Carbon Dioxide Capture Using Amine Functionalized Carbonaceous Materials from Bio-Refinery Waste Streams

Emmanuel Atta-Obeng

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CARBON DIOXIDE CAPTURE USING AMINE FUNCTIONALIZED CARBONACEOUS MATERIALS FROM BIO-REFINERY WASTE STREAMS

Emmanuel Atta-Obeng

A dissertation submitted to the College of Agriculture, Natural Resources and Design at West Virginia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Forest Resource Science

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Morgantown, West Virginia
2017

Keywords: Lignin, hemicellulose, carbonaceous material, hydrothermal carbonization, activation

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ABSTRACT
Carbon dioxide capture using Amine functionalized carbonaceous materials from biorefinery waste streams
Emmanuel Atta-Obeng

One of the greatest challenges in the world today is to replace exhaustible fossil fuel resources with renewable alternatives that will satisfy the increasing worldwide energy and chemical demands in a sustainable way. Using renewable precursors has a low impact on environmental health since it reduces pollution, greenhouse gas emissions and limits global warming and problems associated with waste management. Lignocellulosic biomass is the most available feedstock for developing sustainable chemicals and energy. A major challenge to the efficiency of the forest biorefinery industry is lack of suitable technologies for the conversion of its waste or by-products (lignin and hemicelluloses) into value-added products. In this research, lignin was hydrothermally treated at different temperatures, and the resulting carbonaceous materials (CMs) were functionalized with amine groups to capture carbon dioxide (CO$_2$).

Experimental measurements and characterization techniques were used to evaluate optimum temperature for the hydrothermal treatment of lignin. The yield of CMs decreased with increasing temperature. Thermal degradation analysis showed that at 350°C, a more carbonaceous material was formed, which showed more coal-like features. This was further supported by Raman spectroscopy and X-ray diffraction analysis. Scanning electron micrographs of the CMs also showed both open and closed vesicles after hydrothermal carbonization.

The chemical transformations occurring during hydrothermal carbonization of lignin was investigated. Overall, major structural changes in the HP-L™ lignin only occurred after 300°C. Fourier transform infrared (FTIR) analysis and X-ray photoelectron spectroscopy (XPS) analysis
showed that bands due to lignin functionalities disappeared at 350°C. Deconvolution and peak analysis using nuclear magnetic resonance (NMR) revealed the evolution of a more condensed structure characterized by aromatic C when temperature reached 350°C. Lignin remained relatively unchanged up until 350°C where significant aromatization occurs. Based on the above characterizations, a mechanism for HTC was suggested.

Activated samples were functionalized with polyethylenimine (PEI) at different loadings to evaluate their synergistic effect in capturing CO₂. Activation improved to surface area from 2.8 m²/g to 1341 m²/g. The highest CO₂ uptake (2 mmolg⁻¹) was attained by samples loaded with 5% PEI after which sorption capacity decreased with increasing PEI loadings. This was ascribed to blockage of the micropores in the activated samples during PEI impregnation. Also, activated samples showed faster adsorption kinetics compared with PEI functionalized activated samples.

Lastly, the hydrothermal treatment (HTT) or carbonization (HTC) of three commercial types of lignin to carbonaceous materials was also investigated. SEM analysis showed that hydrothermally derived carbonaceous materials from Mascoma lignin contained spherical particles with diameters ranging from 50 to 250 nm whereas that from ammonium and sodium ligno-sulfonate lignins contained similar particles but were highly agglomerated. The better characteristics of the post- HTC Mascoma carbon vis-a’-vis post-HTC ammonium and sodium carbons are also evident in the results obtained from XRD, TGA and FTIR analysis. It is possible to produce carbonaceous materials from low-value commercial lignins via HTC and their properties are influenced by the type of lignin.
DEDICATION

I do not believe I could have completed this research without the love and support of my family. This dissertation is dedicated to my wife and daughter Wendy and Nana Ahema, my sisters Lilian and Christie, and my brothers James and Papa Derby. You were always there for me and it has made all the difference.
ACKNOWLEDGMENT

I would like express my sincere gratitude to Dr. Benjamin Dawson-Andoh (Major Advisor) for his continued guidance, discussion, motivation and support during my dissertation work. His enthusiastic and professional approach to research has taught me a valuable tool for the future.

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I am also indebted to the providers of the North-East Sungrant and McStennis Fellowship, without whose financial sponsorship I wouldn’t have made it this far. A special thank you to Attorney David Fryson and Sharon Mallow of the Division of diversity, equity and inclusion for their support as well.

