Molten Salt Gasification of Biomass

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Abstract

Biomass is a renewable resource that shows great promise in a wide variety of applications including alternative fuels and synthetic chemical processes. The use of molten salts as a catalyst for the breakdown of biomass is a venue with potential that has barely been explored. This report will analyze molten salts with varying compositions of Li_2CO_3, Na_2CO_3, K_2CO_3, KOH, and NaOH and their effects on the biomass gasification. It is proposed that the highly ionic molten salt media acts to break down the lignin binding the cellulose and hemi cellulose and to further breakdown the long-chain cellulose strands into smaller sugars in a manner that does not alter the molten salt. In addition, the molten salt increases the surface interactions between the deconstructed carbonaceous materials with gaseous carbon dioxide and water vapor that catalyzes the formation of carbon monoxide and hydrogen (syngas). Experimental results indicate the production of syngas from the proposed process. In addition, experiments suggest that the molten salts catalyze the reaction between carbon dioxide, water, and the char left over from pyrolysis to produce additional carbon monoxide.

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1. Introduction and Rationale

In today's world, there are several major technological and fundamental impending shifts associated with synthetic chemicals and energy related technologies. Current world demand for electricity is upwards of 18 trillion kilowatt-hours per year, but is predicted to rise to over 33 trillion kilowatt-hours by the year 2030.[1] With such astounding growth figures for electricity demand, the natural question facing society is where will all this electricity come from?

For decades the global society has relied on carbon based fossil fuels to power the world. Petroleum fuels, coal, and natural gas have all proven themselves as great, dependable fuel sources which have sustained life and driven industrialization. In the future, however, mankind is faced with a finite amount of carbon fossil fuels and a seemingly infinitely increasing level of demand. To ensure the future of society, new technologies must be introduced that can produce the quantity of electricity demanded in a sustainable manner.

Currently, the energy industry as a whole has been optimized to the maximum extent of today's technologies. Turbine efficiencies, energy cycles, plant design and separation technology have all been fine tuned to produce the maximum electricity per unit energy to meet societal demand. Currently, however, the energy industry is on the brink of a major transition as new technologies emerge that are more efficient, environmentally conscious and help decrease our dependence on non-renewable fuels.

In addition to energy, carbon fossil resources such as petroleum play a vital role in the synthetic chemicals and materials industry. Production of petroleum derived chemicals such as plastics, oils and aromatics are also important factors to consider when developing a sustainable society. New, renewable

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[1] (Annual Energy Outlook 2009: With Projections to 2030)

sources for synthetic chemicals are being developed and will become more prominent and vital in the future as limited supplies of synthetic feed stocks dwindle.

1.1. Energy

With the cost of oil upwards of $40 per barrel[2] and in limited supply, the need for new forms of energy has never been so pressing. The most current predictions show that oil prices will continue to rise as world demand increases, as depicted by Figure 1-1.[2] Although there is no definitive answer as to what the future of global energy will look like, it is clear that a dynamic shift in the energy sources will take place over the next century.

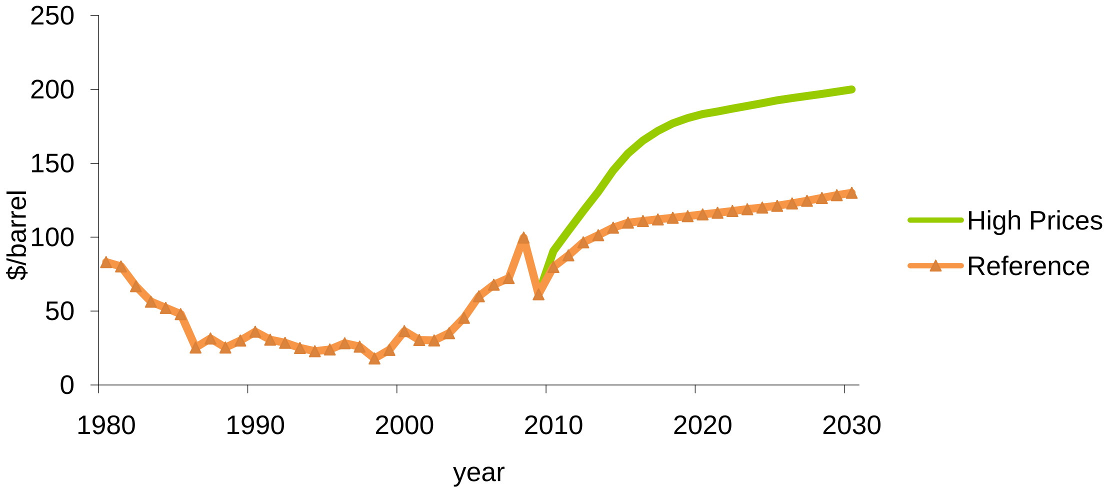

Figure 1-1: Oil prices predictions[3]

Plausible solutions for energy conversions include wind, solar, geothermal, and tidal energy. They are renewable sources of energy with relatively few side effects to the local environment and society. Many are still in their developmental phases, and are currently pricey solutions. In the future, the onset of new technologies and mass production cost reductions will make the technologies more widely available. Skeptics have criticized that these options will only be able to account for a small

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[2] (Weekly United States Spot Price FOB Weighted by Estimated Import Volume (Dollars per Barrel))
[3] (Annual Energy Outlook 2009 Early Release Summary Presentation)

portion of the total energy demand, citing large land and energy input requirements compounded by poor conversion efficiencies.

In the long-term, the only viable fuel source is renewable. Solar conversion is ideal, though costs are great, conversion is low and effective lifespan is limited. Photovoltaic conversion, currently between 10 and 20%[4], is the best means of man-made solar conversion. In nature, plants perform this process through the process of photosynthesis. Research efforts have focused on using biomass forms to convert energy stored in long hydrocarbon chains to useable energy forms. This report focuses on the breakdown of biomass in waste forms into fuel or feedstock for chemical production.

1.2. Synthetic Chemicals and Fuels

Research is underway to find new methods to synthesize new chemicals and fuels driven in large by a limited supply of fossil resources. Currently, petroleum and its derivatives contribute the bulk of the automotive and aviation fuels as well as synthetic polymers used in plastics. As there is only a limited supply of fossil fuels, it is vital that new technologies are developed to synthetically derive these materials from renewable and sustainable sources.

Methods for synthetically forming liquid fuels from other fuel sources, such as coal and biomass, have promising potential for the future. Although energy is lost in the conversion stages, this method of solid to liquid synthesis still shows promise because it can easily integrate into current liquid hydrocarbon fuels economy. Other feedstocks also provide additional synthetic formation methods. For instance, natural gas can be reacted with water in a process known as steam reforming to form a gas composed of carbon monoxide, hydrogen (Equation 1-1).

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[4] (Denis Lenardic)

$$\mathrm{CH_4 + H_2O \rightarrow CO + 3H_2}$$

Equation 1-1

Synthetic gas, or syngas for short, is a mixture varying in composition but made up of carbon monoxide and hydrogen gas. The syngas can be further oxidized to provide energy for electricity generation or provide a feedstock to synthetically form liquid fuels. Syngas also forms under the proper conditions by catalytically breaking down biomass feedstocks.

1.3. Waste

Another key societal and environmental problem needing consideration is waste management in the future. With Americans producing over 250 million tons of solid waste per year (see Figure 1-2), roughly one for every citizen, and trends increasing significantly, the question then becomes where the waste will go in the future.

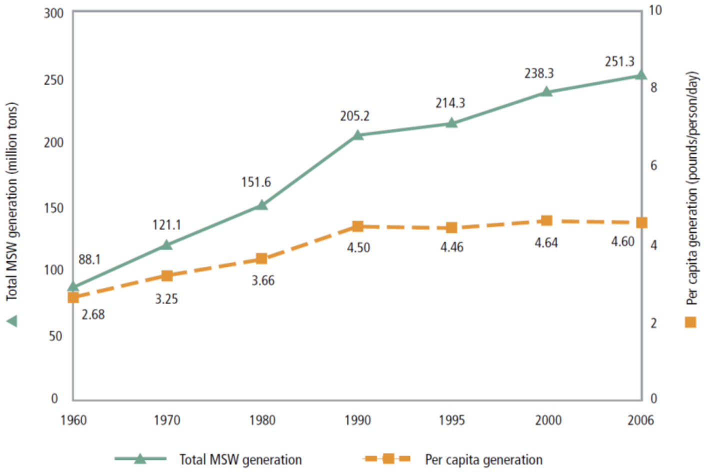

Figure 1-2: Municipal Solid Waste Generation as of 2006[5]

Urban cities constantly increase in population density due to the limited amount of land available for housing construction. The sheer volume needed to accommodate all this waste has forced

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[5] (Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2006)

major cities such as New York to truck their waste out to neighboring states which are reaching their capacity.

In the future, strategies for accommodating this waste must be developed to insure to ensure the future of metropolitan cities. Current recycling programs efficiently reuse aluminum and glass bottles. Paper waste is also efficiently reprocessed into newspapers and assorted products. Unfortunately, for these processes to be effective, each waste product requires a pure, clean feed. In addition, it is difficult to reprocess many plastics, and often requires large energy input to reprocess much of the waste.

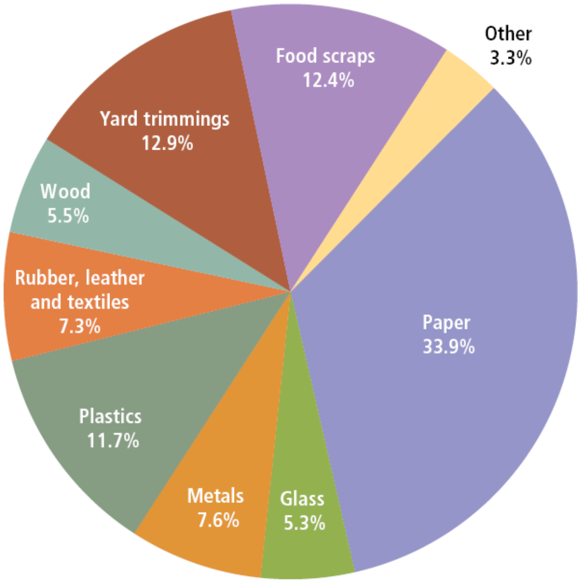

Figure 1-3: Total MSW Generation (by Material), 2006[6]

Out of the 251 million tons of Municipal Solid Waste (MSW), 33.9% was paper and other forms of biomass constitute 64.7%[7]. The purpose of the biomass processing is to target this market of waste.

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[6] (Wastes - Non-Hazardous Waste - Municipal Solid Waste)
[7] (Wastes - Non-Hazardous Waste - Municipal Solid Waste)

1.4. Depletion and Decentralization

In the United States today, the most abundant natural domestic resource for energy generation is coal (Figure 1-4). Other resources include natural gas, petroleum and nuclear. Each energy form comes with its own problems.

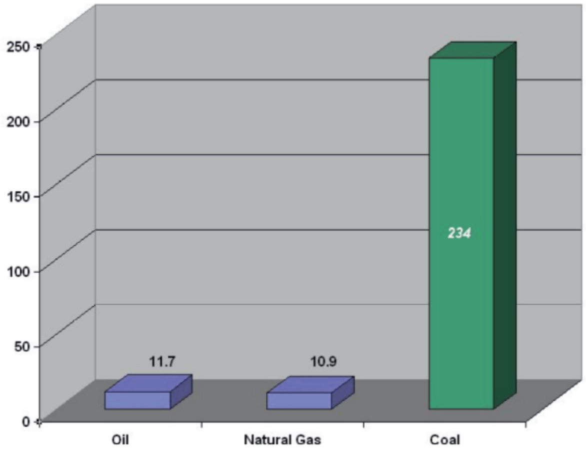

Figure 1-4: 2007 Expected Reserve Life, BP[8]

Coal is only abundant in certain regions of the United States. Natural gas also and petroleum have limited availability. Nuclear, though available in many regions, requires secure transport of uranium and management of nuclear waste, for it has no foolproof storage solution. This often creates centralized dependencies on specific regions. Many often rely on remote locations of the country to be their chief supplier of electricity to power their daily operations. Ideally, this energy generation will be done on a localized level. Unfortunately, the resources simply are not available to do this. Though space is also a reason, the major reason is the lack of a fuel source.

Technology in waste management and treatment has progressed greatly in the past decade, and emerging technologies show great promise in converting waste into usable energy forms.

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[8] (Coal: an abundand energy resource)

1.5. Pollution

Pollution is a hot topic in politics, with scientists and among ordinary people. It affects daily life through the air we breathe, water we drink, and the land we inhabit. Arguably, the largest contributor to pollution in the world is our energy generation. Non renewable energy generation plants such as coal, natural gas, nuclear, and even diesel are the most widely criticized.

1.5.1. *Greenhouse Gas and Global Warming*

Global warming is a scientific theory which is attracting a significant attention in today's scientific and political circles. The theory outlines that the increasing pollution of greenhouse gases have contributed toward a greenhouse effect in which the average global temperature is increasing from year to year.

These greenhouses gases most prominently include carbon dioxide, methane and nitrous oxide. Carbon dioxide and nitrous oxides are products of combustion reactions including those used in coal and other carbon fuels. With increasing efficiencies and scrubbing technologies, NO_x gases can be reduced, however CO_2 will always be a product as carbon is being removed from fossil resources and being returned in its oxidized state as CO_2. This is the greatest issue with the use of coal and other fossil resources.

Current alternative fuel research is primarily focused on carbon neutral processes. In terms of biomass, this means using plants to absorb CO_2 and use it in the photosynthesis process, then use the plants to form a combustible fuel which will return the CO_2 to the atmosphere in a cycle, thus stopping the accumulation of CO_2 in the atmosphere and increase of the greenhouse gas effect. The process developed in this work ultimately creates a carbon neutral system.

1.5.2. *Acid Rain*

Depending on the burning conditions and effluent scrubbing technologies, the reactions result in the formation of nitrous oxides (NO_x) and SO_2 in varying concentrations. These gases in small concentrations are often undetectable to most people, however an accumulation of them in the air can lead toward smog formation. In addition, they dissolve in water in the atmosphere to form their conjugate acids, creating what is commonly referred to as acid rain.

Clearly, the current energy and chemical production processes are unsustainable due to finite resources and the detrimental effect on the environment. Sustainable processes need to be developed. One such approach is described here. Next, a review of the relevant literature is provided.

2. Literature Review

2.1. Biomass

The use of biomass as a source of fuel is not a new movement; in fact, it has only been a little over a century since they were eradicated from common use and replaced entirely by petroleum oils and their derivatives. Recently, however, the use of biomass to offset the consumption of petroleum was seriously reconsidered. Specifically, lignocellulosic biomass sources such as unused forest resources (tree barks and scrap wood), solid waste from agricultural resources (leaves and stems of spent crops), and urban residues (wood and other building materials), are currently disposed of or simply burned rather than being processed to produce energy. It is estimated that, all over the world, these sources alone could contain as much energy as 3.8 billion barrels of oil.[9]

2.1.1. *Biomass Forms*

Biomass is available in a variety of forms. Much of what is considered waste today can actually be considered biomass.

On a most simplistic level, biomass contains solar energy stored as sugars, such as sucrose. These carbon backbone rings are made up of carbon, hydrogen, and oxygen has the structure shown in Figure 2-1. Sugars contain high oxygen content within the molecule and are relatively small, flexible molecules.

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[9] (Walker)

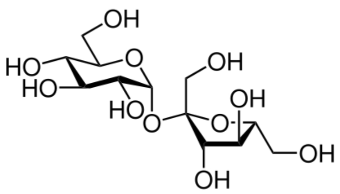

Figure 2-1: Sucrose structure

Cellulose, on the other hand, is a polymer chain made up of a large number of smaller glucose molecules (Figure 2-2). The structure is rather large, though still somewhat flexible as it is a long unbranched chain with (β-1,4)-glucosidic bonded glucose molecules. These chains are linked to other chains via hydrogen bonding to create a rigid, but flexible structure. Hemi cellulose, on the other hand, has a more random, amorphous structure that has little strength. Cellulose is found in green plants, cell walls and most commonly thrown away as wastepaper. One source that is growing in popularity as a potential biomass resource is switchgrass, which is a quick growing crop that can be easily harvested.

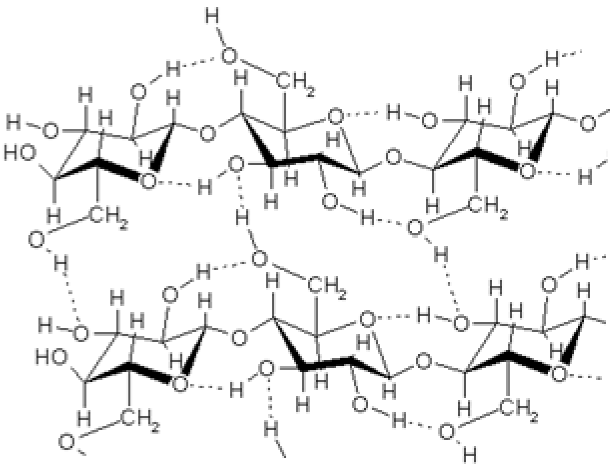

Figure 2-2: Cellulose structure

The last major form of biomass commonly found in waste products is lignin. Lignin is a naturally occurring rigid structure that is comprised of long aromatic ring systems. It is interesting in that there is no predefined structure for lignin, yet it is still very effective at strengthening things such as tree bark, and corn stocks. Lignin is the glue that links cellulose and hemicellulose within plant cell walls.

