

**Hot Water Pretreatment to Improve the Selectivity of Cellulose  
Thermo-chemical Reactions Towards the Production of  
Anhydrosugars.**

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of Robert Johnson find it satisfactory and recommend that it be accepted.

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# **Hot Water Pretreatment to Improve the Selectivity of Cellulose Thermo-chemical Reactions Towards the Production of Anhydrosugars.**

Abstract

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Hot water pretreatment of biomass was systematically studied to determine if reaction selectivity of cellulose towards the production of anhydrosugars and furanics could be improved. Samples of wheat straw and  $\alpha$ -cellulose were treated using hot compressed water at temperatures ranging between 150 and 260°C. The effect of hot water pretreatment on pyrolysis selectivity was studied by Py-GC/MS. Various representative peak area ratios were compared and used as an index of pyrolysis selectivity. The chemical analysis and Py-GC/MS of solid residues of hot water pretreatment suggest that as the temperature increased the hemicelluloses and amorphous cellulose were solubilized. Py-GC/MS results showed that the relative areas associated with levoglucosan increased for both straw and cellulose with increasing treatment temperature. Our results indicate that the selectivity of thermo-chemical reactions towards the production of sugars and furanics can be enhanced and the amount of acetic acid is reduced if the material is treated in hot water at temperatures between 220 and 260°C. Hot water pretreatment may be a viable method to improve the quality of bio-oils produced via fast pyrolysis.

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## **DEDICATION**

This thesis is a dedication to my family, who has been a support for me throughout my life and to my wonderful wife Sara.

# Chapter 1

## Energy Situation and Biomass Pyrolysis

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### 1.1- Introduction

Ubiquitous consumption of fossil fuels in the last century has created many economic and environmental problems that need to be urgently addressed in the next decades. Many known sources of crude oil have become depleted, and therefore remaining oil reserves are more energy intensive to extract and refine. World oil production is facing new challenges to meet demand leading to higher energy prices. Moreover, what remains of easily extractable oil is located in volatile regions of the world. These facts create major problems for U.S. national security and threaten economic growth. Burning fossil fuels has also led to elevated atmospheric concentrations of carbon dioxide which is believed to be responsible for both global warming, and ocean acidification.<sup>1-3</sup> Relying on fossil resources to produce fuels and chemicals poses a significant threat to economic prosperity, environmental stability, and therefore national security. For these reasons renewed interest to develop technologies to convert renewable biomass into liquid transportation fuels has become apparent.<sup>4,5</sup> Biomass derived fuels are renewable, carbon neutral or negative,<sup>6-8</sup> and have great potential to offset significant amount of current fossil fuel consumption.

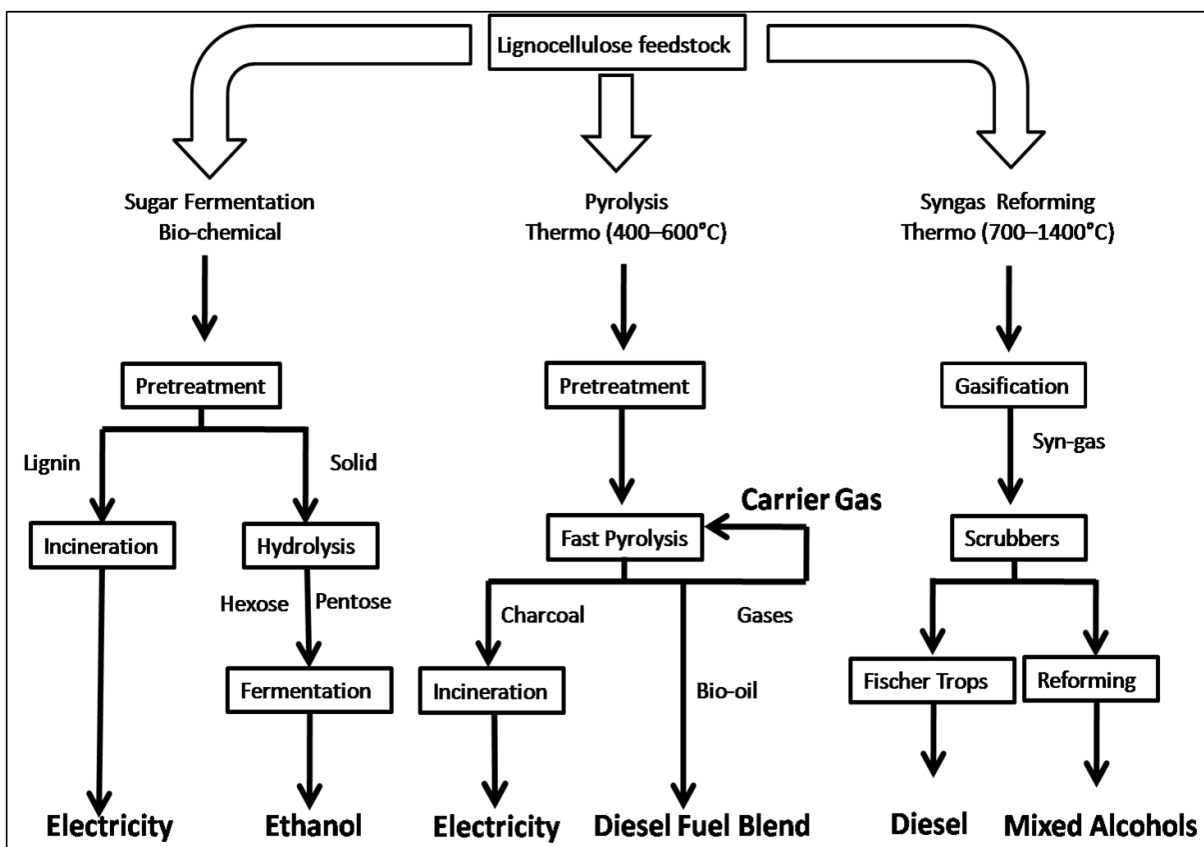
The U.S. Department of Energy has determined that more than 1 billion dry tons of biomass could be sustainably harvested, and would offset roughly 30% of the United States current demand of liquid transport fuel.<sup>9</sup> Increasing the use of clean technologies, and meeting the carbon emission standards of the Kyoto protocol are top priorities with the US government calling to produce 60 billion gallons of second generation bio-fuels by 2030.<sup>10</sup> The American Fuels Act introduced to reduce the risks associated with investing in bio-fuel technologies should help ensure investors that the demand for bio-fuels will be sustained in the long term. The United State is increasingly partnering with other nations and is intensifying its own efforts to develop new avenues to reduce our dependence on fossil fuels, and mitigate global warming.

Recent oil prices beyond 150\$/barrel is a clear indication that current supply of oil cannot satisfy the demand in periods of economic growth. World fossil fuel demand is not predicted to decrease in the near future. Rapid economic growth and industrialization in developing countries and sustained demand in United States, coupled with depletion of known petroleum reserves has drastically affected the demand-supply equilibrium. The U.S. Energy Information Administration predicts that world oil demand will grow by approximately 37% by 2030. Given current consumption this increase in demand translates to an additional 31.7 million barrels/day, which is the equivalent of three times the current output of Saudi Arabia. Moreover, 94% of this spike in demand is to provide liquid transportation fuel.<sup>4,11</sup> Not investing in new technology will ultimately lead to major economic problems in the near future. It is noteworthy that although, numerous clean sources and technologies exist for the production of electricity, biomass is our only renewable source to produce liquid carbon based fuels.<sup>12</sup>

The technologies so far proposed to produce bio-fuels are not exempt of problems and controversies. For example, most bio-fuels currently produced in the United States (first generation bio-fuels) are derived from the fermentation of corn starch. The use of food for fuel has sparked political opposition to bio-fuel production. Alternatively, biofuels could be produced from non-edible, low value, underutilized lignocellulosic materials (second generation bio-fuels).

## **1.2.- Conversion Platforms**

Several biomass conversion platforms are currently being pursued by industry and research institutions<sup>13-16</sup> (See Figure 1.1). One set of technologies (platform) is based on the use of biological agents (enzymes) to hydrolyze cellulose into sugars that are fermented into ethanol. The other conversion platform uses thermo chemical processes (pyrolysis, gasification) to depolymerise the biomass into intermediaries (bio-oil, synthesis gas) that can be further converted (Fischer-Tropsch, hydrotreatment) into green gasoline, methanol, ethanol or mixed alcohols (see Figure 1.1). In general it can be stated that while enzymatic hydrolysis is a very good pathway to convert cellulose into ethanol, this technology makes a very poor use of lignin. Conversely, pyrolysis followed by bio-oil hydrotreatment is an excellent approach to convert lignin into green gasoline and green diesel but the conversion of cellulose into transportation fuels (e.i., ethanol) is low. Gasification, on the other hand, is able to transform all biomass components into a synthesis gas that can be further converted into transportation fuels via Fischer Tropsch. The main drawback of this technology is that the yields of transportation fuels so far achieved by this technology are relatively low (around 14 mass %).

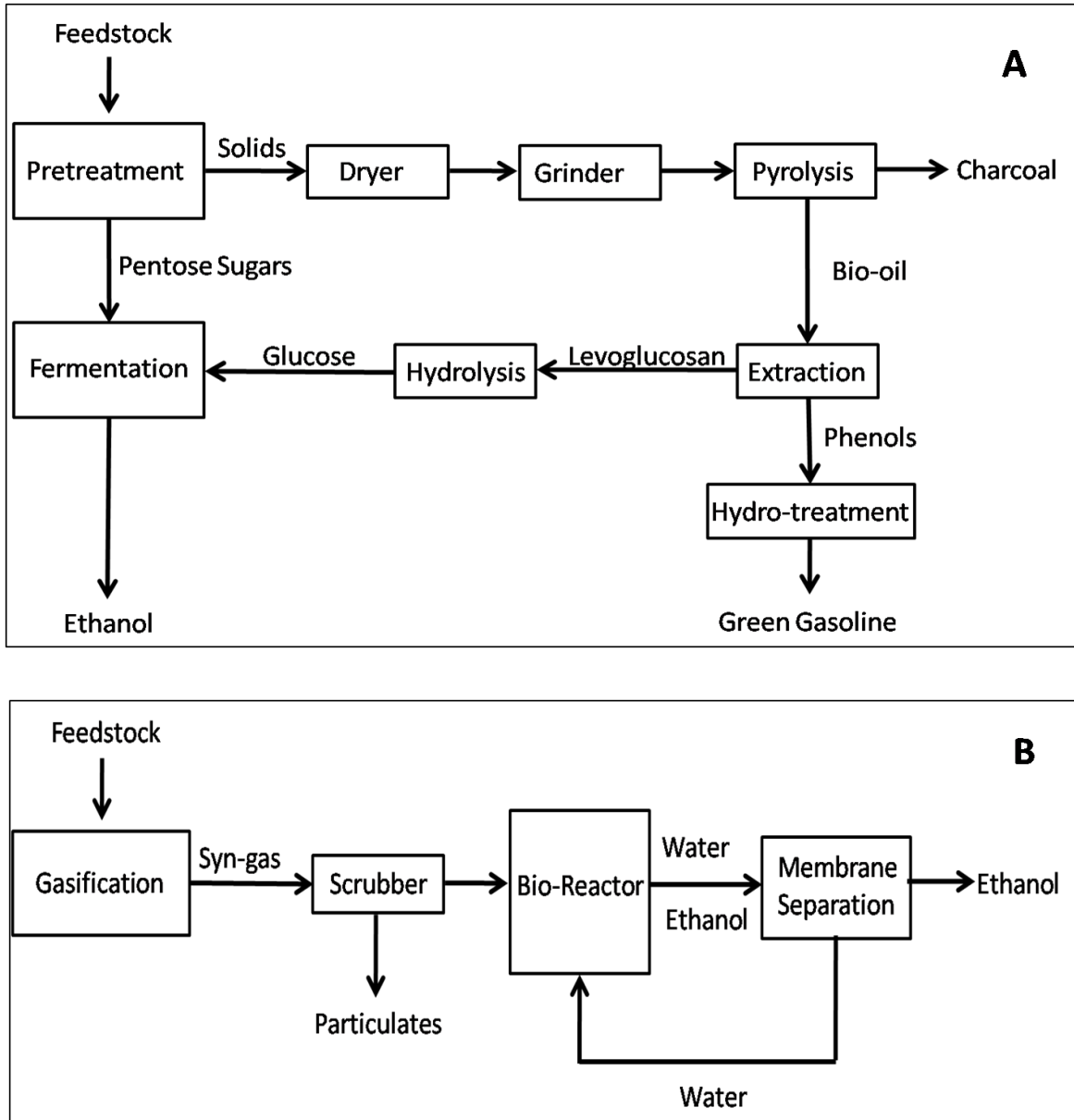


**Figure 1.1.-** Classical biomass conversion schemes

Combining technologies resulting from the classical thermo-chemical and biological platforms, taken advantage of the strengths of each of these pathways, is receiving increasing attention.<sup>13</sup>

Figure 1.2 shows two hybrid concepts to produce transportation fuels from biomass. The first one, a technology is shown in which the biomass is pretreated to remove the C<sub>5</sub> sugars (hemicelluloses) and part of the amorphous cellulose. These sugars are then fermented to produce ethanol. The remaining material is pyrolysed to produce bio-oil and charcoal. The oil is further separated into a fraction rich in sugars and a fraction rich in lignin. The fraction rich in lignin is hydrotreated to produce green gasoline and green diesel and the anhydrosugars are hydrolyzed, detoxified and fermented to ethanol. The process shown in Figure 1.2 (B) is another

hybrid concept but here the biomass is gasified and the synthesis gas is converted to ethanol in a bio-reactor.



**Figure 1.2.-** Bio-thermo hybrid conversion schemes<sup>13</sup>

Although the technologies shown in Figure 1.2 are technically viable, many logistical, technical and economic problems remain unsolved. Biomass fractionation and conversion requires large



initial capital investment for needed infrastructure. Bio-refineries based on thermo-chemical or biological conversion technologies must take advantages of economies of scale to be competitive with petroleum derived fuels. Compared to fossil fuels, biomass is a low energy density material which cannot be transported long distances without densification. Clearly, transporting large volumes of biomass to feed a large bio-refinery is a major economic bottleneck impeding economic competitiveness of second generation bio-fuels.<sup>17</sup>

### **1.3.- Feedstock costs**

Feedstock associated costs can be as high as 70–80% of the total production cost.<sup>18</sup> For example, a study funded by DOE showed that the delivery costs for corn stover ranges from \$43.1 per dry ton for a 500 dry ton/day ethanol facility (1,800 square miles collection area, 22 miles average one-way hauling distance) to about \$51.6 per dry ton for a 4000 dry ton/day facility (14,000 square miles collection area, 62 miles average one-way hauling distance).<sup>19</sup> The difference in delivered costs between facility sizes reflects transport costs, which account for 33% of total delivered costs for a 500 dry ton/day facility and 40% for a 4000 dry ton/day facility. This study clearly demonstrates that a key limitation for economically competitive bio-fuel production is the feedstock availability.

Preprocessing to increase the energy density prior to significant transport is a vital logistic barrier that is currently inhibiting the potential scale of a given bio-refinery. Technologies that increase the economical transport distance improve the potential biomass available for a given facility, and larger refineries can be constructed to take full advantage of economies of scale. For example an assessment of cost to hydro-treat bio-oil to produce green gasoline that was conducted by the UOP Corporation and PNNL predicted a cost of 2500 barrel per day (BPD)

facility is \$2.60/1000 BPD. By increasing the facility size to 30,000 BPD the cost /1000 BPD decreased to \$0.96.<sup>20</sup> Larger centralized refineries provide a strong economic incentive for industry to adopt widespread fuel production from biomass feedstocks. Pre-processing operations can increase economical transport distance by; using physical compaction, conversion to bio-oil, torrefaction, and/or cellulose enrichment prior to transport. Biomass logistic transport problems can be attenuated by biomass chemical or physical densification, by deploying mobile bio-refineries.<sup>21, 22</sup>

#### **1.4.- Densification Strategies and Fast Pyrolysis**

Fast pyrolysis to convert biomass into bio-oil is a promising densification approach. Bio-oil produced via fast pyrolysis is 7.5 times more energy dense than the original biomass.<sup>18</sup> Moreover, handling of liquids poses fewer obstacles, and is more compatible with existing infrastructure. Some prototypes of mobile pyrolysis units are currently being tested,<sup>23</sup> therefore near term implementation is feasible. Furthermore, small scale pyrolysis reactors are less dependent on the economies of scale compared to enzymatic hydrolysis and gasification. One potential solution is to use small scale pyrolysis units to produce char and oil to supply a centralized biomass to liquids (BTL) facility (See figure 1.3).<sup>18</sup> This approach provides a practical means to overcome logistical problems for economically competitive bio-fuels.

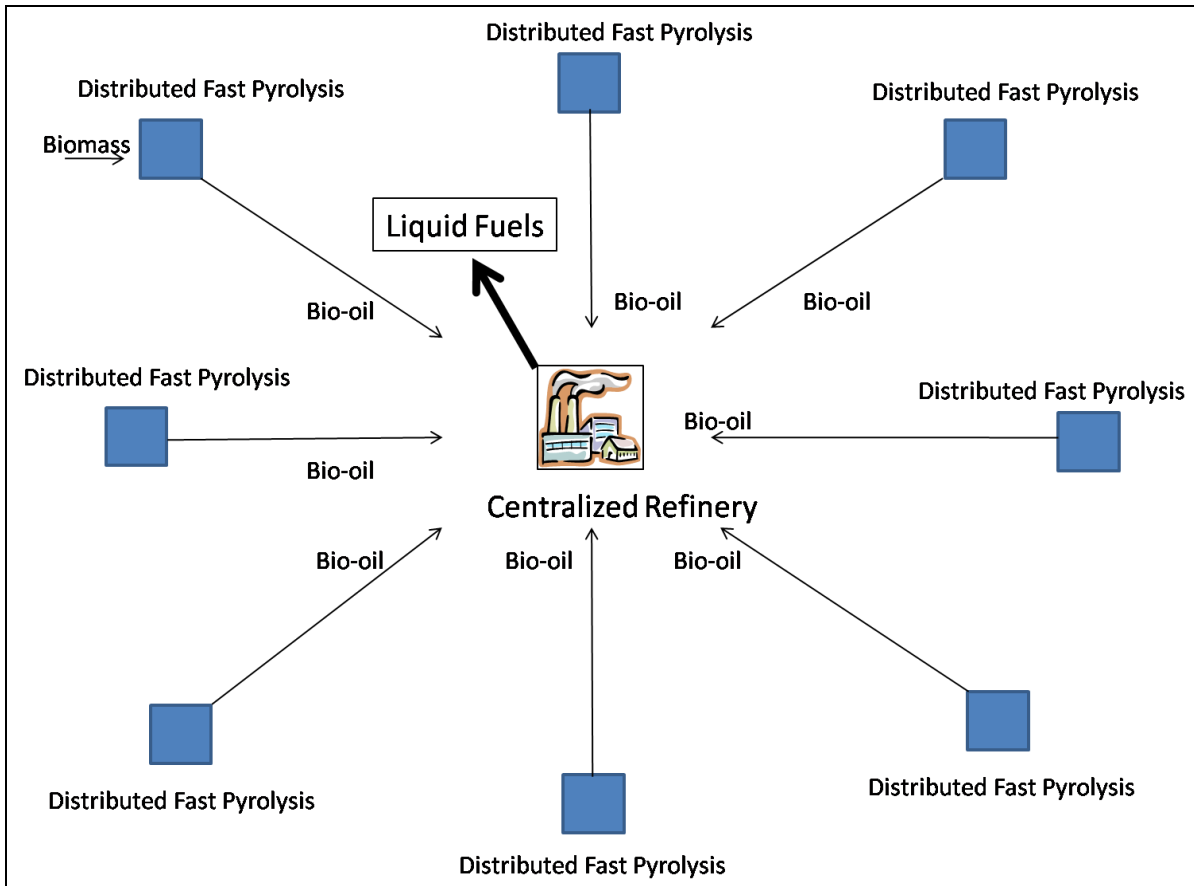


Figure 1.3: Distributed Pyrolysis Bio-refinery Concept

Although bio-oil as a direct substitute for diesel has many fundamental problems,<sup>24, 25</sup> it may be a suitable feedstock to produce second generation bio-fuels.<sup>26-28</sup> Technology currently exists to convert bio-oils into green gasoline, ethanol and syngas.<sup>24, 28, 29</sup> Many of these conversion routes would be similar to what is currently required for petroleum refining or fermentation technology.

### 1.5.- Fast Pyrolysis Reactors

Heating rate is one of the most important factors influencing the distribution of pyrolysis products. If biomass is heated very quickly (1,000°C–10,000 °C/min), it is said that the reactions

happens in the fast pyrolysis region. It is clear that due to low thermal conductivity of biomass (0.1 W/mK along the grain, and 0.05 W/mK cross grain),<sup>30</sup> the primary parameter for production of high yields of liquid is heating rate, which is controlled by the biomass particle size and design of the reactor. If gradients of temperature exist within a given particle, many regions of the particle spend substantial amounts of time in the 200-350 C range and crosslinking reactions predominate, resulting in substantial conversion to char. Processes using large particles and slow heating rates are termed as “slow pyrolysis”.

Slow pyrolysis of biomass is an extremely old technology that has been used primarily for the production of charcoal for cooking and home heating. Charcoal produced from slow pyrolysis is still a major source of energy used in daily life in Africa. Although this technology is established, low tech, and effective there are numerous environmental and economic reasons to substitute this practice with more efficient and environmentally benign approaches. During slow pyrolysis most of the biomass is released to the atmosphere as gases or vapors which greatly contribute to green house gas emissions.