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CHAPTER 1: STRUCTURE OF DISSERTATION, INTRODUCTION AND OBJECTIVES

1.1 Structure of Dissertation

This dissertation contains seven chapters. Chapter one contains the structure of the dissertation, the introduction as well as the objectives of this study.

Chapter two is the literature review on the whole study.

Chapter’s three to six contain four publications to be submitted from the findings of this dissertation. Specifically, chapter three examined the effect of temperature on yield, thermal and physical properties of carbons produced from hydrothermal carbonization of lignin and hemicellulose. Chapter four investigated the chemical changes and suggested a mechanism for the degradation of lignin during HTC. Carbon dioxide capture properties of amine functionalized carbons from HTC lignins were investigated in Chapter five. Finally, Chapter Six compared the properties of CMs produced from HTC of three commercially produced lignins

The general conclusions and future recommendations of this dissertation are presented in chapters seven.

1.2 Overview of project

Carbon dioxide (CO₂) from stationary, anthropogenic point sources such as fossil fuels (e.g. coal), is a major contributor to global warming due to its significant emission quantities [1]. Currently, fossil fuels supply over 85% of global primary energy demand and will likely dominate, at least, for the next few decades [2]. To mitigate the effect of global warming on the environment, large CO₂ emissions from stationary sources should be capped. Also, removal of CO₂ from power plant flue gas is presently the most effective way to remove CO₂ from an energy stand point. In
this regard, post-combustion CO₂ capture technologies have been extensively studied since they can be easily retrofitted into existing conventional plants [3].

Chemical absorption is one of the most widely researched capture techniques for CO₂ in plant sourced flue gases. The process involves bubbling the flue gas through a basic solvent (e.g. monoethanolamine – an alkanolamine). The CO₂ is preferentially absorbed into the solvent by the formation of a chemically bonded compound [3]. The biggest drawback to this technique is the huge cost (up to 20% of plant output energy) involved in regenerating the amine solution. Alternatively, physical adsorption based on pressure, temperature and vacuum swing approaches, by porous solid sorbents are cost effective and have been a subject of intense research in recent years [4]. To make these adsorbents competitive, they must have high selectivity and high adsorption capacities.

While a range of solid sorbents including zeolites, metal organic frameworks (MOFs), silica and alumina have been researched, amine modified activated carbons have recently been identified as promising sorbents for CO₂ capture [4,5]. The adsorptive performance of these materials relies on their large surface areas, pore volume, tunable pore structures [3,6]. Furthermore, their sorption capacities can be enhanced through surface functionalization using various amine groups to mimic liquid phase CO₂ absorption [5]. Besides adsorptive properties, the choice of adsorbent materials is influenced by factors such as easy synthesis, availability of untreated material, scalability, sustainability, cost and toxicity etc. For instance, although most reported MOF’s have high sorption capacities, they are expensive, not scalable and suffer from chemical and hydrothermal instabilities. Carbon based materials have shown to be more promising and can be easily tuned to several applications.
Hydrothermal carbonization (HTC) is an alternative, sustainable, lower-cost thermochemical treatment process for converting biomass and other organic waste streams to carbonaceous “coal-like” products mimicking the natural coalification process [7,8]. Although an old technology, it has gained much prominence recently because of its many advantages. HTC uses an environmentally benign solvent (i.e. water) as the reaction medium, under relatively low-temperature (160 – 374°C) and self-generated pressure (10-22 MPa) conditions. Unlike pyrolysis, substrates for HTC do not have to be pre-dried, a significant saving in energy. The process generates a much higher carbon yield, relatively lower amounts of GHGs and energy efficient since it’s an exothermic reaction [9]. Few studies have looked at the potential application of hydrothermal carbons in CO2 capture. Sevilla and Fuertes (2011) reported very high CO2 uptake of 4.8 mmol/g at room temperature (25°C) for hydrothermally treated sawdust activated at 600°C [10]. No information exists on the performance of carbons from the hydrothermal treatment of biorefinery waste like lignin and hemicellulose in GHG (CO2) capture.