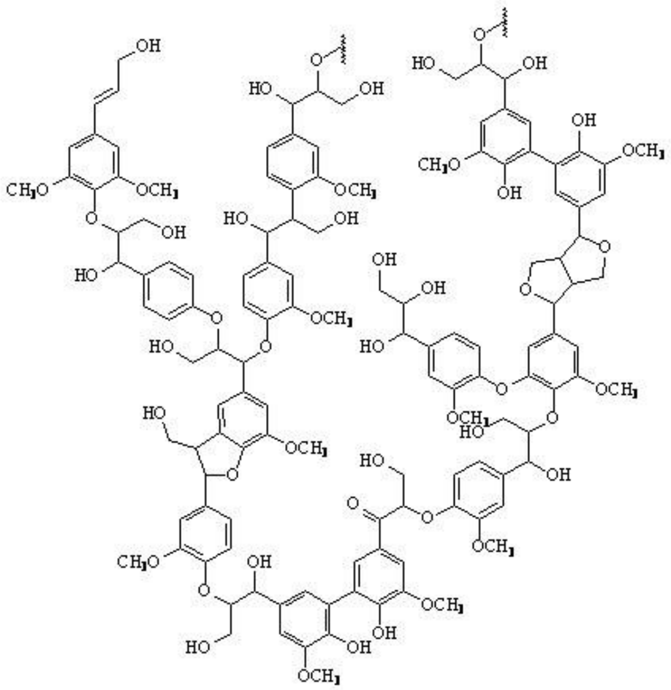

Figure 2-3: Lignin structure[10]

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[10] (Glazer)

2.1.1.1. Biomass Cycle

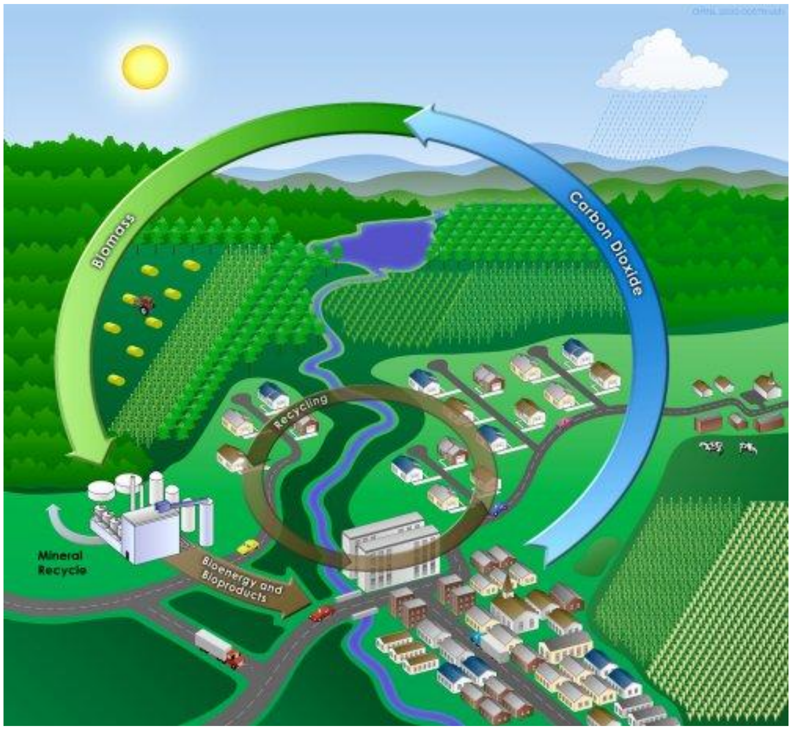

Figure 2-4: The Biomass Cycle[11]

Biomass is often considered a carbon neutral energy source. During its life, plants absorb from the air the same amount of carbon dioxide via photosynthesis that they later return upon decomposition. This process is often called the Biomass Cycle. Plants, and products derived from them such as wastepaper and agricultural waste, can then be broken down into useful products such as syngas and liquid fuels. These products are then used as fuel or in the creation of other products and along the way, return carbon dioxide to the atmosphere. The CO_2 is then absorbed by other plants and the cycle begins anew.

2.1.2. *Processing Methods*

Using biomass as an energy source is not a new revelation. Earliest accounts date as far back as 1.8 million years ago when fire was first used by humans.[12] In the eighteenth century, steam engines

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[11] (Hoexter)

were driven by heat from wood furnaces. In addition, grass clippings and waste biomass has been used in compost by the early farmers as fertilizer.

In modern day energy technologies, maximization of waste energy is critical. Landfills across the country are being fitted with gas collection taps. The gas, approximately 560 million tons in 2006[13], can be capered and burned for electricity generation or other industrial processes. There a large number of start-up companies and individual entrepreneurs who are converting waste vegetable oil from restaurants into biodiesel to run their vehicles or home heating.[14]

Another alternative for this waste is as recycling. Programs now exist for recycling paper, plastics, glass and aluminum for the general public. In addition, there are composting and scrap metal collection facilities that collect their respective waste materials. These forms of waste management effectively find new uses for the materials, but require significant effort and energy consumption in separation and purification.

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[12] (World Heritage Cente)
[13] (An Overview of Landfill Gas Energy in the United States)
[14] (Zhang, Dubé and McLean)

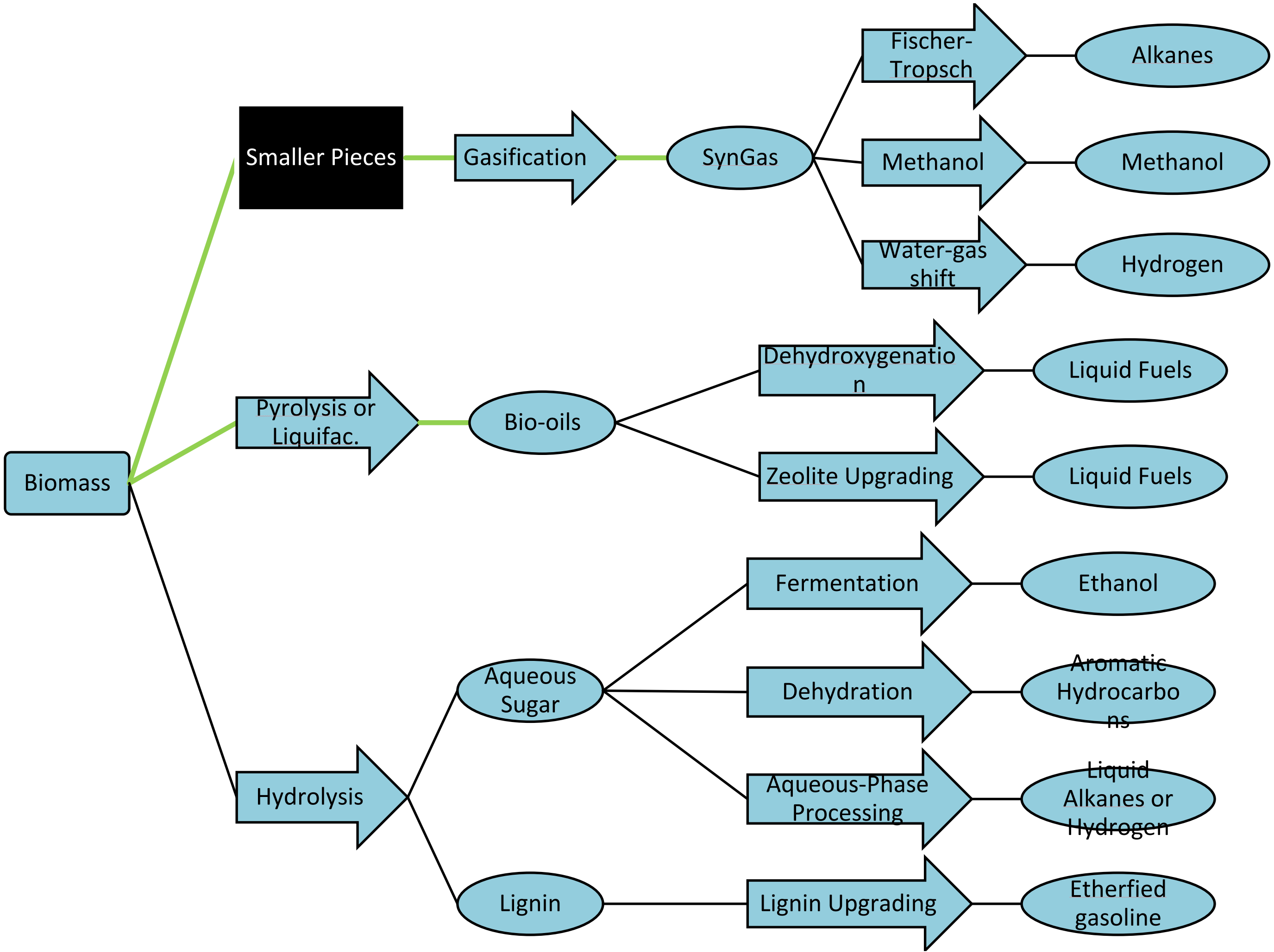

Figure 2-5: Biomass processing pathways[15]

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[15] (George W. Huber)

2.1.2.1. Liquid Fuels

The production of liquid fuels from biomass, aptly named biofuels, can be accomplished via several different methods. These processes typically have shorter residence times, with faster heating rates and moderate temperatures. Biofuel is produced from bio-oil which can be created by processes such as liquefaction and pyrolysis. Liquefaction uses high pressure and low temperatures in conjunction with catalysts and other gases to produce a bio-oil. This process is especially good for feed stocks that have high moisture content.

Bio-oil production by fast pyrolysis requires a dry, finely ground feed fed into a reactor that reaches temperatures between 450 and 550°C. The high temperature breaks down and vaporizes the biomass in smaller chunks, which are then quickly condensed to produce a liquid. This process, though very quick and efficient, builds up char, which can cause problems with liquid fuel production and is also very difficult to remove.[16]

Overall, biofuels have a number of benefits, but production is often limited by its high cost and its numerous difficulties such as coking, corrosiveness, and its high viscosity resulting from inorganic molecules, which cause the fuel to polymerize.[17]

2.1.2.2. Hydrolysis

Hydrolysis is the process by which organic material is reacted with water which results in cleavage of organic molecules.[18] Hydrolysis typically cannot proceed on its own, so there is often a catalyst involved, typically either an acid or base, which causes the hydrogen and hydroxyl ions to dissociate making them all the more reactive.

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[16] (George W. Huber)
[17] (George W. Huber)
[18] (Hydrolysis)

Hydrolysis of biomass can occur by a number of routes, including the method described above to break down the cellulose molecules. The solution is then neutralized and fermented to produce ethanol. The breakdown process can also be enzymatic in which the enzyme, cellulase, breaks down cellulose into glucose which can be further converted into ethanol by yeast fermentation.[19]

2.1.2.3. Biomass Gasification

Biomass can also be processed via gasification a process by which solid and liquid hydrocarbons are converted to syngas, a product containing CO, H_2, CO_2, CH_4, and N_2 that has a multitude of uses. Gasification mainly consists of three types of reactions, pyrolysis (thermal decomposition without oxygen or steam), partial oxidation (processes that completely combust without the use of a stoichiometric amount of oxygen), and steam reforming (the use of steam to convert part of the feed to CO, H_2, and CO_2).[20]

2.1.3. *Problems with Biomass*

2.1.3.1. Growing it

A major concern with developing methods for biomass processing is the shear amount of biomass needed, and land to grow that biomass. Table 2-1 assumes a total conversion of current fuel technology to fuels derived from plants. Areas of 5-500% of the US land area are required to meet the energy demands for transportation gasoline and diesel fuels under this system. In addition, this land would be competing with ordinary agricultural demand and land usage.

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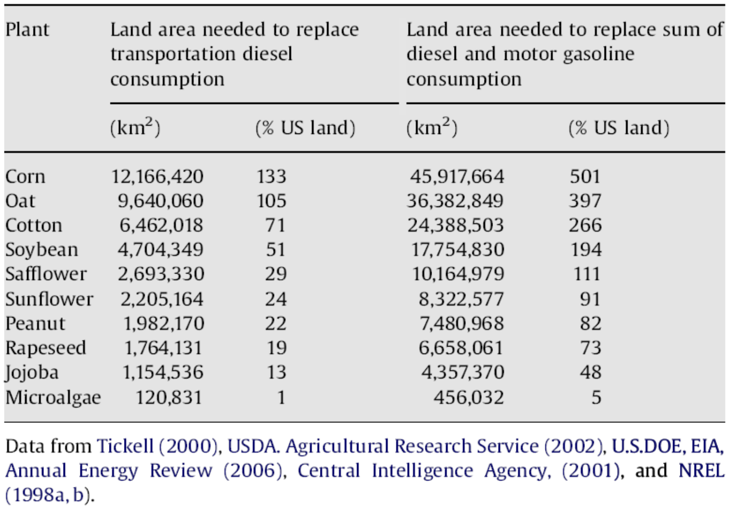
[19] (George W. Huber)
[20] (George W. Huber)

Table 2-1 Land area needed to satisfy 2006 US transpiration fuel consumption with energy from selected agricultural oils (more data in Akinci (2002) and Electronic Annex #1)[21]



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

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

2.1.3.2. Processing it: Collection, Separation, Reactions

A great deal of energy is used to farm, fertilize, and transport biomass for processing. This is true for directly grown biomass, and recycled forms that require a great deal more energy in collection and separation. Many processes are overly energy intensive, requiring more energy to obtain the fuel than is regained from using it. In the case of ethanol production, chemical processing, agricultural, transportation and distribution costs cause it to show little to no net energy gain, as shown in Figure 2-6.

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[21] (Akinci, Kassebaum and Fitch)

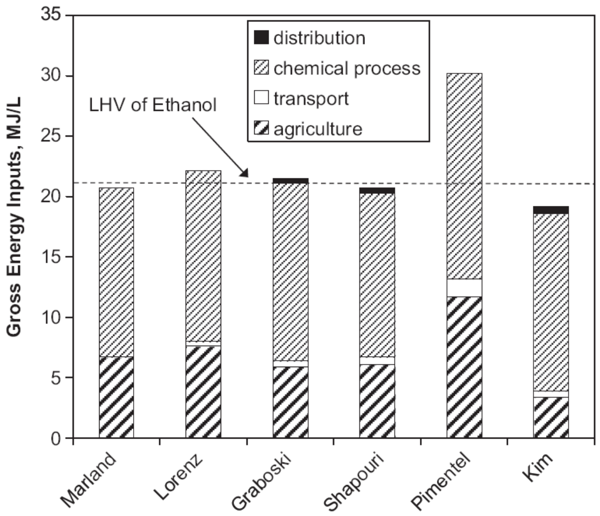

Figure 2-6: Energy required producing ethanol from corn[22]

2.2. Molten Salts and Ionic Liquids

Molten salts and ionic liquids are two terms that at one point in time referred to the same class of chemicals, liquid salts. However, since the discovery of salts that melt below 100°C, they have been separated into the two categories, as they are known today. “Molten Salts” refers to inorganic salts that melt above 100°C, while “Ionic Liquids” typically refer to organic salts that melt below 100°C[23].

One of the best aspects of ionic liquids is the fact that they can melt at temperatures as low as room temperature with similar properties to salts, which melt at much higher temperatures. They are also interesting because of their greater versatility. Unlike molten salts for the most part, Ionic liquids can be modified by the addition of various functional groups to achieve different purposes. They have even been used in a process to dissolve cellulose, which they can do quite effectively.[24] Ionic liquids have numerous benefits, but all seem to be overshadowed by their problems such as high cost and

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[22] (Akinci, Kassebaum and Fitch)
[23] (Wilkes)
[24] (Li Feng)

specificity. In addition, being a new type of chemical, they must be approved for use, which can sometimes be a problem.[25]

Molten Salts tend to have much higher melting points than modern ionic liquids. For example, NaCl has a melting point of 801°C and NaOH has a melting point of 318°C whereas a typical imidazolium salt will melt at 80°C or lower. However, in mixtures, particularly at eutectic compositions, molten salts can melt at much higher temperatures. Molten salt eutectics are used to obtain more favorable properties out of molten salt catalysts. Eutectics can be used to increase the reactivity of the system, lower the melting point of the salts, or change other characteristics to make the salt more desirable for the proposed uses. For example, individual carbonate salts have melting points upwards of 700°C as opposed to a eutectic of potassium carbonate and lithium carbonate, which decreases the melting point to around 500°C[26] allowing the reactor to function almost 200°C cooler. By doing this, operation costs are reduced, and the conditions become easier to meet. A study conducted by Jin et al compared the reactivity of wastepaper with carbon dioxide with various molten salt eutectics (see Figure 2-8). This study revealed that a eutectic of K_2CO_3-Li_2CO_3-Na_2CO_3 allowed a much greater reactivity than the use of no eutectic. By finding the optimal eutectic of hydroxides and carbonates comprised of lithium, sodium, and potassium cations (Table 2-1), we plan to obtain the highest reactivity at the lowest temperature for our proposed reaction[27].

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[25] (BCS Incorporated)
[26] (Center for Research in Computational Thermochemistry)
[27] (Jin, Iwaki and Arai)

Table 2-2: Example Eutectics and Their Melting Points[28]

Example Eutectics and Their Melting Points			
	Salts	Comp. (mol %)	Melting Point
1	LiOH	100	450-470°C
2	NaOH	100	318°C
3	KOH	100	360°C
4	Li_2CO_3	100	723°C
5	Na_2CO_3	100	851°C
6	K_2CO_3	100	891°C
7	Li_2CO_3-LiOH	10.2-89.8	442°C
8	Na_2CO_3-NaOH	7.2-92.8	283°C
9	K_2CO_3-KOH	9.3-90.7	366°C
10	K_2CO_3-KOH-LiOH	2.1-71.8-25.6	221°C
11	K_2CO_3-Li_2CO_3-LiOH	16.4-26.4-57.1	372°C
12	NaCl-Na_2CO_3-NaOH	7.8-6.4-85.8	282°C
13	Li_2CO_3-Na_2CO_3	52-48	500°C
14	Li_2CO_3-K_2CO_3	62-38	488°C
15	K_2CO_3-Li_2CO_3-Na_2CO_3	26.8-42.5-30.6	393°C

Molten salts are very strong oxidizing agents. These, such as nitrates, should be kept away from organic material as they will cause them to combust with exposure to oxygen. Other salts, like hydroxides, are also very corrosive, and they are able to corrode many materials. Also, molten salts only are in the molten state at very high temperatures; due to this, precautions against burns must be taken. Molten salts must be handled with care and placed in appropriate containers.

