 1074 1076 PV 6    89641    2748233   0.19%   0.050%
 19   6.768  1076 1077 1089 VV 8    87065    3020293   0.20%   0.055%    6
 20   6.868  1089 1093 1098 VV 7    26599     665448   0.05%   0.012%

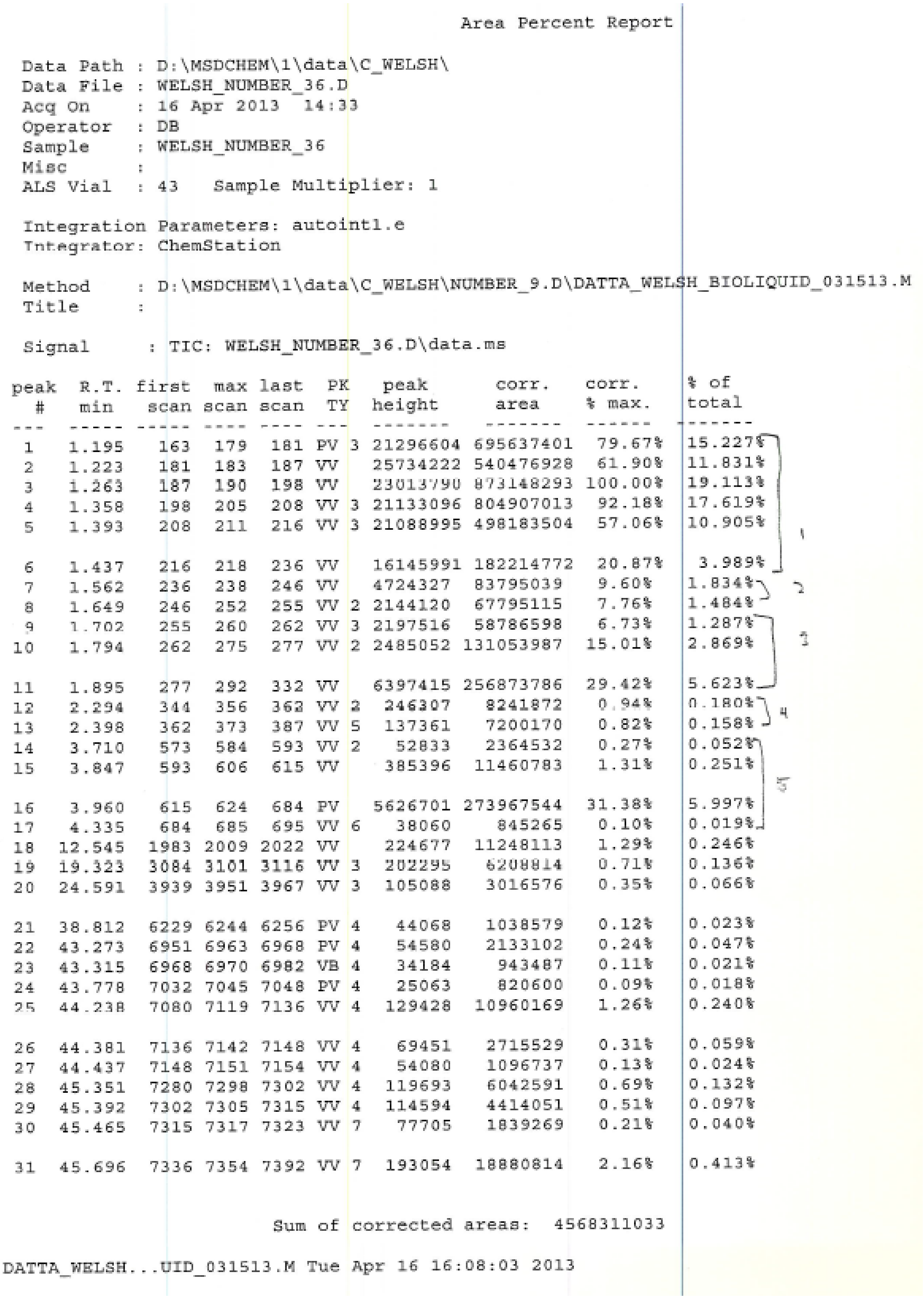
 21  12.524  1994 2005 2018 VV 4    45527    2166944   0.15%   0.039%
 22  19.319  3090 3101 3112 PV 8    49667    1692438   0.11%   0.031%
 23  24.592  3944 3951 3968 VV 7    34472     950532   0.06%   0.017%
 24  44.276  7114 7125 7126 PV 7    14052     480930   0.03%   0.009%
 25  44.303  7126 7129 7131 VV 4     8298     124130   0.01%   0.002%

 26  45.753  7347 7363 7370 VV 4    63898    3706147   0.25%   0.067%
 27  45.807  7370 7372 7391 VV 4    48767    1896160   0.13%   0.034%


                         Sum of corrected areas:   5508755255

DATTA_WELSH...UID_031513.M Tue Apr 16 16:07:40 2013
```

Figure 89: Percentage Report Run 35



```
                                         Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_36.D
  Acq On    : 16 Apr 2013  14:33
  Operator  : DB
  Sample    : WELSH_NUMBER_36
  Misc      :
  ALS Vial  : 43   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_36.D\data.ms

peak  R.T. first  max last  PK   peak      corr.    corr.     % of
  #   min   scan scan scan  TY  height     area     % max.    total
---  ----- ----- ---- ---- ---  -------  -------   ------   -------
  1  1.195   163  179  181 PV 3 21296604 695637401  79.67%  15.227%
  2  1.223   181  183  187 VV   25734222 540476928  61.90%  11.831%
  3  1.263   187  190  198 VV   23013790 873148293 100.00%  19.113%
  4  1.358   198  205  208 VV 3 21133096 804907013  92.18%  17.619%
  5  1.393   208  211  216 VV 3 21088995 498183504  57.06%  10.905%
                                                                      1
  6  1.437   216  218  236 VV   16145991 182214772  20.87%   3.989%
  7  1.562   236  238  246 VV    4724327  83795039   9.60%   1.834%   2
  8  1.649   246  252  255 VV 2  2144120  67795115   7.76%   1.484%
  9  1.702   255  260  262 VV 3  2197516  58786598   6.73%   1.287%
 10  1.794   262  275  277 VV 2  2485052 131053987  15.01%   2.869%   3

 11  1.895   277  292  332 VV    6397415 256873786  29.42%   5.623%
 12  2.294   344  356  362 VV 2   246307   8241872   0.94%   0.180%
 13  2.398   362  373  387 VV 5   137361   7200170   0.82%   0.158%  4
 14  3.710   573  584  593 VV 2    52833   2364532   0.27%   0.052%
 15  3.847   593  606  615 VV     385396  11460783   1.31%   0.251%
                                                                     5
 16  3.960   615  624  684 PV    5626701 273967544  31.38%   5.997%
 17  4.335   684  685  695 VV 6    38060    845265   0.10%   0.019%
 18 12.545  1983 2009 2022 VV     224677  11248113   1.29%   0.246%
 19 19.323  3084 3101 3116 VV 3   202295   6208814   0.71%   0.136%
 20 24.591  3939 3951 3967 VV 3   105088   3016576   0.35%   0.066%

 21 38.812  6229 6244 6256 PV 4    44068   1038579   0.12%   0.023%
 22 43.273  6951 6963 6968 PV 4    54580   2133102   0.24%   0.047%
 23 43.315  6968 6970 6982 VB 4    34184    943487   0.11%   0.021%
 24 43.778  7032 7045 7048 PV 4    25063    820600   0.09%   0.018%
 25 44.238  7080 7119 7136 VV 4   129428  10960169   1.26%   0.240%

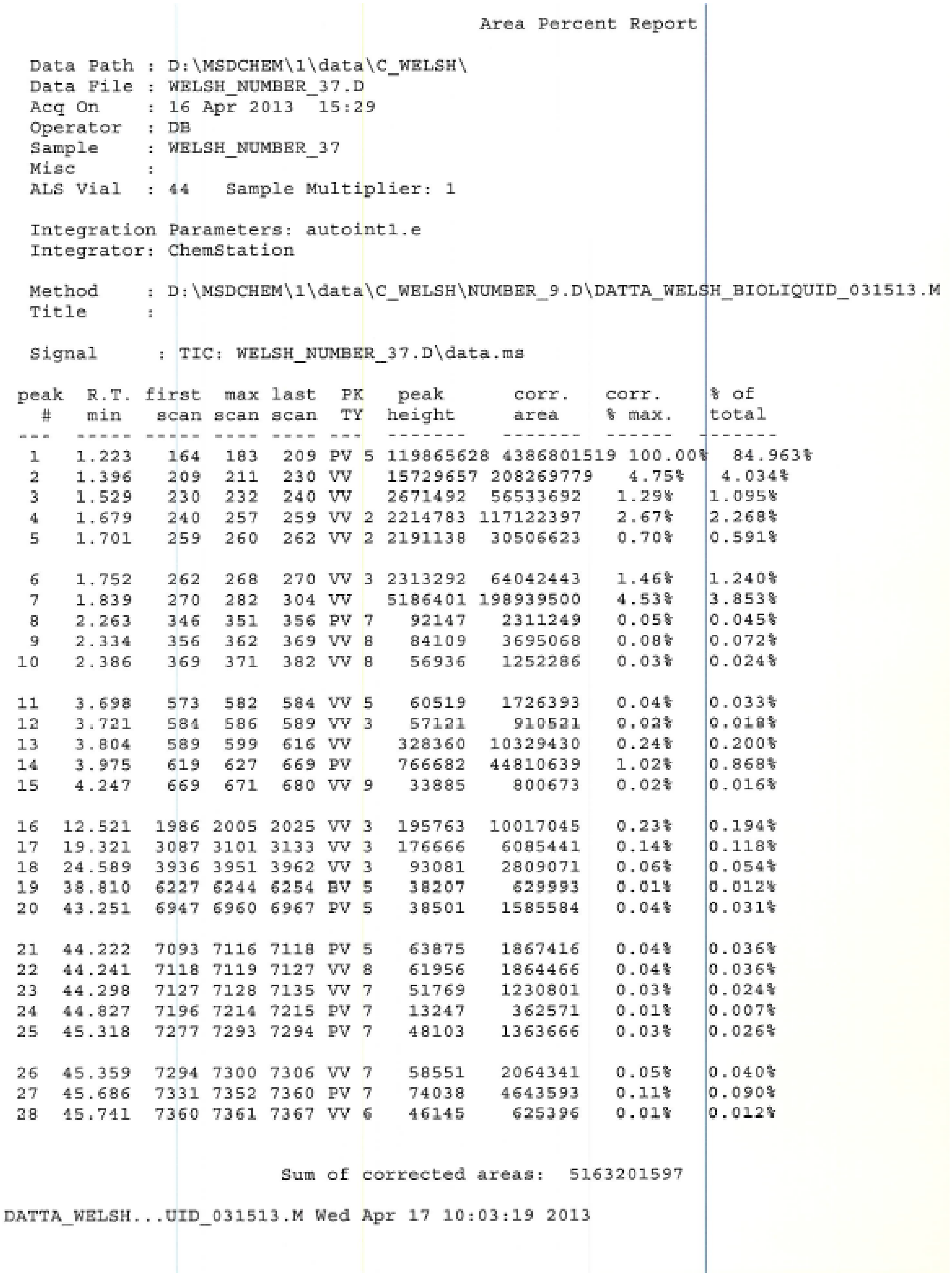
 26 44.381  7136 7142 7148 VV 4    69451   2715529   0.31%   0.059%
 27 44.437  7148 7151 7154 VV 4    54080   1096737   0.13%   0.024%
 28 45.351  7280 7298 7302 VV 4   119693   6042591   0.69%   0.132%
 29 45.392  7302 7305 7315 VV 4   114594   4414051   0.51%   0.097%
 30 45.465  7315 7317 7323 VV 7    77705   1839269   0.21%   0.040%

 31 45.696  7336 7354 7392 VV 7   193054  18880814   2.16%   0.413%


                     Sum of corrected areas:    4568311033

DATTA_WELSH...UID_031513.M Tue Apr 16 16:08:03 2013
```

Figure 90: : Percentage Report Run 36