This study aimed at the efficient utilization of low value bio-refinery waste stream (lignin) as precursor for CO2 adsorption. In a biochemical refinery, the target is D-glucose from cellulose, which when separated can be converted into ethanol by fermentation. The main by-products are lignin and hemicelluloses. Lignins have found recent uses such as carbon fibers, binders or surfactants, whereas hemicelluloses have also been explored as films or gels in packaging, and as sweeteners [11-14]. The sustainable operation of these refineries will mean finding alternative low cost processes for converting these low value waste streams into high value functional materials such as GHG capture. This study investigated CO2 capture capacity based on amine functionalized carbonaceous materials synthesized from the hydrothermal carbonization of biorefinery waste streams.
1.3 Overall objectives of study

The overall research objectives of this study are:

1. Determine optimum processing conditions for the conversion of biorefinery waste streams into carbonaceous materials

2. Evaluation of surface chemistry properties of carbonaceous materials after chemical functionalization

3. Evaluate the CO₂ sorption capacity of amine functionalized carbonaceous materials
1.4 References


CHAPTER 2: LITERATURE REVIEW

2.1 Global warming and carbon economy

Increased industrialization, coupled with rapid economic growth have led to today’s rise in energy demands. The result is an over dependence on fossil fuel resources like coal, oil and natural gas [1]. Combustion of fossil fuels for electricity and transportation impact the environment negatively by emitting greenhouse gases (GHG’s) such as carbon dioxide CO$_2$, nitrous oxide (N$_2$O), sulfur dioxide (SO$_2$), methane (CH$_4$), and ozone (O$_3$). Table 1 gives a breakdown of harmful pollutants released into the atmosphere from burning fossil fuels [2]. Despite emerging non-fossil energy sources like nuclear and hydropower which are considered non-emitting, fossil fuels still supply over 85% of the world’s energy needs [3,4].

Anthropogenic (human source) CO$_2$ is a major contributor to global warming and climate change. Global warming leads to changes in snow cover, high latitude ice cover, decrease in upper ocean pH and an expected economic loss of 5-20% of the world’s gross domestic product [5,6].

It has been reported that atmospheric CO$_2$ level increased significantly, from 280 ppm to 397 ppm since pre-industrial times. Among anthropogenic sources, use of energy is by far the largest (68%) source of CO$_2$ emissions. Specifically, coal combustion generated the highest (46%) CO$_2$ emissions worldwide, twice as much as that of natural gas per unit of electricity sent out [4]. This is due to its high carbon content per unit energy released.

The U.S relies on coal for about 50% of its electricity generation, the equivalent of more than five hundred 500 MW coal fired plants. CO$_2$ emissions from fossil fuels accounted for 78% of all greenhouse gas emissions from human activities in the U.S. [7,8].
Table 2.1 Contributions of green-house gases to global warming [2].

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Natural Gas</th>
<th>Oil</th>
<th>Coal</th>
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<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>117,000</td>
<td>164,000</td>
<td>208,000</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>40</td>
<td>33</td>
<td>208</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>92</td>
<td>448</td>
<td>457</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>1</td>
<td>1122</td>
<td>2591</td>
</tr>
<tr>
<td>Particulates</td>
<td>7</td>
<td>84</td>
<td>2744</td>
</tr>
<tr>
<td>Mercury</td>
<td>0</td>
<td>0.007</td>
<td>0.016</td>
</tr>
<tr>
<td>Total</td>
<td>117,140</td>
<td>165,687.007</td>
<td>214,000.016</td>
</tr>
</tbody>
</table>

There is therefore a global consensus among climate scientists of the urgent need to reduce CO₂ emissions [9]. Global CO₂ emissions must be cut by 50% by 2050, if the expected average global temperature caused by greenhouse effect is to be reduced to 2°C by 2100 [10]. Globally, energy consumption from fossil sources increases annually, and coal burn is even expected to increase especially in developing countries [11]. Coal use will therefore affect deeply the reduction of CO₂ emissions. The cost of infrastructure required to transition into other non-fossil fuel based resources will be expensive and will take decades. Retro-fitting existing coal (fossil based) power plants with the aim of reducing or capturing CO₂ is promising. Carbon capture and storage (CCS) will enable the continuous use of fossil fuels while reducing CO₂ which would have otherwise been emitted into the atmosphere, thereby mitigating global climate change. Without CCS technology, the cost of a 50% reduction in CO₂ emissions by 2050 will be 70% higher [12].
2.2 CO₂ capture technologies from stationary sources

One option for reducing CO₂ emissions is the capture and storage of CO₂ from flue gases emanating from stationary industrial sources such as coal and gas fired plants. CO₂ storage is a core technology and accounts for 70-80% of the total costs of CCS technologies [13]. Since CO₂ is produced during combustion, the type of combustion affects the choice of a CO₂ capture technology. Currently, there are three main capture systems based on three combustion processes: 1) Pre-combustion capture 2) Oxy-fuel combustion and 3) Post-combustion capture. Figure 1 gives schematic diagrams for the three technological concepts [14].