Molten salts are used to enable reactions consisting of organic material. Molten salt oxidation is used to oxidize and break down molecules in organic materials[5]. Molten salts have been used for many purposes including coal gasification, decomposition of hazardous organics, and destruction of waste oils.[29] The cations in the salts are small enough to break bonds in the organic material allowing

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[28] (Molten Salt Database -Eutectic Finder-)

[29] (Jin, Iwaki and Arai)

reactions to take place that were otherwise unavailable. The effectiveness of the salt catalyst can be increased by using a mixture of different salts. Molten salts can also store thermal energy. They are able to obtain high temperatures and remain in liquid form. Solar collection facilities use giant mirrors to heat salts and use the resulting molten salt to power steam turbines. Another application of molten salts is in batteries. The salt is used as a high conductivity electrolyte. The problem with this is the necessity of operating at very high temperatures. Research is underway to reduce the required temperature to lower temperatures using various eutectics.[30] This has lead to the discovery of ionic liquids, salts that are liquid at very low temperatures.[31] Finally, molten salts are used in many gasification processes. There are many different applications of molten salts, and more are found constantly due to increased research in the subject.

2.2.1. *Molten Salt Application and Research*

The work of Jin et al[30] focused on the use of high temperatures (around 973 K) and a carbonate salt mixture in the gasification process of Biomass. In their study, they used a continuous flow reactor which fed CO_2 into a molten salt/wastepaper mixture where it then reacted by the Boudouard reaction to form CO (Equation 2-1).

$$\mathrm{C} + \mathrm{CO_2} \rightarrow \mathrm{CO}\ \Delta \mathrm{H^o} = 169.2\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Equation 2-1

It is interesting to note, that without the presence of the molten carbonate catalyst, this reaction was not seen at all, but instead there were a large amount of liquid hydrocarbons produced. In addition, the reaction rate shot up in the presence of a molten salt mixture. It was pointed out that the

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[30] (Jin, Iwaki and Arai)
[31] (Wilkes)

properties of a molten salt mixture made the mixture a better catalyst than any individual salt. It was also shown that the reaction proceeded quicker with an increase in the temperature.

The reactor designed used by Jin et al, shown in Figure 2-7, uses a continuous flow system to pump a carbon dioxide-argon gas mixture into a tube reactor. The salt and biomass (wastepaper) were deposited in the reactor prior to heating and the oxygen was flushed from the system by a continuous flow of argon gas. The furnace was then heated up to temperatures in the range of 923 K to 1023 K to ensure the melting of the salt and to test the temperature dependence on the reaction. The reactor itself was a ceramic to withstand the high temperatures. Exiting gases were collected in a cold trap to remove any water vapor and to cool down the gases before sampling in a Gas Chromatograph.

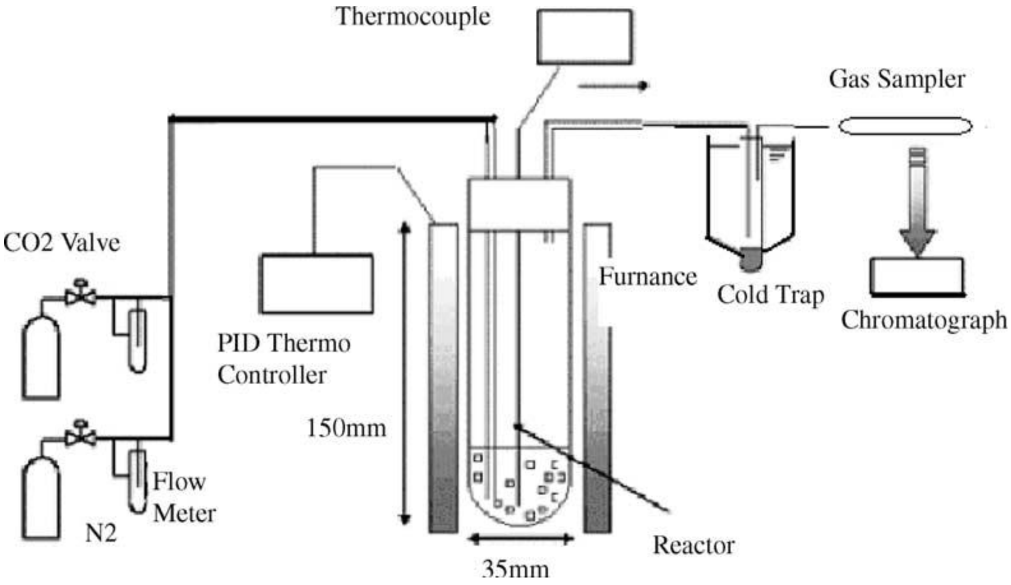

Figure 2-7: Jin et al Reactor Design

A number of aspects were explored to view various conditions and their effect on the molten salt as a catalyst. The first of which was to examine the reaction rate based on the salt mixtures that were used. Shown in Figure 2-8 is a diagram depicting the effects of the composition of the catalyst on the overall production of CO. It’s clear to see that a 3 salt eutectic had much greater results than the same process without a catalyst. In their research, they determined that alkali salts are able to promote reactions more effectively at temperatures higher than their melting point. As a result of the lower melting point through a 3-salt eutectic, the melting point of the salt is greatly lowered thereby increasing the reaction rate as compared to a single salt.

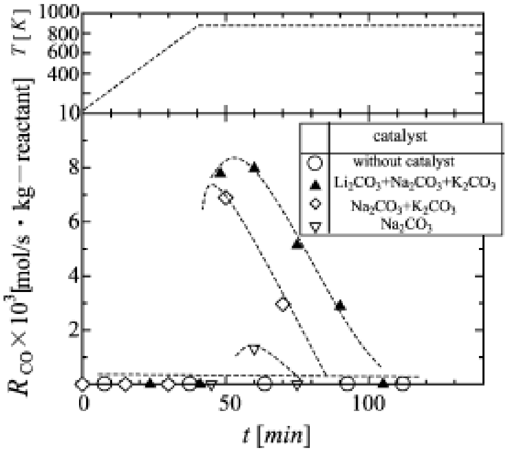

Figure 2-8: Effect of Catalyst on Reaction Rate[32]

Also explored were the effects of temperature and heating rate on the overall reaction (Figure 2-8). Because of the endothermic nature of the Boudouard reaction, an increase in temperature should undoubtedly result in a rise in the reaction rate. Not immediately clear however, is the effect of the heating rate on the reaction rate. Gasification, especially gasification by flash pyrolysis, requires rapid heating to obtain the best results. To optimize their experiment, Jin et al determined that a faster heating rate would boost the effectiveness of the gasification process and thereby increasing the concentration of desirable products.

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[32] (Jin, Iwaki and Arai)

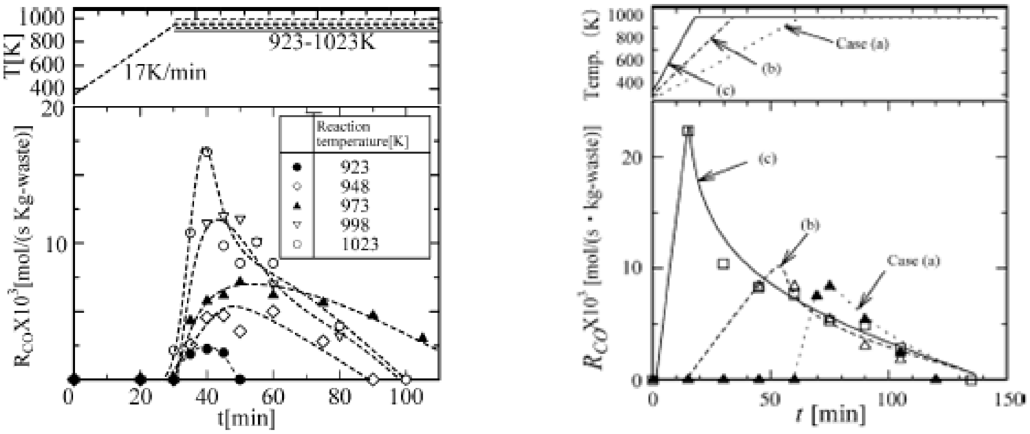

Figure 2-9: Effect of Temperature and Rate of Heating on Reaction Rate[33]

2.3. Gasification

Gasification is the process in which carbon containing material is converted into syngas in the presence of steam and/or carbon dioxide. Syngas is primarily composed of carbon monoxide and hydrogen, but may also contain varying amounts of carbon dioxide, methane, and nitrogen[34]. It is used as a clean energy source because it is carbon neutral; the amount of carbon dioxide produced by combustion is equal to the amount of carbon dioxide used in its creation[35]. Syngas is used in the production of many chemicals such as alkanes, methanol, ethanol, large alcohols, and pure hydrogen[7]. It very versatile and can be used as a reactant in many formation reactions.

Figure 2-10 shows a typical biomass gasifier. In this process, biomass enters into the reactor where it is first dried. It then undergoes the processes of pyrolysis and oxidation which reduce the biomass to ash and gas. The remaining ash is then removed by reacting it with steam and air. The product gases leave through the top where they are carried to the next step in the process.

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[33] (Jin, Iwaki and Arai)
[34] (George W. Huber)
[35] (The gasification process)

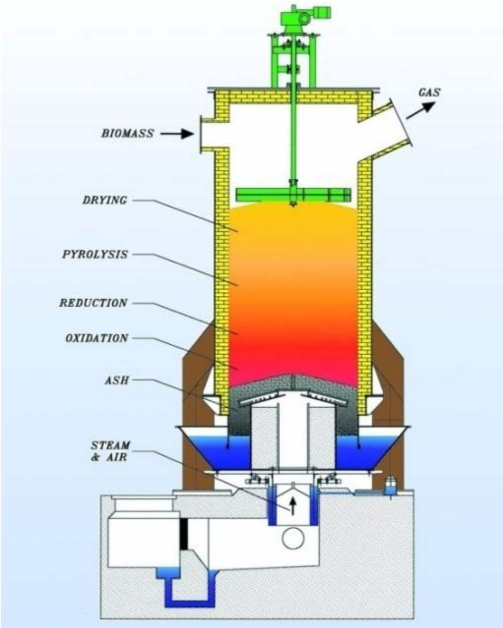

Figure 2-10: Gasification Process Design[36]

Gasification works by super heating biomass in the absence of oxygen. Without oxygen, the biomasses cannot combust and form carbon dioxide. As a result, carbon monoxide is formed instead of carbon dioxide. Also, the hydrogen atoms that are broken off of the carbon atoms form hydrogen molecules as opposed to water molecules due to the limited oxygen available. This can be seen in Table 2-3, gasification occurs in steps, breaking down the cellulose via pyrolysis and partial oxidation. This produces char which is gasified by steam and carbon dioxide. Finally, the resulting gases are reacted via the water-gas shift and the methanation reactions.

In order to limit the oxygen in the system, feed gases of steam or carbon dioxide are generally used. A few advantages of obtaining fuel this way are carbon neutrality, limited pollutants caused by combustion, and the versatility of syngas. However, gasification has its share of problems. For example, the ash remaining after gasification can be very toxic and often acidic[9]. Also, if waste is used in fuel

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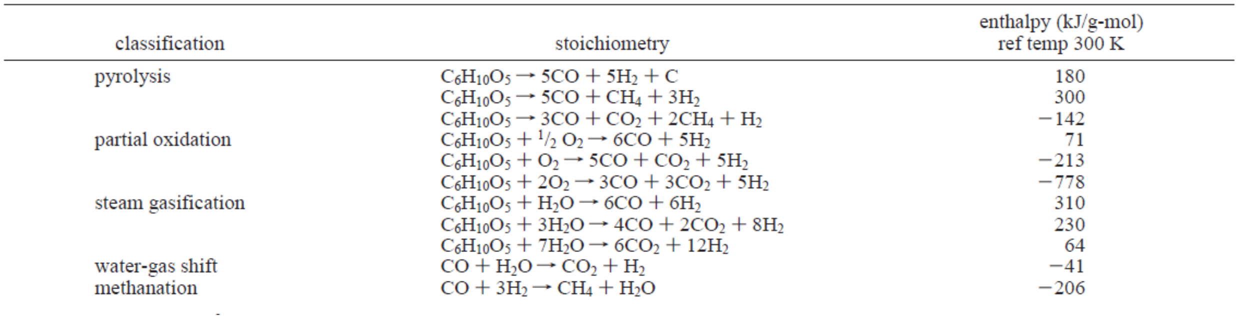
[36] (The gasification process)

production, it may lower incentives for recycling. Finally, large volumes of water are required for cooling purposes due to the obscenely high temperatures.

Table 2-3: Fundamental Reactions and Enthalpy of Selected Cellulose Gasification Reactions[37]



classification	stoichiometry	enthalpy (kJ/g-mol) ref temp 300 K
pyrolysis	$C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$	180
	$C_6H_{10}O_5 \rightarrow 5CO + CH_4 + 3H_2$	300
	$C_6H_{10}O_5 \rightarrow 3CO + CO_2 + 2CH_4 + H_2$	−142
partial oxidation	$C_6H_{10}O_5 + {}^1/_2\,O_2 \rightarrow 6CO + 5H_2$	71
	$C_6H_{10}O_5 + O_2 \rightarrow 5CO + CO_2 + 5H_2$	−213
	$C_6H_{10}O_5 + 2O_2 \rightarrow 3CO + 3CO_2 + 5H_2$	−778
steam gasification	$C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2$	310
	$C_6H_{10}O_5 + 3H_2O \rightarrow 4CO + 2CO_2 + 8H_2$	230
	$C_6H_{10}O_5 + 7H_2O \rightarrow 6CO_2 + 12H_2$	64
water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	−41
methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	−206

In the study by Jin et al, they analyzed the effectiveness of the carbonate salt as a catalyst in the gasification process. Without the presence of any carbonate salt, there were no gases formed by pyrolysis, instead there was a large amount of liquid products formed. It was hypothesized that when the salt melted, the small cations were able to penetrate the (β-1,4)-glucosidic bonds that connect cellulose molecules effectively cleaving the cellulose into smaller parts which could then be decomposed further and reacted via pyrolysis and the Boudouard reaction to produce the desired syngas product[38].

2.3.1. *Pyrolysis*

Pyrolysis is the process by which materials decompose at very high temperatures. From the process of decomposition, there are gaseous, liquid, and solid products produced which include syngas, liquid hydrocarbons and char. There are a few different types of pyrolysis which vary based on the operating temperature, residence time, and heating rate.

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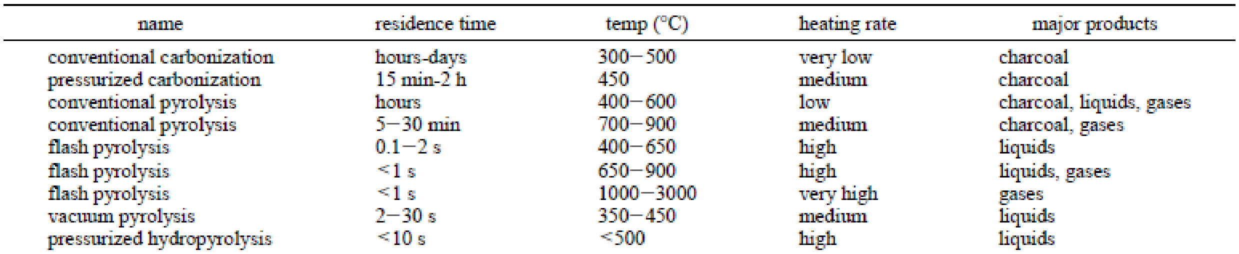
[37] (George W. Huber)

[38] (Jin, Iwaki and Arai)

Table 2-4: Methods of Pyrolysis Decomposition[39]



name	residence time	temp (°C)	heating rate	major products
conventional carbonization	hours-days	300−500	very low	charcoal
pressurized carbonization	15 min-2 h	450	medium	charcoal
conventional pyrolysis	hours	400−600	low	charcoal, liquids, gases
conventional pyrolysis	5−30 min	700−900	medium	charcoal, gases
flash pyrolysis	0.1−2 s	400−650	high	liquids
flash pyrolysis	<1 s	650−900	high	liquids, gases
flash pyrolysis	<1 s	1000−3000	very high	gases
vacuum pyrolysis	2−30 s	350−450	medium	liquids
pressurized hydropyrolysis	<10 s	<500	high	liquids

Table 2-4 depicts the numerous types of pyrolysis and their products. As many of the slower reactions tend to produce a large amount of charcoal either as a main product or a side product, it is very important to have a method of removal for this solid product.

2.3.2. *Partial Oxidation*

Partial Oxidation is a process by which the feed reacts with less than the stoiciometric amount of oxygen necessary for complete combustion. As a result, the gases produced are mainly H_2 and CO with a relatively small amount of CO_2. This is useful because it is yet another method to produce syngas, though it is a route that will not be explored further here.

2.3.3. *Steam/CO_2 Gasification*

In addition to the steam gasification reactions in Table 2-3, there are two other important gasification reactions that use CO_2 and steam shown below:

$$C + H_2O \rightarrow CO + H_2$$ Equation 2-2

$$C + CO_2 \rightarrow 2CO$$ Equation 2-3

These reactions take place on the char that is left behind during pyrolysis and partial oxidation. Equation 2-2 is the process by which pure carbon reacts with water to produce syngas. This is a very common method of char removal from a gasification reactor. Equation 2-3 is known as the Boudouard reaction and reacts carbon dioxide with carbon to produce carbon monoxide. This is especially useful as it allows

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[39] (George W. Huber)

for potential reuse of carbon dioxide used elsewhere in a process. These are very useful as they produce syngas components and use up the char that would otherwise go to waste.

2.3.4. *Water-Gas Shift*

The water-gas shift reaction, shown in Table 2-3, is one that is very important in industry, especially for increasing the yields of hydrogen in various processes. In gasification, the water-gas shift mainly reacts carbon monoxide with steam to produce carbon dioxide and hydrogen. This is especially useful for gasification processes which produce a large amount of CO and not as much hydrogen.

2.3.5. *Methanation*

Methanation is the process by which carbon monoxide and hydrogen are converted to methane and water. The methanation reaction, shown in Table 2-3, is actually the simplest form of the Fischer-Tropsch process (Equation 2-4).

$$(2n+1)\mathrm{H}_2 + n\mathrm{CO} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H}_2\mathrm{O}$$ **Equation 2-4**

This process is normally carried out in industry to produce alkanes and other hydrocarbons from syngas. By using specific catalysts, syngas can be converted to longer chain alkanes and even some alcohols. One of the difficult things to control, however, is the production of methane. Methane is spontaneously created under the conditions of gasification and can be difficult to control.