```
                                  Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_37.D
  Acq On    : 16 Apr 2013  15:29
  Operator  : DB
  Sample    : WELSH_NUMBER_37
  Misc      :
  ALS Vial  : 44   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_37.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- --- -------   -------  ------  -------
  1   1.223   164  183  209 PV 5 119865628 4386801519 100.00%  84.963%
  2   1.396   209  211  230 VV   15729657 208269779   4.75%   4.034%
  3   1.529   230  232  240 VV    2671492  56533692   1.29%  1.095%
  4   1.679   240  257  259 VV 2  2214783 117122397   2.67%  2.268%
  5   1.701   259  260  262 VV 2  2191138  30506623   0.70%  0.591%

  6   1.752   262  268  270 VV 3  2313292  64042443   1.46%  1.240%
  7   1.839   270  282  304 VV    5186401 198939500   4.53%  3.853%
  8   2.263   346  351  356 PV 7    92147   2311249   0.05%  0.045%
  9   2.334   356  362  369 VV 8    84109   3695068   0.08%  0.072%
 10   2.386   369  371  382 VV 8    56936   1252286   0.03%  0.024%

 11   3.698   573  582  584 VV 5    60519   1726393   0.04%  0.033%
 12   3.721   584  586  589 VV 3    57121    910521   0.02%  0.018%
 13   3.804   589  599  616 VV     328360  10329430   0.24%  0.200%
 14   3.975   619  627  669 PV     766682  44810639   1.02%  0.868%
 15   4.247   669  671  680 VV 9    33885    800673   0.02%  0.016%

 16  12.521  1986 2005 2025 VV 3   195763  10017045   0.23%  0.194%
 17  19.321  3087 3101 3133 VV 3   176666   6085441   0.14%  0.118%
 18  24.589  3936 3951 3962 VV 3    93081   2809071   0.06%  0.054%
 19  38.810  6227 6244 6254 BV 5    38207    629993   0.01%  0.012%
 20  43.251  6947 6960 6967 PV 5    38501   1585584   0.04%  0.031%

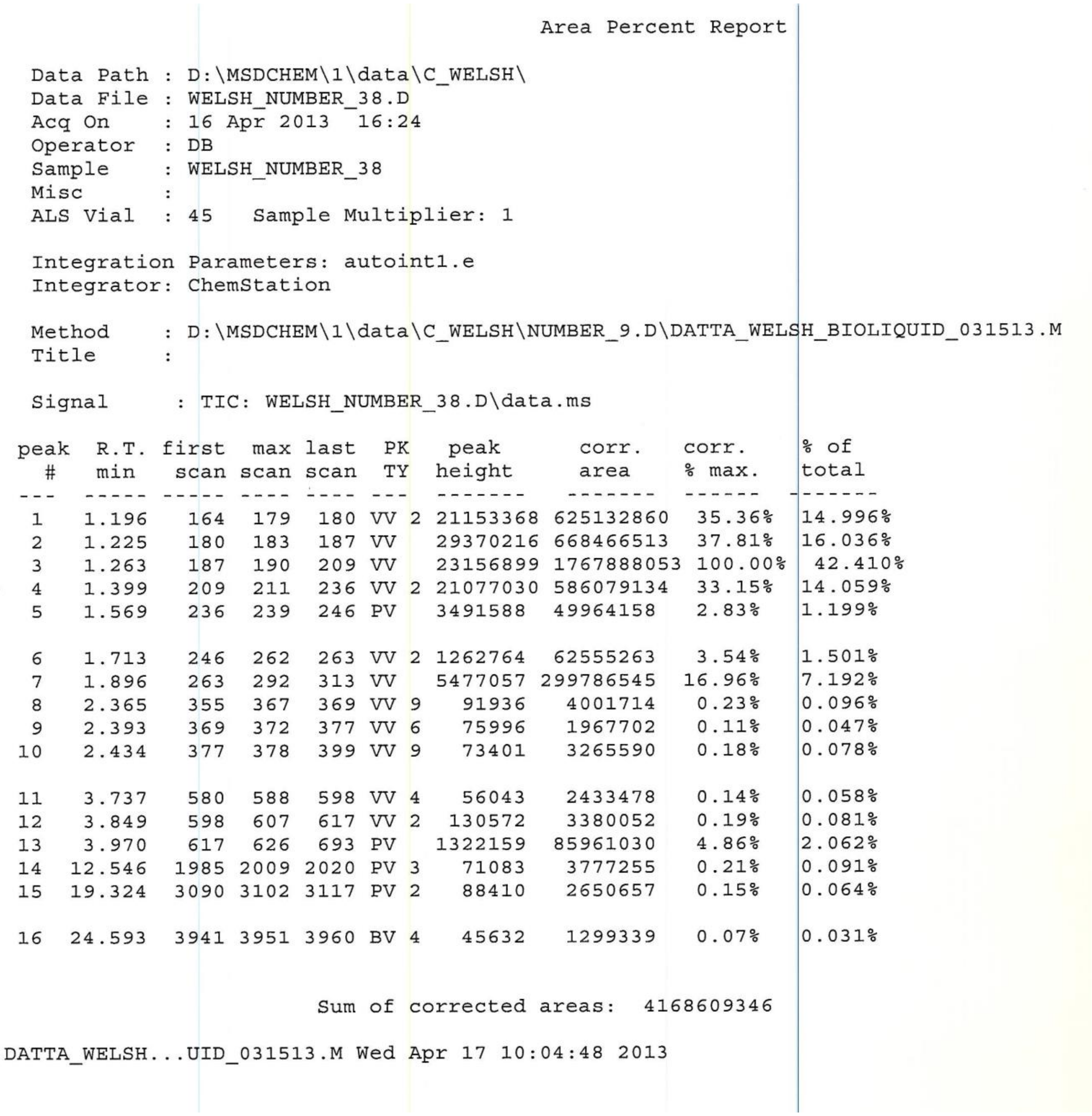
 21  44.222  7093 7116 7118 PV 5    63875   1867416   0.04%  0.036%
 22  44.241  7118 7119 7127 VV 8    61956   1864466   0.04%  0.036%
 23  44.298  7127 7128 7135 VV 7    51769   1230801   0.03%  0.024%
 24  44.827  7196 7214 7215 PV 7    13247    362571   0.01%  0.007%
 25  45.318  7277 7293 7294 PV 7    48103   1363666   0.03%  0.026%

 26  45.359  7294 7300 7306 VV 7    58551   2064341   0.05%  0.040%
 27  45.686  7331 7352 7360 PV 7    74038   4643593   0.11%  0.090%
 28  45.741  7360 7361 7367 VV 6    46145    625396   0.01%  0.012%


                       Sum of corrected areas:   5163201597

DATTA_WELSH...UID_031513.M Wed Apr 17 10:03:19 2013
```

Figure 91: Percentage Report Run 37



```
                                   Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_38.D
  Acq On    : 16 Apr 2013  16:24
  Operator  : DB
  Sample    : WELSH_NUMBER_38
  Misc      :
  ALS Vial  : 45   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_38.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
   #   min   scan scan scan  TY  height     area     % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------   ------  -------
  1   1.196   164  179  180 VV 2 21153368 625132860  35.36%  14.996%
  2   1.225   180  183  187 VV   29370216 668466513  37.81%  16.036%
  3   1.263   187  190  209 VV   23156899 1767888053 100.00%  42.410%
  4   1.399   209  211  236 VV 2 21077030 586079134  33.15%  14.059%
  5   1.569   236  239  246 PV   3491588  49964158   2.83%  1.199%

  6   1.713   246  262  263 VV 2 1262764   62555263   3.54%  1.501%
  7   1.896   263  292  313 VV   5477057 299786545  16.96%  7.192%
  8   2.365   355  367  369 VV 9   91936    4001714   0.23%  0.096%
  9   2.393   369  372  377 VV 6   75996    1967702   0.11%  0.047%
 10   2.434   377  378  399 VV 9   73401    3265590   0.18%  0.078%

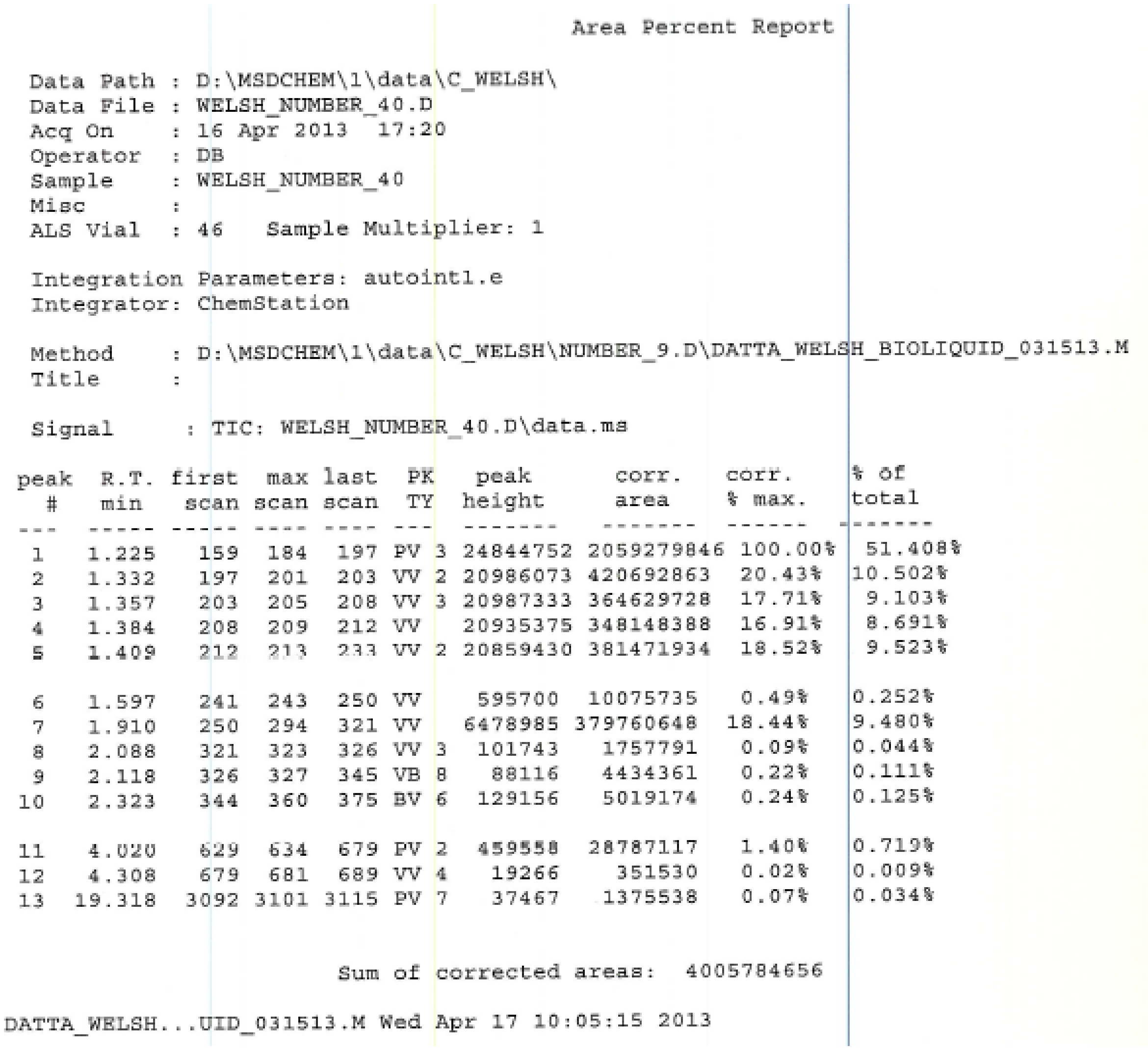
 11   3.737   580  588  598 VV 4   56043    2433478   0.14%  0.058%
 12   3.849   598  607  617 VV 2  130572    3380052   0.19%  0.081%
 13   3.970   617  626  693 PV   1322159   85961030   4.86%  2.062%
 14  12.546  1985 2009 2020 PV 3   71083    3777255   0.21%  0.091%
 15  19.324  3090 3102 3117 PV 2   88410    2650657   0.15%  0.064%