Alternatively, fast pyrolysis relies on biomass being heated very quickly, followed by immediate release of volatiles which are condensed to produce large quantities of bio-oil. This concept was first demonstrated in the 1980's by the Waterloo group in Canada. This group applied fluidized bed technology for biomass pyrolysis. Their results gained much attention due to a substantial change in the ratio of liquids and char produced compared to slow pyrolysis. The Waterloo group used heating rates of (100–1000 °C/min), gas residence times (30 - 1500 ms)<sup>30</sup> and finely ground particles (< 2mm) to convert between 60 and 75 mass % of the dry biomass into a liquid bio-oil, between 15 and 25 mass % of solid char, and 10 - 20 mass % of non-condensable gases. This

process was coined “the Waterloo Fast Pyrolysis Process (WFPP)”. A diagram of a fluidized bed reactor is given in Figure 1.4. The carrier gas enters from the bottom after being heated to the desired temperature. The hot gas is injected into the sand bed through the distributor plate as the means to fluidize the sand bed. The biomass is fed into the fluidized bed and despite efforts to feed low into the sand bed particles are carried to the free board in less than 1 second, and it is therefore in the freeboard where the majority of devolatilization occurs.<sup>31</sup>

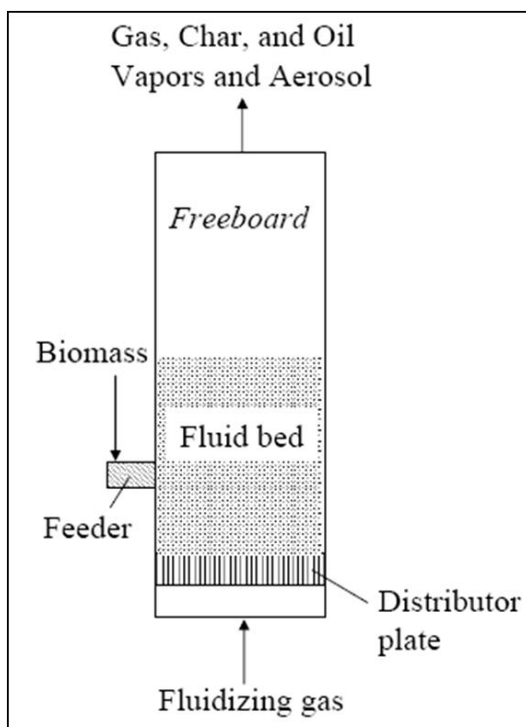


Figure 1.4: Schematic of fluidized bed reactor<sup>32</sup>

One of the major advantages of fast pyrolysis is the very high efficiency of the process. Although devolatilization reactions are endothermic, the poly-condensation reactions are highly exothermic, depending on the final yield of charcoal produced the overall process can be slightly endothermic or exothermic. Moreover, the charcoal that is generated can be used to provide heat for the process, and the non-condensable gases can be recycled to be used as the carrier gas.

With a system configuration that uses both the non-condensable gases and char the process efficiency can be up to 90%.<sup>32</sup>

Since the demonstration by the Waterloo group that a fast pyrolysis using a fluidized bed produced higher yields of bio-oils, other reactor designs capable of similar results have been proposed. All of these specific reactors have advantages and disadvantages. Table 1.1 gives an overview of the advantages and disadvantages of each of these reactors.

**Table 1.1.-** Advantages and disadvantages of Biomass fast Pyrolysis Technologies.

<b>Reactor</b>	<b>Particle Size</b>	<b>Liquid Yeild (wt%)</b>	<b>Inert Gas</b>	<b>Complexity</b>	<b>Scale Up</b>	<b>Specific Size</b>	<b>Status</b>
Fluidized Bed	Small	75	High	Medium	Easy	Meduium	Demo
Circulation (FB)	Medium	75	High	High	Easy	Large	Pilot
Entrained Flow	Small	65	High	High	Easy	Large	Lab
Rotating Cone	Small	65	Low	High	Hard	Small	Pilot
Ablative	Large	75	Low	High	Hard	Small	Lab
Auger	Small	65	Low	Low	Easy	Meduium	Lab
Vacuum	Large	60	Low	High	Hard	Large	Demo
Microwave	Large	50	Low	Medium	Easy	Meduium	Pilot

Adapted from PYNE IEA Bioenergy <http://www.pyne.co.uk>

Some of the most important fast pyrolysis reactors so far developed are:

1. **Ablative pyrolysis** uses physical scraping of wood against a heated surface. This leads to the outer surface being in a fast pyrolysis environment and the char is then scraped away as it is formed to prevent slow pyrolysis from predominating. This process has the advantage of removing the char as it is formed. This process uses larger particles of wood and is typically limited by the rate of heat supply to the reactor. It leads to compact and intensive reactors that do not need a carrier gas, but have the disadvantage of a surface area controlled system and moving parts at high temperature.<sup>33</sup>

- 2. Fluid bed and circulating Fluid bed** are reactors in which the heat is transferred from a heat source to the biomass by a mixture of convection and conduction. The heat transfer limitation is within the particle, thus, requiring very small particles of typically not more than 2 mm to obtain good liquid yields. Substantial carrier gas is needed for Fluidization or transport reducing the overall thermal efficiency of the process.<sup>33</sup>
- 3. Vacuum pyrolysis reactors** do not achieve high heating rates, however, pyrolysis products are rapidly removed from the reactor thus simulating in some ways fast pyrolysis. Larger particles can be used and the vacuum leads to larger equipment and higher costs. Total liquid yields are typically between 60-65% compared to 60-75 mass % from fluidized bed reactors.<sup>33</sup>
- 4. Auger reactor uses a auger to mix hot sand and biomass.** This process requires little carrier gas but has not been as thoroughly studied as fluidized bed reactors.<sup>23,34</sup>
- 5. Entrained flow pyrolysis reactors** are used primary for experimental purposes.<sup>35,36</sup>
- 6. Microwave assisted pyrolysis** this is a new alternative to overcome the need for very fine biomass particles.<sup>18,37,38</sup>

All these reactors have several features in common. All of them are based on the principle of heating the biomass very fast and removing and condensing the vapors as quickly as possible. Ablative reactors can circumvent the need for small particles by scraping char from the surface, these features and its very compact design makes these reactors very promising candidates for transportable pyrolysis units.

## **1.6.- Approaches to enhance the selectivity of primary thermochemical reactions.**

Despite the excellent outlook for a distributed fast pyrolysis systems for biomass densification there exists several factors that could to be improved for more efficient processing and refining of bio-oil. One such factor is *the inability to control the reactions converting the cellulose into molecules that can be used as precursors of transportation fuels (anhydrosugars) (selectivity).*<sup>4</sup> The lack of selectivity of pyrolysis reactions creates bio-oils that are difficult to refine and that are unstable.<sup>39</sup> Controlling these reactions has been an elusive goal.

The use of heterogeneous catalysts to control primary thermochemical reactions is of limited value because the primary thermochemical reactions reactions happen in the solid matrix, and therefore action of catalyst is limited by mass transfer. Another approach to control the selectivity of fast pyrolysis reactions is to alter the composition and structure of the material before undergoing fast pyrolysis.<sup>4, 40-43</sup> Using pretreatment operations to modify the structure of biomass prior to fast pyrolysis could improve the characteristics of bio-oil's produced.

## **1.7.- Conclusions**

Pyrolysis is a promising densification strategy to convert lignocelulosic materials into bio-oils and charcoal. Although controlling the moisture content and particle size has been the primary focus of most of the research reported in the literature, new concepts for biomass pre-processing for thermo-chemical conversion technologies could be developed as a way to produce bio-oils with improved quality and stability. Greater mechanistic understandings of the subtle details that govern thermochemical selectivity add another dimension to preprocessing. It may be possible



to alter the structure of biomass constituents to improve the selectivity of thermochemical reaction towards the production of larger yields of anhydrosugars.

Thus, the next chapter will be devoted to review the thermochemical reactions that needs to be controlled enhance the formation of anhydrosugars.

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# Chapter 2

## Fundamentals of Biomass Thermochemical Reactions

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### 2.1.- Introduction

The composition of bio-oil depends on the process conditions, feedstock composition and technology used. This chapter is devoted review the interrelations between biomass composition, pyrolysis operating variables and the selectivity of thermochemical reactions towards the production of anhydrosugars.

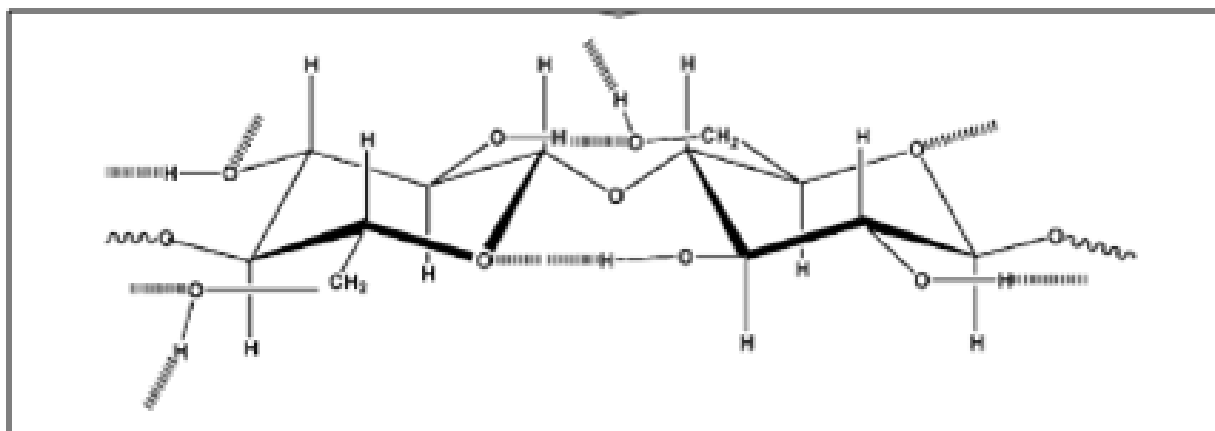
### 2.2.- Biomass Constituents

Biomass is composed of: cellulose, hemicelluloses, lignin, extractives and mineral materials also called ash.

#### 2.2.1- Cellulose

Cellulose is the most abundant source of renewable organic matter on earth, and it is estimated that at any given time  $2.0 \times 10^{15}$  kg of cellulose is present in the biosphere.<sup>1</sup> Cellulose is a major structural component in the cell walls of plants and photosynthetic algae. It is a homogenous polymer that is nearly composed uniformly of glucose, and is considered to be a promising feedstock for fuel production.

Cellulose is responsible for the fibrous properties of plant material. It is an un-branched homopolysaccharide composed of  $\beta$ -D-glucopyranose units linked by  $\beta(1-4)$  glycosidic bonds. Physical properties of cellulose can be in part explained from the three dimensional configuration of this bio-polymer. The 3-D structure of cellulose has the pyranose rings in the chair conformation, with the hydroxyl groups are in equatorial position (Figure 2.1). The beta linkage geometry makes the polymer assume linear three dimensional structures with numerous hydrogen bonding sites to stabilize the linear polymer configuration. Specifically cellulose has intra-molecular hydrogen bonds from O3–H3•••O5 and O2–H2•••O6 and intermolecular hydrogen bonds from O6•••O3 making a highly crystalline material that is insoluble in aqueous solution, and resistant to enzymatic attack.<sup>2</sup> The specific configuration of cellulose can be altered through chemical treatments. In nature cellulose I is the predominant form, it is the kinetically stable allomorph. Cellulose II is more thermodynamically stable and is produced from processing cellulose I. The cellular mechanism of cellulose formation is believed to be a critical factor that favors the natural predominance of cellulose I.



**Figure 2.1-** Cellulobiosan Unit

Cellulose properties are also dependent on other factors, not directly related to 3D configuration. The degree of polymerization and crystallinity are very important parameters affecting the mechanical and thermo-chemical behavior of this bio-polymer. In nature, the degree of polymerization (DP) and crystallinity of cellulose varies depending on the cell type plant species and which layer of the cell wall the cellulose is in. For example wood generally has a DP of 10,000 and cotton has a DP of 15,000.<sup>2</sup> Additionally cellulose in nature contains regions that are not crystalline and are termed amorphous regions of cellulose. There are differences in cellulose properties not only between species but between cell wall regions, and ages of cells. For example there is a drastic difference in the fiber angle when looking at juvenile wood and mature wood. There is substantially more amorphous cellulose in the primary cell wall than secondary cell walls. It has been shown that heat treatment; acid hydrolysis and a variety of biomass processing regimes will alter the DP and the crystallinity, typically reducing the DP and increasing the crystallinity.

In addition to the chemical structure, the macromolecular characteristics of cellulose, defining how the molecules are assembled to form fibers, are also of great importance. Cellulose super structure assembles from individual chains to form micro fibrils that assemble to form fibrils and subsequent fibers.<sup>3</sup>

### *2.2.2.- Hemicelluloses*

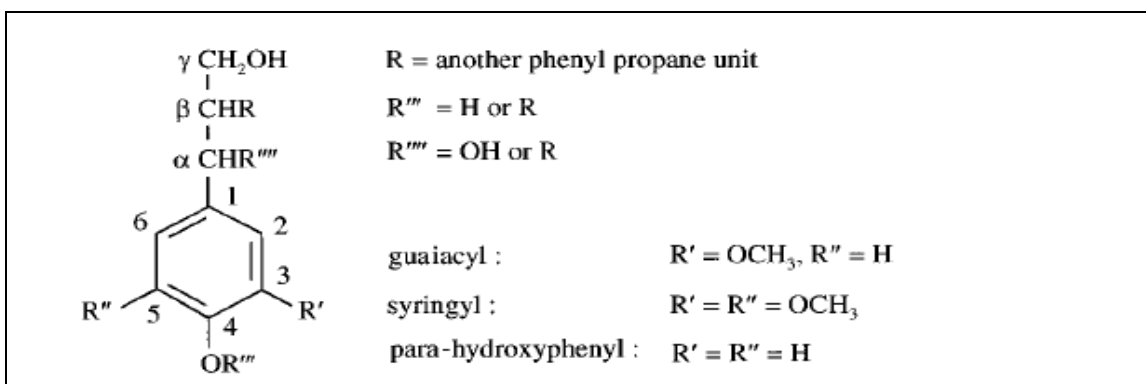
Hemicellulose is an amorphous polymer that acts as a protective coating around the cellulose fibrils. Hemicellulose is substantially more labile and is easily extracted with acid treatments or elevated thermal treatments. The Hemicelluloses are the second major carbohydrate fraction in biomass. Unlike cellulose, they are highly substituted with organic acids and are covalently



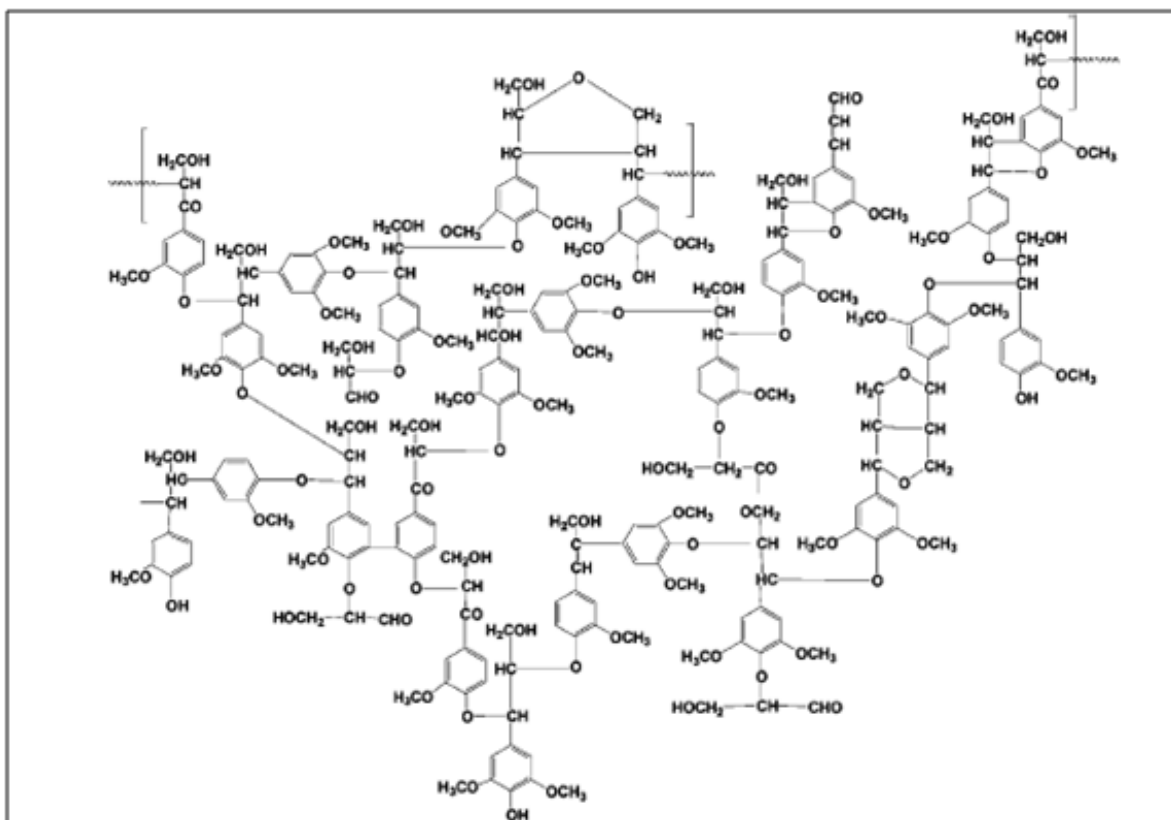
linked to lignin. Hemicelluloses are typically composed of the following sugars: D-glucose, D-galactose, D-mannose, L-arabinose, D-xylose and acid 4-O-methyl D-glucopyranoid. Depending on the type of plant the ratio's of these sugars can be highly variable, but typically xylose is the most predominant sugar, accompanied by various of the other pentoses and hexoses polysaccharides. Woody material tends to have high percentages of xylose and less arabinose compared to straw and grassy plants.

### 2.2.3.- Lignin

Lignin is a heterogeneous polymer consisting of phenyl-propane units linked with numerous ether and alkyl covalent bonds (see Figure 2.2 and 2.3). It is composed primarily of three types of aromatic polymers: guaiacol, syringyl, and phenolic subunits. Due to the random mechanism of lignin polymerization there may be impossible to establish a precise structure of lignin. The function of lignin in plant cells is analogous to cement in a reinforced concrete structure, which encapsulates the fibrous cellulose and hemicellulose matrix. Moreover the high content of phenolics in lignin serves to inhibit microbial growth. Lignin is covalently linked to hemicellulose and associates with cellulose via Van-der-Waals forces and hydrogen bonds.



**Figure 2.2.- Monomer Nomenclature**



**Figure 2.3.-** Proposed structure for Lignin

#### 2.2.4.- Extractives

The “extractives” are another family of compounds present in plant biomass. Wood extracts can be removed by treating the biomass with polar solvents (such as water, methylene chloride, or alcohol) or by using non-polar solvents (such as toluene or hexane). Extractives are generally classified as fats, waxes, alkaloids, proteins, phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils. Extractives function as intermediates in metabolism, serve as energy reserves, and inhibit microbial and insect infestation.

### 2.2.5.- Ash content

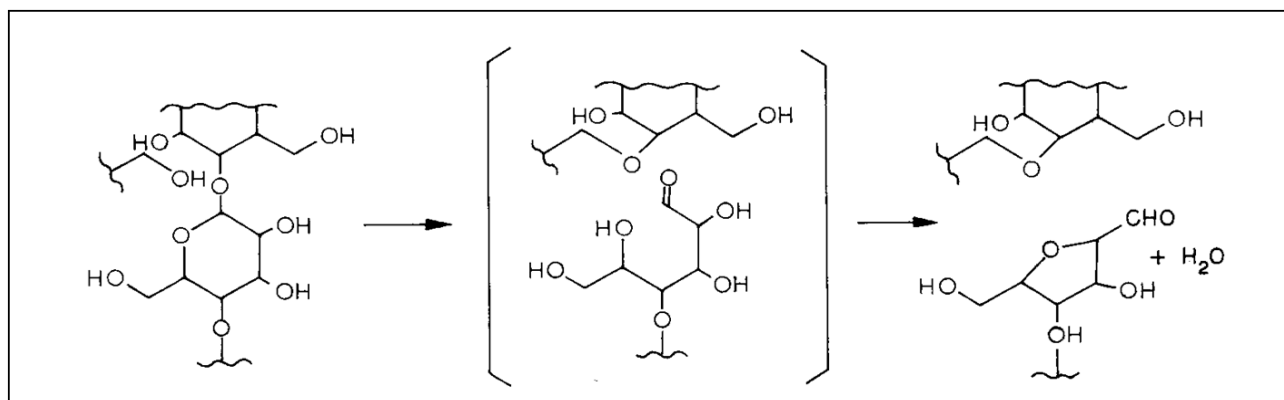
Biomass is also composed of a small amount of metals (K, P, Na, Ca, Si, Mn and Mg). These metals are believed to be present in the form of cations conjugated to esterified acid groups. Straws and grasses also contain relatively high amounts of Si, and SiO<sub>x</sub>.

### 2.3.- Cellulose Thermochemical Reactions

During pyrolysis the initial cracking and condensing of bonds that occurs when biomass is heated is called primary thermal decomposition reactions. These reactions occur mainly on wood cell walls<sup>4-7</sup> and result in the formation of char, tars, and gases. The volatile species formed by these primary reactions may undergo secondary homogeneous and heterogeneous reactions along the diffusion path on their way out of the particle and as the vapors are carried away to the condensers.<sup>8, 9</sup> The products of pyrolysis are both a function of the primary reactions and secondary reactions. It is also important to note that numerous chemical species are produced from the pyrolysis of cellulose, leading to complex mixtures of primary and secondary organics. The review presented in this chapter will focus only on cellulose primary reactions.