2.4. Paper Manufacturing

Molten salts are incidentally involved in the manufacture of paper[40]. A method, known as Kraft Pulping, utilizes a salt comprised of sodium hydroxide and sodium sulfide to separate cellulose from wood. The regeneration of the active pulping chemicals from the spent chemicals is one of the largest

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[40] (Wartena, Winnick and Pfromm)

inorganic chemical processes in the world. This is due to its efficiency, increased capacity, reduced contaminants, and simplified operation.

The Kraft process begins by exposing wood to an aqueous mixture of sodium hydroxide and sodium sulfide at high temperature and pressure which breaks down the paper into a black liquor which is separated from the cellulose fibers. This black liquor contains sodium carbonate, sodium sulfate, sodium sulfide, low concentrations of other organic contaminants, and organics dissolved from the wood.

After some of the water is removed from the black liquor via evaporation, the liquor is fed into a Kraft recovery furnace to combust the organic materials within. Within this reactor, is a molten salt composed of sodium carbonate, sodium sulfide, sodium sulfate, sodium chloride, potassium chloride, carbon, metal and transition metal compounds. The resultant melt is drained through the bottom of the recovery boiler and dissolved in water. Here, the sodium sulfate converts into sodium sulfide. Once the salt has dissolved in the water, the carbonates are turned into hydroxides by heating them over time.

$$\mathrm{Ca(OH)_2}\langle aq\rangle + \mathrm{Na_2CO_3}\langle aq\rangle \xrightarrow{\text{yields}} \mathrm{2NaOH}\langle aq\rangle + \mathrm{CaCO_3}\langle s\rangle$$

Equation 2-5

As shown in Equation 2-5, the calcium carbonate precipitates out of the solution, and it is burned in Equation 2-6 to produce calcium oxide. In Equation 2-7, the calcium oxide is reacted with water to provide the calcium hydroxide to fuel the previous equation.

$$\mathrm{CaCO_3} + \mathrm{heat} \xrightarrow{\text{yields}} \mathrm{CaO} + \mathrm{CO_2}$$

Equation 2-6

$$\mathrm{CaO} + \mathrm{H_2O} \xrightarrow{\text{yields}} \mathrm{Ca(OH)_2}$$

Equation 2-7

This process of replacing the carbonates with hydroxides is known as the lime cycle because it takes place in a high-temperature lime kiln. The goal of doing this is to remove all carbon from the pulping chemicals, to produce sodium hydroxide, and to maintain a sulfur balance in the melt, preferably sulfide. Once this is accomplished, the Kraft melt composed of the resulting salt is then re-used to separate the cellulose from wood.

This relates to our experiments since we are using molten salts to break down lignocellulosic structures. Unlike paper manufacturing however, we will be using pure salts rather than aqueous salt solutions. Though it is conceivable that if successful, our process could be combined with that of paper manufacturing to reuse the salt and break down any waste.

3. Reactor Design

An ideal reactor design allows for interactions between the solid (feed stock), liquid (molten salt) and gaseous (CO_2 and/or H_2O) phases while also providing a controlled environment where the results can be accurately examined. For preliminary laboratory tests, the reactor design described below will be utilized for feasibility studies and as a proof of concept. It leaves room for further refinement for product optimization further investigation of the process in greater detail later on.

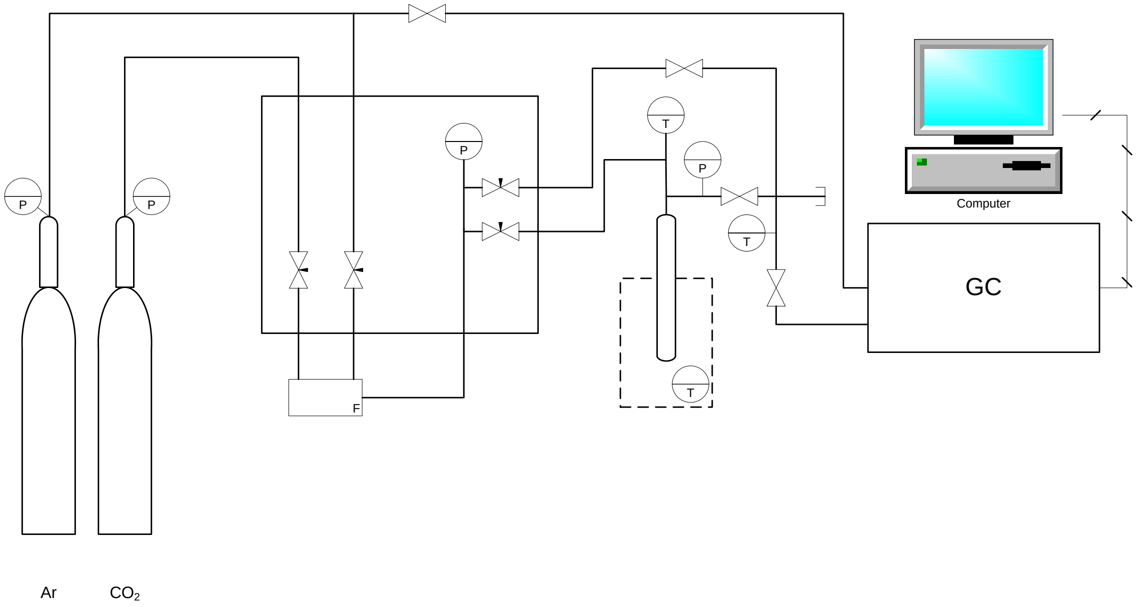

Figure 3-1: Reactor Schematic

3.1. Reactor Type

The reactor system was designed to operate under two conditions: batch and semi-batch. A fluid gas system is used to control operating atmosphere, flow rates, pressures and pathways. Argon and CO_2 gas cylinders feed into a control system which allows for gas flow control through MKS-mass flow controllers and an MKS 247C 4-channel readout device.

From the flow controllers, the gas stream can be cut off or fed into the reactor or bypass streams. The bypass stream leads directly into the Gas Chromatograph (GC) or can be vented to a fume hood. The reactor line extends into a 1/8" tube that is fed 2/3 of the way into the reactor. The outlet is atop the 3/4" reactor and is monitored with a pressure gauge. The outlet line then feeds into the GC sampling port.

The reactor was initially run as a batch process. The carbon dioxide, argon feed ran through the reactor for approximately 15 - 30 minutes until a GC sample registered negligible undesired gas flow. The feed and exiting valves were then cut off from the reactor and remained closed until sampling of the exiting stream after the reactor had cooled.

Due to the corrosiveness of the molten salts, certain precautions were made when selecting materials of construction. For optimal protection against the carbonates, a low carbon-content steel would be optimal. An alloy of Ni-Cr-Fe-Mo would be well suited.[41] The hydroxides, on the other hand, are far more corrosive and often form the metal oxides of the salts. Mo, Fe and Si alloys are detrimental alloying elements, and the ideal is a high Ni low C alloy.[41] Due to economics and availability, the reactor used for these experiments is SS 304, comprised of a Cr-Ni alloy with relatively low carbon. In the future, lower carbon contents would be optimal due to the high operating temperatures. Nonetheless, the reactor managed to hold up quite well to the molten salts used so far.

To ensure the useful life of the reactor is maximized and avoid any side reaction with the reactor vessel, temperatures was planned to be restricted to 500°C for initial experimentation.

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[41] (Davis)

The reactor can also be run as semi-batch. By loading in the feed stock and salt mixtures then running a continuous stream of reactant gas through, it will allow for continuous reaction. To remove oxygen from the system, the reactor was flooded with the reactant gas. In addition, running the process as a semi-batch would allow for the reactor to be operated at considerably lower pressures.

3.2. Design Specifications and Operating Conditions

The reactor was charged with specified feedstock and molten salt and water if needed. It was then sealed at atmospheric pressure, at which point it was heated to 500°C. Calculations have shown that the resulting pressure have the potential of exceeding 400 psi.[42] The vessel is ¾" stainless steel, with Swagelok fittings and high pressure valves in anticipation of the high operating temperature and pressure. Maximum operating pressure is 2000 psi and temperature was capped at 500 °C. In addition, the reactor is air tight, and has been leak tested at high pressure. If operated under semi-batch conditions, operating pressure would be near atmospheric.

3.3. Sizing

To obtain substantial results, the reactor size will be 3/4" x 17" with a 3/4 to 1/4 reducer on the top and a 3/4 end cap on the bottom. A thermocouple was lowered about halfway down the tube length to obtain accurate temperature readings during the reaction. The salt filled about 1-2" from the bottom with an additional 6 or so inches of the compacted feed stock above it.

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[42] See Appendix B for detailed calculations

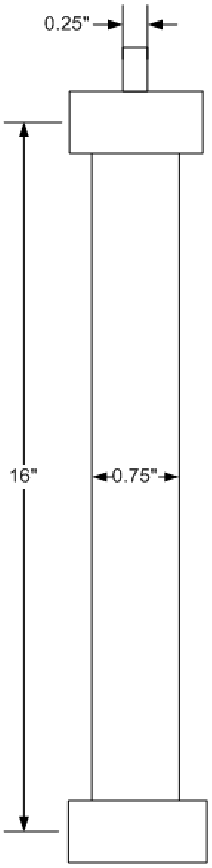

Figure 3-2: Reactor Sizing Specifications

3.4. Heating Element

The reactor was heated with a Lindberg/Blue tubular furnace. It uses PID controls to initially heat then maintain a set-point temperature of 500 °C. The heating element is capped off at the bottom with insulation, and all exiting pipes are insulated as well.

3.5. Safety and Controls

For safety concerns, temperature and pressure were continuously monitored. Temperature was kept below a cap of 500°C. A multi temperature readout system was used to monitor the temperature within the reactor, and at the exiting stream. In addition, pressure was monitored at the gas cylinders, the combined feed stream, and the reactor levels.

When removing the salt from the reactor, respirators and safety goggles were worn at all times to prevent ingestion and exposure to fine hydroxide and carbonate salt particles. In addition, gloves were worn and samples were contained immediately upon removal.

When dealing with carbon monoxide, methane and hydrogen, all lines were securely tightened and fed vented to an adjustable ventilation system. Carbon monoxide feed tanks were kept in the fume hood at all times.

3.6. Calibration and Fluid Flows

The flow controller used to regulate carbon dioxide and argon flows are MKS Mass-Flo Controllers with a 100 sccm range. These are connected to an MKS model 247C 4-Channel Readout which controls the flows. The 4-Channel Readout must first be calibrated using the following equation

SCALING CONTROL FACTOR = GAUGE FACTOR x GAS CORRECTION FACTOR

The Scaling Control Factor is the setting that the 4-Channel Readout is set to. The Gauge Factor is a number based on the range of the Mass-Flo Controller (Gauge Factor = 100 for a 100 sccm Mass-Flo Controller). The Gas Correction Factor can be obtained from the MKS Instruments website for the 4-Channel Readout[43].

3.7. Gas Chromatography Detection

Gas Chromatography is an analytical method commonly used to determine compositions of liquid and gas samples. A sample, in this case gaseous, is fed into the GC where it flows in a carrier gas through a long column, adsorbing and desorbing on the packing, before exiting in separated compounds depending on the volatility and absorption on the packing.

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[43] (MKS 247D Four Channel Power Supply/Readout)

3.7.1. *Column Sizing and Selection*

In the lab, the available SRI 8610C GC was used, with a Carboxen 1000 column. Column sizing, material and packing are all critical to the effectiveness of the column to separate the species. Three factors can be optimized: separation, retention time, and quantity or composition. For the best separation, a really long retention time and long/thin column would be needed. Having a thin column, however, focuses on the separation of trace elements and is not well suited for large concentrations. Depending on the substances being separated, different packing materials may be preferred.

The Carboxen column being used has a diameter of 1/8 inches and is 15 ft stainless steel. The column is able to separate H_2, CO, CH_4, CO_2 and water, however shows some difficulty distinguishing between H_2, Air and CO.

3.7.2. *Carrier Gas Selection*

The most common carrier gases being used today are helium, hydrogen, nitrogen and argon. Helium is commonly used with FID detection. Hydrogen is dangerous, and not preferred due to the necessity to test for hydrogen being generated in the system. Nitrogen and argon are both suitable carrier gases for the system, however due to the high temperatures and pressures of our reactor; argon serves as the preferred inert atmosphere due to its extremely inert nature as a noble gas. It is also preferred over helium because of the large difference in conductivity between hydrogen and argon.

An argon carrier gas was finally settled upon and the GC was calibrated accordingly. Due to the properties of the gas, it registers negative peaks and the polarity of the system must be reversed.

3.7.3. *Temperature and Flow Rate*

Two additional parameters governing gas chromatography are temperature and flow rate. To optimize separation, temperature and carrier gas flow rates can be modified. The greater the temperature or flow, the faster the sample will move through the column. The adsorption will also be affected by temperature. Ideally, a low temperature and flow rate will be used to separate species with similar characteristics, while they can be ramped to separate other compounds which are more easily separated.

In the SRI 8610C, the flow rate is modulated by adjusting the pressure and measuring the resulting flow with a bubble meter on the outlet stream. The pressure was set to 15 psi and temperature was set to 25 C, but only achieved temperatures of 38 C due to ambient heat.

3.7.4. *Detection Method*

Several detection methods can be used in gas chromatography; however the most common two are flame ionization detection (FID), and thermal conductivity detection (TCD). For our experiments, we chose to use TCD due to its ability to detect a wide range of compounds including water. In the future, the system can be modified to run in series with FID.

4. Preliminary Results and Discussion

4.1. Preliminary Salt Analyses

In order to design the reactor and the operating conditions, we initially experimented with different salts in an atmosphere of air that were available to compare their melting points, how well they broke down biomass, and other noteworthy characteristics. These experiments helped to determine characteristics such as optimal conditions and compositions for the salts that would be used. These results would eventually lead to appropriate reactor materials and operating conditions.

4.1.1. *Experiment 1: Molten Hydroxides*

Initial testing was performed with hydroxide salts at 250°C; the salts used were sodium hydroxide, potassium hydroxide, and lithium hydroxide. When tested individually, only the potassium hydroxide melted at this temperature, which was attributed to its water content.

Paper was then added to the molten salt which turned yellow after a few seconds of exposure, and eventually dissolved into the salt. Once fully dissolved, the molten salt turned yellow and became very thick in consistency.

After we tried the salts individually, we began mixing them in an attempt to lower the melting point by forming a eutectic. These mixtures did not melt very well; they partially melted, and the part that melted was most likely the potassium hydroxide. We believe that the potassium hydroxide was beginning to dissolve and mix with other salts in the mixture. Had we left the salt in the furnace for a greater period of time at a higher temperature, the salts may have completely melted, though our experiments were not conclusive to this effect. We decided to add paper to these partially melted salts. When we did, the salt solidified suggesting that the addition of paper to the salts raises their melting point. This will be critical for future experiments. Our reactor design and experiments will have to operate at slightly elevated levels due to its possibility to have a raised melting point temperature.

4.1.2. *Experiment 2: Molten Nitrites, Nitrates and Chlorides*

In order to expand upon the varieties of salts used, we also included nitrites, nitrates, and chlorides in our experiments. This round of experiments was conducted at around 500°C. Nitrate and nitrite salts are extremely oxidizing, especially with organic material and in the presence of air. When we added paper to the molten sodium nitrite, the paper ignited and the salt turned yellow. For nitrates, we used sodium, lithium, and potassium nitrate. When we added paper to them, the paper charred and turned black while the salt turned yellow or dark brown.

Figure 4-1: Non catalytic reaction of nitrates with paper

After we tried the nitrates, we placed sodium chloride, potassium chloride, and copper (II) chloride into the furnace. None of them melted, but the copper (II) chloride changed from light green in color to brown, suggesting that the powder decomposed into copper or copper oxide. Due to the high reactivity of the nitrates, we decided to try a few of them in mixtures with carbonates.

4.1.3. *Experiment 3: Molten Carbonates with Other Salts*

After our previous trials, we added salts to potassium carbonate in order to observe their interactions. For these trials, we used a furnace at 500°C. Our first trial of 10 wt% K_2CO_3 and NaOH melted and behaved violently with the addition of paper. Paper placed in the center of the crucible repelled all of the salt to the edge of the crucible. The paper rapidly turned brown and broke down into smaller pieces, and the salt turned brown during this process.

Our second salt composed of 10 wt% K_2CO_3 and 90 wt% KCl did not melt at these temperatures.

Finally, we tested two salts consisting of 10 wt% K_2CO_3, 5 wt% $NaNO_2$, and 85 wt% NaOH and 10 wt% K_2CO_3, 5 wt% $NaNO_3$, and 85 wt% NaOH. The nitrite mixture behaved similarly to our K_2CO_3 and NaOH salt, but it combusted the paper as well. The nitrate mixture gave us the most interesting results. Once the salt melted, we added a small sample of paper. The paper quickly dissolved after turning light brown around the edges, and the salt turned slightly brown. After remaining in the furnace, the salt returned to its previous state with a slight blue-green tint. This process repeated itself with the addition of increasing amounts of paper with no noticeable change to the salt. Exceedingly large samples resulted with some smoke, but the salt eventually reverted to its previous state. We believe that the discoloration was due to impurities in the paper. This showed promise because the salt remained the same indicating the possibility of it being a good catalyst.

Figure 4-2: Molten carbonate salt

Once we obtained a furnace that could reach 800°C, we were able to test carbonate eutectics. Using a ternary diagram in Figure 4-3, we were able to predict ideal eutectic compositions of sodium carbonate, lithium carbonate, and potassium carbonate. The compositions we used were 27% Na_2CO_3, 40% Li_2CO_3, and 33% K_2CO_3 by weight.

Using the data from the ternary diagram, we tested three different salt mixtures: this pure carbonate eutectic, 50% carbonate eutectic and 50% NaOH, and pure NaOH. The first salt we tested, hydroxide and carbonate combination, gave unexpected results. When it had reached 680°C, it began to bubble. We did not anticipate this, and we believed it was a decomposition reaction, possible a reaction with the crucible or the air. To determine which component of the mixture caused this effect, we tested the eutectic and the hydroxide separately.

We tested the carbonate eutectic in two separate runs. In the first run, we heated the eutectic to 810°C to see if it would melt. Once it melted, we took it out, cooled the furnace, and placed the sample back in to see if it would re-melt at a lower temperature. We repeated this process until we brought the temperature down to 440°C. At this point, the eutectic ceased to melt, and the crucible cracked, halting further experiments. With these results, we reversed the experiment and slowly started heating a new sample without pre-melting it. This new sample started melting at around 540°C, and by the time it reached 580°C, it had completely melted. These results are critical, because it proves that we should be able to melt the eutectic within the reactor itself rather than preparing it in advanced.