 16  24.593  3941 3951 3960 BV 4   45632    1299339   0.07%  0.031%


                         Sum of corrected areas:  4168609346

DATTA_WELSH...UID_031513.M Wed Apr 17 10:04:48 2013
```

Figure 92: Percentage Report Run 38



```
                                     Area Percent Report

 Data Path : D:\MSDCHEM\1\data\C_WELSH\
 Data File : WELSH_NUMBER_40.D
 Acq On    : 16 Apr 2013  17:20
 Operator  : DB
 Sample    : WELSH_NUMBER_40
 Misc      :
 ALS Vial  : 46   Sample Multiplier: 1

 Integration Parameters: autoint1.e
 Integrator: ChemStation

 Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
 Title     :

 Signal      : TIC: WELSH_NUMBER_40.D\data.ms

peak  R.T. first  max last  PK   peak       corr.     corr.    % of
  #   min   scan scan scan  TY  height      area     % max.   total
---  ----- ----- ---- ---- ---  -------   -------   ------  -------
 1   1.225   159  184  197 PV 3 24844752 2059279846 100.00%  51.408%
 2   1.332   197  201  203 VV 2 20986073 420692863  20.43%  10.502%
 3   1.357   203  205  208 VV 3 20987333 364629728  17.71%   9.103%
 4   1.384   208  209  212 VV   20935375 348148388  16.91%   8.691%
 5   1.409   212  213  233 VV 2 20859430 381471934  18.52%   9.523%

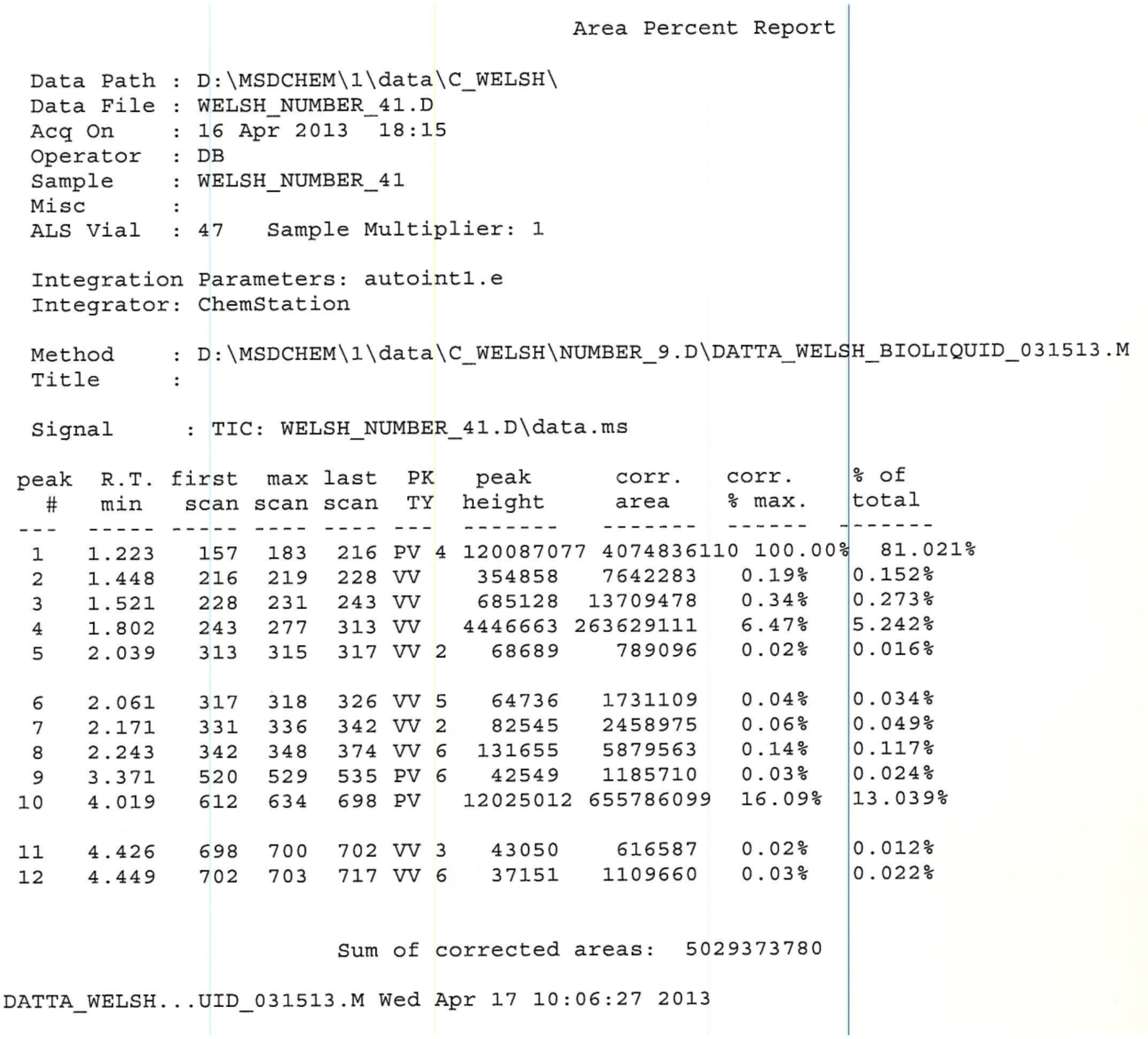
 6   1.597   241  243  250 VV     595700  10075735   0.49%  0.252%
 7   1.910   250  294  321 VV    6478985 379760648  18.44%  9.480%
 8   2.088   321  323  326 VV 3   101743   1757791   0.09%  0.044%
 9   2.118   326  327  345 VB 8    88116   4434361   0.22%  0.111%
10   2.323   344  360  375 BV 6   129156   5019174   0.24%  0.125%

11   4.020   629  634  679 PV 2   459558  28787117   1.40%  0.719%
12   4.308   679  681  689 VV 4    19266    351530   0.02%  0.009%
13  19.318  3092 3101 3115 PV 7    37467   1375538   0.07%  0.034%


                      Sum of corrected areas:   4005784656

DATTA_WELSH...UID_031513.M Wed Apr 17 10:05:15 2013
```

Figure 93: Percentage Report Run 40



```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_41.D
  Acq On    : 16 Apr 2013  18:15
  Operator  : DB
  Sample    : WELSH_NUMBER_41
  Misc      :
  ALS Vial  : 47   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_41.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min  scan scan scan  TY  height      area   % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   1.223   157  183  216 PV 4 120087077 4074836110 100.00%  81.021%
  2   1.448   216  219  228 VV     354858   7642283   0.19%  0.152%
  3   1.521   228  231  243 VV     685128  13709478   0.34%  0.273%
  4   1.802   243  277  313 VV    4446663 263629111   6.47%  5.242%
  5   2.039   313  315  317 VV 2    68689    789096   0.02%  0.016%

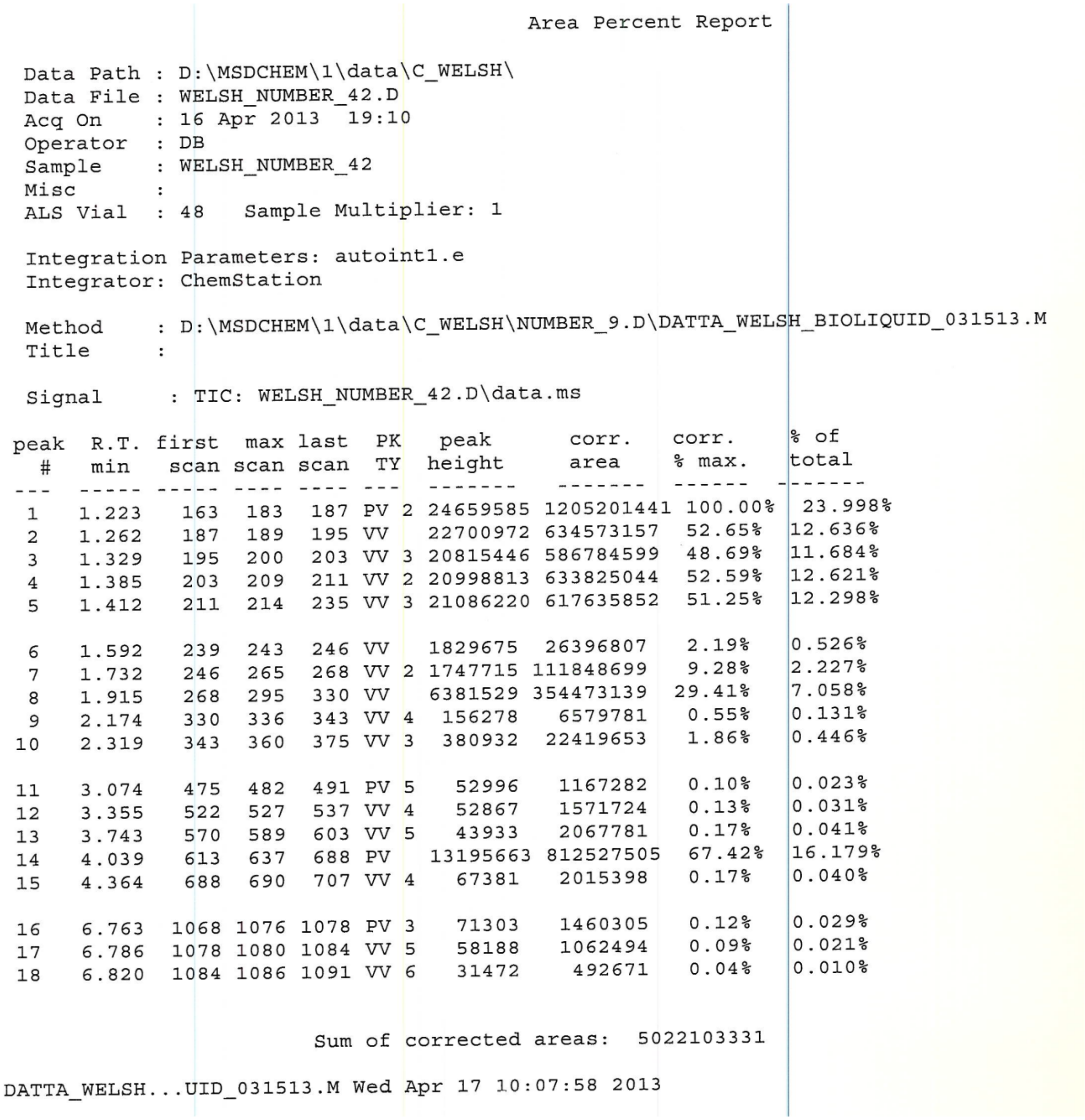
  6   2.061   317  318  326 VV 5    64736   1731109   0.04%  0.034%
  7   2.171   331  336  342 VV 2    82545   2458975   0.06%  0.049%
  8   2.243   342  348  374 VV 6   131655   5879563   0.14%  0.117%
  9   3.371   520  529  535 PV 6    42549   1185710   0.03%  0.024%
 10   4.019   612  634  698 PV   12025012 655786099  16.09%  13.039%

 11   4.426   698  700  702 VV 3    43050    616587   0.02%  0.012%
 12   4.449   702  703  717 VV 6    37151   1109660   0.03%  0.022%


                        Sum of corrected areas:   5029373780

DATTA_WELSH...UID_031513.M Wed Apr 17 10:06:27 2013
```

Figure 94: Percentage Report Run 41



```
                                        Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_42.D
  Acq On    : 16 Apr 2013  19:10
  Operator  : DB
  Sample    : WELSH_NUMBER_42
  Misc      :
  ALS Vial  : 48   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_42.D\data.ms

peak  R.T. first  max last  PK   peak       corr.    corr.    % of
 #    min   scan scan scan  TY  height      area    % max.   total
---  ----- ----- ---- ---- ---  -------   -------   ------  -------
 1   1.223   163  183  187 PV 2 24659585 1205201441 100.00%  23.998%
 2   1.262   187  189  195 VV   22700972 634573157  52.65%  12.636%
 3   1.329   195  200  203 VV 3 20815446 586784599  48.69%  11.684%
 4   1.385   203  209  211 VV 2 20998813 633825044  52.59%  12.621%
 5   1.412   211  214  235 VV 3 21086220 617635852  51.25%  12.298%