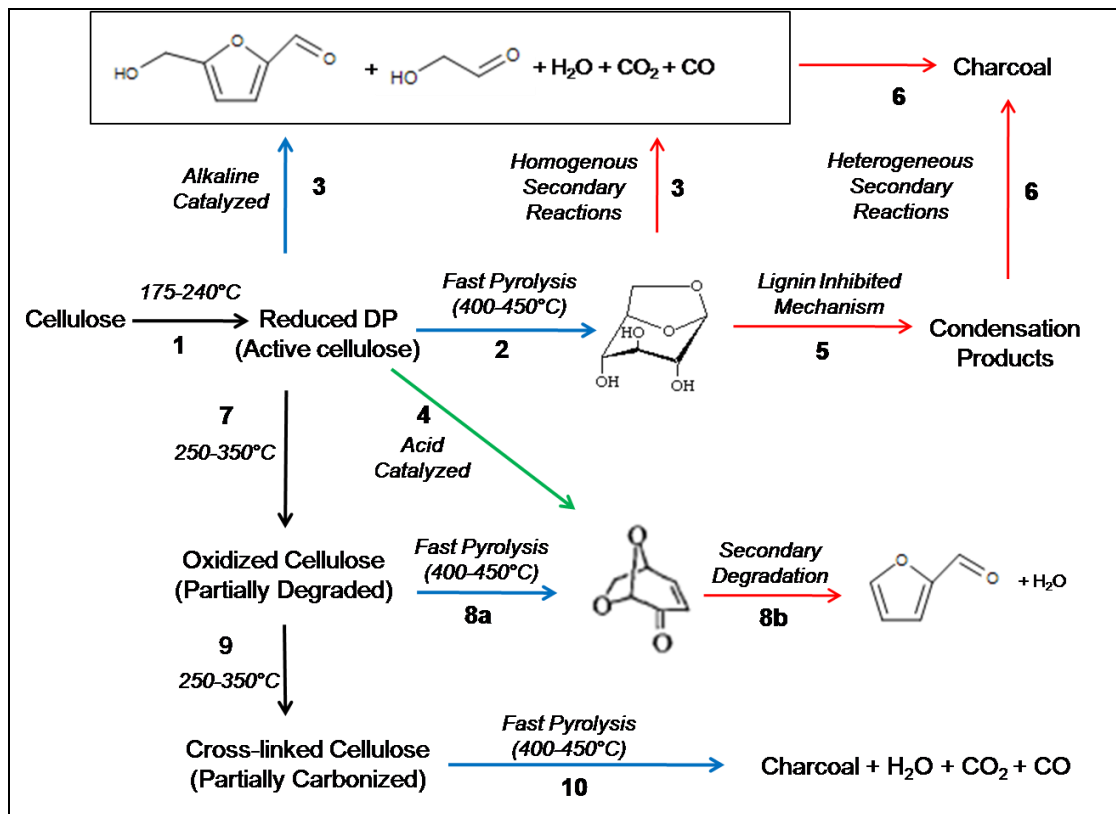
Cellulose thermo-chemical reactions can be divided based on the range of temperature at which the reactions happen into: low temperature reactions (<300°C) and high temperature reactions (>350°C). When Cellulose is heated below 350°C oxidation, dehydration and crosslinking reactions predominate. These reactions are characteristic of slow pyrolysis processes. At temperatures between 200 and 250°C a drastic reduction in the degree of polymerization of cellulose as well as an increase in crystallinity occur. Prolonged heating at higher temperatures induces cross linking reactions that lead to the formation of extra-charcoal and higher yields of

water.<sup>10, 11</sup> Figure 2.4 shows the Broido mechanism typically used to explain cellulose crosslinking. At temperature higher than 350°C depolymerization and fragmentation reactions predominate.



**Figure 2.4.-** Broido rearrangement reaction mechanism

Figure 2.5 provides an overview of the major degradation pathway of cellulose in the temperature range between 200 and 600 °C. Much experimental evidence suggests that cellulose thermal degradation proceeds following seven major reactions: (1) weak bond breaking reactions to produce active cellulose;<sup>12-18</sup> (2) de-polymerization of active cellulose to produce mono- and oligo-sugars;<sup>19-22</sup> (3) fragmentation or open ring reactions controlled by the presence of alkalines<sup>23-27</sup>; (4) acid catalyses dehydration reactions;<sup>28-30</sup> (5) polymerization of anhydrosugars;<sup>31-34</sup> (6) crosslinking reactions of fragmentation products to produce char. If cellulose is treated with heat or oxidizers active cellulose can be converted to a mildly oxidized form<sup>28</sup> (7) that under the action of heat will lead to higher yields of levoglucosenone and furfural (8).<sup>30</sup> Continued heating will lead to (9) crosslink cellulose that when heated to pyrolysis temperatures form predominantly char (10).<sup>35 36</sup>



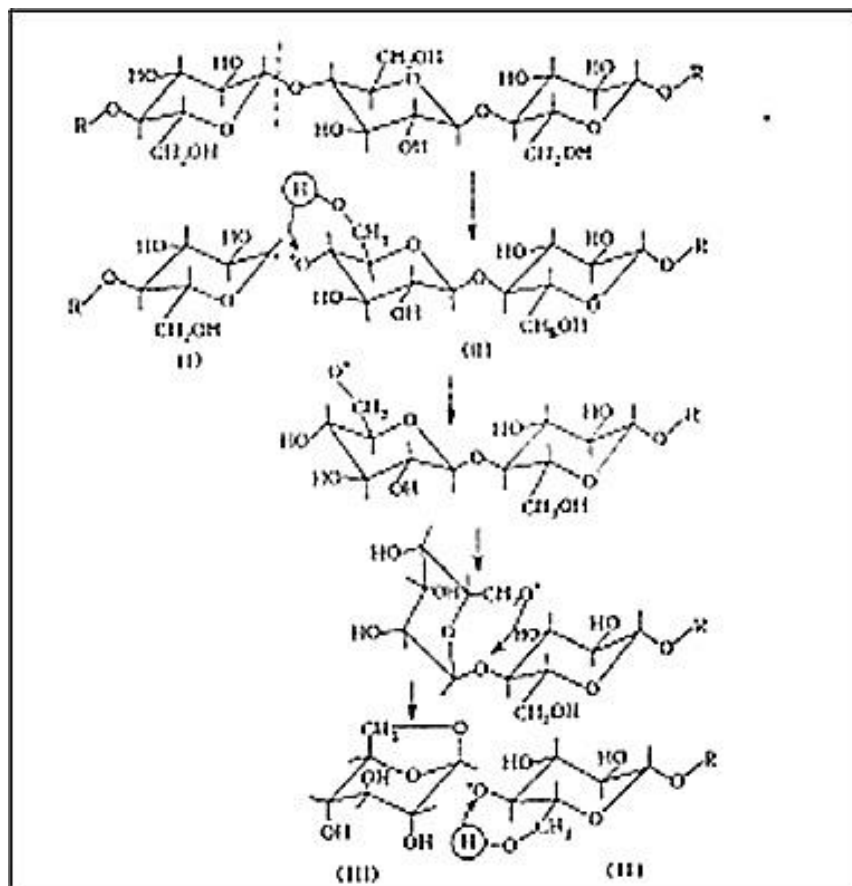
**Figure 2.5.-** Cellulose degradation Pathways

It has been well established that sustained heating cellulose at temperatures of 220–250°C cause a drastic reduction in the degree of polymerization, increase in crystallinity, evolution of water, formation of carbonyl, carboxyl and hydroperoxide groups, and evolution of carbon monoxide and carbon dioxide, finally leaving a charred residue.<sup>22</sup> A classic review<sup>12</sup> shows evidence that supports a two step thermal decomposition of cellulose. The literature shows that decomposition begins with a sharp decrease in DP with moderate losses in weight of 5% and 20–30% for cotton cellulose and cellulose hydrate respectively. The degree of polymerization then remains constant until nearly 80% of the cellulose is decomposed, and typically has DP of 200-300 and 30-50 for the two modifications. It is important to note that the mass loss during the first stage

results in a low yield of levoglucosan and a sharp drop in the DP; the subsequent mass loss gives substantially greater yields of levoglucosan, in which DP remains constant. A similar phenomenon is also observed during cellulose acid hydrolysis<sup>27</sup> and can be explained by the existence of 4-5 disordered units in every 300 ordered units in the cellulose micro-fibrils. Cellulose molecules with a degree of polymerization between 200 and 300 glucose units are known by the thermo-chemical research community as “active cellulose.”

### *2.3.1.- Mechanisms of depolymerization reactions*

Two theories (free radical and heterolytic de-polymerization) have been proposed to explain the mechanism of depolymerization reactions. Experiments have been conducted using addition of dinaphthylphenylenediamine as a free-radical scavenger to test the affect on levoglucosan yields. These results showed that the levoglucosan yield was reduced from 30 to 5 % with the addition of this free radical scavenger. This experiment provides strong evidence that a free radical scission is required during the cleavage of the beta linkages. The free radicals can act as triggers of depolymerization reactions. The mechanism for radical mediated formation of levoglucosan begins with the formation of a radical in the glycosidic linkage. Next a proton is donated from carbon 6 and a new radical is formed. This alkoxy radical can then attack carbon 1 and form the 1-6 anhydro linkage and liberate levoglucosan. The carbon four radical then repeats the transfer and the process continues. (Figure 2.6)

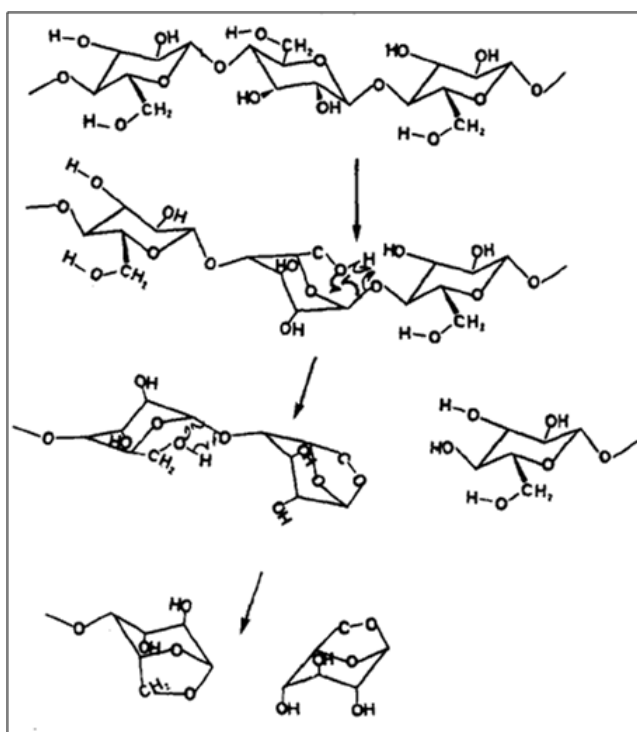


**Figure 2.6.-** Radical mediated depolymerization mechanism for levoglucosan formation<sup>12</sup>

Experiments conducted by Shafizadeh support the heterolytic de-polymerization theory. The author used phenyl glycosides model compounds to study the ring substitution effects on transglucosidation. His results suggest that a heterolytic mechanism predominates as evident by a strong effect of ring substitution on the formation of anhydrosugars. It should be noted that these experiments were conducted using model compounds, and that the model system used may not be truly representative of the environment surrounding cellulose molecules.

The proposed mechanism for heterolytic de-polymerization to form levoglucosan speculates that several possible transformations could be occurring that contribute to the reduction of the rate-limiting step. High temperature causes a decrease in DP, the breaking of inter- and intra-

molecular hydrogen bonding to form a less rigid structure (i.e., a glass transition zone), the formation of a reactive intermediate by the cleavage of the glycosidic linkage (free radical or ionic species), or the inter-conversion from the chair to the twist conformation so that the carbon in the 6-position will be in the axial position as it is in levoglucosan. These changes allow for the oxygen on carbon 6 to be mobile for a  $S_N2$  substitution on C1 liberating levoglucosan and rendering the next monomer in the chain available to repeat the process<sup>6</sup> (Figure 2.7). Recent evidence using 2D Infrared spectroscopy shows that intra-molecular hydrogen bonds are broken at 220°C which provides a solid evidence to support Evans hypothesis and may provide a mechanistic explanation for the large reduction of DP observed at this temperature<sup>37</sup> Elucidation of the specific role heating plays in the subtle changes in hydrogen bonding and Structural conformations is one research area that should be further explored.



**Figure 2.7.-** Heterolytic mechanism for levoglucosan formation



Another source of debate in the literature is if the cellulose de-polymerize in a random or in a sequential manner. The first mechanism hypothesis, proposed by Broido<sup>13</sup> suggests that the de-polymerization of cellulose occurs by random cleavage of glycosidic linkages. The second mechanism, proposed by Golova,<sup>12</sup> states that once a chain reaction is initiated, the whole chain “unzips” to form mono and oligo anhydrosugars. The evidence presented by Golova to support a un-zipping mechanism relies on data comparing levoglucosan formation from cellulose hydrate and cotton cellulose. Cellulose hydrate has DP of 30-50, and cotton cellulose has DP of 200-300 of cotton cellulose, and the rate of decomposition of the cellulose hydrate exceeds that of the latter by 50%. This indicates the importance of the absolute number of terminal monomer units in thermal decomposition. Therefore if the rate of decomposition is dependent on the number of terminal end groups the processes is presumed to follow a chain de-polymerization that is initiated at the terminal end, thus more terminal ends available leads to a higher rate of decomposition. Golova<sup>12</sup> concludes that since high yields of levoglucosan occur without, sharp changes in the DP the thermal de-polymerisation of cellulose can be regarded to begin in some activated region of the macromolecule, and proceeds via the complete breakdown of cellulose with the detachment of one glucose anhydride molecule after the other from the initiated end of the chain. The presence of radicals may act as a trigger of depolymerization reactions.

In addition to evidence that relies on the DP the effect of cations on the production of anhydro-sugars also provides significant evidence supporting the unzipping hypothesis: It is well established that even trace amounts of cations lead to formation of very little sugars and mostly gases. This is occurring despite concentrations that are as low as 1 ion/ 3-5 thousand monomeric units. This demonstrates that the interaction of cations with only a few end chain groups can potentially affect the overall degradation mechanism. It is interesting that as little as 0.1 mass %

potassium or sodium has a strong effect to catalyze: the formation of low molecular weight carbonyl compounds such as acetaldehyde and acetol and high molecular weight condensed species leading to the formation of extra-char. The cations act to modify the terminal moiety and disrupt the first monomer to un-zip. Essentially if the terminal monomers are perturbed from formation of levoglucosan the entire levoglucosan formation mechanism is abolished. This has been described by Piskorz<sup>11</sup> as a capping of the end groups. In these circumstances fragmentation reactions tends to predominate.

There are evidences suggesting that the cellulose chains can also de-polymerize in a random fashion. Currie point pyrolysis studies at high heating rates and temperatures close to 500 °C have shown the presence of large quantities of cellulobiosan and other oligosugars in the tars. The decomposition of cellulose to form cellobiose and other sugars cannot be explained by the classical unzipping mechanism based on the end group concerted depolymerization. It has been proposed that there is a molten transition state that the cellulose undergoes prior to de-polymerization at 450°C, and that from this molten state the cellulose de-polymerizes in a random chaotic manner.<sup>21</sup>

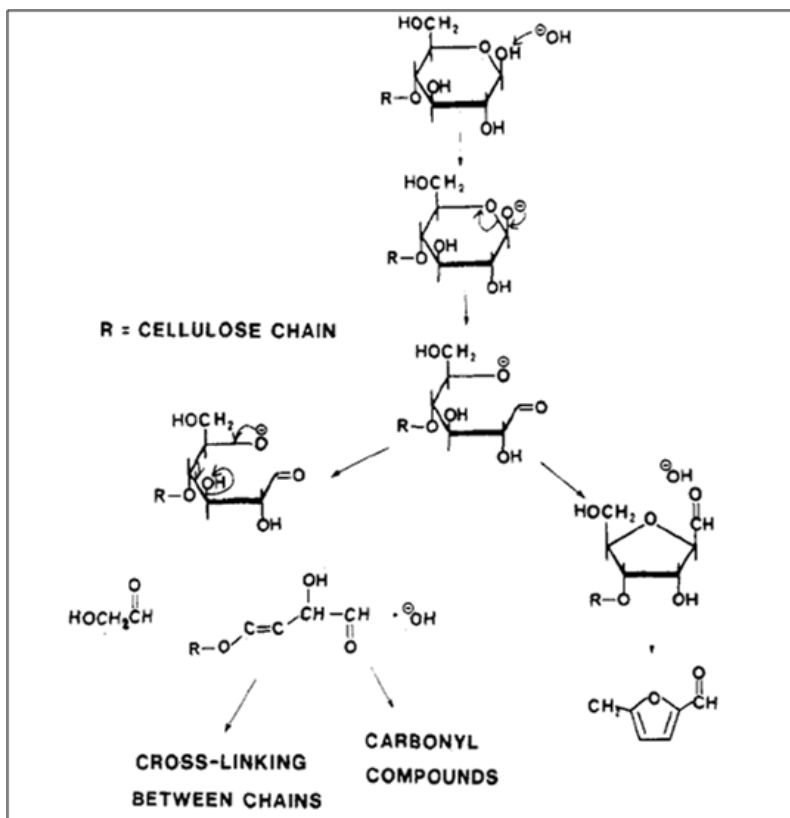
### *2.3.2.- Mechanisms of fragmentation reactions*

A good description of fragmentation of sugars has been summarized elsewhere.<sup>38, 39</sup> Aldoses are enolized to form more reactive 2-ketoses. Ketohexoses undergo dehydration to form hydroxy methyl furfural (HMF). Furanics can undergo further dehydration and fragment to yield formic acid and levulinic acid from hexoses. 2-ketoses can be fragmented to yield dihydroxyacetone and glyceraldehyde, glycolaldehyde, and four carbon carbonyl compounds. Dehydration of trioses to yield acetol and pyruvaldehyde; dismutation of biose, trioses, and tetroses and their dehydration

products to yield lactic aldehyde, pyruvic aldehyde, lactic acid, glycolic acid, acetaldehyde, acetic acid, formaldehyde, formic acid, and acetone also happen. These aldehydes and ketones further react to form intra or inter molecular cross linked structures. There may also be re-polymerization of aldoses and ketoses to form di-, tri-, and higher oligosaccharides. Dimerization of fructose to difructose anhydrides; cyclodehydration of aldoses to glycosans, and then polymerization; enolization and dehydration of the synthetic oligosaccharides have been also reported.<sup>39</sup>

Essentially the fragmentation of cellulose in primary reactions leads to the formation of furanics and small molecules. Experimental results shown in the literature<sup>40</sup> suggest that furfural and HMF are fairly thermally stable. Pyrolysis of furfural at 500°C only degraded about 10% of the original starting furfural. Therefore the secondary fragmentation of furfural is of minor importance for production of small molecules during pyrolysis.

Another experiment to address the questions pertaining to fragmentation de-polymerization was conducted by Kato.<sup>40</sup> This experiment compared the volatiles produced from pyrolysis of cellulose, cellobiose, glucose, and levoglucosan between temperatures of 250-500°C. The results showed that the relative amounts of furfural and HMF from cellulose were higher than those arising from levoglucosan. If most of the pyrolytic degradation proceeded through levoglucosan, the amounts of volatiles furanics and small molecules should be higher in the levoglucosan condition and not the cellulose. Kato concluded that the mechanism calling for the formation of furanics and small molecules via levoglucosan intermediate step seems to be a minor reaction in the overall process. Evans has proposed a mechanism to explain the fragmentation to form furanics and small molecules.<sup>6</sup> (Figure 2.8)



**Figure 2.8.-** Alkaline catalyzed fragmentation mechanism <sup>6</sup>

## 2.4.- Conclusions

The description summarized above reveals the competitive nature of several reaction mechanisms in the pyrolysis of cellulose. Conditions which result in the selective formation of levoglucosan from cellulose realize very low yields of hydroxy-acetylaldehyde, and char. The pyrolysis temperature, cellulose degree of polymerization and the presence of trace amounts of alkaline cations have a major effect on the selectivity of thermochemical reactions towards the production of anhydrosugars and determines the product distribution.<sup>11</sup>

The most important factors controlling the selectivity of cellulose thermochemical reactions towards the production of anhydrosugars are: degree of polymerization, crystallinity, presence of antioxidant (lignin) controlling the concentration of radicals, content of alkalines and pyrolysis

temperature. In the next chapter we will review how these parameters can be modified through pretreatment to enhance the production of anhydrosugars via fast pyrolysis.

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## Chapter 3

### Pretreatment Technologies to Enhance the Production of Anhydrosugars During Fast Pyrolysis

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#### 3.1.- Introduction

Pretreatment is critical for all chemical and biological conversion technologies (i.e. pulp and paper, enzymatic hydrolysis). Although, numerous technologies have been developed to weaken the recalcitrance, improve fiber quality, and fractionate lignocellulosic materials for biological, mechanical and chemical conversion; research of pretreatment technologies for thermochemical conversion is still in its infancy. Many biologically based bio-refineries consider thermochemical conversion the last step to convert only the material that can't be biologically converted. It is therefore necessary to re-examine pretreatment technologies while keeping in mind what effects these technologies could have to enhance the selectivity of thermochemical reactions towards the production of anhydro-sugars. This section will give an overview of the pretreatment technologies that have been studied as part of the biological platform and will stress on effect these technologies will have on the structure and content of cellulose, hemicelluloses and lignin. This information is important to better understand how to improve conversion of cellulose into anhydrosugars via fast pyrolysis.

#### 3.2. Drying

Reducing biomass moisture content is critical to minimize both logistic and processing problems. Transport of wet biomass can add extra transportation cost to material that is already very

difficult to transport economically. Grinding biomass into small particles is far less energy intensive when biomass is dry.<sup>1</sup> Fast pyrolysis of dry biomass is preferred because pyrolysis of a wet biomass consumes a substantial amount of energy to evaporate and heat the water. It has been reported that extensive biomass drying reduces the yields of chars and gases<sup>2</sup> and the water content and acidity of bio-oils.<sup>3</sup> Furthermore, lower moisture content reduces the residence time needed in the reactor.<sup>4,5</sup> For fast pyrolysis processes, it is strongly advised to reduce the moisture content below 10 mass%.<sup>6</sup>

### *Process Description*

Biomass can be dried in the open air, by being exposed to direct sun-light or with kilns. Air and sun drying are the most common methods used to dry agricultural residues (wheat straw or corn stover) which are left in the field until dry. Air drying is also commonly used for lumber production. Although air drying is cheap and effective the time requirement is not suitable for many large industrial applications. Getting biomass moisture content below 20% is very difficult with air drying.