When we tested the sodium hydroxide alone at 800°C, we achieved results similar to what we had when it was mixed with the eutectic. After melting, the salt started bubbling and turned dark yellow/brown. This suggests a reaction of some kind; we believe it is reacting with the crucible itself. We should not experience this problem with our reactor, however, as it is made of stainless steel and not ceramic.

Over the course of testing different salt combinations, we were also developing design for our stainless steel reactor. We were also trying to adapt a previous reactor system in the lab to work with our reactor. The system in place should be able to measure the pressure and flow of the gases we intended to use and it could be used to regulate them.

4.2. Determining Ideal Eutectic

In order to get our salts to melt in our reactor, we had to determine a composition that would reduce the melting point to a reasonable temperature, say 500˚C or lower. A eutectic is a specific mixture where the melting point is at its lowest. In addition, at this composition, the components of the eutectic must crystallize at the same time if the liquid were to cool. These compositions are very specific and can be found in tables and in graphs. On the ternary diagram (Figure 4-3), there is a range of compositions at which the three carbonates we intended to work will melt at 700K.

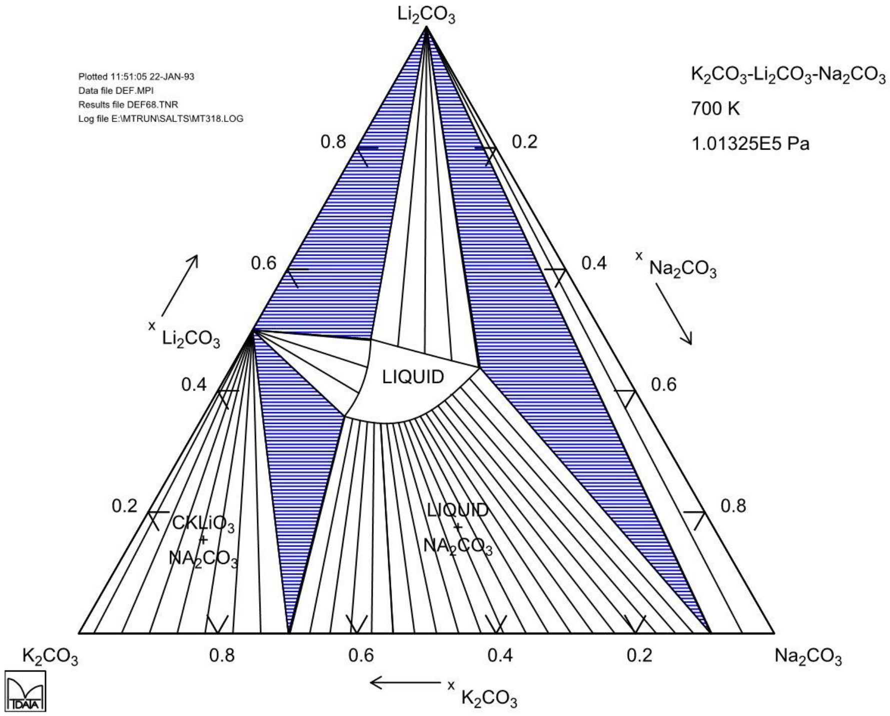

Figure 4-3: Carbonate Salt Ternary Diagram[44]

Further research revealed an appropriate eutectic of sodium carbonate, lithium carbonate, and potassium carbonate, 27 wt%, 40 wt%, and 33 wt% respectfully. To this eutectic we added 25% hydroxide salts, a 50-50 of potassium hydroxide and sodium hydroxide. The resultant composition had a melting point of about 440 C. This melting point is more for the stainless steel reactor which can oxidize at 500 C. The reason we used only 25% hydroxide was because we thought that the carbonates played the greater part in our desired reaction. Had we used greater compositions of the hydroxides, we could have lowered the melting point to a lower temperature, but it would have changed to the composition of our salt more than we wanted.

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[44] (MTDATA – Phase Diagram Software from the National Physical Laboratory)

5. Experimentation

5.1. Running the Process

5.1.1. *Preparation*

Before each run, the reactor was prepared for a batch reaction process. This included filling it with the salt, the biomass, water, and the reactant gas. Before that, the biomass and salt were prepared. To prepare the biomass, a sample was measured by weight and then physically broken down into smaller particulate sizes. This was necessary due to the size of the reactor, for if the biomass samples were too large, they would not fit inside.

Figure 5-1: Wood Chips feedstock

Next, the salt was prepared. The salt eutectic used was comprised of five different salts: lithium carbonate, sodium carbonate, potassium carbonate, sodium hydroxide, and potassium hydroxide. Through using the desired weight percents and sample size, the individual weights for each salt was measured out and added to a crucible. Once all the desired salts had been added, the salt was stirred together to increase the uniformity of the mixture. By being well mixed, the salt would melt faster.

Figure 5-2: Sample of molten salt

Once both the salt and the biomass samples had been prepared, they were added individually to the reactor, most commonly with the salt first. Once they both had been added, they were packed down with the packing rod. Some runs included water; for these runs, the water was added at this point. A water sample that had been volumetrically measured to the desired amount was poured into the reactor on top of the salt and biomass. Once all solid and liquid materials were within the reactor, the reactor was reattached to the rest of the system in order to remove undesired air.

Figure 5-3: Reactor vessel

In order to insure the desired reaction takes place, and not a side reaction, all unwanted gases were flushed out by the feed gas. This was accomplished by allowing the desired feed gases to flow through the system for approximately thirty minutes. Samples of the exiting gas were periodically sampled in the gas chromatograph during this time in order to check the concentration of undesired gases remaining in the reactor. Once the gas in the reactor had reached a satisfactory level, the exiting valve was closed, and the reactor was allowed to reach twenty pounds per square inch before the feed valve was closed as well. Once the reactor had been sealed, the furnace was turned on, and the reaction was allowed to take place.

5.1.2. *Running a Sample*

Once the reactor had been filled with its various reactants and the molten salt catalysts, the furnace was set to five-hundred degrees Celsius. At this temperature, the salt was able melt thus enabling it to serve as a catalyst for the desired reactions. The furnace remained at this temperature for roughly an hour and a half before being shut down. At this time, the reactor was left to cool before running samples through the gas chromatograph. Once the reactor had returned to room temperature, multiple samples of the product gas were run through the gas chromatograph. These results were saved and compared with each other and other runs from other samples.

After all necessary gas samples were taken, the reactor was removed from the system in order to remove and analyze the remaining solids. The reactor was first inverted in order to remove the majority of the biomass remains and drain any fluids that were still in the reactor. After this has been completed, the bottom of the reactor was removed, and the packing rod was pushed through the system in order to expel the salt plugged in the bottom (Figure 5-4). After this had been accomplished, the reactor was cleaned, reassembled, and prepared for the next run.

Figure 5-4: Solidified salt at bottom of reactor

5.2. Variables

5.2.1. *Constant Variables*

Some variables were held constant in order to better compare results. Also, some were held constant for safety purposes. The initial pressure of the system was held at twenty pounds per square inch gauge to prevent over pressurization of the system at high temperatures, yet still provide enough reactant gas to carry out the reactions. The temperature of the system was set to five-hundred degrees Celsius in order to melt the salt, but to avoid heat damage to the stainless steel in the reactor. The composition of the salt eutectic was kept constant due to its low melting point. Also, its consistency allowed for better comparisons in different runs.

5.2.2. *Adjusted Variables*

In order to test different combinations, the inputs for the biomass and the reactant gases were varied in type and composition. To compare the reactivity of the salts to different feeds, varying biomasses were used. First, paper, such as printer paper, was used due to ease at which it could be obtained and uniformity. Because paper is mostly cellulose, sticks were tried afterwards because they are neither uniform nor comprised mostly of cellulose. Sticks have greater amounts of lignin due to the bark. However, sticks were a little too non-uniform, and easily contaminated by dirt and other things, so pine chips were used. Pine chips were fairly uniform in composition, and obtainable in large quantities. It had more lignin than paper, but more uniform than sticks making it a very viable medium. Supposedly, the molten salt breaks cellulose into small sugar molecules, so sucrose was used to compare results of something that has already started as a sugar. In addition to changing the biomass feeds, the feed gas was adjusted to see its effect on the reaction.

Argon was used as a control gas for the system since it would not react with anything in the reactor. The two gases assumed to partake in the reaction are water vapor and carbon dioxide. In order to put water vapor into the system, water was added along with the biomass and the salt before the gases were added. As the furnace heats the system, the water evaporates and would react with the biomass at the appropriate temperature. Carbon dioxide was added directly into the system. It provides a different type of reactant than water vapor due to its lack of hydrogen, and the fact that it already has carbon. Many runs were carried out containing both water vapor and carbon dioxide in order to optimize the reaction. Other runs used solely one or the other to determine their individual effects.

6. Results and Discussion

6.1. Qualitative

Over the course of experimentation, there were a variety of changes that could not be quantified, but were important to take note of. The first indication that there was gas in the reactor after running was a vastly increased pressure even after the reactor was cooled. This was often higher than 200psi suggesting a significant increase in the number of moles of gas. Another indication of the reaction was the presence of water in the reactor, and more importantly, the presence of thick oil that coated the top cap of the reactor on numerous occasions (Figure 6-1).

Figure 6-1: Yellow oil within upper end cap

In regards to the salt itself, it could be determined that biomass was reacting while in contact with the salt due to the presence of small bubbles in the salt after it had hardened. Another indication of this was the presence of char in the core of the hardened salt, as seen in Figure 6-2.

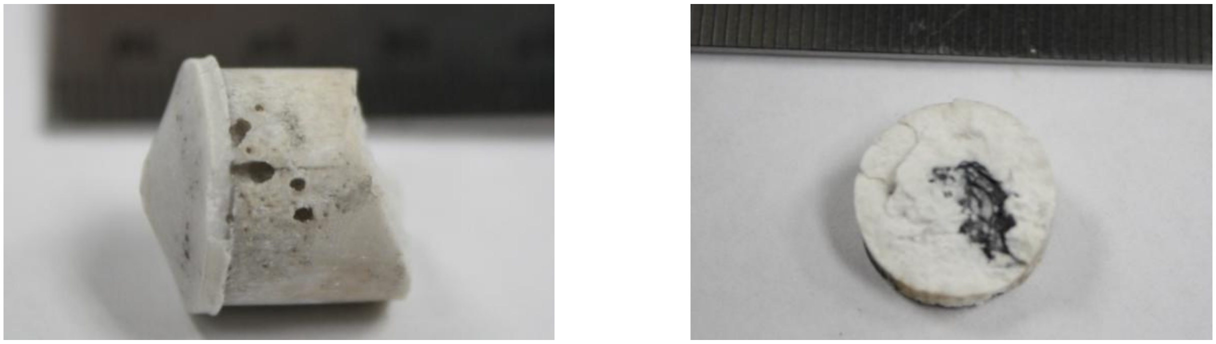

Figure 6-2: Solid salt core

When water was used in the reactor, the salt would turn gray after hardening suggesting that it absorbed some water. In addition, when the water was removed after a completed run, it was yellow, suggesting that it had mixed with another liquid, possibly oil, or had dissolved a solid (Figure 6-3).

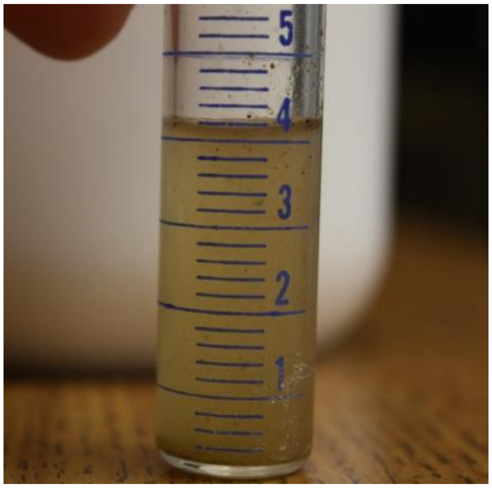

Figure 6-3: Suspension of solid/liquid residue

After the reaction had run for approximately 1.5 hours and everything was removed from the reactor, there was a lot of char built up which implies that the reaction did not completely remove the solid product.

Figure 6-4: Solid residue post-reaction

The differences in how each feed stock reacted are also important to note. For example, paper, though only tested in very small amounts, 0.2g - 1g, was the only feed stock to completely react into gas and a small amount of liquid product. 5g of sucrose formed a thick black syrup which may have been the result of caramelization, a breakdown and reformation of the sugar molecules. The twigs (10g) and pine chips (10g and 5g) were fairly similar in that both produced a fine black powder with several large chunks. In addition, some of the larger chunks contained small holes, possibly sites where a reaction was taking place on the pure carbon.

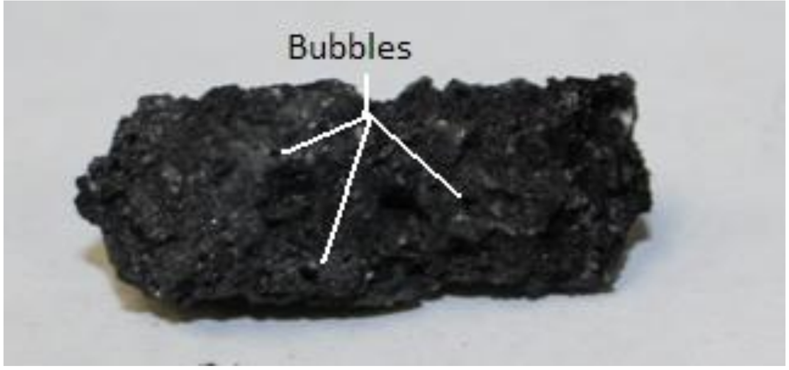

Figure 6-5: Solid residue with absence of molten salt

A run without salt was also performed to get an idea on how the reaction would proceed without a salt present. The first noticeable difference was in the smell. Without the salt, the smell of the reactor was a pungent, sour smell a sharp contrast to every other run. In addition, it seemed like there was a lot more char built up in the bottom of the reactor and there were hardly any bubbles in the large chunks. There also seemed to be a larger presence of liquids coating the inside of the reactor and the endcap than normal.

6.2. Quantitative

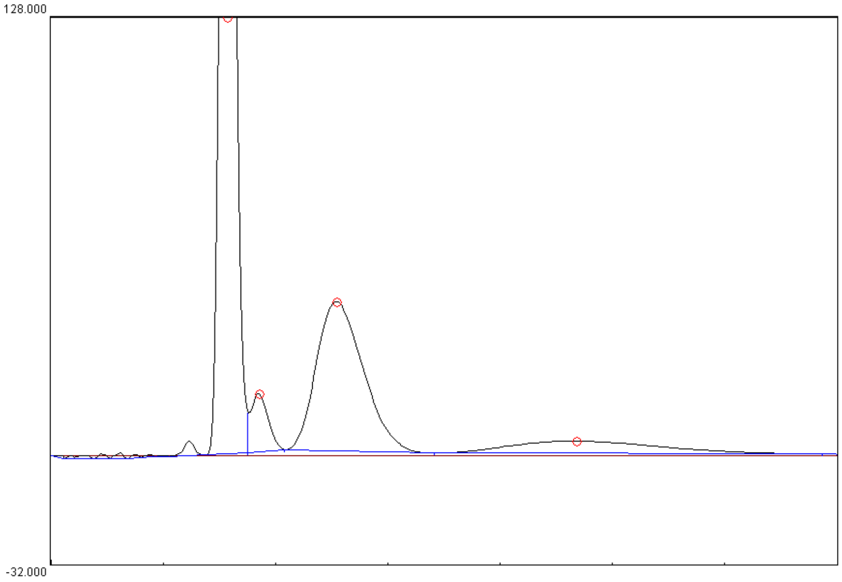

Figure 6-6: Sample chromatogram

Shown above is the result of a sample run in the gas chromatograph. The peaks, in order, are hydrogen, carbon monoxide, methane, and carbon dioxide. To determine the mole fraction of each species, pure runs were performed for each anticipated gas to confirm retention times and determine the standard area for each. The following relation was then used to find the Calibration Constant ("C") using the knowledge the mole ratio of a pure sample is 1:

$$\frac{n_{standard}}{A_{standard}} = C \text{ , where } n \text{ is the mole ratio} \qquad \text{Equation 6-1}$$

On the chromatogram of the sample, the ratio of the area under each peak to the total area could be determined using the integration function within the PeakSimple software. The mole ratios of each could be determined by multiplying the sample area by C. Finally, the mole fraction of each gas could be found by dividing each ratio by the sum of all the ratios.

Table 6-1 depicts some example runs, the corresponding chromatograms can be found in Appendix A: Gas Chromatography Data.

Table 6-1: Mole fractions from experimental runs

Biomass	Gas	H_2	CO	CH_4	CO_2
10g Twigs	CO_2\H_2O	0.258	0.0838	0.3048	0.353
10g Pine	CO_2\H_2O	0.2689	0.0724	0.2459	0.4128
5g Sucrose	CO_2\H_2O	0.5146	0	0.0166	0.4688
5g Pine	CO_2\H_2O	0.3233	0.1312	0.1416	0.404
5g Pine	Ar\H_2O	0.5393	0	0.3534	0.1073
5g Pine	Ar	0.3697	0.1346	0.2704	0.2254
5g Pine	CO_2	0.6406	0	0.3594	0
5g Pine	No salt\CO_2	0.1298	0.1338	0.2146	0.5218

It’s immediately evident that, in most cases, hydrogen is the main product, followed closely by methane and carbon dioxide. What is surprising is the low concentration of carbon monoxide. However, this can be explained by the presence of methane in the reactor. It’s conceivable that a water-gas shift reaction or even a basic Fischer-Tropsch process in which the carbon monoxide reacts to form methane:

$$\mathrm{H_2O + CO \rightarrow CO_2 + H_2} \quad \text{Equation 6-2}$$

$$(2n+1)\mathrm{H_2} + n\mathrm{CO} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O} \quad \text{Equation 6-3}$$

The Fischer-Tropsch reaction seems to be a very feasible side reaction. The simplest reaction (where *n*=1) results in the production of methane and water and is often called methanation. It's very likely that this process occurs, not only by the presence of methane in the Gas Chromatograph results, but also by the presence of water in the reactor even after runs that did not include water in the initial sample. In addition, the Fischer-Tropsch process tends to take place around 100-300°C and typically isn't taken above this point because higher temperatures favor methane production. Since we are operating at 500°C, it is likely that significant quantities of methane were being produced very quickly.[45] Also, the reverse reaction of methanation occurs above 550-600°C. This means any methane that does get formed does not go away.

$$\mathrm{CH_4} + \mathrm{H_2O} \leftrightarrow \mathrm{CO} + 3\,\mathrm{H_2} \tag{Equation 6-4}$$

It is also important to add that, as evident by the run with pure carbon dioxide, carbon dioxide plays a major role as a reactant in this process. It is likely that the carbon dioxide participates in the Boudouard reaction as suggested by the literature and is catalyzed by the salt. This is made more evident by a comparison with the run without any salt. In that run, there was a large concentration of CO_2 and not very much of the other gases. According to a set of calculations (Appendix D: Char Conversion Calculation) it was determined that 0.011 mol of char would react given the amount of CO_2 put into the reactor, a 5.85% conversion of the carbon feed.