 6   1.592   239  243  246 VV    1829675  26396807   2.19%   0.526%
 7   1.732   246  265  268 VV 2  1747715 111848699   9.28%   2.227%
 8   1.915   268  295  330 VV    6381529 354473139  29.41%   7.058%
 9   2.174   330  336  343 VV 4   156278   6579781   0.55%   0.131%
10   2.319   343  360  375 VV 3   380932  22419653   1.86%   0.446%

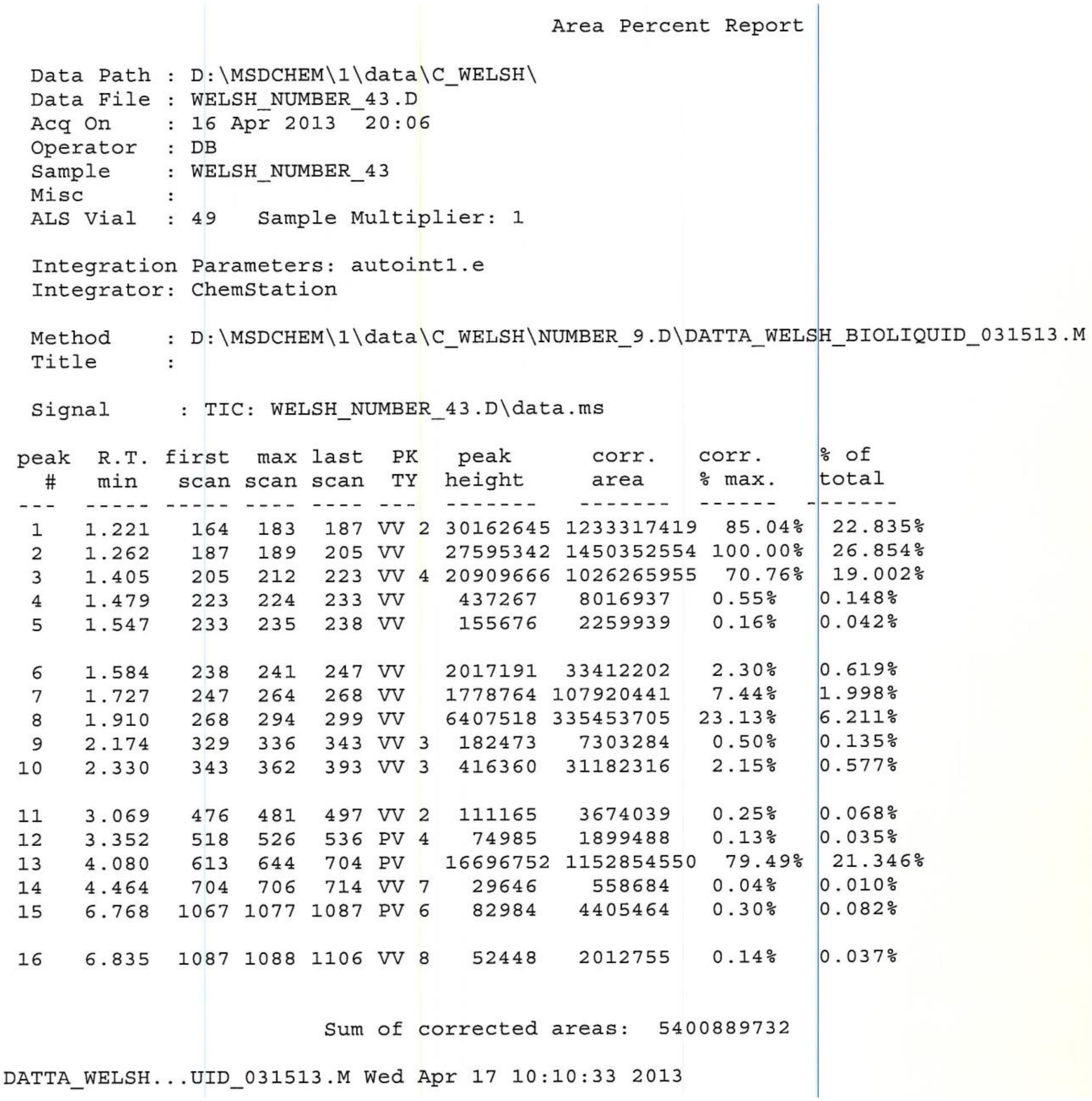
11   3.074   475  482  491 PV 5    52996   1167282   0.10%   0.023%
12   3.355   522  527  537 VV 4    52867   1571724   0.13%   0.031%
13   3.743   570  589  603 VV 5    43933   2067781   0.17%   0.041%
14   4.039   613  637  688 PV   13195663 812527505  67.42%  16.179%
15   4.364   688  690  707 VV 4    67381   2015398   0.17%   0.040%

16   6.763  1068 1076 1078 PV 3    71303   1460305   0.12%   0.029%
17   6.786  1078 1080 1084 VV 5    58188   1062494   0.09%   0.021%
18   6.820  1084 1086 1091 VV 6    31472    492671   0.04%   0.010%


                          Sum of corrected areas:   5022103331

DATTA_WELSH...UID_031513.M Wed Apr 17 10:07:58 2013
```

Figure 95: Percentage Report Run 42



```
                                         Area Percent Report

  Data Path : D:\MSDCHEM\1\data\C_WELSH\
  Data File : WELSH_NUMBER_43.D
  Acq On    : 16 Apr 2013  20:06
  Operator  : DB
  Sample    : WELSH_NUMBER_43
  Misc      :
  ALS Vial  : 49   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\MSDCHEM\1\data\C_WELSH\NUMBER_9.D\DATTA_WELSH_BIOLIQUID_031513.M
  Title     :

  Signal     : TIC: WELSH_NUMBER_43.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
   1  1.221   164  183  187 VV 2 30162645 1233317419  85.04%  22.835%
   2  1.262   187  189  205 VV   27595342 1450352554 100.00%  26.854%
   3  1.405   205  212  223 VV 4 20909666 1026265955  70.76%  19.002%
   4  1.479   223  224  233 VV     437267    8016937   0.55%   0.148%
   5  1.547   233  235  238 VV     155676    2259939   0.16%   0.042%

   6  1.584   238  241  247 VV    2017191   33412202   2.30%   0.619%
   7  1.727   247  264  268 VV    1778764  107920441   7.44%   1.998%
   8  1.910   268  294  299 VV    6407518  335453705  23.13%   6.211%
   9  2.174   329  336  343 VV 3   182473    7303284   0.50%   0.135%
  10  2.330   343  362  393 VV 3   416360   31182316   2.15%   0.577%

  11  3.069   476  481  497 VV 2   111165    3674039   0.25%   0.068%
  12  3.352   518  526  536 PV 4    74985    1899488   0.13%   0.035%
  13  4.080   613  644  704 PV   16696752 1152854550  79.49%  21.346%
  14  4.464   704  706  714 VV 7    29646     558684   0.04%   0.010%
  15  6.768  1067 1077 1087 PV 6    82984    4405464   0.30%   0.082%