Drying biomass in kilns using high temperatures greatly reduces the time required to reduce the moisture content below 20 mass %. Due to the high energy requirements to dry excessively wet biomass,<sup>7</sup> most systems use air drying first, followed by kiln drying in a second step employing process waste heat. Drying ground biomass is typically faster and can be operated continuously. Common designs for dryers are rotary drum dryers and suspension dryers. Rotary drum driers are the most common type of drying equipment used in industry.<sup>7</sup> Hot flue gas or super heated steam are commonly used for drying biomass.<sup>8</sup> Excellent reviews on the most common driers can be found elsewhere.<sup>7</sup>

### *Mode of Action and Utility for Pyrolysis Pretreatment*

Removing water from biomass requires the existence of moisture concentration gradients within the biomass and the outer surface. In this condition water transport can be described by two phase transport model: movement of water from the interior to the surface of the wood and evaporation of water from the surface. Water is transported within the interior as both a liquid and vapor and moves through voids in the structure and through cell walls. Generally the rate of transfer is faster through the openings than through cell walls, and explains why denser wood species require longer drying time than lighter species.<sup>9</sup>

### **3.3.- Grinding**

One aspect of biomass processing that is often overlooked is particle size reduction. This step affects the economy of the process. Size reduction doesn't lead to any additional value to the material, and grinding material into particles fine enough for fast pyrolysis is energy intensive.<sup>10</sup> The amount of energy required is highly dependent on the incoming feed, grinder used, moisture content, and final size required.<sup>1</sup> The effect of moisture content is positively correlated to increased energy requirements.<sup>1</sup> Additionally the type of feedstock and the type of grinder may be an important consideration. For example the energy required to grind hardwood is substantially lower using a knife mill compared to a hammer mill.<sup>10</sup> Generally grinding woody material is more energy intensive than agricultural residues. The energy required to grind a material from 22 mm to 1.6 mm particles will be between 10-130 kWh/ton.<sup>10</sup> Doing the energy balance this is equal to between 0.036 and 0.468 MJ/kg. Comparing this energy with the high heating value of incoming biomass (typically 17 MJ/kg) it can be said that the energy to grind varies from 0.2 % to 2.7% of the total energy in the original biomass. If we take into account that

conventional efficiencies to convert heat into electricity are below 30 %, then the electricity consumed by the grinders in fast pyrolysis units could represent between 0.66 and 9 % of the total energy available in the feedstock.

Sieving is another very energy intensive operation. Biomass must be sieved to ensure that a uniform particle size distribution is fed to the reactor. Furthermore, biomass passes over magnets to remove any metals, and metered to control the rate of biomass feed.<sup>11</sup>

### *Process Description*

Biomass is reduced in size by a combination of chipping, grinding and milling. Size reduction machines for large particle sizes, i.e. particles above 40 mm, are known as **crushers or shredders**, while smaller particles are processed by **mills**. Size reduction instruments have been developed for meeting the different demands placed on the mechanical preparation of solid substances. These comminution principles always stand in close relationship to the breaking properties of the sample, however, each case has to be considered individually. The *two most common designs for mills are knife or hammer mills*, although other low velocity comminution systems do exist.<sup>12</sup> Hammer mills use is limited to dry material with incoming size that is less than 4 cm.

### *Mode of action and Utility for Pyrolysis pretreatment*

To carry out a size reduction process smoothly and effectively the machine must be matched to the breaking behavior of the particular material. The density, hardness, consistency and biomass particle shape determine the kind of size reduction system to be used.

### 3.4. Torrefaction

Torrefaction is a mild thermochemical process (temperatures between 200 and 300 °C) that improves the fuel properties of biomass. Torrefaction reduces the moisture content and improves grind ability, hydrophobicity, and energy density.<sup>13</sup> The application of distributed torrefaction is similar to that of fast pyrolysis, and serves to improve the energy content of the biomass and reduce transportation costs. Torrefaction does have some promising features as a potential pretreatment for pyrolysis because the temperature ranges at which torrefaction is carried out contribute to hemicellulose<sup>14</sup> decomposition and removal. However, in the same temperature range it cellulose crosslinking resulting in higher yields of charcoal could also happen. A mild treatment, in the temperature range between 200 and 240°C may be a suitable strategy for biomass pretreatment for pyrolysis applications because cellulose crosslinking in this range of temperature is still very limited.

#### *Process Description*

Torrefaction can be carried out in a modified slow pyrolysis reactor or in a dryer connected to combustion gases. Essentially a huge variety of configurations can be used to torrefy biomass. One important environmental consideration is the condensation or combustion of VOC produced.

#### *Mode of Action and Utility for Pyrolysis Pretreatment*

Torrefaction at temperatures over 290°C can result in the dehydration of biomass and in a net decrease in the oxygen content (increase in C and H), making the material more energy dense. Although torrefaction is an excellent pretreatment for gasification, excessive crosslinking of

cellulose occurring at temperatures over 240 °C is not suitable for a fast pyrolysis applications seeking to attain high yields of bio-oils enriched in sugars.

### **3.5.- Acid Pretreatment**

It has been known for over 100 years that acids act as catalyst to convert ("hydrolyze") cellulose and hemicellulose into simple sugars (hexose and pentose, or "C6 and C5" sugars). This technology was applied by both Germans and Russians to produce fuel alcohol from wood to sustain war time fuel necessity. During this same period, in the United States (Springfield Oregon) a 15 million gallon per year ethanol plant was operated, and the Quaker oats company developed technology based on acid hydrolysis to produce furfural. The technology used in all of these plants shared similar problems to being economically competitive with fossil fuels: poor yields, high wastage, and the large volume of unmarketable by-products. Except for a few plants in Russia, and the Quaker oats process these technologies fell out of use after World War II.<sup>15</sup> Most of the current production of furfural is concentrated in China using corn cobs as a feedstock. Furfural is being commercialized primarily as an extraction solvent for petrochemical refining to remove dienes.<sup>15</sup> Recent studies motivated by the high petroleum prices has proven that the furfural or other furanic substitutes can also be used as extenders of transportation fuels.<sup>16, 17</sup>

The use of enzymes became popular in the 1970's, as a way to solve the problems of high degradation of sugars associated with acid hydrolysis. Since then, the cost of enzymes has decreased 20-30 fold.<sup>18</sup> Several companies currently produce cellulase enzymes, (NovoZyme, Genecore) at a cost competitive with acid hydrolysis. The low reaction temperatures, non-corrosive reaction media and no need for a neutralization step are some of the reasons making

enzymes preferable to acids.<sup>19</sup> Much of the recent research using acids focuses on pretreatment to improve the activity and accessibility of the cellulase enzymes. The dilute and concentrated acid hydrolysis systems have been greatly improved with the use of counter current and multistage pretreatments such as those commercialized by Blue Fire Ethanol Corp. Dilute acid pretreatment is performed by soaking biomass in dilute acid (concentrations typically below 4 mass %) followed by heating (140–200°C) for reaction times ranging from several minutes to one hour. Typically for pretreatment applications dilute acid are considered favorable to concentrated acids. This is due to lower cost for acids and acid recovery systems and less neutralization required before fermentation.<sup>20</sup>

#### *Process Description*

Biomass is typically mixed with acids solution into slurry as the material is fed into the reactor, typically (0.5-5 mass % acid). The slurry is heated to temperature range of 100-230°C for well established reaction times. After reaction has been completed the slurry is cooled and filtered. The solid is then used in the next step to produce glucose, and the liquid is treated to recycle the acid. The un-recycled acid is neutralized. Although various mineral and organic acids have been shown to be effective for hemicellulose removal, sulfuric acid is often preferred for industrial applications. Moreover, technology exists to recycle the acid and use the un-recyclable acid to produce gypsum making large scale processing more economical and environmentally friendly.

21-23

Most of the work in acid pretreatment has been done to enhance the biological conversion of cellulose to ethanol. One of the main drawbacks of this pretreatment approach is that some of the



degradation products resulting from acid pretreatment are inhibitory to fermenting organisms.<sup>24</sup>

25

### *Mode of Action and Utility for Pyrolysis Pretreatment*

The acids catalyze the hydrolysis of  $\beta$  (1–4) glycosidic bonds, ester linkages between sugars and organic acids (primarily acetic), aryl ethers between lignin moieties, and ion exchange with cations. This leads to nearly complete removal of pentose sugars and organic acids associated with hemicellulose, removal of some fraction of lignin (species dependent) and the leaching of inorganic materials from biomass.<sup>26, 27</sup> Removing the esterified acids associated with hemicelluloses through pretreatment could result in more stable, less acidic bio-oils.

The biomass resulting from acid hydrolysis typically has an increased crystallinity, lower degree of polymerization (DP) and virtually no inorganic materials.<sup>28</sup> The acid has additional catalytic activity on the sugars liberated from hemicelluloses leading to dehydration reactions to form furanic molecules such as furfural and hydroxy-methyl furfural. The further degradation of these compounds in the presence of acids results in the formation of levulinic acid.<sup>29</sup> The liquid produced from biomass dilute acid hydrolysis is a mixture of pentoses, furanics, organic acids, and some phenolics.<sup>30, 31</sup> Depending on the engineering of the system the degradation product formation can be either minimized to improve fermentation efficiency or maximized to produce furanics. For example, counter current treatment technology<sup>20</sup> has proven to be an effective way to limit the formation of furanics by limiting the time the sugars are in contact with severe conditions. Other Lewis acid solvents such as ionic liquids and other chemical methods have also shown to be very efficient to improve the yields of furfural and hydroxyl-methyl furfural from sugars.<sup>17, 32-35</sup>

Acid pretreatment could be an interesting approach to enhance the production of pyrolytic sugars. The removal of alkalines is critical to control the selectivity of cellulose thermochemical reactions towards the production of anhydrosugars.<sup>36</sup> The literature shows<sup>37</sup> that improved yields of sugars and lower yields of hydroxy-acetaldehyde resulted when the biomass was pretreated with diluted acid. In addition to the removal of alkalines, sulfate ions have been reported to act as catalyst improving the production of pyrolytic sugars.<sup>37-39</sup>

### **3.6.- Alkaline Pretreatment**

The use of alkaline chemical treatments is well established in the field of pulping and paper making. Treatment of biomass with strong bases such as NaOH, Ca(OH)<sub>2</sub> or NaS has the advantage of selectively solubilizing most of the lignin and to a lesser extent carbohydrates. Improvement of carbohydrate yields is still an important area of research.<sup>40</sup> Kraft pulping has advantageous to paper production because it results in paper with low lignin content . With advances in enzyme technology and the drive to produce ethanol via enzymatic cellulose hydrolysis the use of alkaline pretreatment has been extensively explored as a pretreatment technology for cellulose ethanol. The literature reports the used of numerous bases such as ammonia (NH<sub>3</sub>), sodium hydroxide (NaOH) and calcium hydroxide (Ca(OH)<sub>2</sub>) to delignify biomass and reduce cellulose crystallinity.<sup>20</sup>

#### *Process Description*

Alkali pretreatment processes utilize lower temperatures and pressures compared to other pretreatment technologies. It may be carried out at ambient conditions, but pretreatment time is measured in hours or days not minutes.<sup>41</sup> One of the major problems with bases catalyzed

pretreatments is that unlike acid-catalyzed pretreatment, some alkalis are converted to irrecoverable salts or are incorporated as salts into the biomass making recycle of the catalyst difficult.

#### *Mode of Action and Utility for Pyrolysis pretreatment*

Alkaline pretreatment breaks the bonds between lignin and carbohydrates and disrupts the lignin structure, which makes the carbohydrates more accessible to enzymatic attack. During alkaline hydrolysis, the hydroxide ion attacks the anomeric carbon atom, thus cleaving the ether bridge. With the uptake of water and liberation of the OH<sup>-</sup> ion, glucoses are formed. However, it is difficult to obtain a high yield of sugar because mono- and dimeric carbohydrates, such as glucose, fructose, or cellobiose, are severely attacked by alkalis at temperatures below 100 °C. Treatment with alkalis has shown to be effective and it is believed that the reasons are related to a decrease in cellulose crystallinity, lowered degree of polymerization, swelling, (leading to an increase in the internal surface area), and removal of lignin. Lignin is known to be a non-reversible inhibitor of cellulase enzymes and therefore removal of this component improves enzyme half life's and improves enzyme activity by improving the available surface area the enzyme can be in contact with.<sup>42, 43</sup> Moreover lignin monomers are toxic to the majority of fermenting organisms and removal of the lignin limits the inhibition of the organisms from residual lignin presence.<sup>44</sup>

The uses of bases have not been tested as pretreat for pyrolysis. This is in part because the removal of lignin and the decrease of cellulose crystallinity resulting from this treatment, are not desired properties for lignocellulosic material that will be pyrolysed. Furthermore, alkaline pretreatment is very slow, and therefore would require large equipment.

### 3.7.- Steam explosion

Steam explosion is another method to fractionate biomass that has been traditionally used to produce cellulosic ethanol or produce hard board. As early as 1925 steam explosion was developed for hardboard manufacture, and was known as the Masonite process.<sup>45</sup> Steam explosion has several characteristics that make it particularly competitive.<sup>46</sup> For example one striking advantage is that both physical comminution and chemical fractionation are both occurring. Steam explosion is recognized as one of the most cost effective pretreatment processes for hardwoods and agricultural residues, but it is less effective for softwoods.<sup>47</sup> It is currently used for commercial production of cellulosic ethanol by a number of companies including BioGasol ([www.biogasol.com](http://www.biogasol.com)). The solid remaining is physically and chemically modified making it more susceptible to enzymatic hydrolysis. Sugar yields approaching 95% have been reported using steam explosion pretreatment, compared to 15% in the un-treated control.<sup>45</sup>

One advantage of steam explosion is the ability to incorporate catalyst. This gives flexibility as to what feedstocks can be handled, and the severity of the chemical treatments undergone. For example softwood processing with steam explosion is generally not very effective, but the effectiveness can be improved with the addition of an acid catalyst. Acid catalysts, such as H<sub>2</sub>SO<sub>4</sub> or SO<sub>2</sub> improve hemicellulose, and lignin solubilization. If lignin destruction is what is needed, bases or oxidizing agents can be impregnated. Lastly, steam explosion degrades lignin to a point which 15-25% of the lignin can be extracted 90-95% pure using organic solvents or alkaline solution.<sup>48, 49</sup>

### *Process Description*

The commercial process involves first filling a vertical cylinder with wood chips. Once filled with chips, the cylinder is sealed and pressurized with saturated steam at pressures up to 7MPa. Steam-explosion, as a pretreatment process, can be performed either batch wise or continuously.<sup>48</sup> First the slurry is mixed into the tubular plug flow reactor until it reaches a flash tank and pressure is released. Steam is recycled followed by separation of the solids and liquids. The solid undergoes a lignin extraction leaving refined streams of lignin and cellulose.

### *Mode of Action and Utility for Pyrolysis Pretreatment*

The physical structure of the material is destroyed as a result of the material being permeated by the saturated steam which leads to high internal pressures. Instantaneous release of pressure leads to a violent decompression that physically destroys the cellular structural integrity. Essentially this substitutes the need for a separate milling operation. Low temperatures (190–200°C) result in blowing the fibers apart in the middle lamella, intermediate temperatures (217°C) reduces the number of fiber bundles and more fragments are observed, more severe (230–235°C) conditions lead to nearly complete destruction of the cellular structure.<sup>45</sup>

The action of super heated steam leads to hydrolysis of hemicellulose sugars, organic acids, and some lignin mechanistically similar to dilute acid or compressed hot water. Most of the sugars and acids can be recovered in the remaining liquid phase as oligomeric and monomeric sugars. Some of the pentose sugars will be converted to furfural, and other small oxygenated species. Steam explosion produces a material with a depolymerized lignin that can be extracted with aqueous organic solvents or aqueous alkali. When analyzing the degree of polymerization (DP)

of the lignin produced from several extraction method, the steam exploded lignin had the lowest DP, which is a clear indication of substantial bond hydrolysis.<sup>49</sup>

Steam explosion may be a good pretreatment for fast pyrolysis. It has the advantage of removing hemicellulose and esterified acids and causing physical destruction. Cellulose DP is also reduced. The temperature of the process is in the range in which active cellulose forms. The crystallinity of cellulose increases.<sup>48</sup> Another advantage of steam explosion is the reduction in the energy needed to generate fine particle.

Traditional size reduction methods require 70% more energy than steam explosion to achieve the same size reduction<sup>46</sup>. Hemicellulose is solubilized via auto-hydrolysis similar to dilute acid or hot compressed water treatment (LHW). Although sugar recovery is much lower with steam explosion than with LHW or acid hydrolysis, optimal hemicellulose solubilization and hydrolysis can be achieved by either high temperature and short residence times (270°C, 1 min) or by lower temperature and longer residence time (190°C, 10 min).<sup>50</sup> Recent studies indicate that lower temperature and longer residence time are more favorable.<sup>46</sup> Although, steam explosion does remove hemicellulose, organic acids, and modify cellulose into a lower DP more crystalline material, all properties favorable for increased production of sugars, there is little removal of inorganic species and therefore may not be as significant in improving cellulose reaction selectivity as dilute acid, or LHW. Nearly complete removal of alkali is critical for pyrolysis selectivity and therefore herbaceous crops that contain high percentages of ash may require an additional washing step to remove alkalis if steam explosion is chosen as a pretreatment for fast pyrolysis, this issue warrants further studies. Lastly, the mobility of steam explosion reactors

may be problematic for use as part of transportable units where the production of steam may be difficult.

### **3.8.- Organic solvent pretreatments**

Another approach to selectively remove lignin that has gained attention in the last twenty years is the pretreatment at temperatures between 150 and 250 °C in the presence of solvents. Experiments have been conducted using a wide range of solvent systems such as: alcohols (ethanol,<sup>51</sup> methanol,<sup>52</sup> ethylene glycol,<sup>53</sup> glycerol,<sup>54</sup>) acetone,<sup>55, 56</sup> ionic liquids,<sup>57</sup> a variety of acid,<sup>58</sup> and metal salt catalyst.<sup>59</sup> This process has the advantage of producing high value lignin and a pretreated biomass rich in cellulose highly susceptible to enzymatic attack. The quality of the lignin produced is high because the presence of solvents reduces condensed structures typically formed via steam explosion or acid hydrolysis. Solvent-physical pretreatments have been shown to exhibit synergistic behavior with respect to enzymatic hydrolysis as evident by work conducted using H<sub>2</sub>SO<sub>4</sub> free ethanol cooking followed by ball milling.<sup>60</sup> One of the main benefits of organosolv fractionation is that both the product and the solvent can be recovered as one stream which reduces the number of steps needed to obtain high value products. Organosolv processes has proven beneficial for the processing of high lignin softwood biomass.<sup>51</sup> This technology is being commercialized by Lignol, (British Columbia, Canada).

#### *Process Description*

The solid chips are immersed in the solvent system of choice and heated for a given period of time. Depending on the solvent and the amount and type of catalyst temperature for solvent pulping range from 150 to 250°C, and reactions times typically on the order of several minutes to

several hours. In these cases the hydrolyzed lignin is dissolved and recovered in the organophilic phase. Liquid to solid ratio of 7:1 mass % with 50% ethanol, and 1% H<sub>2</sub>SO<sub>4</sub> are typical pretreatment conditions. Filtration is typically used to separate the solvent from the solid rich in cellulose.

#### *Mode of Action and Utility for Pyrolysis Pretreatment*

Most organo-solvent pretreatments use an acid catalyst in much the same way as dilute acid pretreatment, although having this hydrolysis carried out in an organic environment improves lignin solubilization. This is due to lignin's limited solubility in aqueous media, and particularly acidic aqueous media. Lignin is depolymerized by acid catalysed breaking of  $\beta$ -O-4,  $\alpha$ -aryl,  $\beta$ -aryl bonds.<sup>51</sup> Having the lignin solubilize into the solution and not remain in the solid matrix is believed to be the reason that less condensed lignin fragments are obtained as compared to steam explosion or acid hydrolysis.<sup>61</sup>

This process may not be very suitable for application with fast pyrolysis. First, pyrolysis of lignin is fairly efficient and not viewed as a component that is advantageous to remove. Second, mobile pyrolysis units using organo-solvent pretreatment would need to transport large volumes of flammable solvents with the pyrolysis systems. Third long treatment times are needed. The use of organic solvents for pretreatment is often viewed as more applicable for the pulping or pretreatment of biomass for biological conversion routes. Since separation of lignin and sugars from bio-oil is not difficult the removal of lignin prior to pyrolysis seems to be a competing technology with pyrolysis with little potential overlap.



### **3.9.- Biological driven conditioning**

Another alternative pretreatment is the use of microbes or enzymes<sup>62</sup> to condition the material prior to processing. Biological conditioning requires very little energy input, is environmentally friendly, and requires low capital investment and technical knowhow. For these reasons biological conditioning may be well suited for businesses located in isolated regions. Fungal conditioning has been extensively explored by the pulp and paper industry as a means to reduce the energy required for physical refinement to reduce lignin content, and lower the severity of thermo-chemical pulping/pretreatment.<sup>63, 64</sup> Although, fungal conditioning is an effective means to reduce thermo-chemical severity required during pulping, the widespread implementation of this practice is not viewed as a good candidate for industrial scale application due to the slow rate of the biological processes, and losses of carbohydrate required for sustaining microbial growth. Nevertheless, biological conditioning may be used to produce high value low volume products that would grant additional economic incentive for commercial applications. Fungal solid state processes may hold a niche in future bio-refineries as a means to produce high value low volume products with minimal infrastructure investment and improve process economics. For example, the spent material from mushroom farming has been studied as a feedstock for the production of bio-fuels,<sup>65-67</sup> bio-plastics,<sup>68, 69</sup> and animal feed.<sup>70</sup>

#### *Process Description*

Biomass is typically piled and either pasteurized with steam or wetted to obtain an appropriate moisture content (typically 50 mass %).<sup>68</sup> The material is inoculated with fungi in either controlled or outside environments for 1-3 weeks. Typically the parameters controlling the rate and effectiveness of biopulping are moisture content, temperature, humidity, air exchange and

reactor design.<sup>71</sup> For bio-pulping or mushroom production typically white rot species are used, as they are recognized to be more efficient at removing lignin selectively.