In order to maximize the amount of syngas that is being produced, it would be ideal to limit the production of methane by preventing or reversing the Fischer-Tropsch process. This may prove to be difficult, however, since that particular reaction operates better at higher temperatures and pressures. On the other hand, if pure hydrogen was the target, it could be beneficial to use a continuous mixed stream of CO_2 and steam to influence the Boudouard reaction, which would in theory push forward the water-gas shift reaction. In addition, the presence of water in high enough quantities could help to reduce the extent of the Fischer-Tropsch Process.

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[45] (Coal Utilization)

7. Conclusions

In conclusion, the salt composition that we used in our reactor was both catalytic and regenerative. It came out of the reactor in roughly same condition at which it went in. It occasionally had a grayish tint, but this is due to biomass particles trapped in the salt and the possibility of it absorbing some water. This is important because if the salt is meant to be used for extended periods of time, it is necessary for it to be catalytic otherwise the system will cease to function because there will be no salt remaining.

The production of syngas was the most important result of this process. Hydrogen was produced in large amounts and was the main product in many of the experiments run. With additional control structures in place, it's possible that the concentrations of hydrogen and carbon monoxide could be greatly increased. One method would be to run the process with a continuous gas flow to minimize the effect of side reactions.

In our process, we had various undesired results as well. One of which was water. Experiments we tested without water contained small amounts of water within the reactor after the reaction was finished. This is due to the simplest form of the Fischer-Tropsch Process, methanation which explains the appearance of methane. Due to the elevated concentrations of carbon monoxide and hydrogen gas, the Fischer-Tropsch Process took place to reduce the pressure. This is because the products of this reaction has a lesser number of moles than the reactants. This explains why we have much less carbon monoxide than methane.

Another unexpected result was the presence of an oily substance. This substance was thick and yellow. It condensed around the edges of the reactor, the feed tube, and the end caps. This could be a very important result because this means that it may be possible to obtain bio-oil from our process.

As can be seen in Table 6-1, the presence of the salt in the reactor greatly increases the amount of hydrogen and methane produced. Due to this information, it is reasonable to assume that the molten salt plays an important part in the formation of the desired product. This is most likely due to the catalysis of the Boudouard reaction by the molten carbonate salt resulting in an increase in carbon monoxide production. This is backed up by the presence of bubbles in the final salt suggesting a reaction that has taken place inside the salt while it was molten. There's also a strong possibility that the carbonate also helps to break down cellulose prior to complete breakdown by pyrolysis.

8. Recommendations for Future Study

8.1. Reactor Design

In order to run a more efficient and applicable process, several major and minor alterations will be needed to be made in the reactor design. The current design does not allow for immediate sampling upon completion of a run due to the high temperature and pressures at which the system runs. We suggest the installation of a condenser between the reactor and the GC, along with temperature indicators which will ensure that all the low boiling liquids, namely water, will be condensed and the temperature will be low enough to pass through the GC.

The second major change is to switch from a batch to a semi-batch system. From our results, we see that in many cases the CO_2 is a limiting reagent and that the high operating pressures may shift equilibrium away from the preferred products, namely syngas. We suggest the addition of a water boiler system prior to the reactor that will mix with an inlet feed gas. This will allow for experiments with and without either CO_2 or water. In addition, a continuous feed system for biomass with either a hopper system or fluid injection system should be considered.

It is critical that there be no oxygen in the system prior to running the reactor. The current system employs a flushing process in which the reactor is flushed with Argon or the feed gas until a GC sample shows negligible oxygen. To improve upon this, especially if additional apparatus are being added to the lines, a vacuum pump should be installed to completely remove oxygen from the reactor, condenser, boiler and pipelines. In addition, this will allow for precise measurements for mass balances.

Several minor changes include rebuilding a reactor vessel. Due to the high temperatures, the reactor undergoes severe wear and tear over its useful life and needs to be replaced. In addition, the fluid flow system needs to be calibrated and correction factors for each gas need to be properly implemented, especially for continuous flow. Several valves should be replaced on the fluid control system due to leaks. In addition, it may be interesting to determine the effects of a microwave heating process on the reaction.

8.2. Reaction Rate Analysis

In our experiments, we obtained similar results for gaseous atmospheres of pure Ar, CO_2 and water. It is well known that pyrolysis and gasification occur without the aid of the molten salt catalyst, however we believe the catalyst increases the reaction rate by aiding in the breakdown. To test this, rate analyses will need to be conducted with the control as well as with different feed gases and catalyst compositions. This could be conducted by employing various times and temperatures for the reaction or by using a continuous flow which would allow for a greater amount of control on species partial pressures.

8.3. Temperature, Pressure, Energy Dependencies

The two major driving forces for a reaction are kinetics and thermodynamics. Kinetically speaking, experiments should be performed to analyze the effect of temperature and pressure on the system. Due to the high melting salt, lower temperatures cannot be studied, however a study on the change in melting point of the salt due to accumulation of nonreactive species may prove useful. Also, a study on rates of reaction at various temperatures should be performed.

In our experiments, operating pressure ranged between 500-1000 psi. Pressure is a major driving force for gaseous equilibrium and should be studied more closely, especially in a continuous system.

The second major aspect is thermodynamics. A thermodynamic analysis of equilibrium reaction products would shed some light on the overall process. A proper energy balance should also be performed to analyze for the practical feasibility of such a process. Heating effects for the reactor and boiler should be accounted for as well as heat of reaction, decomposition, condensation, etc.

8.4. Mechanistic Breakdown Study

Chemically speaking, sugars, cellulose and lignins are complex structure, however their properties are rather well known. A study of plausible reaction routes and the role of the molten salt as a catalyst should be studied. Analysis into how the salt mechanistically breaks down each structure and how it is regenerated should be performed. By determining the active parts of the catalyst, adjustments and changes to the catalyst should be made. Minor changes might include adjustment to the carbonate hydroxide composition, while major changes might include introduction of a new component such as nitrates.

In addition, a study of the overall reactions should be studied, including proposing a step by step reaction mechanism to explain the chemistry. This may also be useful in mass and energy balances. There should also be an analysis of the liquid products formed possibly by a GC/Mass spectroscopy analysis.

8.5. Study Catalytic Properties

The last major are to study is the effectiveness of the catalyst to act catalytic. Experiments should be performed to quantify the amount of catalyst at the beginning and end to ensure it is not being reacted. End composition should also be studied to ensure that there is no change in the salt due to the hydroxides decomposing into carbonates in the presence of carbon dioxide.

The catalyst should also be studied for reapplication abilities. Within the reactor, this may mean running multiple samples with the same salt and noting any degradation in the catalyst's ability to catalyze the reaction through kinetics or product composition. In addition, for a flow system, this may mean having a continuous flow of the feed for a long period of time and studying the changes.

It is possible that metal catalysts such as Ni, Cu, Sn, Fe, etc. could be used in conjunction with the molten salt to catalyze the reaction. As a liquid, the molten salt could effectively dispense the metals to assist in catalysis.

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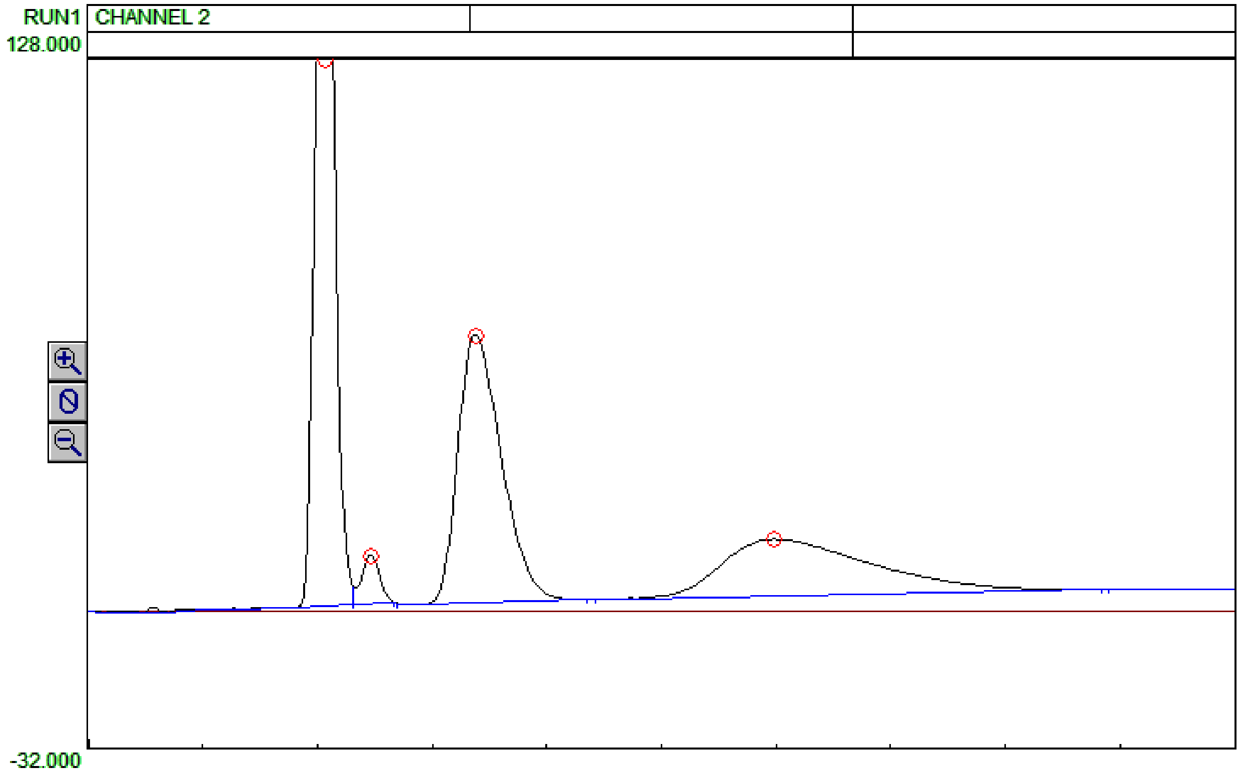
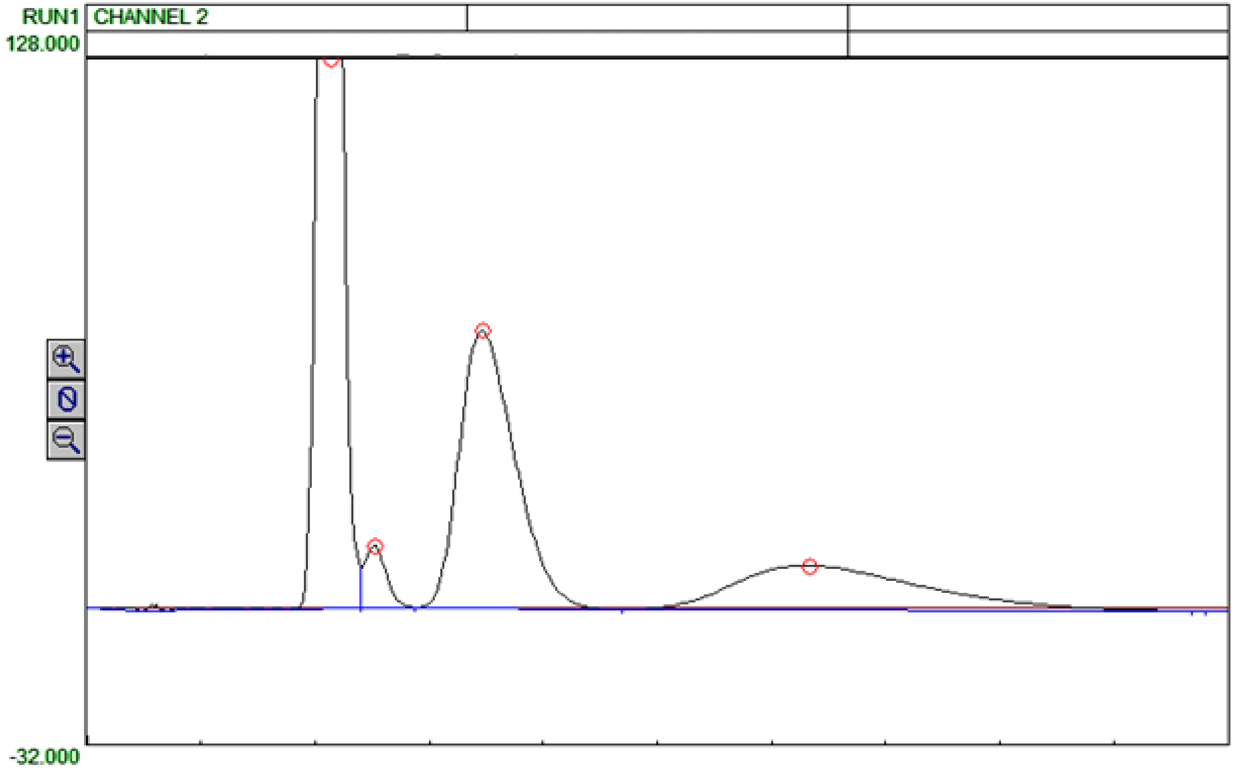
10. Appendices

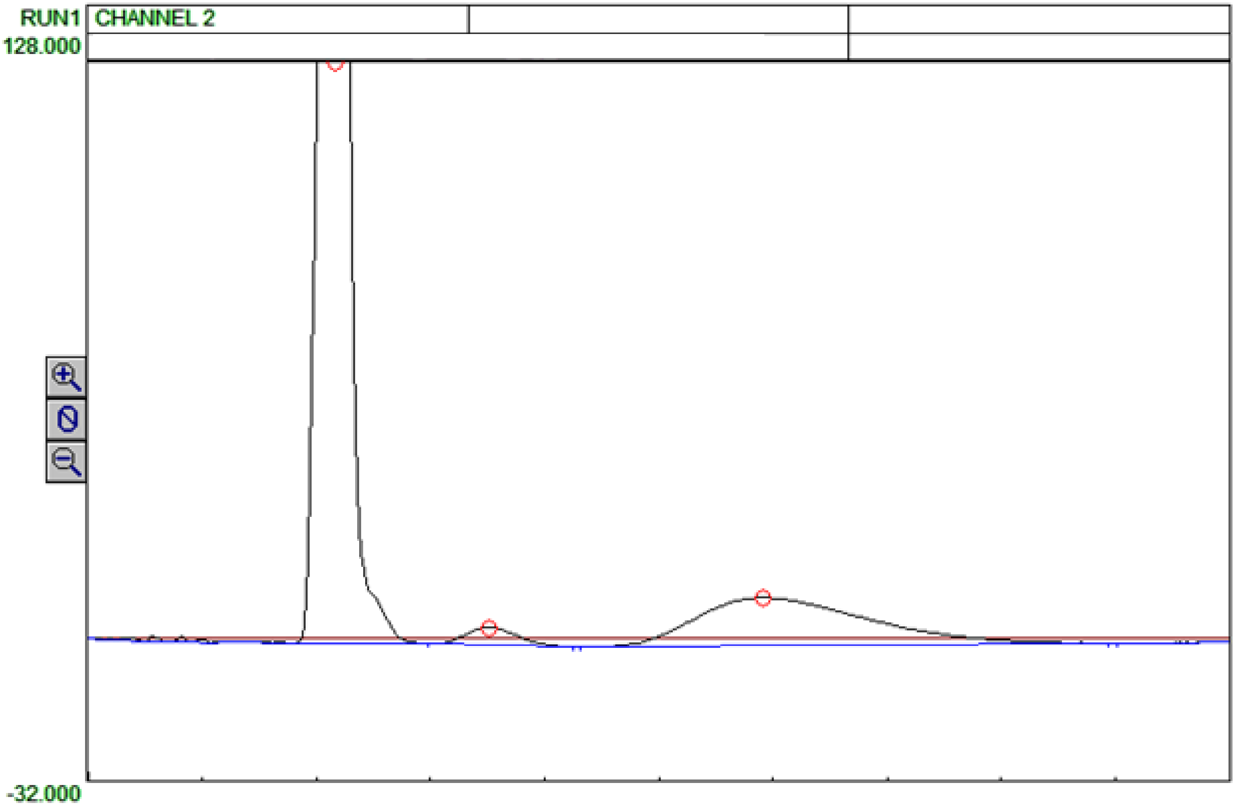
10.1. Appendix A: Gas Chromatography Data