  16  6.835  1087 1088 1106 VV 8    52448    2012755   0.14%   0.037%


                        Sum of corrected areas:   5400889732

DATTA_WELSH...UID_031513.M Wed Apr 17 10:10:33 2013
```

Figure 96: Percentage Report Run 43

Appendix C: GC/MS Results – Product Distribution Graphs

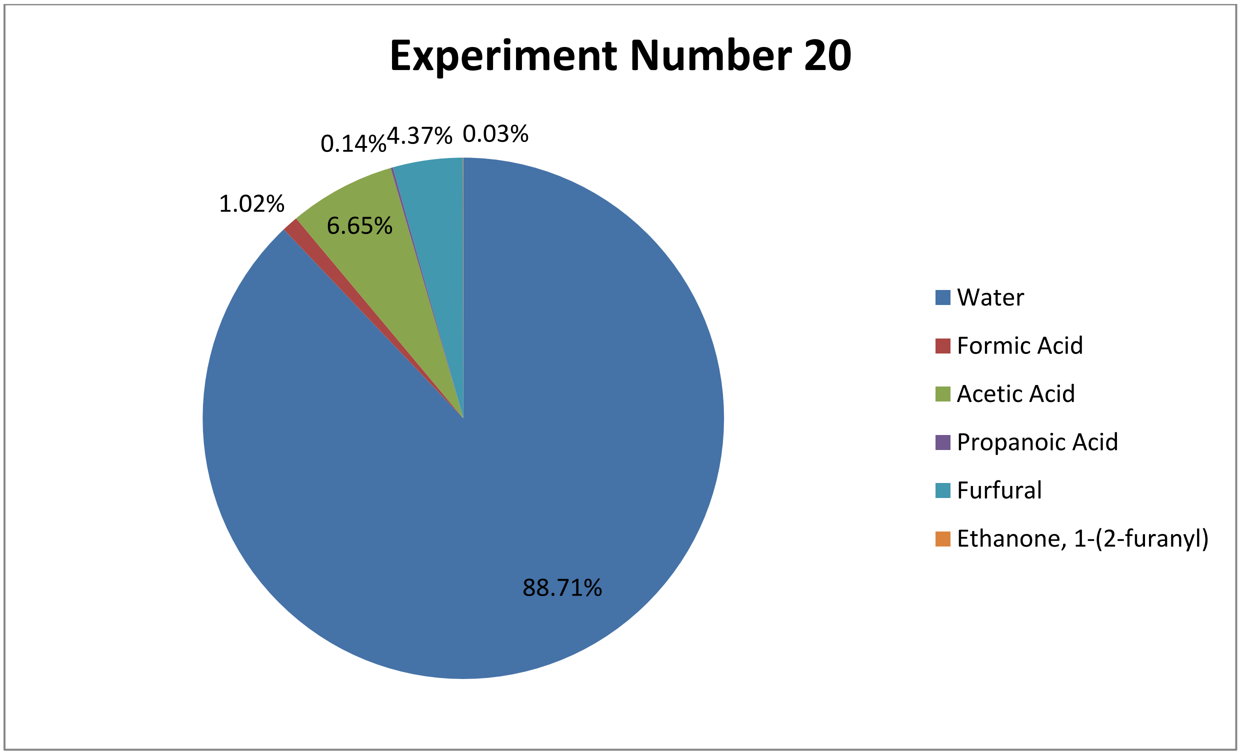


Figure 97: Product distribution for experiment 20

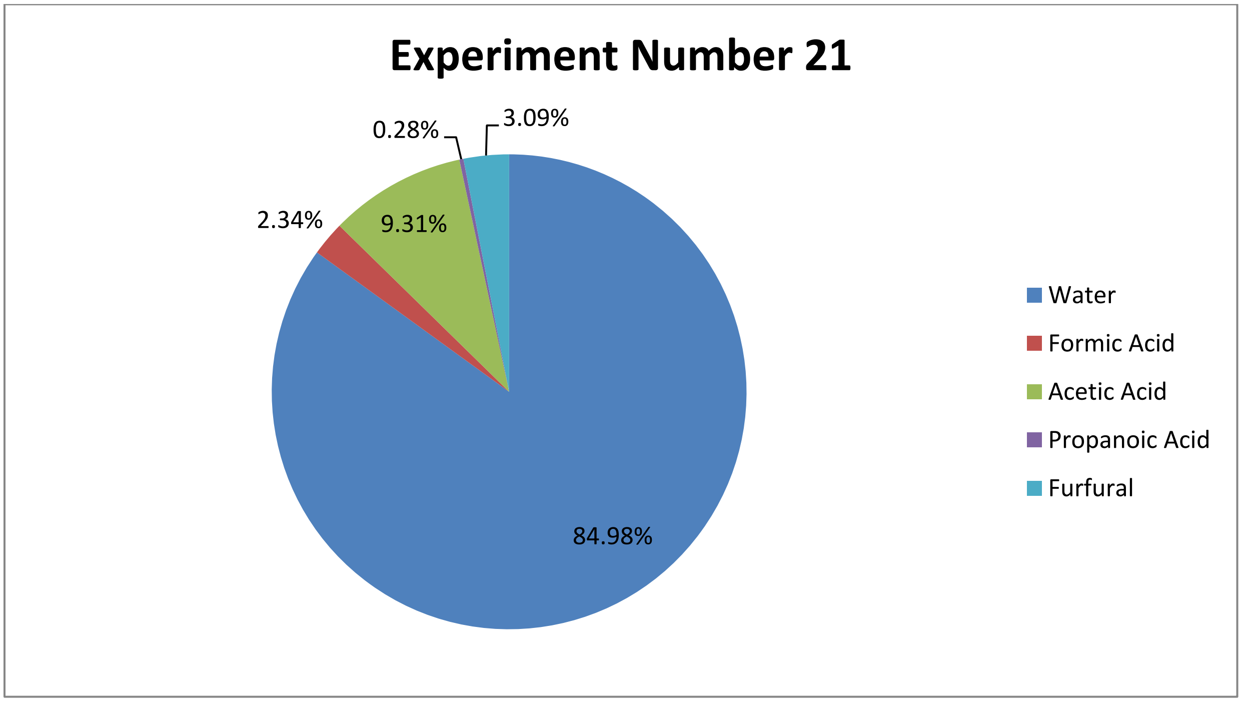


Figure 98: Product distribution for experiment 21

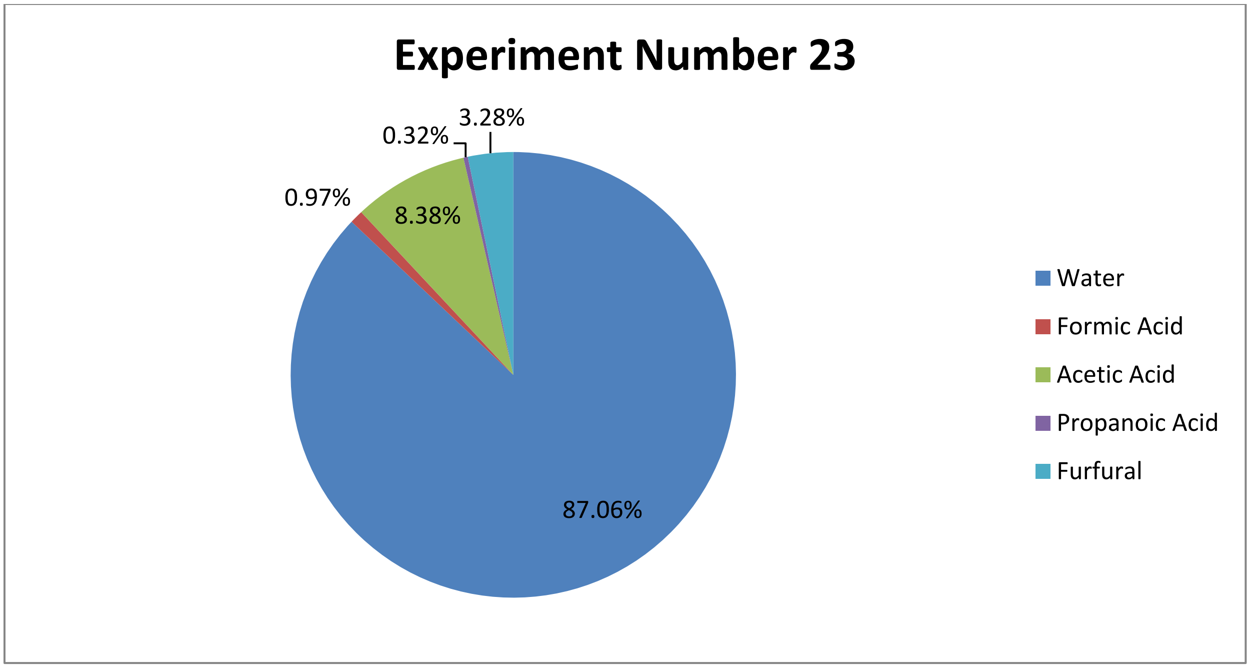


Figure 99: Product distribution for experiment 23

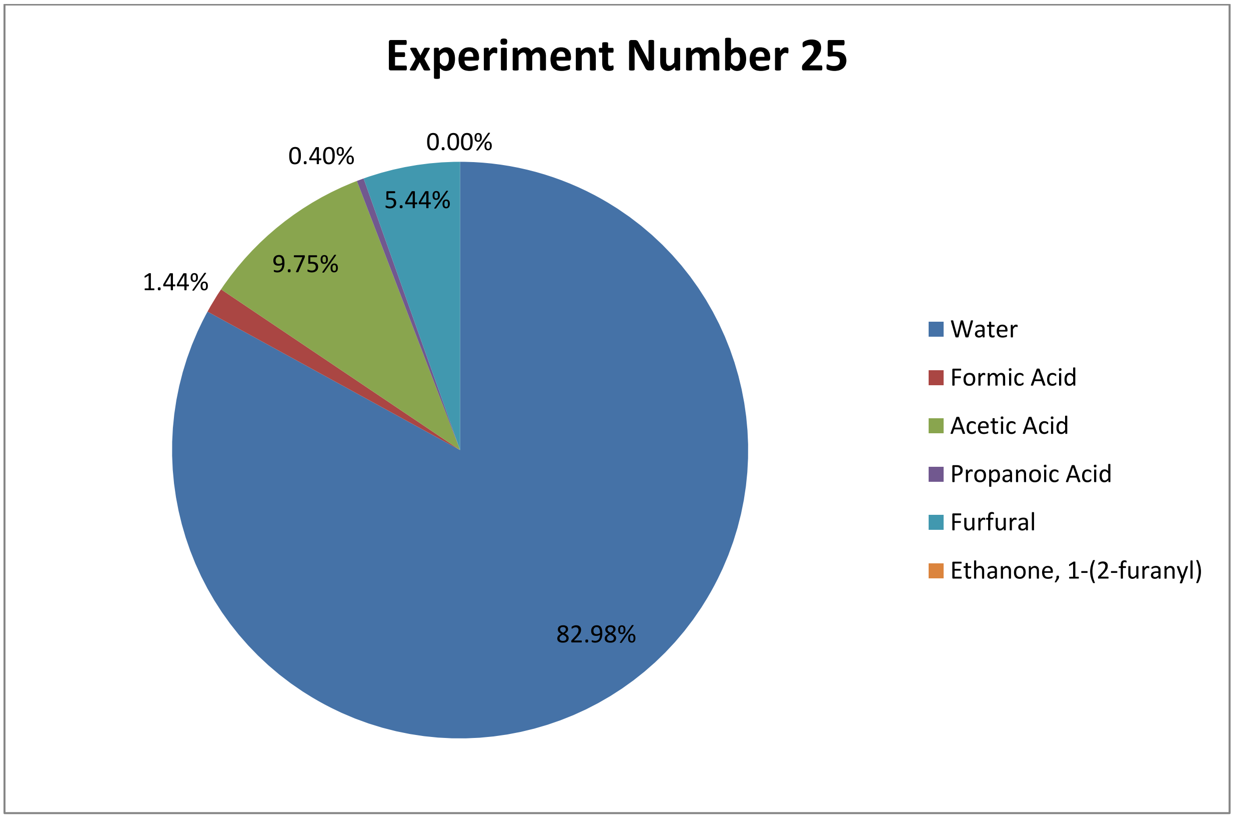


Figure 100: Product distribution for experiment 25

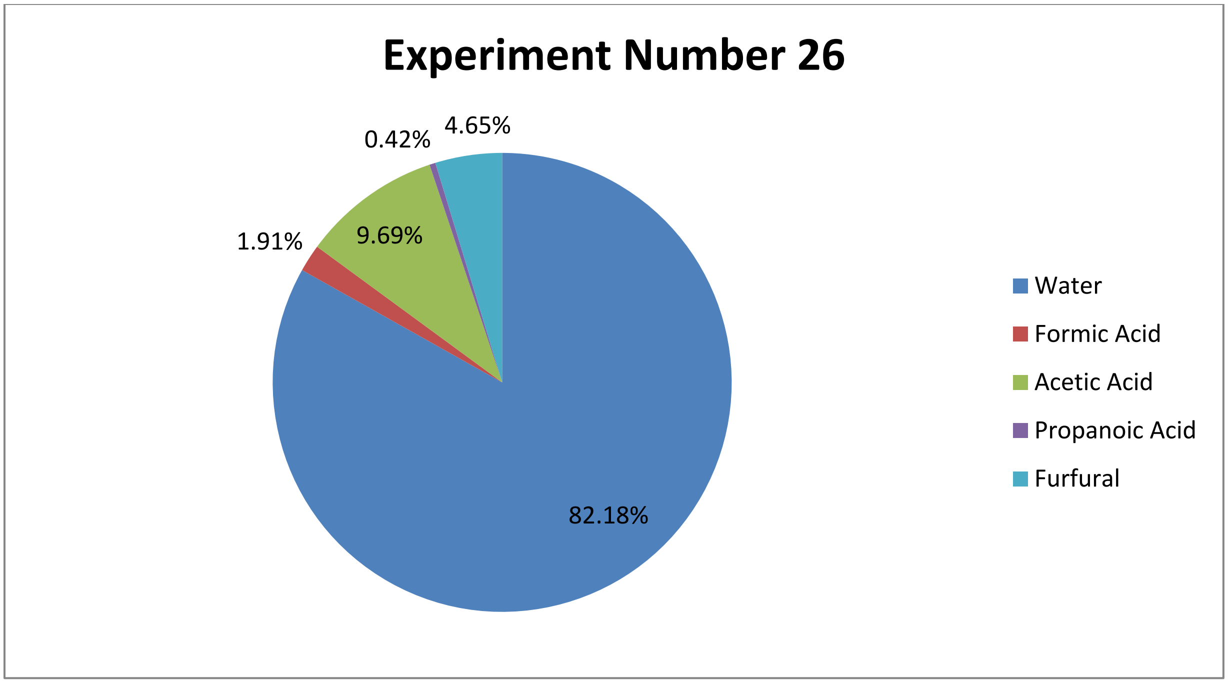


Figure 101: Product distribution for experiment 26

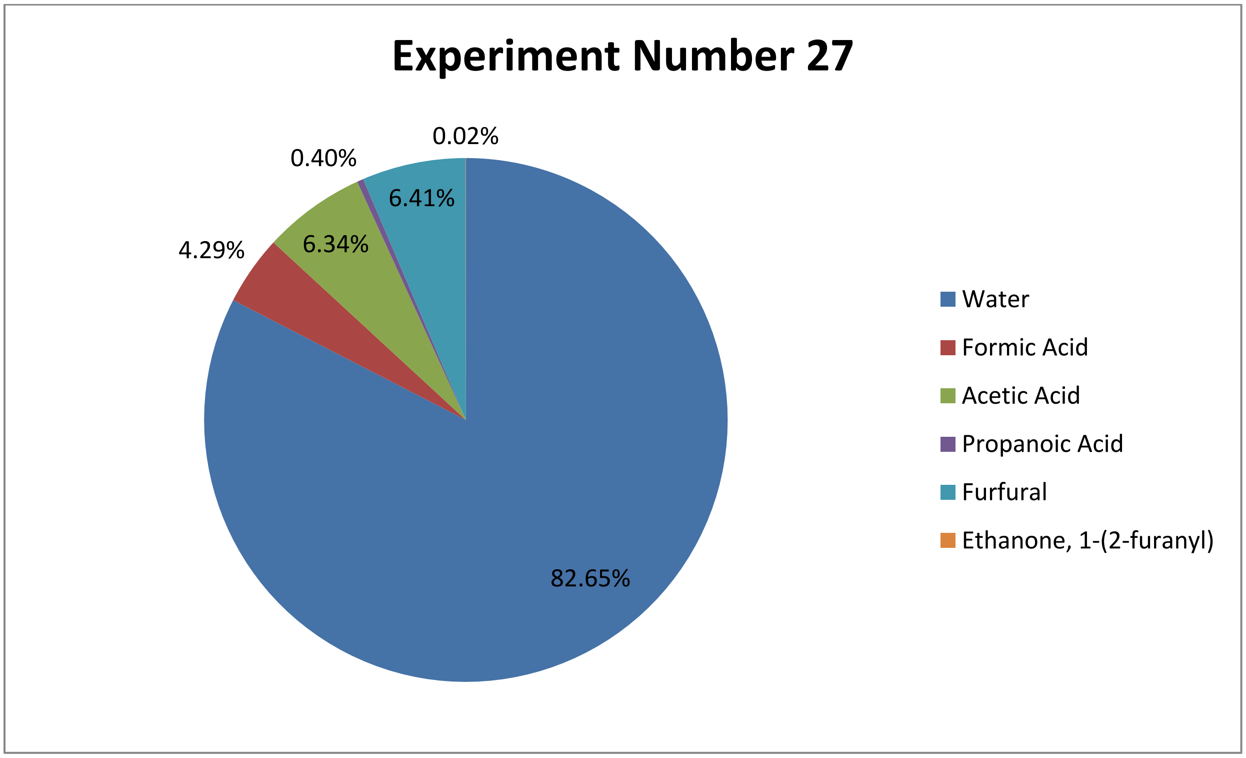


Figure 102: Product distribution for experiment 27

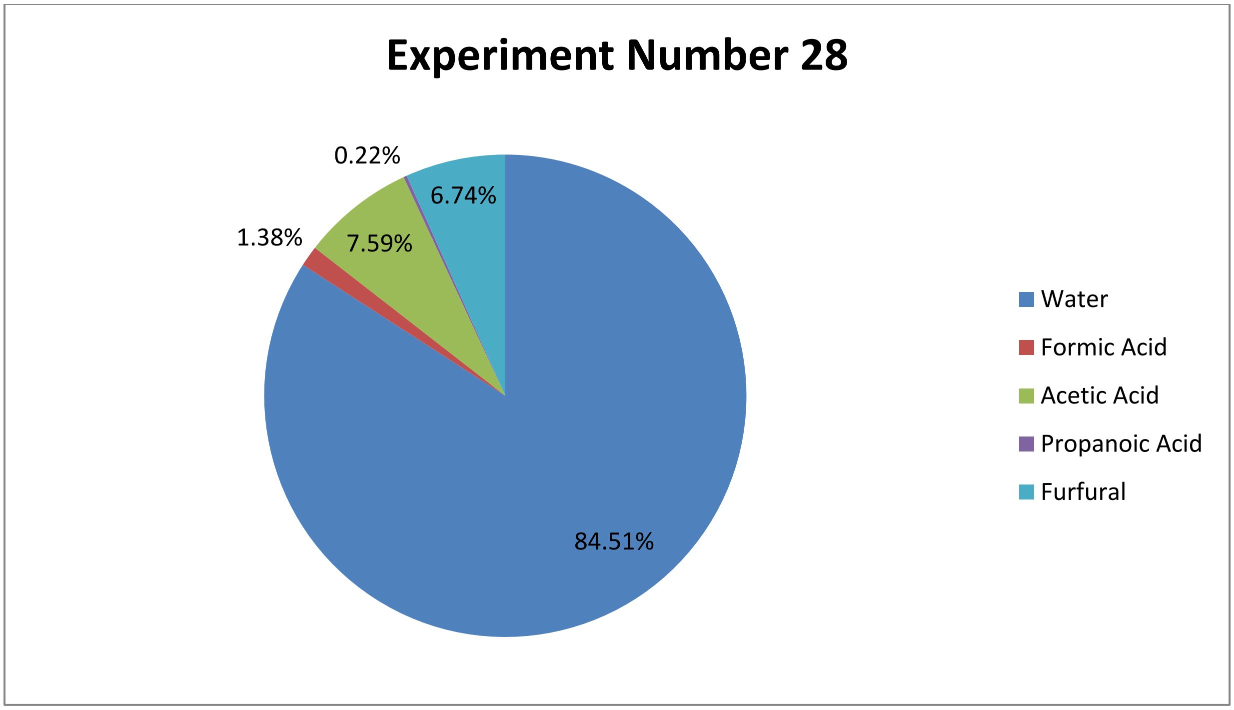


Figure 103: Product distribution for experiment 28

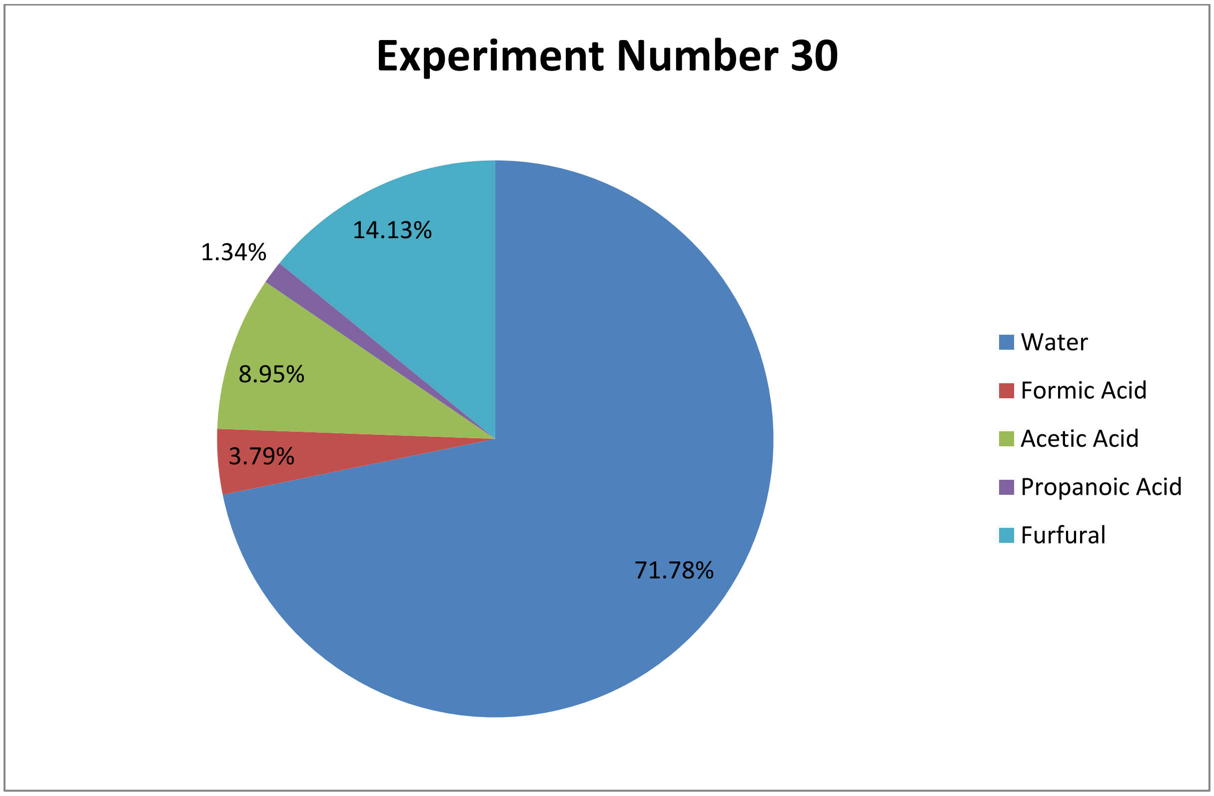


Figure 104: Product distribution for experiment 30

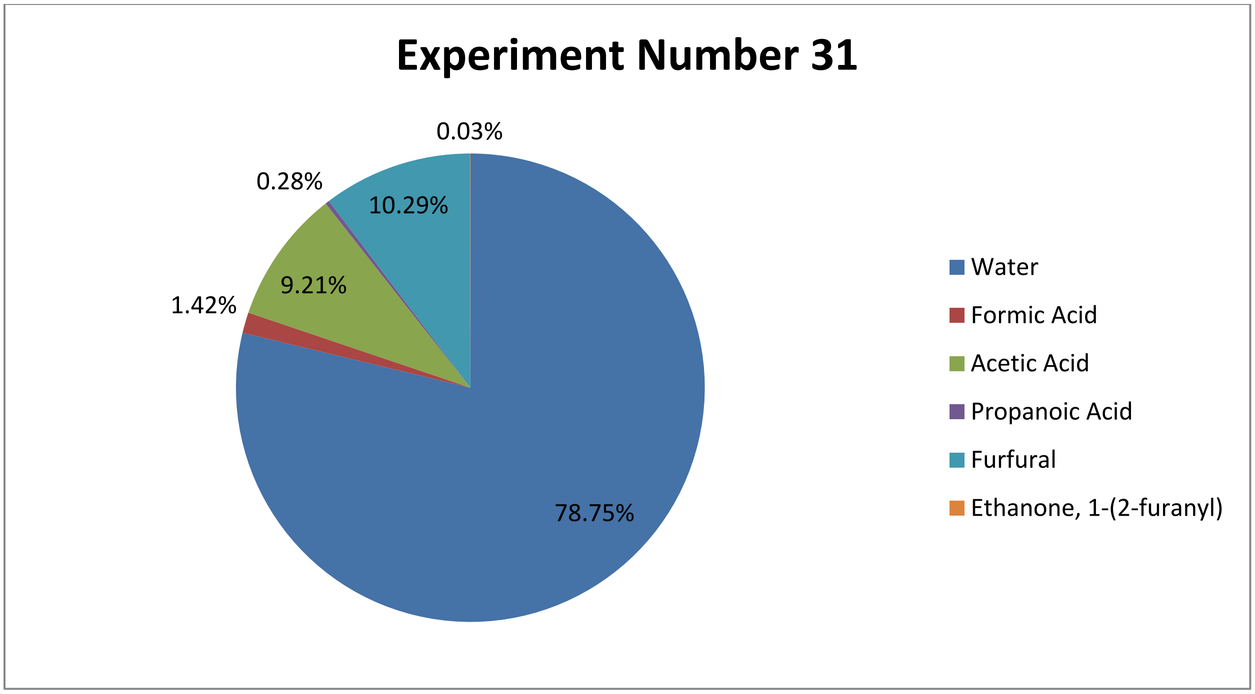


Figure 105: Product distribution for experiment 31

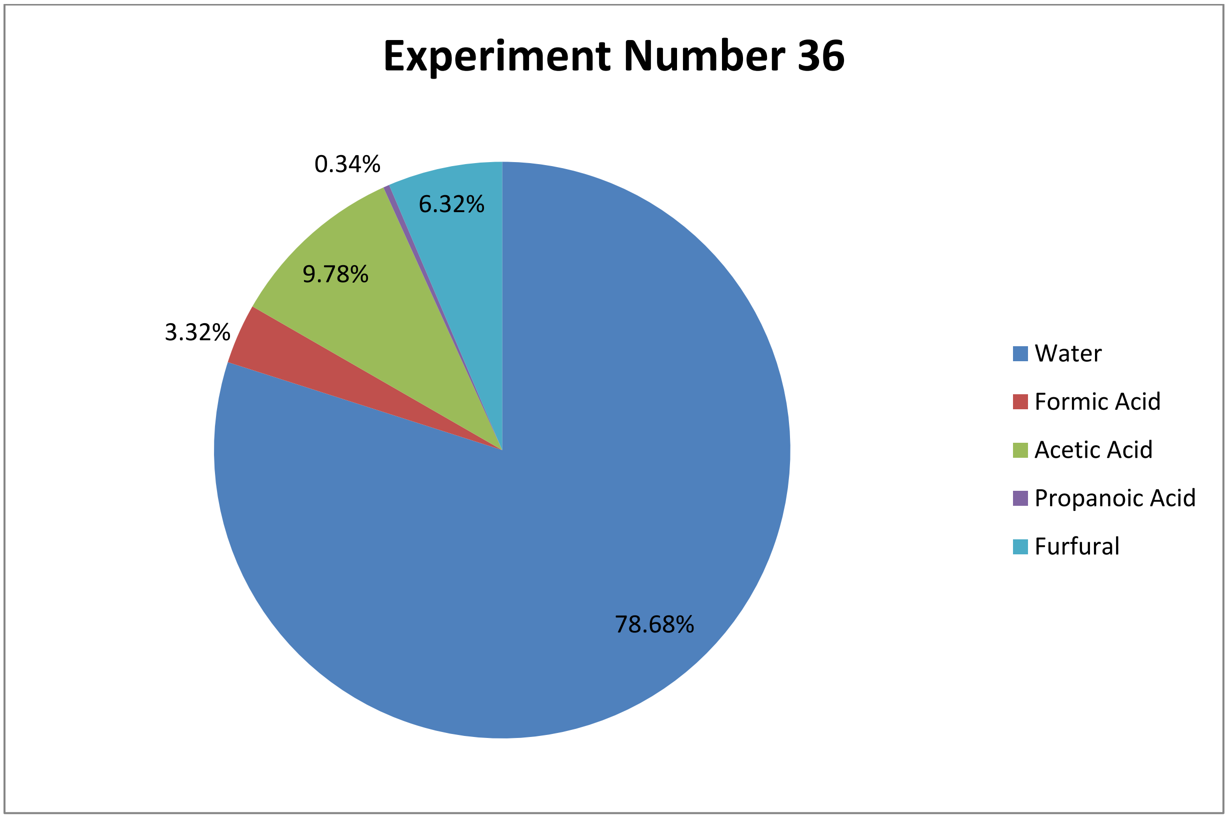


Figure 106: Product distribution for experiment 36

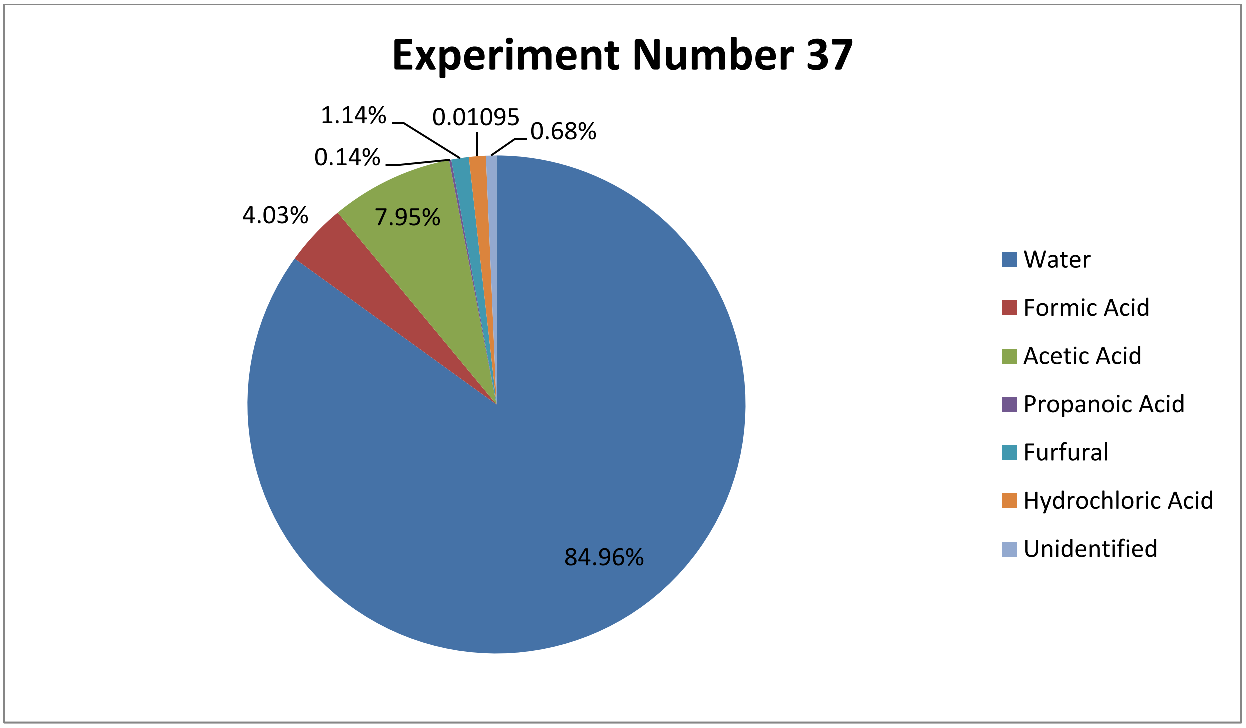


Figure 107: Product distribution for experiment 37

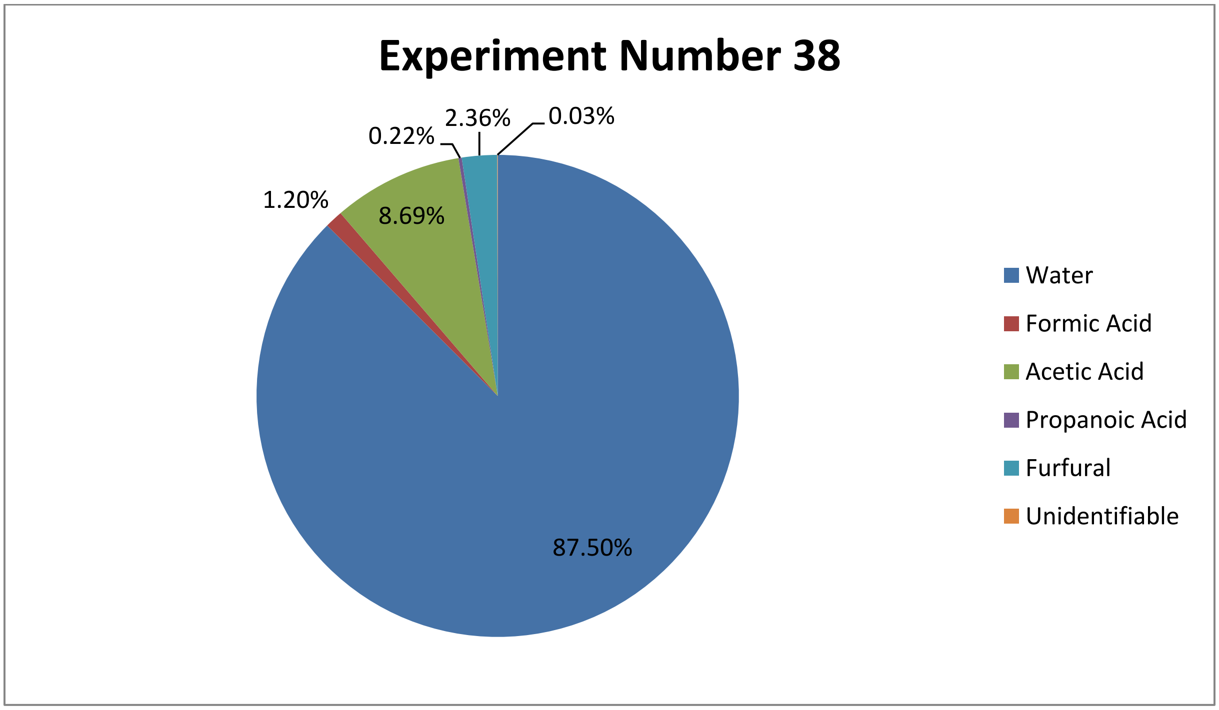


Figure 108: Product distribution for experiment 38

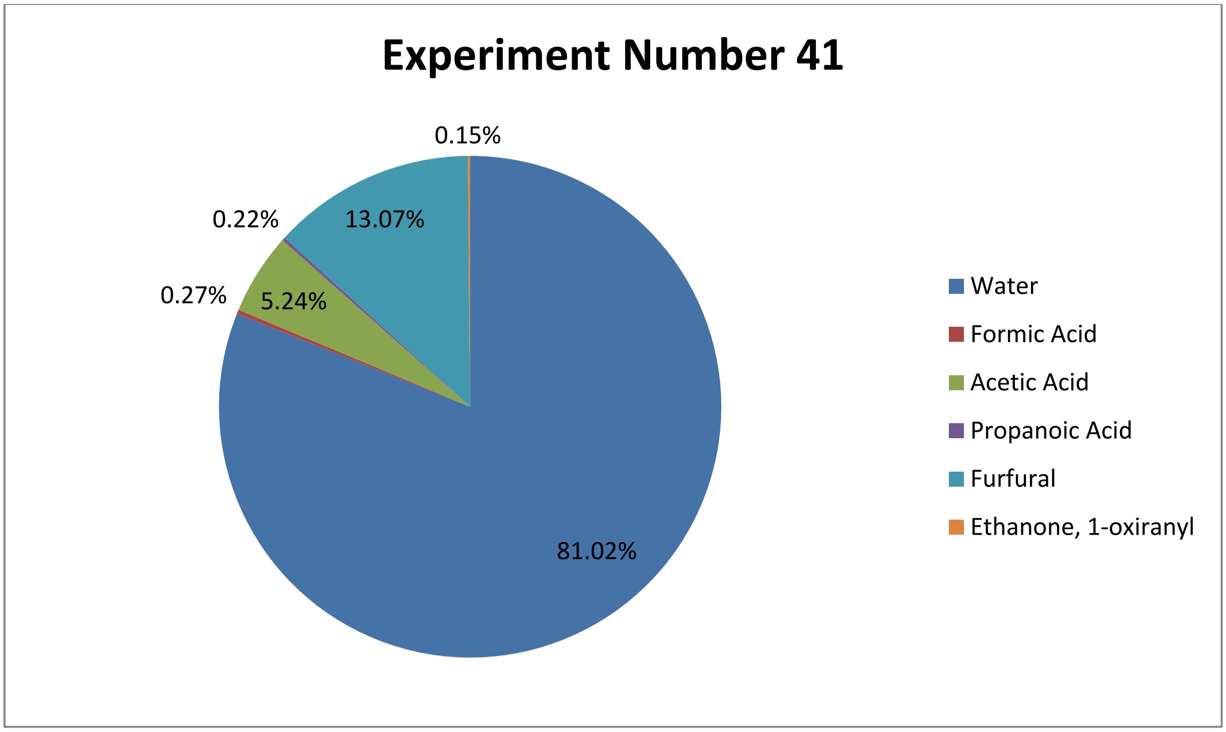


Figure 109: Product distribution for experiment 41

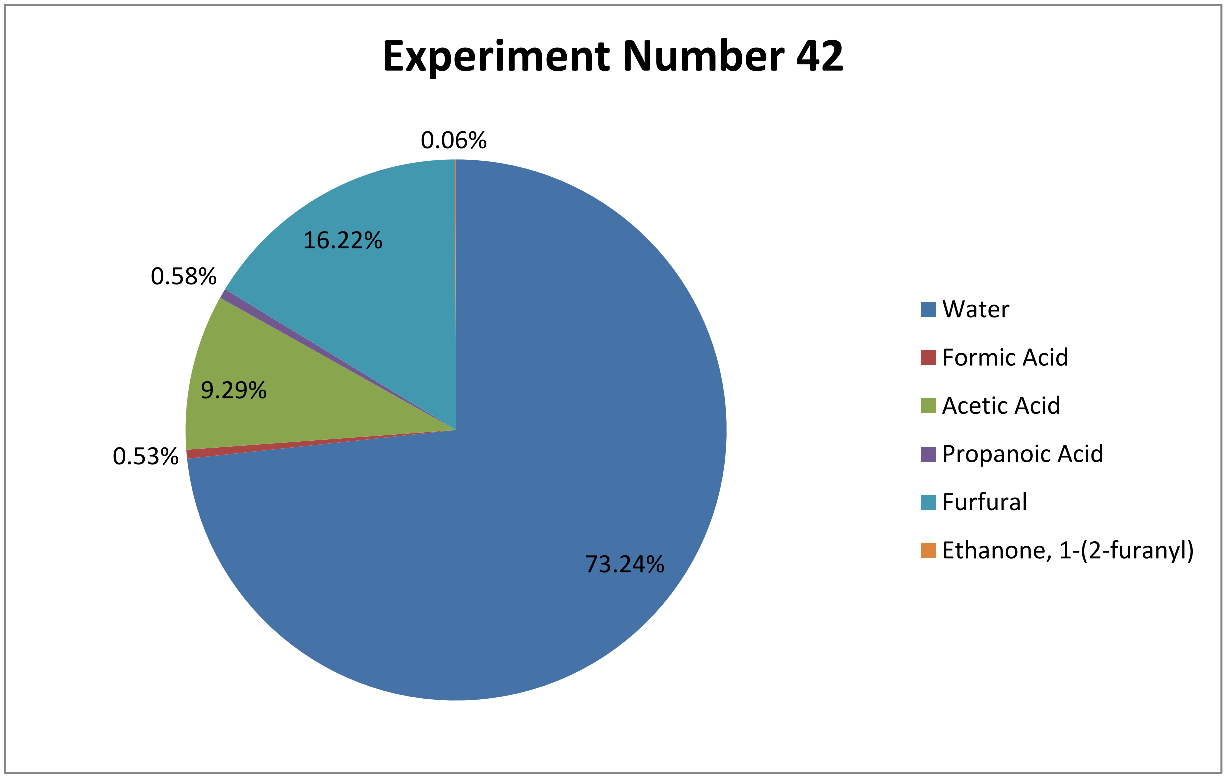


Figure 110: Product distribution for experiment 42

Appendix D: Raw Data

Table 21: Raw data of cellulose baseline tests

Cellulose Baseline Tests								
Experiment Number	Temperature	Mass of Cellulose	Flask Weight		Vile Weight		Liquid Yield	Attainable Liquid Yield
#	Celsius	(g)	Before (g)	After (g)	Before (g)	After (g)	%	%
1*	300	3.2	98.7	98.7	6.2	6.2	0.0	0.0
2*	350	3.2	98.7	99.0	6.2	6.4	9.4	6.3
3*	400	3.2	98.7	99.4	6.3	6.8	21.9	15.6
4*	450	3.2	98.7	99.6	6.2	6.9	28.1	21.9

Table 22: Mole ratio tests raw data

Mole Ratio Tests											