Figure 2.1 Schematic diagram for three types of CO₂ capture technologies.
2.2.1 Post combustion CO2 capture

Post-combustion capture approach removes CO2 from the flue gas stream after combustion of fossil fuel in air. It is the most feasible approach because it can be easily retro-fitted into existing plants [15,16]. The concentration of CO2 from flue gas is typically low (4-14%) as such large volumes must be handled resulting in large equipment sizes and increased capital costs. The low concentration of the gas requires powerful chemical solvents that should be used and the regeneration of these solvents require a large amount of energy. The partial pressure of CO2 from post combustion flue gas is low (0.15atm.), and the thermodynamic driving force is low as such creates problems for a cost-effective separation process from the gaseous mixture [17].

2.2.2 Pre-combustion CO2 capture

In pre-combustion capture, the fuel is pretreated before combustion. The fuel goes through a gasification process to yield a gaseous mixture of hydrogen and carbon monoxide (CO), which further undergoes a water-gas reaction with steam to produce more hydrogen and CO2 [18]. The concentration of CO2 in this mixture can range from 15-50%, and it is captured at a high pressure for storage. The remaining hydrogen is used as fuel. The whole process is equivalent to removing carbon from coal before combustion. CO2 concentration and pressure are both higher in pre-combustion than post-combustion capture. Presently, the fuel conversion steps required for pre-combustion are more complex and energy intensive as such the technology is more difficult to be adapted to existing plants [19].

2.2.3 Oxy-combustion CO2 capture

Oxy-fuel combustion uses high purity oxygen (95% by volume) instead of air for the combustion process; producing gases consisting of mainly water vapor and CO2 that can be separated to produce high purity CO2 [20]. The advantage of this process is that; the flue gas has
a CO₂ concentration of over 80% and relies mainly on a physical separation technique thereby
avoiding the use of chemical solvents that contribute to operating costs and environmental disposal
of any related solid or liquid wastes. Despite its advantages, research is still ongoing on how to
improve its economics i.e. costs of O₂ production and reducing energy penalty due to air separation
and CO₂ purification [21].

2.3 Post-combustion CO₂ capture technologies

Among the current technologies, post-combustion capture is still the most widely applied
since it can be easily retro-fitted into existing plants. It employs wet or dry adsorbents for the gas
separation based on a physical or chemical process. Post-combustion technologies have been
classified into absorption, adsorption, membrane and cryogenics as shown in Fig. 2 [22,23].

2.3.1 Absorption techniques

Chemical absorption of CO₂ from flue gases is possible due to acid-base neutralization
reactions using a basic solvent. CO₂ is an acid and as such reacts with basic chemical compounds
to form weakly bonded intermediate compounds which can be easily broken by heat to regenerate
the solvent and give off a pure CO₂ stream as depicted in Fig. 3 [22,24]. For this reason, amine
based solvents such as monoethanolamine (MEA), diethyl-ethanolamine have been
commercialized and used in the industry for over 60 years [25,26]. Despite being the most
researched of separation technologies, amine based chemical absorbents suffer significant
disadvantages. Integrating a commercial amine-based capture system into a pulverized coal plant
would increase energy cost by about 80% and lead to 25-40% energy penalty [27] Additionally,
amine based absorption processes suffer high equipment corrosion, low CO₂ loading capacity and
amine degradation by other gases (SO₂, NO₂, HF etc.) in flue gas [2].
Figure 2.2 Classification of application technologies for post-combustion CO₂ capture.
2.3.2 Membrane technology

Membrane based separation techniques have been in existence for a long time, with broad industrial applications such as air separation and natural gas purification [29]. Its application to flue gas separation is relatively new. Membrane based techniques operate on physical or chemical interactions between a gas and the membrane material. They preferentially separate gases through various mechanisms such as solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport [30]. Membranes are made from different materials such as organic (polymeric) or inorganic (carbon, zeolite, ceramic or metallic) and can be porous or non-porous [31]. Membrane-based process has the advantage of being simple, easy to operate and low energy consumption; however, they require a high cost module, not durable and not suitable for treating large volumes of emission gases [32].
2.3.3 Adsorption techniques

Adsorption separation operates on a cyclical process by which a gas selectively attaches itself to the surface of a solid material. The adhered molecules form film on the surface of the materials to which they are attached and are called adsorbate, while the material on which they are attached is called the adsorbent. The process is controlled by the properties of the gas (molecular size, molecular weight) and the adsorbent surface (polarity, pore size and distribution) of the sorbent. In the case of CO₂ flue gas, the CO₂ is adsorbed and the remaining gas mixture is emitted into the atmosphere. Adsorption has an advantage because the sorbent is regenerated at different stages by either thermal or pressure modulation to remove CO₂, thereby reducing the net energy used in the whole capture process [33].