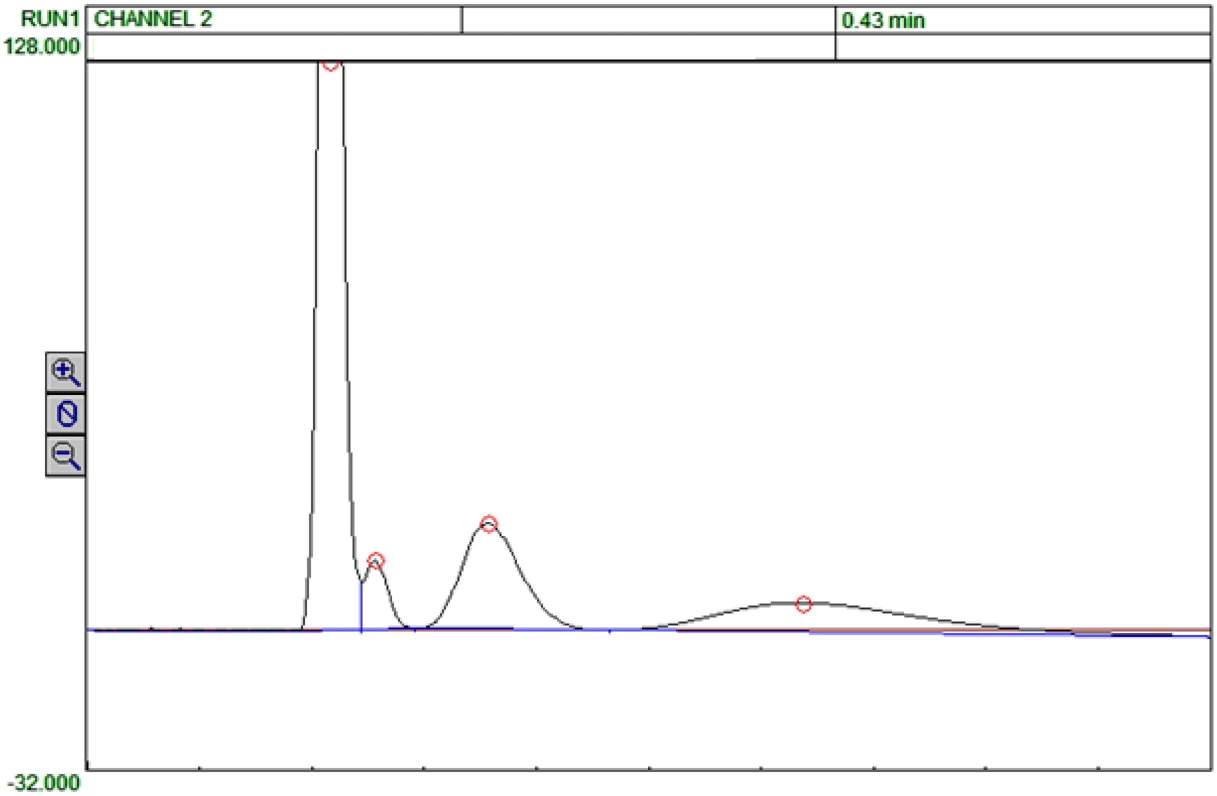
	Biomass	**Gas**	**Area Fraction**	**Mole Ratio**	**Mole Fraction**
	10g twig	CO_2\H_2O			
H_2	2785.827	5761.882	0.483493	4.22E-05	0.176338
CO	126.8555		0.022016	1.47E-05	0.061306
CH_4	1635.413		0.283833	5.54E-05	0.231681
CO_2	1213.786		0.210658	0.000127	0.530675
			1	0.000239	1
H_2	3013.766	5325.901	0.56587	4.94E-05	0.258447
CO	127.915		0.024018	1.6E-05	0.08375
CH_4	1588.316		0.298225	5.82E-05	0.304838
CO_2	595.904		0.111888	6.74E-05	0.352965
				0.000191	1



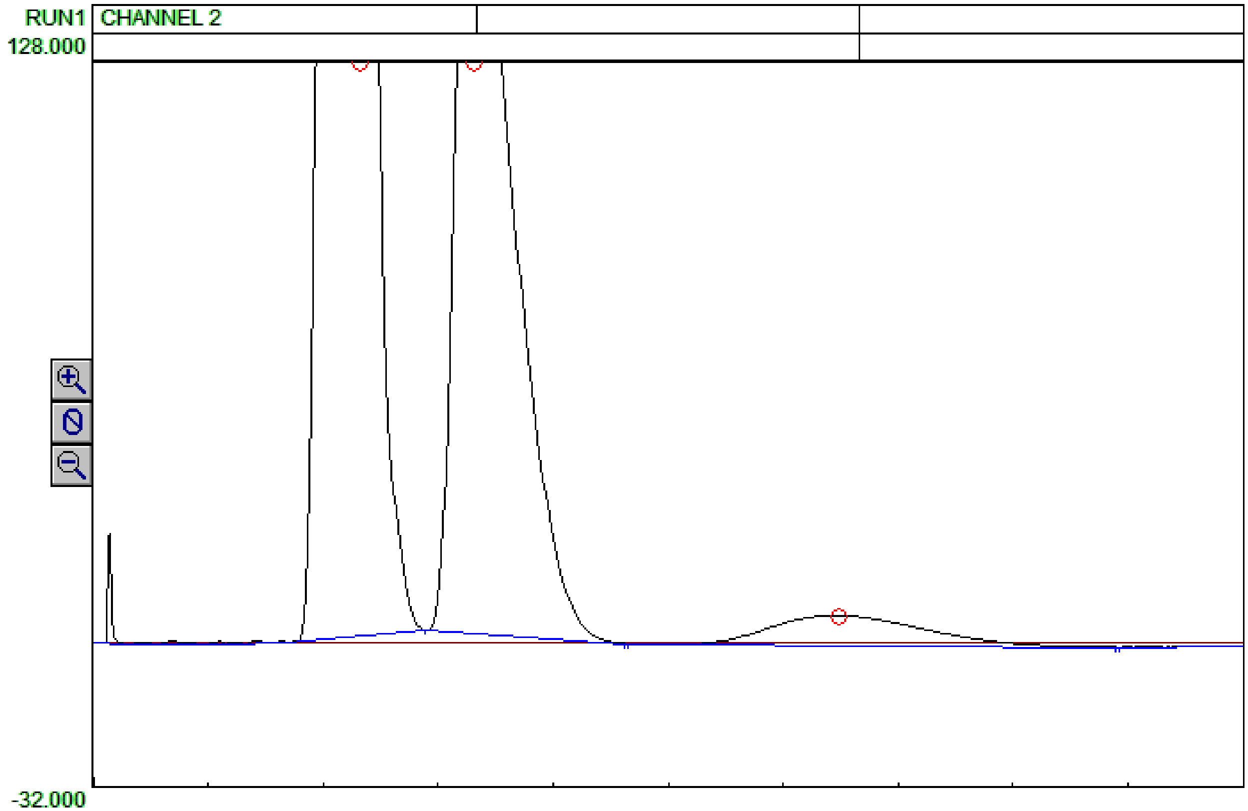
	Biomass	**Gas**	**Area Fraction**	**Mole Ratio**	**Mole Fraction**
	10g pine	CO_2\H_2O			
H_2	5375.444	8955.425	0.600244	5.24E-05	0.268938
CO	189.614		0.021173	1.41E-05	0.072428
CH_4	2195.951		0.245209	4.79E-05	0.245884
CO_2	1194.416		0.133373	8.03E-05	0.41275
				0.000195	1



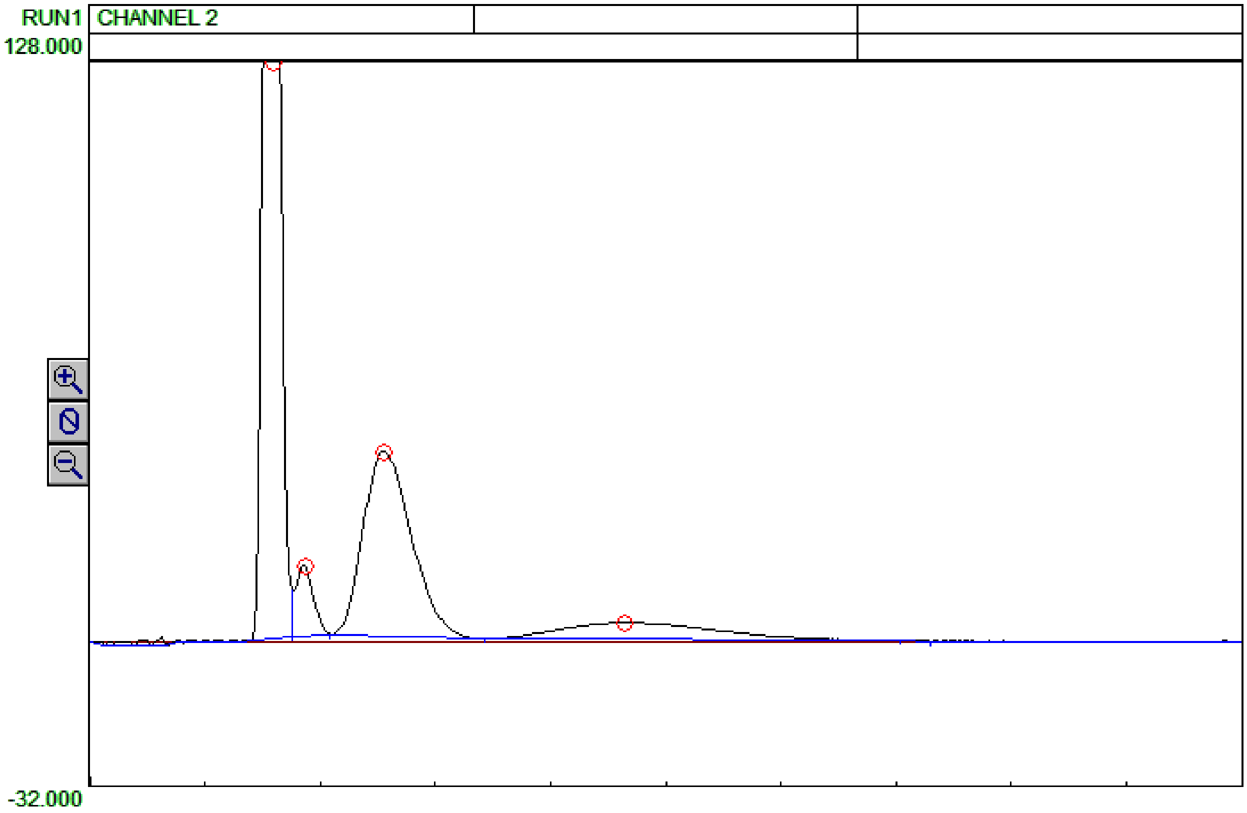
	Biomass	Gas	Area Fraction	Mole Ratio	Mole Fraction
	5g sucrose	$CO_2\backslash H_2O$			
H_2	8367.167	9591.576	0.872345	7.61E-05	0.514564
CO	0		0	0	0
CH_4	120.696		0.012584	2.46E-06	0.016612
CO_2	1103.713		0.115071	6.93E-05	0.468824
				0.000148	1



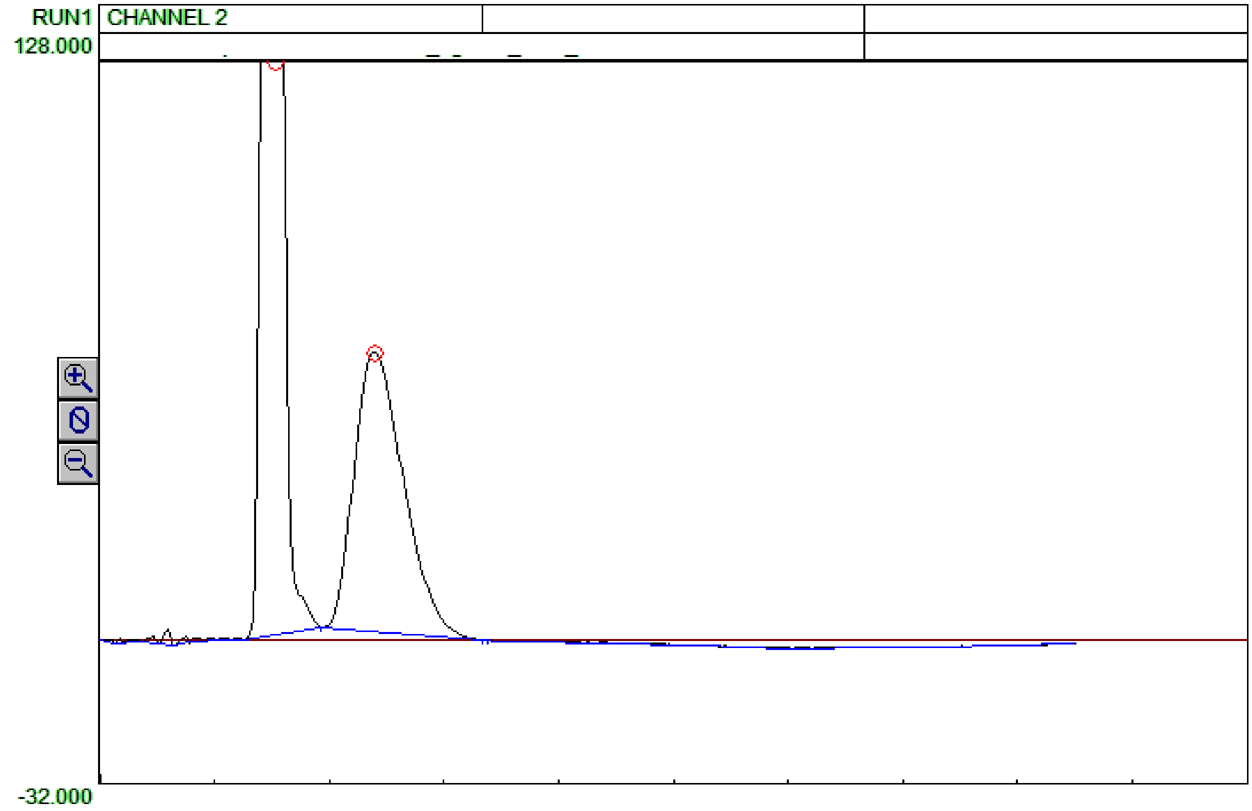
	Biomass	Gas	Area Fraction	Mole Ratio	Mole Fraction
	5g pine	CO_2\H_2O			
H_2	6263.788	8955.768	0.699414	6.1E-05	0.323251
CO	333.027		0.037186	2.48E-05	0.131214
CH_4	1225.602		0.136851	2.67E-05	0.141554
CO_2	1133.351		0.12655	7.62E-05	0.403981
				0.000189	1
H_2	4811.9	6774.668	0.710278	6.19E-05	0.333589
CO	220.556		0.032556	2.17E-05	0.116738
CH_4	879.142		0.129769	2.53E-05	0.136403
CO_2	863.07		0.127397	7.67E-05	0.41327
				0.000186	1
H_2	4334.941	5989.346	0.723775	6.31E-05	0.353391
CO	194.557		0.032484	2.16E-05	0.121093
CH_4	778.948		0.130056	2.54E-05	0.142119
CO_2	680.9		0.113685	6.85E-05	0.383397
				0.000179	1



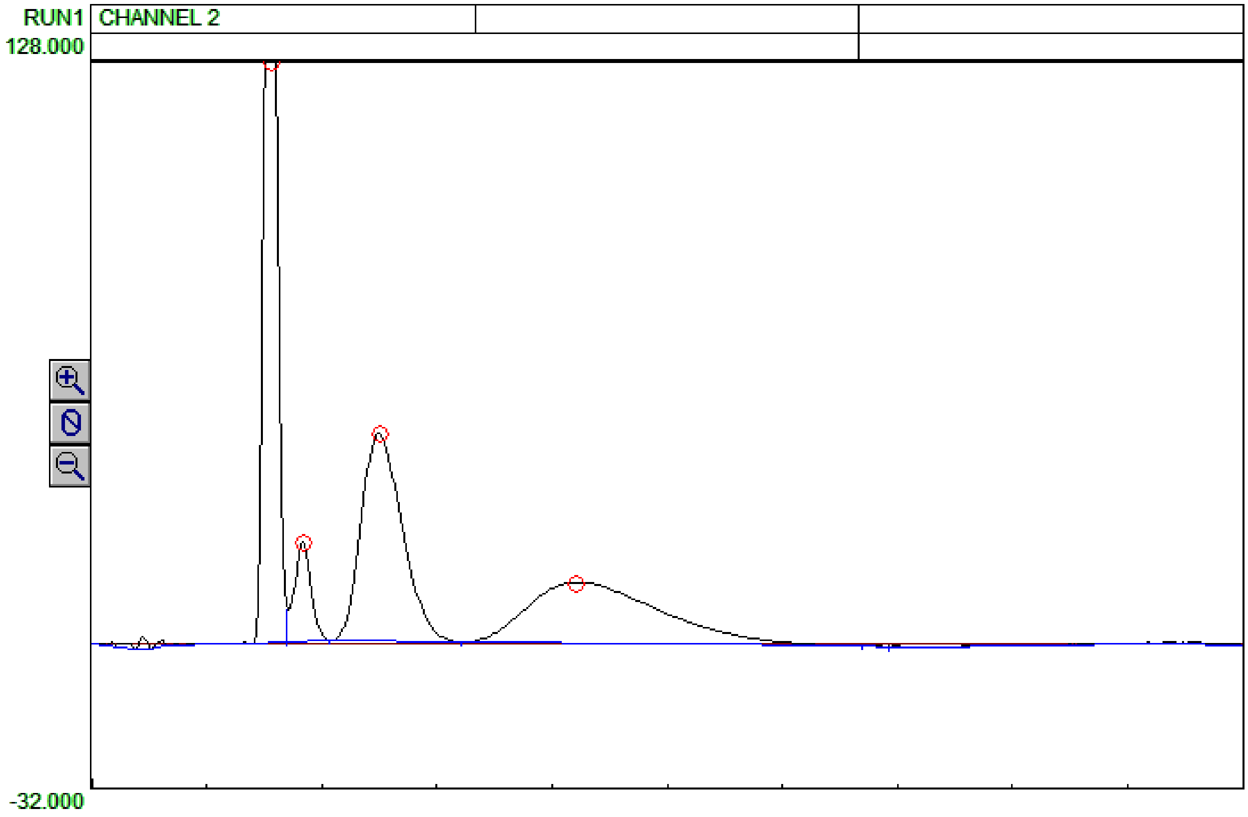
	Biomass	Gas	Area Fraction	Mole Ratio	Mole Fraction
	5g Pine	Ar\\H_2O			
H_2	21692.47	28669.65	0.756635	6.6E-05	0.539267
CO			0	0	0
CH_4	6352.178		0.221565	4.32E-05	0.353417
CO_2	625		0.0218	1.31E-05	0.107317
				0.000122	1
H_2	7942.918	9958.246	0.797622	6.96E-05	0.607001
CO	0		0	0	0
CH_4	1879.926		0.188781	3.69E-05	0.321529
CO_2	135.402		0.013597	8.19E-06	0.071471
				0.000115	1