Experiment	Mole Ratio	Temperature	Mass Cellulose	Mass Eutectic	Total Mass	Reactor Wt Before	Reactor Wt After	Beaker Wt Before	Beaker Wt After	Vial Wt Before	Vial Wt After
#	Cellulose to Eutectic	°C	g	g	g	g	g	g	g	g	g
1	10 to 1	450	5.000	0.113	5.113	415.4	411.8	124.682	126.546	6.194	7.822
2	10 to 3	450	5.000	0.141	5.141	415.2	411.7	98.850	100.808	6.167	7.840
3	10 to 5	450	5.000	0.189	5.189	415.3	411.8	124.820	127.100	6.176	8.208
4	10 to 7	450	5.000	0.283	5.283	415.4	411.9	124.645	126.923	6.170	8.146
5	10 to 9	450	5.000	0.566	5.566	415.7	412.4	124.720	127.030	6.210	8.280
6	10 to 10	450	5.000	1.132	6.132	416.2	412.7	124.628	127.041	6.179	8.287
7	9 to 10	450	5.000	2.264	7.264	417.3	414.0	124.600	127.200	6.180	8.450
8	7 to 10	450	5.000	4.528	9.528	419.6	416.5	124.670	127.160	6.226	8.519
9	5 to 10	450	5.000	6.791	11.791	421.9	418.1	124.663	127.266	6.190	8.575
10	3 to 10	450	5.000	9.055	14.055	423.8	419.6	124.677	127.206	6.123	8.411
11	1 to 10	450	5.000	11.319	16.319	426.0	421.3	124.678	127.292	6.202	8.268
12	1 to 20	450	2.500	11.319	13.819	423.3	420.9	124.673	126.506	6.162	7.836

Table 23: Raw data of varying chloride eutectic tests

Varying Chloride Eutectic Tests																								
Exp.	Cell. to Eut.	Temp	Mass Cell.	Mol Wt	Moles Cellulose	Zinc Chloride			Sodium Chloride			Potassium Chloride			Lithium Chloride			Mass Eut.	Reactor Wt Before	Reactor Wt After	Beaker Wt Before	Beaker Wt After	Vial Wt Before	Vial Wt After
#	Ratio	°C	(g)	g/mol	mols	Mole %	Mol Wt	Mass (g)	Mole %	Mol Wt	Mass (g)	Mole %	Mol Wt	Mass (g)	Mole %	Mol Wt	Mass (g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
13	1 to 20	400	2	162.14	0.012335	40%	65.38	6.452	0%	22.99	0.000	20%	39.098	1.929	40%	6.941	0.685	9.066	420.0	418.0	124.674	126.028	6.1748	7.3635
14	1 to 20	400	1.3	162.14	0.008018	60%	65.38	6.290	20%	22.99	0.737	20%	39.098	1.254	0%	6.941	0.000	8.282	419.3	418.1	124.668	125.387	6.1763	6.7428
15	1 to 20	400	1.3	162.14	0.008018	60%	65.38	6.290	30%	22.99	1.106	10%	39.098	0.627	0%	6.941	0.000	8.023	419.2	418.2	124.663	125.386	6.1505	6.7381
16	1 to 20	400	1.3	162.14	0.008018	60%	65.38	6.290	40%	22.99	1.475	0%	39.098	0.000	0%	6.941	0.000	7.765	418.9	417.9	124.672	125.465	6.1032	6.7427