#### *Mode of Action and Utility for Pyrolysis pretreatment*

Fungal colonization and deconstruction of biomass is a complex process controlled by a variety of factors. Both excretion of enzymes and secondary metabolites onto the fiber surface play significant roles in the fungal decay process.<sup>72</sup> Non-degraded biomass excludes hydrolytic and oxidative enzymes from entering the secondary wall, and 6-8 weeks of incubation is required before significant penetration can occur.<sup>73</sup> Early decay is dependent on secondary metabolites to attenuate the fiber structure to allow greater enzymatic access.<sup>74</sup> Initial fungal (white rot) growth preferentially degrades accessible materials. This includes lignin in the middle lamella as well as hemicellulose and amorphous cellulose in the Primary cell wall.<sup>63</sup>

For bio-pulping applications the effects of fungal colonization in the first three weeks are most desired as they lead to a decrease in fiber strength and structural integrity. These changes in the structure of lignocellulosic materials result in 25 to 35% energy savings during mechanical milling.<sup>64</sup> Fungal spent straw has several characteristics that make its direct use as a feedstock for a thermo-chemical process not optimal. The ash, nitrogen and organic acid composition are enriched during the fungal decay process. Although, the high content of acids and ash in fungal spent substances are undesirable for pyrolysis, there are some changes that may be useful for this process. The fungal growth process leads to a drastic reduction in the DP of the lignin and cellulose which may aid for better liquid yields during pyrolysis. An additional advantage would be that material would be ground into fine particles with reduced energy requirements.

### 3.10.- Hot Water Fractionation

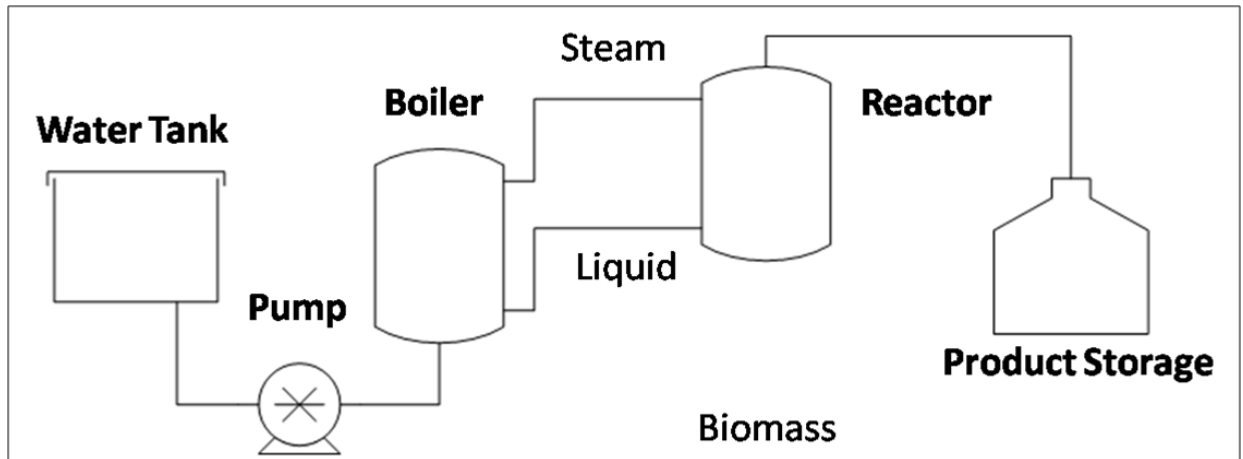
Another biomass pretreatment method is compressed hot-water (LHW). This process uses hot compressed water as a means to fractionate biomass. LHW exhibits very interesting properties which vary depending on temperature and pressure of the process. LHW has advantage of serving as both the solvent and catalyst for biomass hydrolysis.<sup>75, 76</sup> The treatments can be classified into two broad categories: supercritical and subcritical. When LHW is in the subcritical state it acts similar to an acid catalyst and is an effective method for biomass pretreatment for fiber refinement or enzymatic hydrolysis.<sup>77-79</sup> When supercritical state LHW is used, complete hydrolysis/liquefaction of biomass can be achieved. When LHW is in the supercritical state there are numerous interesting properties. Supercritical LHW behaves like a non-polar solvent and depending on the density free radical or ionic reactions are dominant.<sup>76</sup> LHW in the supercritical state is able to swell the microcrystalline material and overcome mass transfer limitations into the crystalline matrix which results in short time requirement for complete hydrolysis of carbohydrates.<sup>80</sup> Subcritical LHW is only able to react with the outer surfaces of the cellulose crystal, making complete cellulose hydrolysis slow. Due to subcritical LHW being the route for pretreatment studied in this thesis, the remainder of this chapter will be devoted to describe this technology.

#### *Process Description*

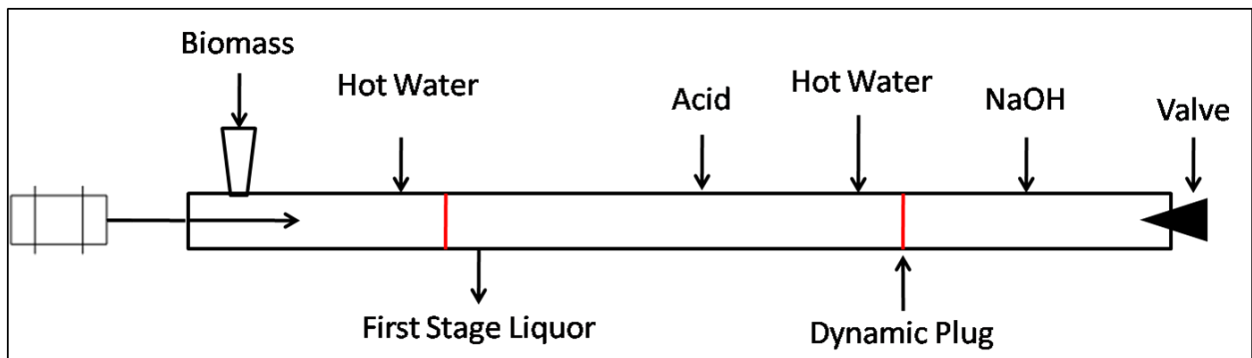
There are a variety of hot water reactor systems that have been developed for biomass pretreatment. It is noteworthy that LHW reactor configuration is similar to dilute or concentrated acid hydrolysis, although the reactors are less susceptible to corrosion with LHW.<sup>75</sup> The most promising reactor designs use counter current flows, or percolation water circulation.<sup>77, 81-83</sup> At

large scale, these designs are preferable to batch reactors for several reasons. Batch reactors lose considerable amounts of energy and the sugar is degraded during heating up and cooling down between runs. One continuous counter current process that has proven effective is the process developed by pure vision INC (Figure 3.2).<sup>77</sup> This technology was demonstrated using corn stover and is depicted in Figure 3. 1. This reactor configuration is divided in two stages. The first stage removes pentose sugars using hot water auto hydrolysis, and has been shown effective to recover up to 95% of hemicellulose sugars. The next stage of this reactor incorporates an alkaline catalyst (NaOH) to remove lignin. One very attractive feature of this system is that both pentose sugars, cellulose and lignin are recovered in relatively pure segregated streams, and the lignin produced is of far lower average molecular weight (180-200 g/mol), and is a suitable feedstock for conversion to specialty chemicals. This is a substantial improvement over traditional kraft pulping processes which produce very condensed high molecular weight lignins (50,000), which are only suitable to provide heat. The remaining solid residue is highly enriched in cellulose that is susceptible to enzymatic hydrolysis and suitable for feedstock for wood products.<sup>78</sup>

Percolation reactors have numerous advantages for commercial scale operation. These reactors are effective using large particles, can be configured for continuous operation, and require very short treatment times (2-5 minutes). LHW technology is of great interest for both the pulp and paper industries and for bio-fuels production. Although there are many designs to accomplish efficient fractionation of biomass, the potential of these systems as pretreatment strategy for fast pyrolysis reactors warrants further investigation.



**Figure 3.1.-** Diagram of a percolation LHW treatment flow diagram<sup>84</sup>



**Figure 3.2.-** Diagram of flow reactor system developed by Pure Vision Inc<sup>77</sup>

*Mode of action*

The reactions occurring during LHW hydrolysis follow similar mechanisms that those occurring during acid hydrolysis. This is due to a change in water ionization with elevated temperature. In addition to the acidic action of water, biomass contains acetic acid associated with hemicellulose that is released in the temperature range between 145 and 190°C.<sup>85</sup> Generally the temperatures used for LHW are between 150 and 235°C and time varies depending on the reactor configuration, and feedstock.<sup>76</sup> Under these conditions LHW has shown to remove virtually all the hemicelluloses, ash and some lignin.<sup>86</sup> At temperatures below 240°C the hydrolysis reactions

predominate, and the resulting liquid products are primary mono and oligomeric sugars.<sup>86</sup> Microcrystalline cellulose is formed due to reduction in degree of polymerization and alterations to the hydrogen bonding networks.<sup>87</sup> At temperatures over 240°C a new set of reactions occur, resulting in significant cross linking of cellulose. These cross linked structures are lead to formation of more char.<sup>76, 88</sup>

### *Utility for Pyrolysis pretreatment*

Understanding the effect of hot water pretreatment on biomass structure and the impact of these changes in the selectivity of thermochemical reactions is critical to evaluate the potential of LHW as a pretreatment for fast pyrolysis. LHW treatments for pyrolysis applications must reduce the degree of polymerization of cellulose, maximize the formation of microcrystalline cellulose, minimize the crosslinking reactions leading to char formation and remove as much hemicellulose and alkalines as possible. This is a complicated task as there are some overlap in the optimum temperature ranges for each of these outcomes.<sup>88</sup> Development of more detailed mechanistic models of the reactions happening during pretreatment is needed to identify the optimum conditions to maximize the yields of sugars from different biomasses.<sup>89</sup>

There are several engineering and economic advantages of using LHW compared to acids for pretreatment. LHW is less corrosive to reactor material than acids based processes. The hydrolysate doesn't require neutralization prior to fermentation or enzymatic hydrolysis. There is no need for equipment to recycle the acid or separate the gypsum that is produce during neutralization. LHW pretreatment yields solids that have several characteristics that are advantageous for a fast pyrolysis process. The solid produced after LHW pretreatment is free of acids and hemicelluloses. LHW is an effective means of removing ash, which catalyses

undesirable fragmentation reactions leading to the formation of low molecular weight compounds. LHW treatment conditions typically will not remove greater than 20% of the lignin. Lignin is considered a good feed material for pyrolysis, and the phenolics in bio-oil can be easily separated and converted into green gasoline. LHW doesn't require expensive reactors and few additional chemicals are needed, which may make LHW more amendable to small scale distributed application than chemical hydrolysis. LHW has been shown to be effective for a wide variety of feedstocks and can be effective with large particle sizes and short residence times. Being able to preprocess large particles before size reduction would reduce the particle strength, result in lower energy requirements for grinding of material into the fine particles required by fast pyrolysis. This feature is very important for feedstocks such as grasses and straw containing substantial amounts of inorganics that cause dulling and damage to grinding equipment, removing ash prior to the size reduction may reduce equipment maintenance.

### **3.12.- Conclusions**

Pretreatment has been used for years to enhance bio-mass biological conversion and as a part of wood products industries. Generally the most important consideration for pretreatment is the feedstock due to the difference in composition and physical properties from biomass types. Table 3.1 provides a summary of some of the most important modifications occurring as the result of each of the pretreatment approaches described in this chapter. Some of the properties modified by pretreatment evaluated are: removal of in-organic material (alkalines), cellulose crystallinity, removal of hemicelluloses, associated organic acids and lignin, and reduction of grinding costs. Given this criteria several conclusions can be made as to what pretreatment would be suitable for fast pyrolysis.

**Table 3.1-** Summary of pretreatment modifications and pyrolysis benefits

<b>Pretreatment</b>	<b>Alkaline Removal</b>	<b>Cellulose Crystallinity</b>	<b>Grinding Energy</b>	<b>Particle Size</b>	<b>Hemicellulose</b>	<b>Lignin</b>	<b>Overall</b>
Acid	High	Increase	Little reduction	Small	Removed	Retained	Good
Base	High	Decrease	Little reduction	Small	Retained	Removed	Poor
Hot Water	High	Increase	Large Reduction	Large	Remvoed	Retained	Good
Steam Explosion	Low	Increase	Large Reduction	Large	Remvoed	Retained	Good
Biological	Very low	Decrease	Large Reduction	Large	Removed	Modified	Poor
Solvent	Little	Little Effect	Little reduction	Small	Retained	Removed	Poor
Torrefaction	None	Increase	Large Reduction	Large	Removed	Retained	Good

As a result of our analysis of Table 3.1 it was concluded that acid pretreatment, compressed hot water, steam explosion and thermal pretreatment in the range of temperatures between 200 and 240°C (mild torrefaction) can be promising pretreatment alternatives to enhance the yields of anhydrosugars via fast pyrolysis.

### **3.13.- Thesis Objectives**

The purpose of this thesis is to examine the use of hot water pretreatment at various temperatures to understand how biomass structural modification will affect the selectivity of cellulose thermochemical reactions towards the production of anhydrosugars. The objectives of this thesis are:

1. To determine the effect of hot water pretreatments at various temperatures on the chemical and physical properties of biomass.
2. To establish the effect of hot water pretreatment on the distribution of products resulting from the fast pyrolysis of  $\alpha$ -cellulose and wheat straw.



### 3.14.- Methodology and Experimental Overview

Two feedstock's with different chemical properties (wheat straw,  $\alpha$ -Cellulose) were tested to elucidate the effects of hot water pretreatment on the selectivity of thermochemical reactions toward the production of anhydrosugars. Wheat straw is an unprocessed feedstock that contains cellulose, lignin, ash, and high content of hemicelluloses.  $\alpha$ -Cellulose is a processed feedstock that has virtually no lignin or alkalines but contains small amounts of pentoses (hemicellulose). The following 4 tasks were performed to accomplish the objectives of this thesis:

*Task 1: Hot water pretreatment of wheat straw and  $\alpha$ -Cellulose in the temperature ranges of 150-260°C.*

*Task 2: Characterization of original and pretreated lingo-cellulosic materials*

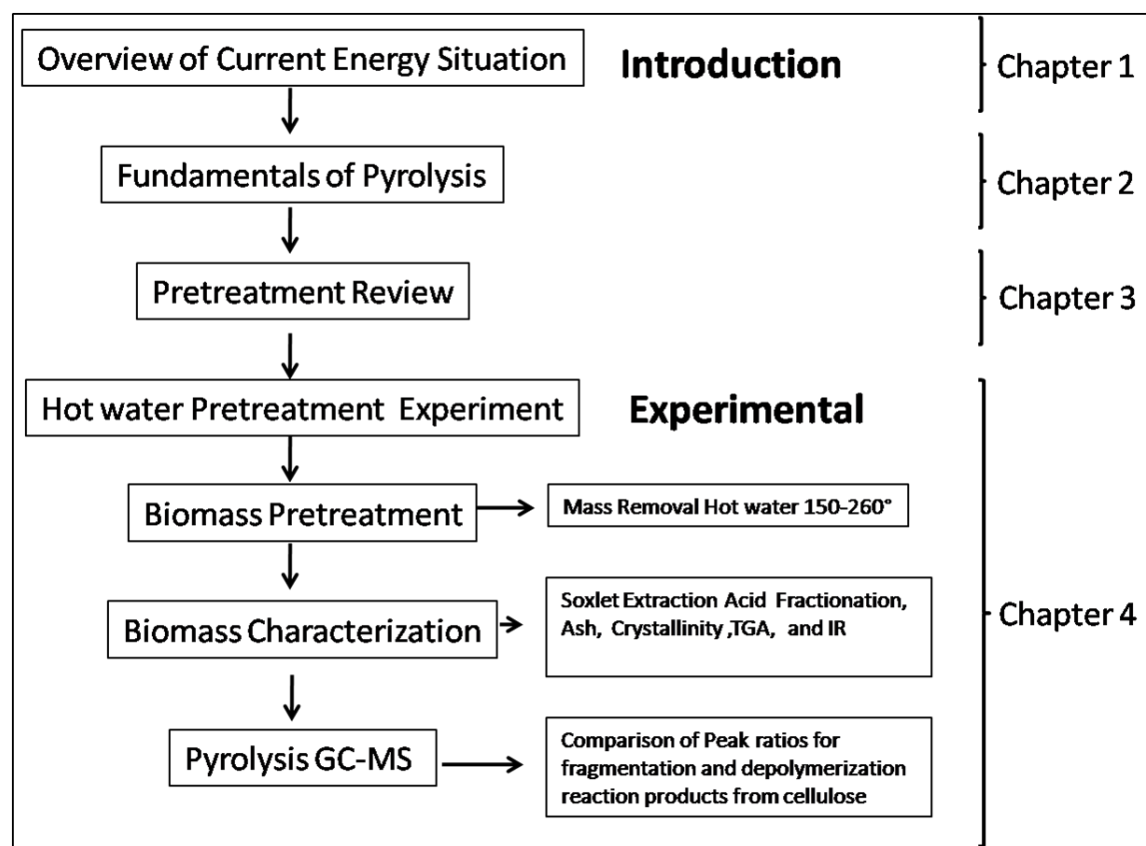
*Task 3: Use of pyrolysis GCMS to evaluate the impact of pretreatment on selectivity of cellulose thermochemical reactions*

*Task 1:* Two different biomass samples were chosen based on the difference in alkalines and lignin content. While, the wheat straw is a herbaceous material with high content of ash and lignin, the  $\alpha$ -cellulose is a processed biomass that is rich in cellulose and contain small amount of hemicelluloses but no lignin and ash. The main aim of this task was to perform the mass balances of the two materials subjected to pretreatment.

*Task 2:* The content of extractives, Klason lignin, acid soluble lignin, cellulose, ash, and hemicelluloses in all pretreated materials was quantified with standardized ASTM methods. X-Ray diffraction experiments were conducted to determine the effect of pretreatment conditions

on biomass crystallinity. Thermogravimetric and infra-red spectroscopic analyses were conducted to provide further evidences of biomass alteration during pretreatment.

*Task 3:* Pretreated samples were pyrolyzed in a small apparatus connected in-line to a gas-chromatography-Mass spectrometry analyser. The ratios of the areas of peaks associated to representative compounds were quantified to determine the impact of hot water pretreatment on the selectivity of cellulose thermochemical reactions Figure 3.3. shows an overview of this thesis.



**Figure 3.3.-** Thesis Overview

### 3.15.- Scientific Contributions

The scientific contribution of this thesis can be summarized as the following:

- It is the first extensive study to determine the effect of liquid hot water pretreatment for the fast pyrolysis of biomass.
- Comparison of two cellulosic materials will give insight as to what are additional factors that may play a role in the chemical modification of biomass from hot water treatment.
- This is the first study reported in the literature suggesting that hot water pretreatment can be used as a viable pretreatment approach to improve the selectivity of cellulose thermochemical reactions towards the production of anhydrosugars. This study also suggests that the overall quality of the bio-oil produced from hot water pretreated biomasses could be also improved (lower content of acids and alkalines).

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## **Chapter 4**

### **Pyrolysis-GC/MS Studies to Evaluate High Temperature Aqueous Pretreatment as a Way to Enhance the Quality of Bio-oil from Fast Pyrolysis of Wheat Straw**

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#### **4.1.- Introduction**

Growing concerns over climate change and national energy security have resulted in renewed interest in replacing gasoline and diesel with bio-fuels. One potential biomass processing approach is distributed fast pyrolysis units to convert up to 70% of the biomass into crude bio-oils which would be transported to centralized bio-refineries and used as the feedstock to produce second-generation transportation fuels.<sup>1</sup> One major economic advantage of distributed preprocessing is that the resulting bio-oil is substantially more energy dense and can therefore be economically transported longer distances for further conversion into transportation fuels in a bio-oil refinery.<sup>2</sup> Making large quantities of feedstock accessible allows the refinery to be designed to take advantage of economies of scale, which is a critical factor for economic viability.<sup>3,4</sup>

One current problem with the bio-oil-based bioeconomy model proposed is the nature of the oils produced via fast pyrolysis. Crude bio-oil is corrosive, thermally unstable, and contains large amounts of small oxygenated species with little economic value.<sup>5</sup> One approach to produce

transportation fuels from bio-oil is hydrotreatment. By this method, approximately 40 mass % of the bio-oil can be converted into green gasoline and green diesel.<sup>6,7</sup> Thus, fast pyrolysis followed by bio-oil hydrotreatment can yield up to 28 mass % of lignocellulosic materials into green gasoline and green diesel. While the conversion of lignin into transportation fuels achieved by this concept is relatively high, the pyrolytic conversion of cellulose to precursors of transportation fuels is very poor. Currently, most of the cellulose is fragmented to produce small molecules (chiefly, hydroxyacetaldehyde) with little economic value. One approach to enhance the conversion of cellulose to precursors of transportation fuels (anhydrosugars) is to alter the properties of the feedstock through pretreatment. The main hypothesis of this paper is that the selectivity of primary thermochemical reactions toward the production of anhydrosugars and furanics can be enhanced by pretreatment in hot water. This, together with the removal of hemicelluloses, could result in a less acidic, higher quality bio-oil.

The initial cracking of bonds (pyrolysis) that occurs when biomass is heated are called primary thermal decomposition reactions. These reactions occur mainly on wood cell walls.<sup>8-11</sup> Attempts have been made to explain the mechanisms for cellulose degradation via pyrolysis. Golova<sup>14</sup> first noted that there is an initial rapid reduction in cellulose degree of polymerization to 200 or 300 units without much change in cellulose weight, followed by a period in which the degree of polymerization remains fairly constant, although the conversion (weight loss) ranges from 4% to 80%. A similar phenomenon is also observed during cellulose acid hydrolysis<sup>12</sup> and can be explained by the existence of four to five disordered units in every 300 ordered units in the cellulose microfibrils. Cellulose molecules with a degree of polymerization between 200 and 300 glucose units are known by the thermochemical research community as “active cellulose.”<sup>10</sup> This active cellulose is further degraded to form volatile species.

To explain the depolymerization of active cellulose, two mechanisms have been proposed. The first one, proposed by Broido et al.<sup>13</sup>, suggests that the depolymerization of cellulose occurs by random cleavage of glycosidic linkages. The second mechanism, proposed by Golova,<sup>14</sup> states that once a chain reaction is initiated, the whole chain “unzips” to form mono- and oligo-anhydrosugars. Under well-controlled conditions, most of the cellulose can be converted to levoglucosan and cellobiose.<sup>15, 16</sup> The mechanisms triggering the unzipping of active cellulose and the effect of the crystallinity of active cellulose on sugar yields are not completely understood. There is abundant evidence proving that the presence of alkaline cations inhibit this “unzipping” and that this inhibition induces undesirable ring fragmentation reactions.<sup>17, 18</sup> It has been established that microcrystalline cellulose gives higher yields of anhydrosugars than native cellulose during fast pyrolysis.<sup>18</sup> Thus, biomasses with low content of alkaline cations and with high crystallinity generate more mono- and oligo-sugars.