	Biomass	Gas	Area Fraction	Mole Ratio	Mole Fraction
	5g Pine	Ar			
H_2	3877.96	5672.459	0.683647	5.96E-05	0.369665
CO	184.886		0.032594	2.17E-05	0.134558
CH_4	1267.238		0.223402	4.36E-05	0.270354
CO_2	342.375		0.060357	3.64E-05	0.225424
				0.000161	1
H_2	8089.262	12193.18	0.663425	5.79E-05	0.361961
CO	377.7875		0.030984	2.06E-05	0.129063
CH_4	3075.976		0.25227	4.92E-05	0.308039
CO_2	650.151		0.053321	3.21E-05	0.200937
				0.00016	1
H_2	3642.661	5342.238	0.68186	5.95E-05	0.364469
CO	172.7		0.032327	2.15E-05	0.131927
CH_4	1180.765		0.221024	4.31E-05	0.264409
CO_2	346.112		0.064788	3.9E-05	0.239195
				0.000163	1



	Biomass	Gas	Area Fraction	Mole Ratio	Mole Fraction
	5g Pine	CO_2			
H_2	7103.268	8883.662	0.799588	6.97E-05	0.640634
CO	0		0	0	0
CH_4	1780.394		0.200412	3.91E-05	0.359366
CO_2	0		0	0	0
				0.000109	1
H_2	6766.735	8622.505	0.784776	6.84E-05	0.619662
CO	0		0	0	0
CH_4	1855.77		0.215224	4.2E-05	0.380338
CO_2	0		0	0	0
				0.00011	1



No salt	Biomass	Gas	Area Fraction	Mole Ratio	Mole Fraction
	5g Pine	CO_2			
H_2	6863.138	16858.4	0.407105	3.55E-05	0.129759
CO	926.7		0.05497	3.66E-05	0.133769
CH_4	5072.612		0.300895	5.87E-05	0.214643
CO_2	3995.948		0.23703	0.000143	0.521829
				0.000274	1
H_2	1746.631	3973.359	0.439585	3.83E-05	0.14311
CO	198.018		0.049836	3.32E-05	0.123872
CH_4	1085.036		0.273078	5.33E-05	0.198967
CO_2	943.674		0.2375	0.000143	0.534051
				0.000268	1
H_2	1873.44	4320.449	0.433622	3.78E-05	0.137359
CO	221.741		0.051324	3.42E-05	0.124126
CH_4	1134.591		0.26261	5.13E-05	0.186177
CO_2	1090.677		0.252445	0.000152	0.552339
				0.000275	1

10.2. Appendix B: Calculations for reactor pressure

Reactant amounts

$$nCO_2 + (C_6H_{10}O_5)_n \rightarrow n7CO + n5H_2$$

$$\therefore \sim 1\ mole\ CO_2\ per\ mole\ glucose$$

Assume reactor is full of CO_2 (best case scenario)

$$V_{CO_2} = \pi\left(\frac{D}{2}\right)^2 * L = \pi\left(\frac{0.75}{2}\right)^2 * 16 = 7.068\ in^3 = 1.16 * 10^{-4}\ m^3$$

$$n_{CO_2} = \frac{PV}{RT} = \frac{101325 * (1.16 * 10^{-4})}{8.314 * 298} = 0.004737\ mol$$

$$n_{C_6H_{10}O_5} = 0.004737\ mol$$

$$m_{C_6H_{10}O_5} = n_{C_6H_{10}O_5} * MM = 0.004737\ mol * \left(162.14\frac{g}{mol}\right) = 0.768\ g\ Cellulose$$

If this is a batch reactor, this is a small amount of cellulose. Side reactions with the salt and products may occur.

Final Pressure Calculation:

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Assume preferred reaction (low pressure reaction):

$$CO_2 + C_6H_{10}O_5 \rightarrow 7CO + 5H_2$$

$$n_1 : n_2 = 1:12$$

$$\frac{P_1V}{n_1T_1} = \frac{P_2V}{12n_1T_2}$$

$$P_2 = \frac{1\ atm}{298\ K} * \frac{12 * 800\ K}{1} = 32\ atm = \mathbf{470\ psi}$$

Assume other reaction (high pressure reaction):

$$6CO_2 + C_6H_{10}O_5 \rightarrow 12CO + 5H_2O$$

$$n_1 : n_2 = 1:17$$

$$\frac{P_1V}{n_1T_1} = \frac{P_2V}{17n_1T_2}$$

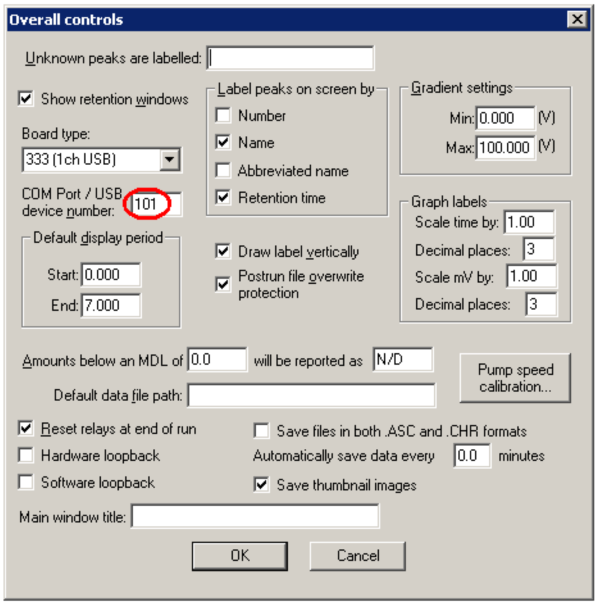
$$P_2 = \frac{1\ atm}{298\ K} * \frac{17 * 800\ K}{6} = 7.6\ atm = \mathbf{112\ psi}$$

In addition, Le Chatelier's principle will drive the reaction in the backward direction due to the high pressures.

10.3. Appendix C: Gas Chromatograph Operation

The Gas Chromatograph was controlled mainly by a program published by SRI called PeakSimple. PeakSimple is a program that can receive data from a Gas Chromatograph from various channels based on the type of detector used. Multiple detectors can be used at once, but for the purpose of these experiments, only the Thermal Conductivity Detector was used which was set as Channel 2.

To begin, it must be confirmed that PeakSimple is reading from the proper COM channel on the back of the computer. If it is not reading properly, the program will return the error message "Acquisition System Not Functioning." At this point this dialog box must be closed. From there, the COM channel that PeakSimple is reading from can be changing by clicking on "Edit" in the menu bar and selecting "Overall..." The dialog box shown in Figure 10-1 is from a newer version of PeakSimple than that which was used, but the concept remains the same. Circled in Red is the value that needs to be changed, the COM port used for this experiment was 2.



Overall controls

Unknown peaks are labelled:

☑ Show retention windows

Board type: 333 (1ch USB)

COM Port / USB device number: 101

Default display period
Start: 0.000
End: 7.000

Label peaks on screen by
☐ Number
☑ Name
☐ Abbreviated name
☑ Retention time

☑ Draw label vertically
☑ Postrun file overwrite protection

Gradient settings
Min: 0.000 (V)
Max: 100.000 (V)

Graph labels
Scale time by: 1.00
Decimal places: 3
Scale mV by: 1.00
Decimal places: 3

Amounts below an MDL of 0.0 will be reported as N/D

Default data file path:

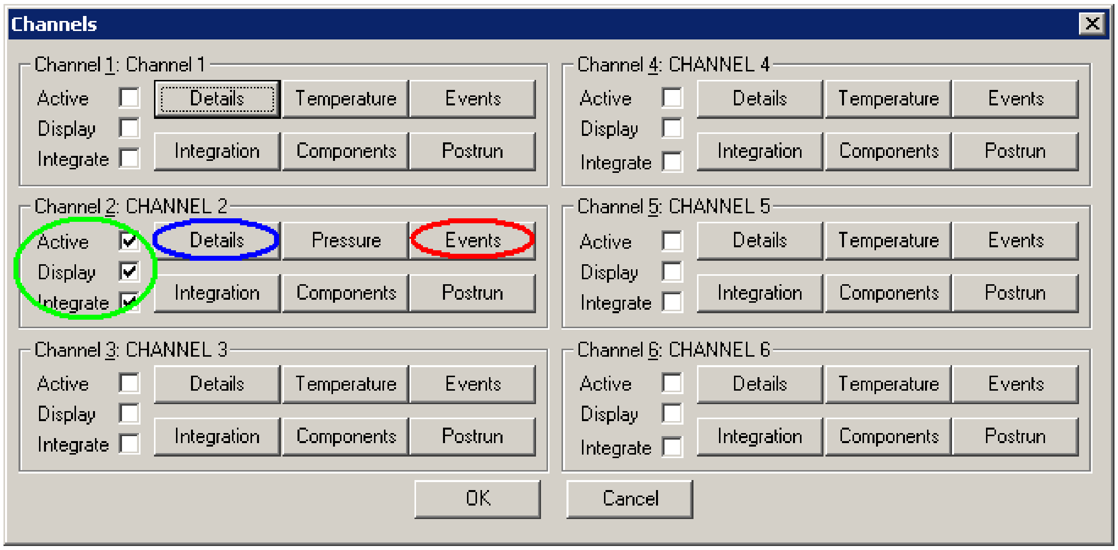
☑ Reset relays at end of run
☐ Hardware loopback
☐ Software loopback

☐ Save files in both .ASC and .CHR formats
Automatically save data every 0.0 minutes
☑ Save thumbnail images

Main window title:

Figure 10-1: "Overall..." Dialog Box

Next, it must be confirmed that PeakSimple is reading from the proper Gas Chromatograph channel. The channel is displayed on the top of the Gas Chromatograph right next to the appropriate detector. The channel for the TCD on the Gas Chromatograph used was Channel 2. To change which channel it reads from, click on "Edit" in the menu bar and select "Channels..." The dialog box that appears is shown in Figure 10-2.



Channels

Channel 1: Channel 1
Active ☐
Display ☐
Integrate ☐

Channel 2: CHANNEL 2
Active ☑
Display ☑
Integrate ☑

Channel 3: CHANNEL 3
Active ☐
Display ☐
Integrate ☐

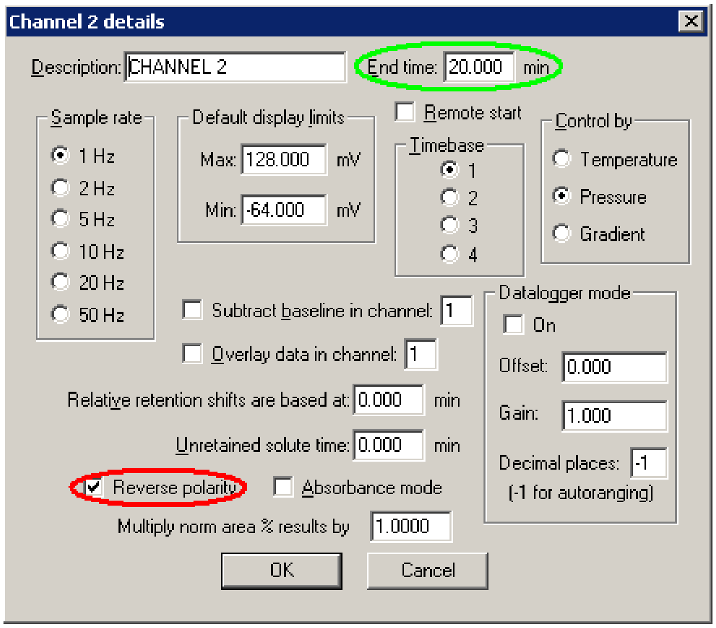
Channel 4: CHANNEL 4
Active ☐
Display ☐
Integrate ☐

Channel 5: CHANNEL 5
Active ☐
Display ☐
Integrate ☐

Channel 6: CHANNEL 6
Active ☐
Display ☐
Integrate ☐

Figure 10-2: Channels Dialog Box

Circled in green are the three checkboxes that must be selected in order for the program to read, display, and integrate the selected channel. The "Details" button, circled in blue, is necessary to change specific aspects of each run. The "Events" button, circled in red, is used to adjust the time when controllable events occur. The "Pressure" button, can be used to control pressure in the TCD, "Integration" can be used to modify Integration settings, "Components" controls how PeakSimple labels peaks based on retention time, "Postrun" controls what happens after the run including autosaving the chromatogram and logs as well as setting the Gas Chromatograph up for another run. "Details" and "Events" will be described in more detail below.



Channel 2 details

Description: CHANNEL 2

End time: 20.000 min

Sample rate
● 1 Hz
○ 2 Hz
○ 5 Hz
○ 10 Hz
○ 20 Hz
○ 50 Hz

Default display limits
Max: 128.000 mV
Min: -64.000 mV

☐ Remote start

Timebase
● 1
○ 2
○ 3
○ 4

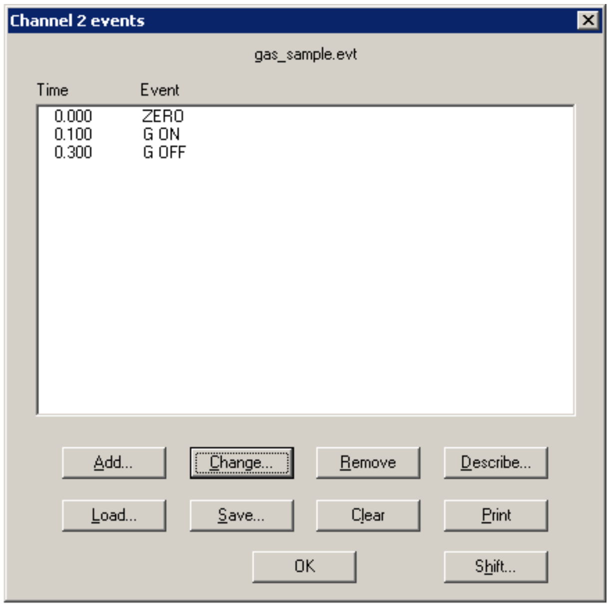
Control by
○ Temperature
● Pressure
○ Gradient

☐ Subtract baseline in channel: 1
☐ Overlay data in channel: 1
Relative retention shifts are based at: 0.000 min
Unretained solute time: 0.000 min
☑ Reverse polarity ☐ Absorbance mode
Multiply norm area % results by 1.0000

Datalogger mode
☐ On
Offset: 0.000
Gain: 1.000
Decimal places: -1
(-1 for autoranging)

Figure 10-3: Details Dialog Box

Shown in Figure 10-3 is the Details Dialog box. End Time, circled in green, controls the length of the run. The Reverse Polarity check box, circled in red, is important when running the Gas Chromatograph with an Argon carrier gas which displays peaks upside-down. This option will reflect the sample line over the baseline to correct for this.



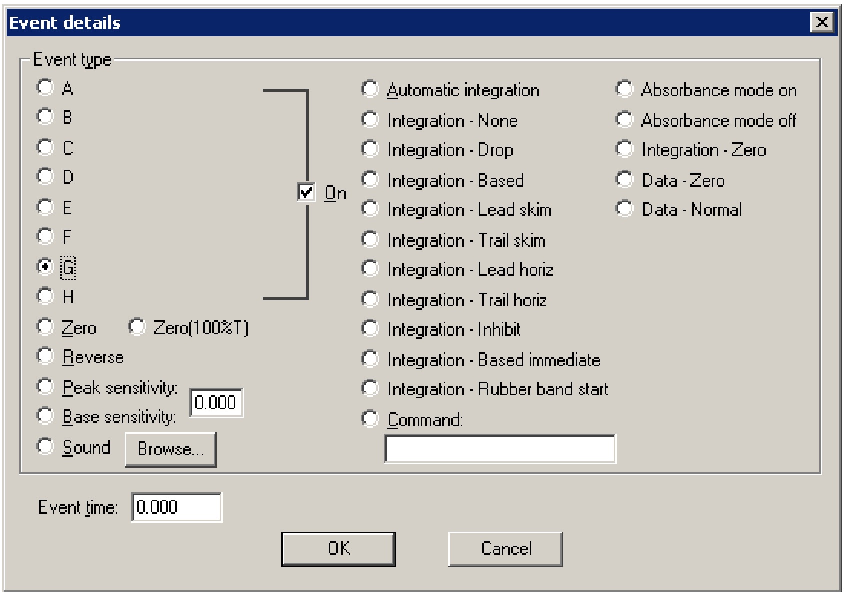
Channel 2 events

gas_sample.evt

Time	Event
0.000	ZERO
0.100	G ON
0.300	G OFF

Figure 10-4: The Events Dialog Box

The Events dialog box, shown in Figure 10-4, allows the user to program event to happen at specific times. Events are loaded into the system by selecting add, and selecting the event and inputting the time. Figure 10-4 also shows the suggested events for these experiments. Figure 10-5 shows the Event Details window which allows the user to choose one of many functions to occur at a time specified by the value in the "Event time" box.



● G

☑ On

Peak sensitivity / Base sensitivity: 0.000

Event time: 0.000

Figure 10-5: The Event Details Dialog Box

10.4. Appendix D: Char Conversion Calculation

Feed Stock Calculation

$$V_{reactor} = \pi r^2 * h$$

$$V_{reactor} = \pi \left(\frac{0.75}{2}\right)^2 * (16) = 7.068\, in^2 = 1.158 * 10^{-4} m^3$$

$$P^*_{CO_2,0} = 20\, psig = 239{,}248\, Pa, \qquad T_0 = 300K$$

$$n_{CO_2,0} = \frac{P^*_{CO_2,0} * V}{R * T_0} = 1.111 * 10^{-2} mol\ \mathrm{CO_2}$$

$$n_{C,feed} = 5g * \frac{\text{mol Cellulose}}{158g} * \frac{\text{6 mol C}}{\text{mol Cellulose}} = 1.899 * 10^{-1}\, mol\ \mathrm{C}$$

$$\mathrm{C} + \mathrm{CO_2} \rightarrow 2\mathrm{CO}$$

$$X_{Feed} = 1 - \frac{n_{Feed}}{n_{Feed,0}} = 1 - \frac{1.899 * 10^{-1} - 1.111 * 10^{-2}}{1.899 * 10^{-1}} = 0.0585 = 5.85\%$$

Limiting reagent: CO_2*. It can only react up to 5.85% of the total* C*, residual or in tact feed.*