17	1 to 20	400	1.3	162.14	0.008018	70%	65.38	7.339	30%	22.99	1.106	0%	39.098	0.000	0%	6.941	0.000	8.445	419.3	418.1	124.666	125.460	6.1732	6.8067
18	1 to 20	400	1.3	162.14	0.008018	80%	65.38	8.387	20%	22.99	0.737	0%	39.098	0.000	0%	6.941	0.000	9.125	419.7	418.6	124.667	125.366	6.1169	6.6645
19	1 to 20	400	1.3	162.14	0.008018	50%	65.38	5.242	50%	22.99	1.843	0%	39.098	0.000	0%	6.941	0.000	7.085	417.4	416.5	124.657	125.354	6.1647	6.6594
20	1 to 25	400	1.3	162.14	0.008018	40%	65.38	5.242	40%	22.99	1.843	20%	39.098	1.567	0%	6.941	0.000	8.653	419.2	418.0	124.672	125.203	6.1676	6.5972
21	1 to 25	400	1.3	162.14	0.008018	100%	65.38	13.105	0%	22.99	0.000	0%	39.098	0.000	0%	6.941	0.000	13.105	423.4	422.0	124.664	125.410	6.0850	6.6142
22	1 to 20	400	1.5	162.14	0.009251	70%	65.38	8.468	30%	22.99	1.276	0%	39.098	0.000	0%	6.941	0.000	9.744	420.6	419.6	124.670	125.287	6.1882	6.6157
23	1 to 20	400	1.7	162.14	0.010485	70%	65.38	9.597	30%	22.99	1.446	0%	39.098	0.000	0%	6.941	0.000	11.043	422.5	421.5	124.670	125.453	6.2094	6.8192
24	1 to 20	400	1.9	162.14	0.011718	70%	65.38	10.726	30%	22.99	1.616	0%	39.098	0.000	0%	6.941	0.000	12.342	424.3	423.0	124.665	125.538	6.1504	6.7859
25	1 to 20	400	1.3	162.14	0.008018	70%	65.38	7.339	30%	22.99	1.106	0%	39.098	0.000	0%	6.941	0.000	8.445	421.4	420.5	124.676	125.372	6.1418	6.6800
26	1 to 20	400	2.5	162.14	0.015419	70%	65.38	14.113	30%	22.99	2.127	0%	39.098	0.000	0%	6.941	0.000	16.240	428.1	426.3	121.682	123.027	6.1673	7.3140
27	1 to 20	400	2.5	162.14	0.015419	60%	65.38	12.097	20%	22.99	1.418	0%	39.098	0.000	20%	6.941	0.428	13.943	428.1	426.1	124.676	125.858	6.1735	7.1249
28	1 to 20	400	2.5	162.14	0.015419	60%	65.38	12.097	30%	22.99	2.127	0%	39.098	0.000	10%	6.941	0.214	14.438	428.5	426.7	121.679	122.936	6.1826	7.2268
29	1 to 20	400	2.5	162.14	0.015419	50%	65.38	10.081	30%	22.99	2.127	0%	39.098	0.000	20%	6.941	0.428	12.636	426.5	424.2	124.678	125.976	6.1014	7.1266
30	1 to 20	400	2.5	162.14	0.015419	40%	65.38	8.065	30%	22.99	2.127	0%	39.098	0.000	30%	6.941	0.642	10.834	422.4	420.3	121.564	123.043	6.1635	7.2823