The volatile species formed by the primary reactions may undergo secondary homogeneous and heterogeneous reactions along the diffusion path on their way out of the particle and as the vapors are carried away to the condensers.<sup>19, 20</sup> Although the overall distribution of products resulting from fast pyrolysis of biomass is a function of both primary and secondary thermochemical reactions, there are very few technological options to control primary thermochemical reactions in the solid phase. Low heating rate, the presence of inorganic species, and high contents of hemicelluloses and lignin are well established factors known to reduce the quality and yield of bio-oil, and increase of char production. Thus, design of pretreatments to improve selectivity will need to address the need to remove alkalines, hemicellulose, and potentially alter cellulose structure into a more active form.

Pretreatment technologies as a way to enhance the production of fermentable sugars has not been systematically studied. Heating biomass in the presence of water between 180°C and 250°C has been shown to contribute to an increase in cellulose crystallinity.<sup>21,22</sup> Radlein et al.<sup>17</sup> reported that one biomass sample which had been accidentally preheated in poorly controlled experimental conditions (probably around 180°C) for several hours yielded an abnormally high yield of sugars. The causes for this interesting but unexpected result could not be explained in the original experiment. The hypothesis of this work is that formation of a high-temperature crystalline phase with a lower degree of polymerization (active cellulose) will result in higher yields of sugars in the bio-oil produced during fast pyrolysis of biomass.<sup>23-31</sup> This hypothesis is consistent with the well-known impact of thermal pretreatment on cellulose crystallinity,<sup>21, 22, 32,</sup><sup>33</sup> with the studies describing the formation of a high-temperature crystalline phase,<sup>24-26</sup> and with the previous reports of Piskorz et al.,<sup>18</sup> suggesting that higher cellulose crystallinity enhances the production of mono- and oligo-sugars during fast pyrolysis.

Shafizadeh and Stevenson<sup>34</sup> first proposed the use of prehydrolysis with sulfuric acid at 160°C as a way to enhance the production of fermentable sugars from pyrolysis. This was carried out to remove the hemicellulose and inorganic impurities. Later, the group at the University of Waterloo used a similar approach and demonstrated that nearly 80% of pretreated hollocellulose (cellulose + hemicellulose) can be converted to sugars via fast pyrolysis.<sup>17</sup> The increase in the observed sugar yield was explained by the removal of alkalines which are known to be strong catalysts of fragmentation reactions. In addition to removal of alkalines, there is also the advantage of removal of much of the acetic acid present in the hemicellulose, in part responsible for the low pH of bio-oils. Although pre-hydrolysis with dilute acid has been proven a viable means to improve selectivity and bio-oil quality, there exist several technical issues with

incorporation into a distributed bio-oil-based bio-economy such as waste management, corrosion resistant reactors, and catalyst recycle equipment.

An alternative to using acids to fractionate biomass is compressed hot water (CHW). At elevated temperatures and pressures, liquid water can be used to remove virtually all hemicellulose and a significant amount of lignin<sup>35</sup> because of its increased ionization and reduced pKa. Subcritical water has a major reduction in dielectric constant and results in a lower pKa than water at Standard atmospheric Conditions (SAC), which is the explanation as to why it can act as both a solvent and a catalyst. Subcritical CHW is able to efficiently hydrolyze the hemicellulose sugars, some lignin, and ash with reactions times as little as 4 minutes without the need for prior size reduction.<sup>35</sup> This, coupled with hydrolysis of hemicellulose-linked acetic acid, is responsible for autocatalysis of biomass in CHW.<sup>36</sup> Compressed hot water hydrolysis results in high overall recovery of pentose sugars, although much of this is in oligomeric form and requires a mild post-hydrolysis.<sup>37,38</sup>

Thus, the main objective of this paper is to investigate how CHW biomass pretreatment affects the biomass structure and how these changes affect the selectivity of pyrolysis reactions toward the production of anhydrosugars.

## **4.2. Experimental**

### *4.2.1. Feedstock and Materials Preparation*

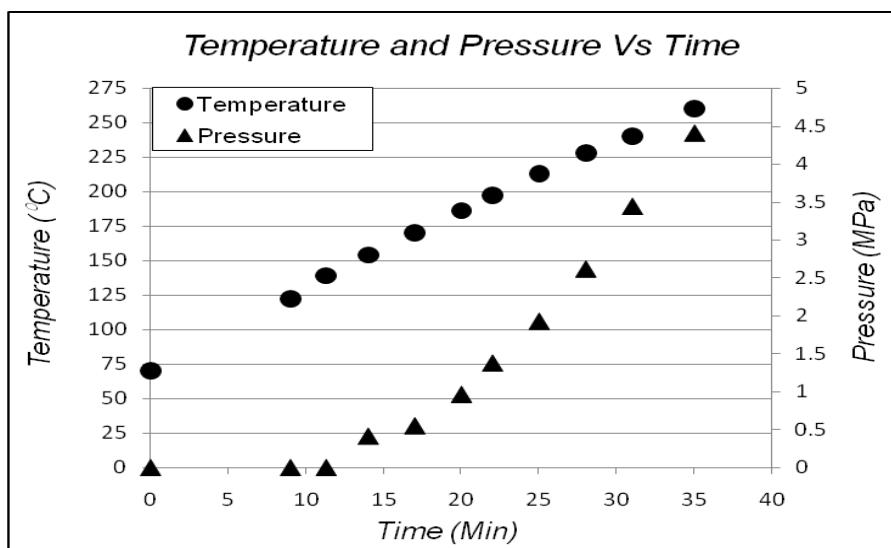
Wheat straw (*Triticum sativum*) used in the experiment was grown in Moscow, Idaho. It was milled and sieved to particles below 24 mesh (Tyler Mesh Size, 0.707 mm).  $\alpha$ -Cellulose was obtained from Sigma-Aldrich (St. Louis, Missouri). It was received as a fine powder. The process to obtain  $\alpha$ -Cellulose employs treatment of fibrous material with chlorine gas and two amino ethanol, followed by extraction with 17.5% sodium hydroxide (TAPPI 249, ASTM D



1104.2; ASTM D 1103). The  $\alpha$ -Cellulose was analyzed in our lab; it was determined to be composed of 85% glucan and 15% hemicellulose with a negligible amount of ash.

#### *4.2.2.- Hot Water Pretreatment of Wheat Straw and Cellulose*

Hot water treatments were carried out in a Parr pressure reactor model 4521 with 1-L filling capacity. Both wheat straw and  $\alpha$ -cellulose samples were subjected to treatment under temperatures ranging from 150°C to 260°C. Parameters such as mass loadings (5 mass %), mixing (200 rpm), and heating rate (5.5°C/min) were constant for all trials. The reactor was filled with a total volume of 300 mL of water with 15.0 grams of straw and allowed to wet for 1 hour prior to heating. The samples were heated until the target temperature was reached, and immediately cooled by running tap water through a heat exchanger inside the pressure reactor. Temperature and pressure profiles of the reactor, given the loading conditions, are presented in Figure 1. The pressure recorded in the reactor was close to the vapor pressure of water. Independent of the final temperature, cooling to below 70°C took less than 5 minutes. Immediately after thermal treatment, liquid and solids were separated by vacuum filtration (Whatman #1), solids were washed with an additional 300 mL of distilled water, and then were oven-dried overnight at 105°C. The dry mass of the treated solids was recorded and compared to the original dry weight. The liquid resulting were refrigerated and analyzed within 1 week after treatments.



**Figure 4.1.-** Temperature and pressure profiles for experimental conditions

#### 4.2.3. Biomass Characterization

As received and treated biomass samples were initially extracted with ethanol:touluene using a soxlet apparatus as described by ASTM method 1107. Following overnight extraction, the liquor was evaporated under vacuum and the extractive content was determined gravimetrically. Samples were prepared and characterized by the two-stage acid hydrolysis method described elsewhere ([http://www.nrel.gov/biomass/analytical\\_procedures.html](http://www.nrel.gov/biomass/analytical_procedures.html) accessed June 2009) The first hydrolysis step used 72% sulfuric acid at 30°C for 1 hour. Immediately following the 1-hour incubation, the samples were diluted to 4% and autoclaved for 1 hour. The resulting solid residues were reported as acid-insoluble lignin. The sugars in the aqueous phase were quantified with ion-chromatography using an ion exchange chromatography apparatus (Dionex ICS-3000 DC IC) equipped with an electrochemical detector. All samples were separated using a Dionex Pac PA20 (3 mm × 150 mm) with CarboPac PA20 Guard (3 mm × 30 mm). The flow rate was 0.5 mL/min and the column temperature was maintained at 30°C. Samples were eluted isocratically with 20% 52-mM NaOH and 80% water. The column was flushed between samples

with 100% 200-mM NaOH followed by double-deionized water. Sugars content was quantified by running a standard curve ranging from 1 to 20 ppm for each sugar species of interest, and validated against a QC sugar sample. The sugars concentrations reported were measured in duplicate. Acid-soluble lignin was determined by UV absorbance at 205 nm (0.2–0.7) with an extinction coefficient of 110 L/g cm.<sup>39</sup> Ash content was determined by burning the material in an oven at 575°C and checking for constant weight every 4 hours, following the method NREL/TP-510-42622.

#### *4.2.4. Thermo-gravimetric analysis*

Prior to these experiments, the pretreated wheat straw was run through a Wiley mill and sieved through No. 20 mesh to ensure uniform particle size. Thermogravimetric analysis (TGA) of pretreated solid samples was conducted using a Mettler-Toledo TGA/SDTA851<sup>°</sup>. Approximately 5- to 10-mg samples were loaded into an aluminum pan and heated (10°C/min, 50°C–600°C) under a nitrogen atmosphere (20 mL/min).

#### *4.2.5. X-ray powder diffraction*

X-ray powder diffraction spectra were collected by a Phillips X'Pert MPD 3040 diffractometer equipped with an Anton-Parr sample holder and a position sensitive detector (PSD). The X-ray source was a cobalt anode operated at 40 kV and 45 mA. The X-ray beam was Fe-filtered and passed through a 1/4-in. divergence slit and a 1/8-in. anti-scatter slit before it reached the sample powder. The data in a  $2\theta_{\text{cobalt}}$  ranging from 10° to 40° were collected with a step size of 0.01673°. The XRD spectra were deconvoluted to determine the peak height of the cellulose 200 peak ( $I_{200}$ ,  $2\theta_{\text{cobalt}} = 26.2^\circ$ ) and the peak height of the amorphous material ( $I_{\text{am}}$ ,  $2\theta_{\text{cobalt}} = 22.1^\circ$ ). The Segal method<sup>40</sup> was used to calculate the sample crystallinity.

#### 4.2.6 Infrared Spectroscopy

Ground treated and un-treated samples were used to obtain infrared spectra of wheat straw . Spectra were collected on a Shimadzu IR-Prestige-21 equipped with a Pike Miracle ATR compression clamp. 32 scans were carried out and averaged from  $750\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$  with  $2\text{ cm}^{-1}$  resolution. Raw spectra were modified with an ATR correction; baseline smoothed ed, and normalized to the  $1100\text{ cm}^{-1}$  cellulose peak. Peaks were compared on qualitative basis as described by.<sup>41</sup>

#### 4.2.7. Py-GC/MS

Pyrolysis GC/MS was carried out using a CDS pyroprobe 5000 connected in-line to an Agilent GC/MS. Samples were loaded into a quartz tube and gently packed with quartz wool prior to pyrolysis. The samples were kept a few seconds (3–5 s) at  $230^{\circ}\text{C}$  to ensure adequate removal of air prior to pyrolysis. Samples were pyrolyzed by heating nearly instantaneously to  $500^{\circ}\text{C}$  and held at this temperature for 3 minutes. The GC/MS inlet temperature was maintained at  $250^{\circ}\text{C}$  and the resulting pyrolysis vapors were separated by means of a  $30\text{ m} \times 0.25\text{ }\mu\text{m}$  inner diameter (5%-phenyl)-methylpolysiloxane non-polar column, with a split ratio of 50:1. The gas flow rate was  $1\text{ mL/min}$  and helium was the carrier gas. The column was heated at  $3^{\circ}\text{C/min}$  from  $40^{\circ}\text{C}$  to  $280^{\circ}\text{C}$  to ensure that the all the heavy molecules were removed from the column, and the oven was held at  $280^{\circ}\text{C}$  for 10 minutes. The gas was then sent into a mass spectrometer (Agilent Technologies Inert XL MSD). The mass spectra of predominant peaks were then compared to an NBS mass spectra library to establish the identity of each compound. Typical mass spectrometer conditions were: transfer line  $150^{\circ}\text{C}$ , ion source  $230^{\circ}\text{C}$ , and electron energy  $70\text{ eV}$ . The peak area values reported were calculated from the summation of the predominant ion peaks in the mass spectrum for the given compound. The ions that were chosen as representative ions per

each compound are shown in Table 1. To determine whether hot water treatment resulted in greater selectivity, a semiquantitative method comparing the ratios of total area for selected compounds to determine the treatment effect was proposed. Levoglucosan and hydroxy methyl furfural (HMF) are both cellulose products which, if produced in greater abundance, would be advantageous for bio-oil refinement. Consequently, the peak area ratio between levoglucosan, HMF, and compounds resulting from fragmentation reactions (e.g., hydroxyl-acetaldehyde) was used as an indicator of the pyrolysis selectivity.

**Table 4.1.-** Main ions used in the quantification of Py/GC-MS spectra

Peak No	Name of Compound	Retention Time (min)	Formula	<i>m/z</i>	MW
1	Carbon dioxide	1.53	CO <sub>2</sub>	44/45	44
2	1-Propen-2-ol, acetate	1.78	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	42/43/58/72	100
3	Acetaldehyde, hydroxy	2.10	CHOCH <sub>2</sub> OH	40/42/56/60	60
4	Acetic acid	2.53	CH <sub>3</sub> COOH	43/45/60	60
5	2-Propanone, 1-hydroxy-	2.75	CH <sub>3</sub> COCH <sub>2</sub> OH	42/43/45/74	71
6	1,2-Ethanedial, monoacetate	4.14	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	42/43/73/74	194
7	Butanedial	4.38	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	39/43/57/58	86
8	Propanoic acid, 2-oxo-, methylester	4.52	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	42/43/44/102	102
9	Furfural	5.34	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	39/40/95/96	96
10	2-Furanmethanol	5.86	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	41/53/81/98	98
11	1,2-Cyclopentanedione	7.57	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	42/55/69/98	98
12	2H-Pyran-2, 6(3H)-dione	9.27	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	55/56/84/112	112
13	-Cyclopenten-1-one, 2-hydroxy-3-methyl	10.12	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	41/55/60/112	112
14	Levoglucosenone	12.17	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	68/81/98	126
15	5-hydroxy methyl furfural	15.20	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	41/97/126	126
16	Phenol, 2,6-dimethoxy	17.86	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	93/96/139/154	154
17	Levoglucosan	22.23	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	42/57/60/73	162
18	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	24.87	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	77/91/119	194

### 4.3.- Results

#### 4.3.1.- Hot Water Pretreatment of Wheat Straw and Cellulose

Figure 4.2 shows the percent of solid biomass remaining (oven-dry) following pretreatment at different temperatures. The mass loss of wheat straw and  $\alpha$ -Cellulose followed very different trends. For wheat straw samples, the pretreatment temperatures 150°C to 200°C showed a rapid reduction in the final weight mass retained. Increasing the pretreatment temperature to 225°C–260°C showed little additional solubilization, and the solids retained leveled off at 40% for temperatures above 250°C. It is well established that hot water treatment in the temperature ranges of 175°C to 225°C will hydrolyze hemicellulose and will remove an important part of the alkalines and some extractives.<sup>42,43</sup>

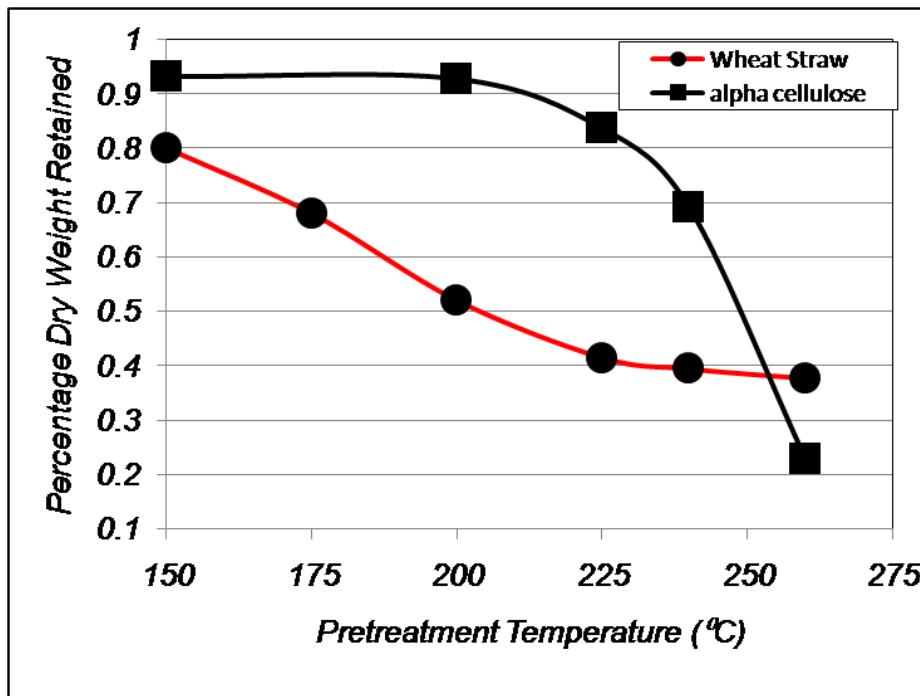


Figure 4.2.- Yield of pretreated biomass vs. pretreatment temperature

The mass loss for  $\alpha$ -Cellulose shows less susceptibility to hydrolysis from 150°C to 225°C, perhaps due to the lower content of hemicelluloses (approximately 15 mass %). But, in contrast to wheat straw, the rate of thermal degradation is accelerated when heated to 240°C and 260°C. These drastic differences can be explained by the differences in composition: essentially,  $\alpha$ -cellulose is free of lignin and ash. When  $\alpha$ -Cellulose is heated beyond 240°C the solubilization increases (30%), but when it is heated to 260°C the solubilization drastically increases and 70% of the material is solubilized. Clearly, at the same temperatures the susceptibility of  $\alpha$ -Cellulose to hydrolysis is much higher than wheat straw. Our hypothesis is that removal of lignin from  $\alpha$ -Cellulose improves the accessibility of subcritical water to the cellulose polymers, and the cellulose is rapidly solubilized. This is in agreement with the differences with sub- and supercritical water hydrolysis, as an accessibility limitation to cellulose molecules.<sup>44</sup> It has been shown previously that near critical water (at temperatures as low as 250°C) it is possible to hydrolyze cellulose,<sup>45</sup> although these results demonstrate that the molecular environment of the polymer also plays a role in the rates of hydrolysis.

#### *4.3.2. Changes in the Composition of Pretreated Wheat Straw*

The compositional analysis that was determined for treated and untreated wheat straw samples is shown in Table 2. The content of ash in the pretreated biomass decreases from 7.4 mass % in the fresh samples to 2.3 mass % for samples pretreated at 260°C. Under these conditions, most of the alkalines are removed.<sup>46</sup> The content of extractives in the pretreated biomass increases from 2.1 mass % to more than 22.9 mass %. Analyses conducted of these extractives clearly indicate that they are products of lignin thermal degradation reactions. While the content of solid insoluble lignin in the pretreated biomass increases from 14.5 to 18.4 mass %, the content of acid-soluble

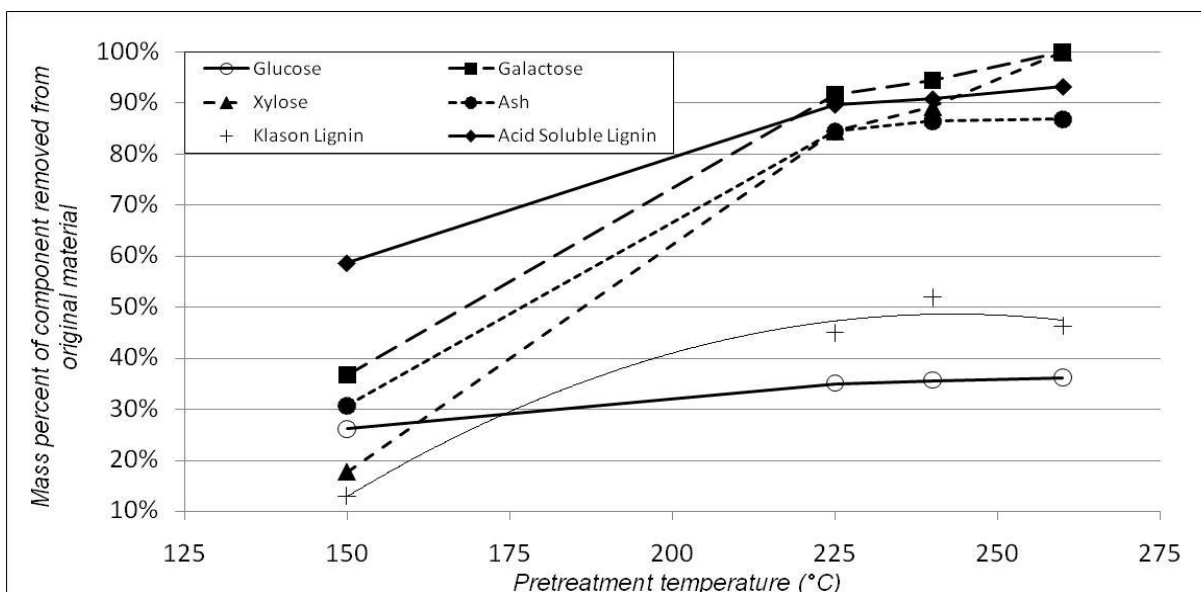
lignin in the pretreated biomass decreased. All sugars derived from hemicelluloses gradually solubilize while the concentration of cellulose in the solid phase increases.

The composition of wheat straw residues (pretreated biomass) shown in Table 4.2 and the yields shown in Figure 4.3 were used to obtain the mass percent of each of the components removed from the original material (see Figure 3). Almost 28 mass % of the glucose was removed at temperatures as low as 150°C. Further hydrolysis was induced with more severe treatment. Glucose removal reaches a maximum at 35% of the total available glucose, and levels off in temperatures greater than 225°C. We attribute these observations to the removal of amorphous cellulose. The hemicelluloses (arabinose, galactose, glucose, mannose/xylose) were almost completely removed when treated at 260°C. Lignin was also extracted; at 150°C almost 14 mass % of the lignin was removed, but when treated at 225°C to 260°C, roughly 42% to 48% of the lignin was removed. Although increasing severity had little effect on additional removal of lignin, there is significant evidence that chemical modification is occurring, as is evident by the increase in the amount of extractible material obtained with increasingly severe treatments; this is consistent with steam explosion fractionation experiments.<sup>47</sup> These results show that the cellulose and Klason lignin fractions are less susceptible to hydrolysis by the CHW treatment. Finally, almost 90 mass % of the ash was removed.

**Table 4.2.-** Compositional Percentages of various biomass components on oven dry basis

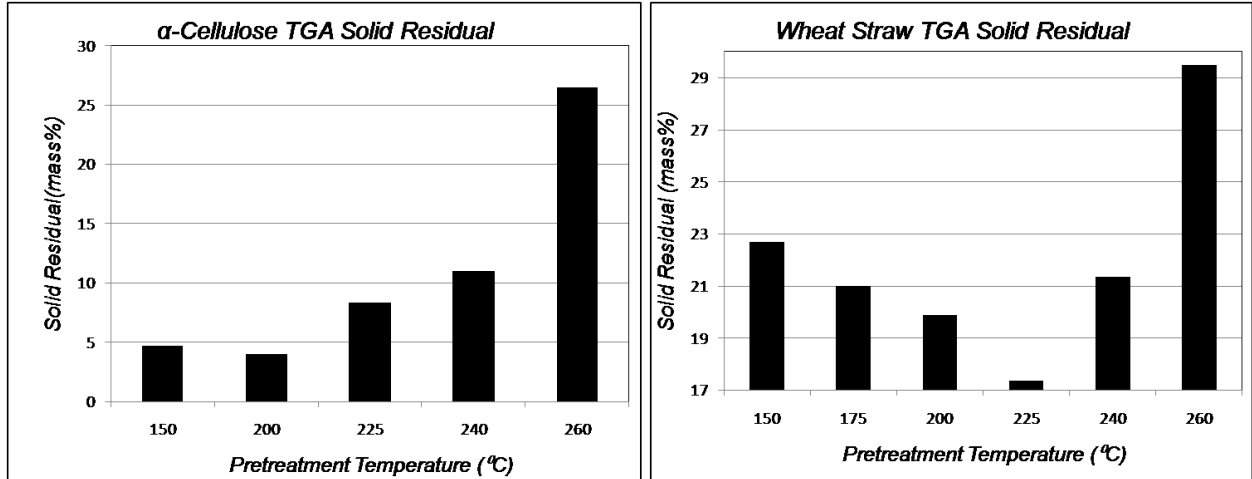
Pretreatment Temperature	Ash	Extractives	Acid insoluble		Arabinose	Galactose	Glucose	Mann/Xylo	Total
			Lignin	Acid Soluble Lignin					
Fresh	7.36	2.10	14.47	3.81	3.32	0.73	36.68	15.15	83.62
150	6.56	1.54	16.20	2.03	3.30	0.61	35.36	17.50	83.10
225	2.64	10.36	18.38	0.91	0.14	0.14	53.91	5.31	91.79
240	2.33	16.25	16.28	0.82	0.00	0.10	54.46	4.16	94.39
260	2.28	22.86	18.41	0.61	0.00	0.00	56.32	0.00	100.48





**Figure 4.3.-** Component percent removal from wheat straw.

The solid samples resulting from hot water pretreatment were subjected to TGA. Figure 4.4 shows the effect of pretreatment temperature on the solid residue mass left after heating the biomass to 500°C at 10°C/min. For the  $\alpha$ -cellulose, we observed a gradual increase in the yield of carbonaceous solid residue obtained by TGA. In the case of wheat straw, a minimum in the carbonaceous solid residues was obtained at temperatures between 200°C and 225°C. These differences in behavior between  $\alpha$ -Cellulose and wheat straw can be due to the lignin antioxidant effect enhancing the oxidation stability of the cellulose and wheat straw. In both cases an increase was observed in the solid residue when the biomass was pretreated at 260°C. This increase in the solid residue at pretreatment temperatures above 225°C is a indication that the cellulose is undergoing cross-linking reactions leading to charcoal formation.<sup>13</sup>



**Figure 4.4.-** TG solid residue vs. pretreatment temperature.

Figure 4.5 shows the deconvolution of typical differential thermogravimetric (DTG) curves considering that the thermal degradation of wheat straw was an additive function of three major pseudo-components (cellulose, hemicelluloses, and lignin). The procedure for kinetic fitting has been described elsewhere.<sup>48</sup> Briefly, the general equations used to describe the decomposition of the fractions are:

$$\frac{d\alpha}{dt} = \sum_{j=1}^N Z_{j0} \frac{d\alpha_j}{dt} \quad (1)$$

$$\frac{d\alpha_j}{dt} = A_j \exp\left(-\frac{E_j}{R \cdot T}\right) (1 - \alpha_j)^n \quad (2)$$

$$\sum_{i=1}^N z_{j0} = 1 \quad (3)$$

$$z_{j0} = \frac{W_{j0} - W_{j\infty}}{W_0 - W_{\infty}} \quad (4)$$

Where:

$\frac{d\alpha}{dt}$  instantaneous reaction rate

$\frac{d\alpha_j}{dt}$  instantaneous reaction rate for component j

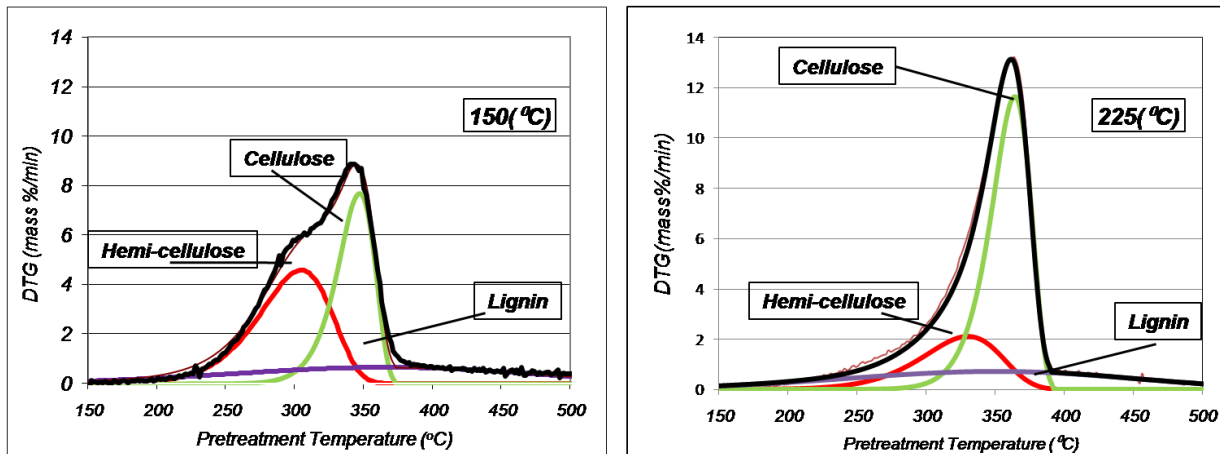
$\alpha_j$  parameter defined as:  $\alpha_j = \frac{W_{j0} - W_j}{W_{j0} - W_{j\infty}}$

$Z_{j0}$  mass fraction of volatile solids from component j

$A_j$  pre-exponential factor corresponding to thermal degradation of component j

$E_j$  activation energy corresponding to component j thermal volatilization

$W$  mass of solid residue



**Figure 4.5.-** Fractioned DTG curves for pretreated wheat straw with independent reaction model

The kinetic parameters used to fit the DTG curves are shown in Table 4.3. In general, the kinetic parameters ( $E$ ,  $\log A$ , and  $n$ ) were kept constant for all fittings. The only exemption was the activation energy used to simulate the behavior of cellulose. A substantial change in the shape of the DTG curve forced us to change the values of activation energy used to describe the thermal behavior of  $\alpha$ -Cellulose for samples that were treated at temperatures above 225°C. The values

of  $Z_{j0}$  shown in Table 3 are a good indication of the fraction of volatiles assigned to each of the peaks (cellulose, hemicelluloses, and lignin), and when compared to the chemical analysis the trends are very similar.

**Table 4.3.-** Parameters used to deconvolute the DTG curves.

Pretreatment Temperature (°C)	Component	E(kJ/mol)	Log A (min <sup>-1</sup> )	n	Heating Rate (°C/min)	Mass fraction of released gases ( $Z_{j0}$ ) (%)
150	Cellulose	230	19.23	1	10	0.36
175	Cellulose	230	19.176	1	10	0.38
200	Cellulose	230	19.041	1	10	0.45
225	Cellulose	200	19.041	1	10	0.64
240	Cellulose	200	19.041	1	10	0.62
260	Cellulose	200	19.041	1	10	0.58
150	Hemicellulose	100	8.602	1	10	0.41
175	Hemicellulose	100	8.602	1	10	0.33
200	Hemicellulose	100	8.602	1	10	0.26
225	Hemicellulose	100	8.602	1	10	0.13
240	Hemicellulose	100	8.602	1	10	0.12
260	Hemicellulose	100	8.602	1	10	0.12
150	Lignin	26	1	1	10	0.23
175	Lignin	26	1	1	10	0.29
200	Lignin	26	1	1	10	0.29
225	Lignin	26	1	1	10	0.24
240	Lignin	26	1	1	10	0.26
260	Lignin	26	1	1	10	0.29

The values of  $Z_{j0}$  shown in Table.4.3 are in agreement with the compositional analyses shown in Table 4.2 and confirm that continued heating beyond 225°C will result in a material with very low content of hemicelluloses. This is consistent with a large number of experiments that have been conducted using pretreatment of biomass with hot water and dilute acid.<sup>49</sup> Consequently, weight losses observed for wheat straw (more than 60 mass %) can be explained by the removal of most of the hemicelluloses, extractives, and ash as well as by the partial solubilization of amorphous cellulose and lignin.<sup>43, 50</sup>

### 4.3.3. X-ray diffraction

Figure 4.6 shows the X-ray diffraction (XRD) spectra for  $\alpha$ -Cellulose and wheat straw pretreated at different temperatures. The major peak at  $26.4^\circ$  is representative of the amorphous and crystalline cellulose in the material. The minimum around  $22.1^\circ$  represents only the amorphous material<sup>40</sup>. Figure 4.7 shows the relative crystallinity obtained from the XRD data by the Segal method for wheat straw and  $\alpha$ -Cellulose. It clearly shows an increase in crystallinity as pretreatment temperature increases. Both  $\alpha$ -cellulose and wheat straw become more crystalline with increased pretreatment temperature. It noteworthy that the content of cellulose in pretreated wheat straw at temperatures between  $150^\circ\text{C}$  and  $260^\circ\text{C}$  is very close to the crystallinity values shown in Figure 4.7. This result suggests that the increase in crystallinity observed is most likely caused by the significant solubilization of amorphous cellulose and hemicelluloses and the increase in the concentration of crystalline cellulose. The increase in the crystallinity of  $\alpha$ -Cellulose observed at temperatures between  $225^\circ\text{C}$  and  $260^\circ\text{C}$  can be explained by the removal of hemicelluloses and amorphous cellulose. Clearly, not all the  $\alpha$ -Cellulose at  $260^\circ\text{C}$  is crystalline. At these temperatures it is likely that an important part of the  $\alpha$ -Cellulose is oxidized and cross-linked, forming amorphous structures. The cross-linking mechanism proposed by Broido<sup>17</sup> can be used to explain why the crystallinity of  $\alpha$ -Cellulose obtained at  $260^\circ\text{C}$  is lower than the content of cellulose. The cellulose that remains in the material is the crystalline cellulose or oxidized cross-linked amorphous cellulose. Almost all of the non-oxidized amorphous cellulose in the biomass was likely removed during the CHW treatment. This evidence suggests the presence of lignin may be protecting cellulose from oxidation and cross-linking, and may be explained by the antioxidant properties of lignin preventing a decrease in crystallinity in the wheat straw pretreated at higher temperatures.<sup>44, 51, 52</sup>

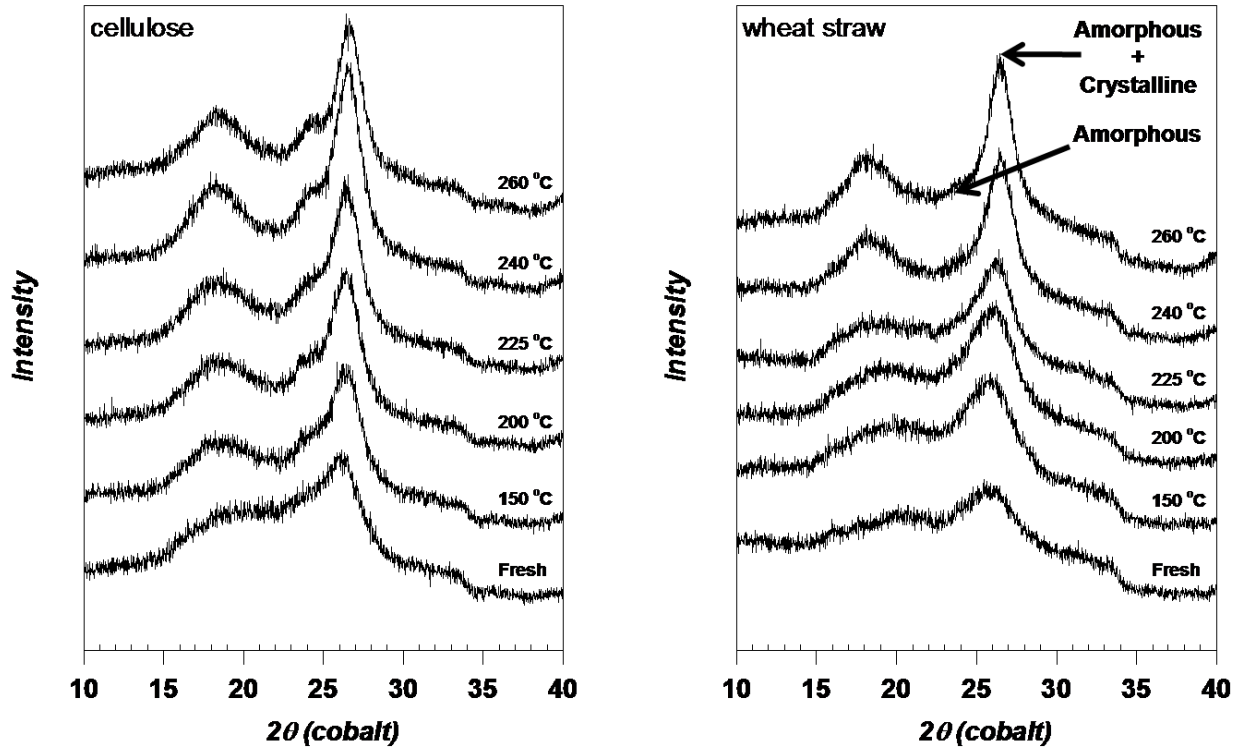


Figure 4.6.- X-ray diffraction of  $\alpha$ -cellulose and wheat straw pretreated at different temperatures

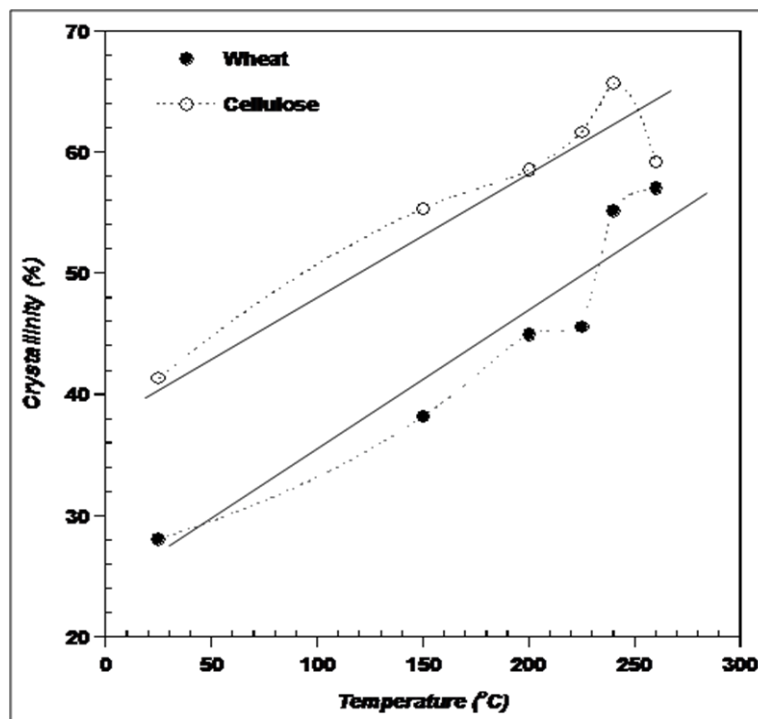
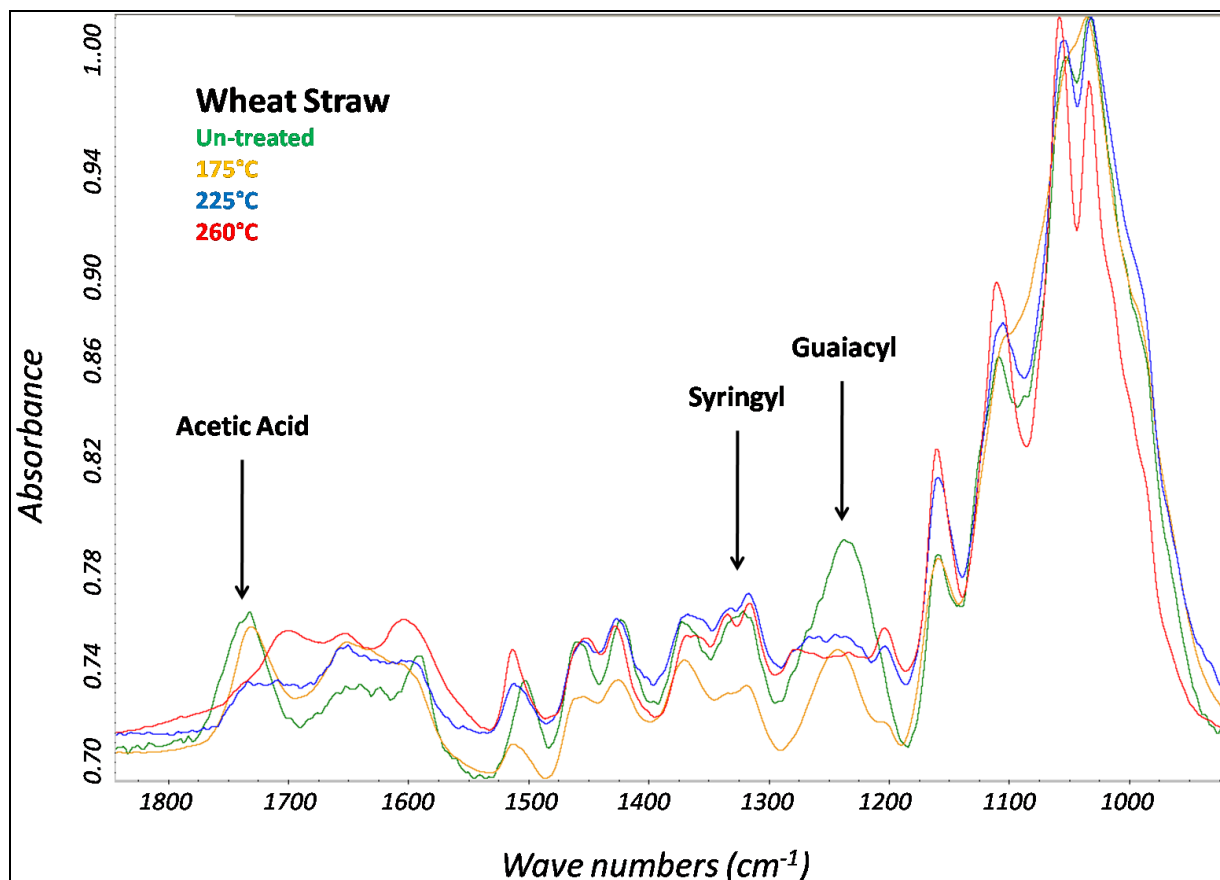


Figure 4.7.- Comparison of cellulose crystallinity % as determined by the Segal Method.

#### 4.3.4 Infrared Spectroscopy

Figure 4.8 shows the IR spectra of wheat straw treated at different temperatures in the range of wavelengths between 1150 and 1790  $\text{cm}^{-1}$ . The spectra obtained from the treated wheat straw samples clearly show changes in the prominent peaks that are typically associated with lignin guaiacol and syringyl (1250  $\text{cm}^{-1}$  and 1311  $\text{cm}^{-1}$ , respectively) <sup>41</sup>. The guaiacyl units are more drastically removed than the syringyl units. This result is consistent with those reported in the literature showing that 40% of guaiacyl and 5% of syringyl are connected through  $\beta$ -O-4 structures <sup>53</sup>. The removal of higher amounts of guaiacyl units happens despite the greater tendency of these units to form condensed structures. It is noteworthy that the peak at 1750  $\text{cm}^{-1}$ , commonly associated to esterified acetic acid, is also being degraded as a result of CHW treatment. This is another indication confirming that acetic acid esters are being degraded during the treatment <sup>54</sup>. The IR spectra confirm that CHW pretreatment removes part of the lignin (mostly the guaiacyl) and most of the hemicelluloses.