31	1 to 20	400	2.5	162.14	0.015419	40%	65.38	8.065	40%	22.99	2.836	0%	39.098	0.000	20%	6.941	0.428	11.329	425.4	423.7	124.670	125.709	6.1246	6.9819

Table 24: Raw data of heating rate tests

Heating Rate Tests																								
Exp.	Cell. to Eut.	Temp	Mass Cell.	Mol Wt	Moles Cell.	Zinc Chloride			Sodium Chloride			Potassium Chloride			Lithium Chloride			Mass of Eutectic	Reactor Wt Before	Reactor Wt After	Beaker Wt Before	Beaker Wt After	Vial Wt Before	Vial Wt After
#	Ratio	°C/min	(g)	g/mol	mols	Mole %	Mol Wt	Mass (g)	Mole %	Mol Wt	Mass (g)	Mole %	Mol Wt	Mass (g)	Mole %	Mol Wt	Mass (g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
33	25	20	2.500	162.14	0.01542	40%	65.38	10.081	0%	22.99	0.000	20%	39.098	3.014	40%	6.941	1.070	14.165	428.1	426.1	121.677	123.808	6.1667	6.4515
34	20	40	2.000	162.14	0.01234	40%	65.38	6.452	0%	22.99	0.000	20%	39.098	1.929	40%	6.941	0.685	9.066	420.5	419.1	124.676	126.381	6.1474	7.5282
35	25	40	2.500	162.14	0.01542	40%	65.38	10.081	0%	22.99	0.000	20%	39.098	3.014	40%	6.941	1.070	14.165	428.3	426.3	121.687	122.857	6.1754	7.1623
36	20	40	2.500	162.14	0.01542	70%	65.38	14.113	30%	22.99	2.127	0%	39.098	0.000	0%	6.941	0.000	16.240	428.6	426.9	121.677	122.754	6.1768	7.0346
37	20	20	2.500	162.14	0.01542	70%	65.38	14.113	30%	22.99	2.127	0%	39.098	0.000	0%	6.941	0.000	16.240	429.2	427.6	124.678	125.741	6.2163	7.0851
38	20	10	2.500	162.14	0.01542	70%	65.38	14.113	30%	22.99	2.127	0%	39.098	0.000	0%	6.941	0.000	16.240	428.6	427.1	107.821	108.400	6.1312	6.633
39	20	20	2.500	162.14	0.01542	40%	65.38	8.065	0%	22.99	0.000	20%	39.098	2.411	40%	6.941	0.856	11.332	424.7	-	107.696	107.859	-	-
40	20	10	2.500	162.14	0.01542	40%	65.38	8.065	0%	22.99	0.000	20%	39.098	2.411	40%	6.941	0.856	11.332	425.6	424.1	126.213	126.815	6.1909	6.7945
41	20	30	2.500	162.14	0.01542	40%	65.38	8.065	0%	22.99	0.000	20%	39.098	2.411	40%	6.941	0.856	11.332	425.6	423.6	126.197	127.500	-	-
42	20	60	2.500	162.14	0.01542	40%	65.38	8.065	0%	22.99	0.000	20%	39.098	2.411	40%	6.941	0.856	11.332	425.7	424.1	117.285	118.475	6.1775	7.2278
43	21	60	2.500	162.14	0.01542	40%	65.38	8.468	0%	22.99	0.000	20%	39.098	2.532	40%	6.941	0.899	11.899	425.7	423.8	126.213	127.246	6.2152	7.0372