**Figure 4.8.-** IR spectra of treated wheat straw samples.

#### 4.3.5 Py-GC/MS

The Py-GC/MS experiment was conducted to determine whether CHW treatments would significantly alter the distribution of products formed during fast pyrolysis. Experimentally, this was determined by comparing peak area ratios for major peaks. A typical chromatogram with the peaks associated with the most important compounds analyzed in the paper (hydroxyacetaldehyde, furfural, levoglucosanone, hydroxymethyl furfural, acetic acid, 2-methoxy-4-vinyl phenol, and phenol, 2,6 dimethoxy) is shown in Figure 4.9. Figure 4.10 shows how the ratio levoglucosan/hydroxy-acetaldehyde and levoglucosan/furfural vary as a function of pretreatment temperature when the sample was pyrolyzed at 500°C. This figure indicates that the peak area ratios are being altered as a result of the CHW treatment. The data in Figure 4.10

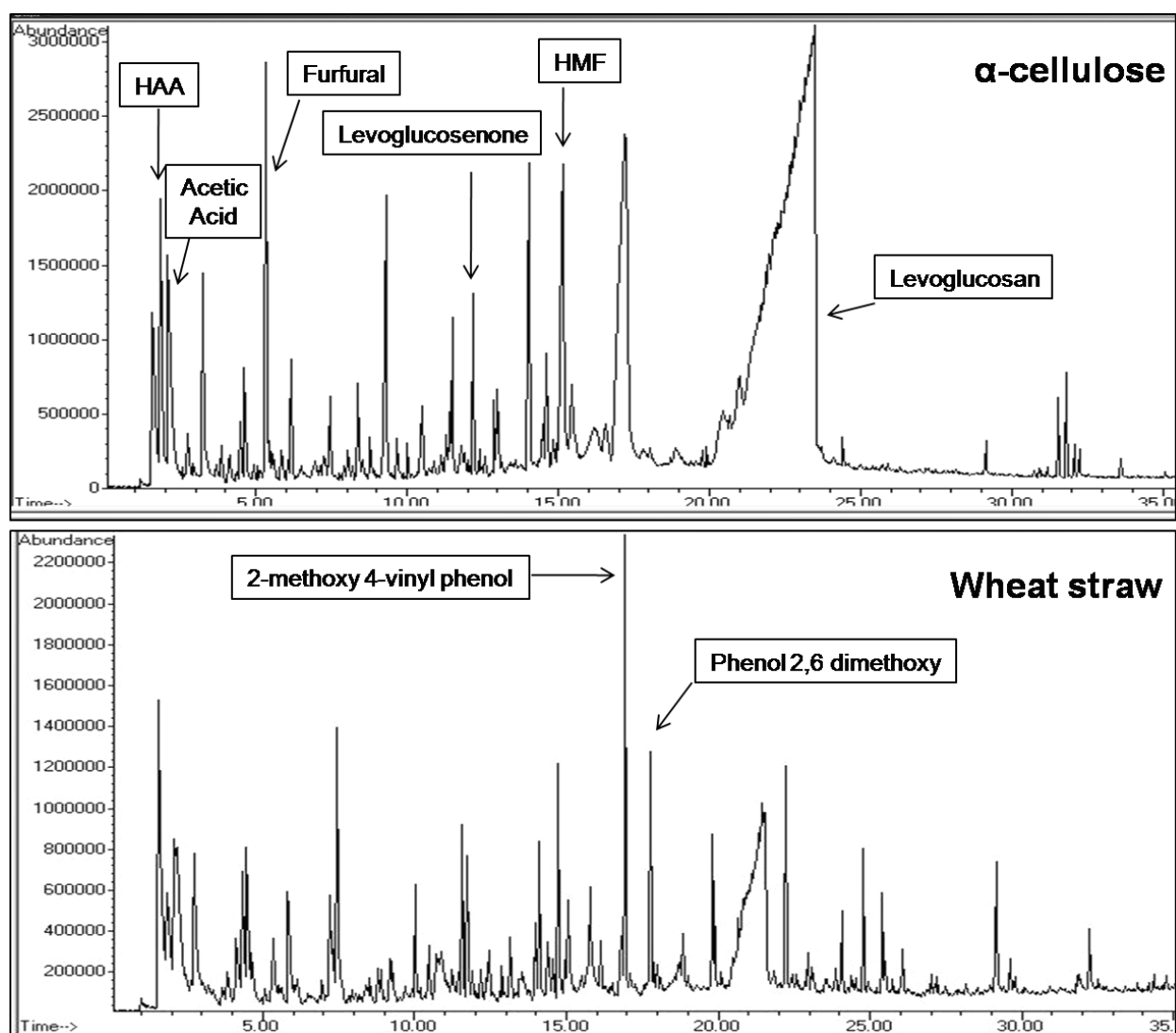


indicate that the ratio levoglucosan is increasing with respect to hydroxy acetyl aldehyde (HAA) for both  $\alpha$ -Cellulose and wheat straw. This ratio increases from 2.5 to 5.5 for wheat straw treated at 175°C and 260°C, respectively.  $\alpha$ -Cellulose in general had a much higher ratio of levoglucosan/HAA, but showed a similar linear increase as a result of the CHW treatment. Specifically, levoglucosan/HAA increased from 13 to 31 when treated at 150°C and 260°C, respectively.

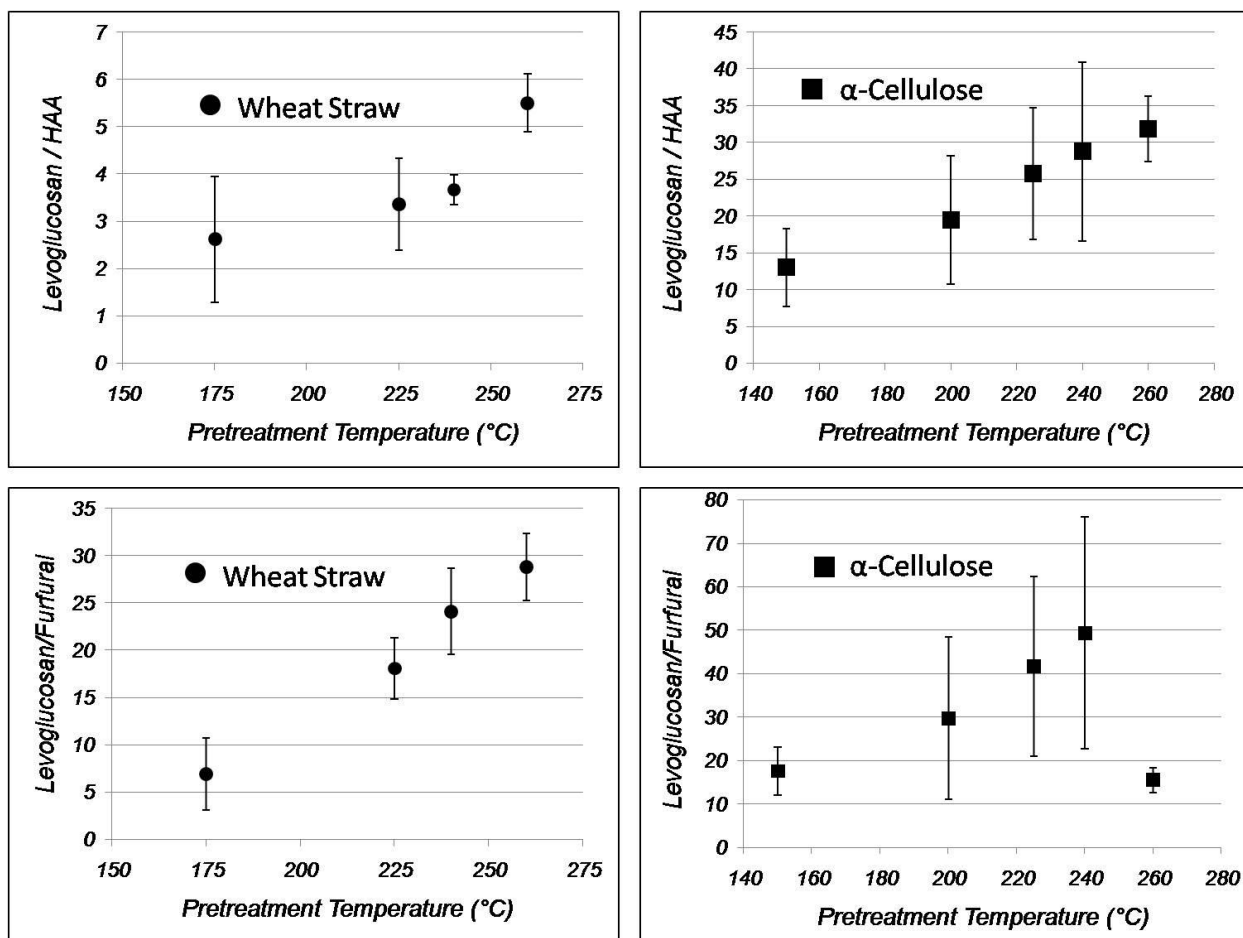
This result is an indication that cellulose primary reaction selectivity is being altered to favor depolymerization reactions leading to the formation of levoglucosan over fragmentation reactions leading to the formation of hydroxy acetyl aldehyde. One explanation for this result could be the reduction in alkalines in the material, which are well known to be a strong catalyst of cellulose fragmentation. However, this explanation alone would not be sufficient evidence because there was a similar increase observed for  $\alpha$ -Cellulose, which is virtually ash-free material. Moreover, virtually all the ash was removed from the wheat straw when treated at 225°C, which also showed an increase in the levoglucosan/HAA ratio.

Another explanation could be that the increase in levoglucosan is proportional to the increase in the content of “active cellulose” in the material. The ratio levoglucosan/furfural also increases steadily as the pretreatment temperature augments; the only exception is a drastic reduction observed for  $\alpha$ -Cellulose treated at 260°C. When comparing the ratio of levoglucosan to furfural, we see a linear increase for both wheat straw and  $\alpha$ -Cellulose, as would be expected from removal of pentose sugars from the material. This trend did not hold for  $\alpha$ -Cellulose when treated at 260°C. Experimental evidence and the literature support the hypothesis that the cellulose is undergoing mild oxidation as a result of the treatment, and oxidized cellulose could lead to the formation of furfural. Py-GC/MS data show that for  $\alpha$ -Cellulose there is a substantial

increase in levoglucosenone (data not shown) typically formed with addition of acid catalyst and cellulose oxidation.<sup>55</sup> Furthermore levoglucosenone has been shown to degrade to furfural.<sup>56</sup> The more intense oxidation of  $\alpha$ -Cellulose is also supported by the TGA data that shows the highest amount of char formation at the 260°C condition. Surprisingly, the wheat straw samples did not seem to form any levoglucosenone; this may in part be due to the lignin serving as an antioxidant that is protecting the cellulose.



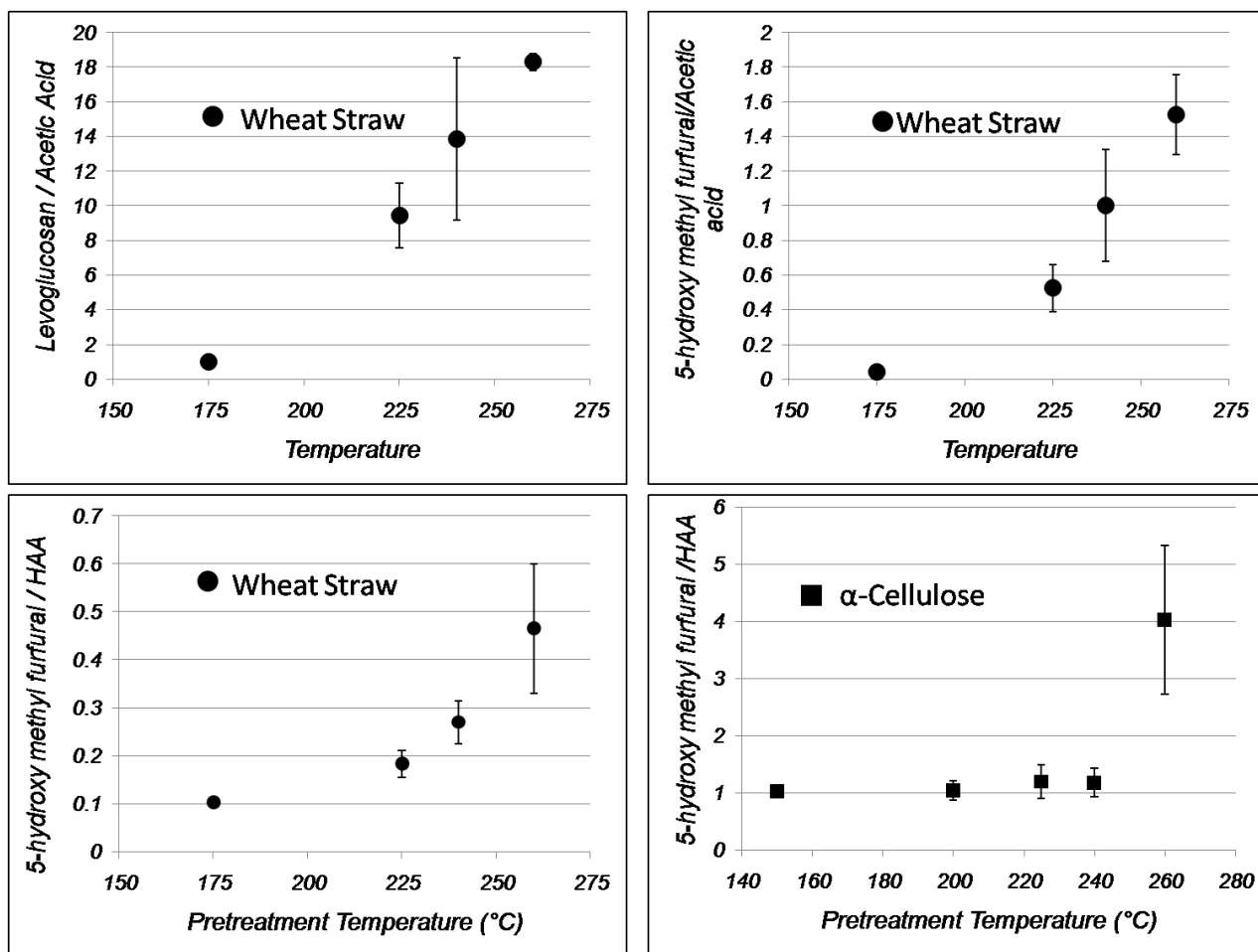
**Figure 4.9.-** Py-GCMS Chromatograms for wheat Straw and  $\alpha$ -Cellulose



**Figure 4.10.** - Pyrolysis GCMS peak ratios for levoglucosan HAA and furfural.

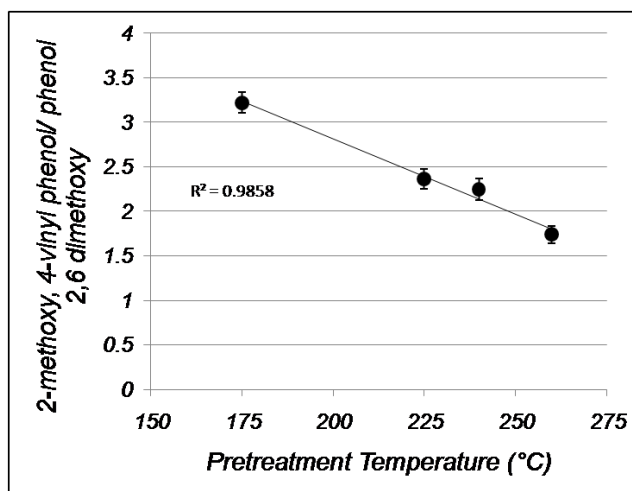
Figure 10 shows the ratio levoglucosan and 5-hydroxy methyl furfural (HMF) to acetic acid for treated wheat straw samples. Both ratios increased nearly 15 to 20-fold and this suggests that the bio-oil produced may be less reactive and corrosive. Additionally, the ratio of HMF to HAA increases substantially for both  $\alpha$ -cellulose and wheat straw. Specifically, wheat straw increases from 0.1 to 0.48 from 175°C to 260°C, respectively.  $\alpha$ -Cellulose increases from 1 to 4 for 150°C and 260° conditions. When taking all the data into account, it seems clear that as an effect of the treatment there seems to be selectivity to favor more oxidation and depolymerization and less fragmentation. This evidence suggests that CHW pretreatment may produce bio-oil that is

composed of a greater amount of sugars and furanics and fewer small molecules, and may therefore be a viable option to improve the bio-oil quality.



**Figure 4.11.-** Levoglucosan HMF acetic acid and HAA peak area ratio comparisons

To determine the effect of CHW treatment on the lignin fraction of the wheat straw, a comparison of peak area ratios of lignin monomers derived from either syringyl or guaiacol subunits (phenol 2,6 di-methoxy and 2-methoxy, 4-vinyl phenol) is shown in Figure 4.12. The Py-GC/MS data show a linear decrease in these two ratios, suggesting that CHW preferentially removes the guaiacol subunits. The lignin plays a very important role in protecting the cellulose against oxidation and cross-linking when subjected to intense hot water pretreatment.<sup>52</sup>



**Figure 4.12.-** Comparison of peak area ratios for compounds derived from guaiacol and syringyl sub-units.

Our results show that it is possible to improve the production of sugars and furans if the cellulose is pretreated in the temperature ranges of 200°C to 240°C in CHW. A viable explanation for this phenomenon is that the increased temperature induced the formation of an “active cellulose,” which is an intermediary for depolymerization reactions leading to the formation of anhydrosugars. Although the existence of “active cellulose” has been proposed for more than 40 years, the nature of this active cellulose is not well known. Recent literature reports a phase transition from  $1\beta$  to a high-temperature cellulose phase in the same range of temperature where the active cellulose is formed. It has been demonstrated<sup>24-26, 57</sup> that there is a reduction in intramolecular hydrogen bonds at 220°C and that the hydrogen bonds from O3–H3•••O5 and O2–H2•••O6 are broken. These changes, together with reductions in cellulose degree of polymerization and chain rigidity, could result in the formation of a unique type of cellulose favoring depolymerization reactions. The further oxidation of active cellulose provides a reasonable explanation for the increase in the yields of furfural and hydroxy methyl furfural as the pretreatment temperature increases.

#### **4.4. Conclusions**

The results presented herein suggests that hot water pretreatment in the temperature range between 200°C and 260°C could be an efficient method to improve the quality of bio-oil produced from fast pyrolysis of wheat straw. Our data suggest that CHW fractionation to remove hemicelluloses and ash may provide a novel method to improve the composition of bio-oils by reducing the content of acids and increasing the content of oligo-sugars. Our results support the hypothesis that thermochemically induced changes may dictate the proportions of different pyrolysis products. This experiment suggests that thermochemical pretreatment of biomass can alter the composition of the bio-oil that is produced; moreover, compressed hot water treatments in the temperature range of 150°C to 260°C seem to increase the conversion of cellulose into levoglucosan and hydroxy methyl furfural.

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# Chapter 5

## Conclusions and Recommendations

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### *5.1.- Conclusions*

LHW could be a suitable approach to pretreat and fractionate biomass to improve the quality of bio-oil resulting from fast pyrolysis. This method has been proven effective for both biological conversion for bio-fuel production and for the wood products industry. To the best of the author's knowledge this is the first attempt to use LHW as a pretreatment for thermo-chemical conversion, specifically fast pyrolysis. The experiments that were conducted suggest that LHW will modify cellulose structure, remove hemicellulose, and modify lignin in a manner that improves the overall quality of the bio-oil produced. Our Py-GC/MS studies suggest that this pretreatment approach will result in the production of higher yields of anhydrosugars.

### *5.2.- Recommendations*

#### *5.2.1 Science Recommendations*

The experimental results presented in this thesis show that hot water pretreatment has a significant effect on the ratio of levoglucosan to hydroxy acetyl-aldehyde formed from pyrolysis

of cellulose. The data show that there is a connection between the increases in production of levoglucosan and the increase in crystallinity of cellulose. Although, this trend is not ideal it does seem to be present. New experiments to characterize the changes in the molecular weight of cellulose as a function of pretreatment temperature would be useful to elucidate the relationship between cellulose DP and the selectivity toward the formation of anhydrosugars (levoglucosan).

The Py-GCMS experiments for  $\alpha$ -Cellulose present some interesting results regarding potential oxidation that is occurring when treated at 260°C. It seems clear that the treatment at 260°C leads to a partially oxidation, as evident by the sharp increase in levoglucosenone, furfural and hydroxymethyl furfural. This leads to the conclusion that while mild pretreatment conditions will result in a reduction of the DP of cellulose, more severe pretreatment conditions will lead to oxidation and crosslinking. Experiments with  $^{13}\text{C}$  NMR may be useful to determine the extent of cellulose oxidation. Kinetic studies making use of  $^{13}\text{C}$  NMR and molecular weight distribution information could help to gain deeper understanding of the mechanisms of the reactions in solid phase happening during pretreatment. This information is needed to develop mathematical models to design and optimize pretreatment units. Further, use of 2D spectroscopic techniques on model polymers coupled with molecular modeling may elucidate the specific carbons most susceptible to oxidation. Lastly, it seems clear that lignin is acting as an antioxidant protecting cellulose against oxidation and crosslinking. New experiments could be carried out to better understand the mechanisms of cellulose oxidation.

Another interesting observation is that the presence of lignin does seem to drastically reduce the ratio of levoglucosan/hydroxy acetyl aldehyde as evident by substantially different ratios from treated wheat straw and  $\alpha$ -Cellulose. This observation may provide ground work to validate the

depolymerization mechanism via free radical scission as lignin is a known antioxidant. Experiments could be conducted using DSC to monitor the position of exothermic crosslinking reactions with various mixtures of cellulose and lignin to attempt to correlate oxidation and crosslinking kinetic parameters as affected by the presence of lignin. This information could be used to develop new technologies to mitigate the inhibitory effect lignin has on cellulose depolymerization reactions.

### *5.2.2 Engineering Recommendations*

This project demonstrated that LHW pretreatment may improve the quality of bio-oil produced during fast pyrolysis. This finding should be validated by treating larger amounts of material under the same pretreatment and pyrolysis conditions in a fluidized bed reactor. Analysis of the content of anhydrosugars, furanics, and lignin in the resulting oils will provide conclusive validation of this thesis.

It is well established that LHW and steam explosion modifies the structure of lignin making it easily extractible with solvents or alkali. The extractible lignin may be a suitable feedstock for hydrotreatment. It is very important to investigate if this lignin would be efficiently converted into green gasoline.