Two forms adsorption exist i.e. physi-sorption and chemi-sorption. In physi-sorption, the adsorbate (CO₂ gas) is weakly bound to the surface of the solid by van der Waals forces and heat is released upon adsorption. Chemi-sorption on the other hand, occurs when there is a covalent bond between the gas and the sorbent, as such adsorption capacity is higher. Solid sorbents that have been used in CO₂ capture include activated carbons, zeolites, activated alumina, metal organic frameworks, and siliceous materials [34-38]. At present, chemical absorption and physical adsorption are the major areas of research focus for post-combustion CO₂ capture.

Solid sorbents are advantageous because they can be used over a wider temperature range (25-700°C), yielding less waste during cycling, and the spent solid sorbents can be disposed without causing environmental problems [39]. However, the economic viability and practical application of these solid sorbents in post-combustion CO₂ capture will depend on factors such as working temperature, sorption capacity, selectivity, durability (regeneration of sorbent after multiple use) and cost.
2.3.4 Cryogenics

In cryogenics separation, all components of the flue gas are removed except N₂ and CO₂ prior to cooling. These two gases are then sent to the cryogenic chamber temperature and pressure are manipulated to cause the CO₂ to liquefy. Under right distillation conditions, CO₂ condenses which can be collected at bottom of chamber, while N₂ escapes from an outlet at top chamber as a gas [40]. Cryogenic technology is a suitable process because of its low investment cost and high reliability. However, it is not included in most (economical) comparison studies, as it has been considered as an unrealistic candidate for post-combustion CO₂ capture due to expected high cooling costs, but also because it has been considered as a gas–liquid separation [41].

1.4 Carbon and its applications

Carbons are classified according their degree of structural order i.e. C-C bonding based on $sp$, $sp^2$ or $sp^3$ hybrid orbitals. There are carbons which are graphitizable/anisotropic (exhibit X-ray diffraction lines of three-dimensional graphite) or become graphitic upon heating to temperatures beyond 2000°C. Graphene layers of graphitizable carbons also show considerable planarity and stacking. Another group of carbons which are non-graphitic/isotropic do not show X-ray diffraction lines even when heated beyond 2000°C [42]. This is depicted in Figure 4.

![Graphitizable vs. non-graphitizable carbons](image-url)

Figure 2.4 Graphitizable (left) vs. non-graphitizable carbons [43].
Carbon can also exist (allotrope) as a) diamond b) graphite c) graphene d) single wall nanotube e) Buckminster fullerene, each member being unique in terms of structure, texture and ability to accept foreign atoms/compounds into their structures (Fig. 5). Detailed literature review exists on carbon science, structure and technology, activated/porous carbons and their applications in adsorption [42-46].

![Allotropes of carbon](image)

Figure 2.5 Allotropes of carbon a) diamond b) graphite c) graphene d) single wall nanotube e) Buckminster fullerene [47].

Carbon materials play a part in our daily lives in many ways, some not obvious. They have found wide applications in energy conversion technologies (energy storage, catalysis, biofuels etc.), water purification, gas separation and storage, soil amelioration etc. [48-51]. Independent of source and processing conditions, carbon materials can easily be tuned to obtain such beneficial properties as high surface area and porosity, chemical inertness, high mechanical strength, electrical conductivity and thermal stability.
Carbon based materials such as activated carbons, charcoal and coal are considered promising sorbent materials for CO₂ capture [52]. Although these materials mainly consist of a single element (i.e. carbon), they are widely used because of their availability, high surface areas and have highly tunable pores for modification and surface functionalization [53]. Unlike liquid sorbents, carbon sorbents are particularly good for CO₂ capture because 1) they are widely available and cheap to produce 2) have high thermal and chemical stabilities 3) the adsorption/desorption temperatures are well below 100°C 4) can be used at atmospheric pressure and 5) their energy consumption is comparatively low [54,55].

Amine groups have been incorporated into various carbon sorbents to increase their polarization which in turn increases CO₂ selectivity and capture. Amine functionalized sorbents have the advantage of eliminating corrosion problems and lower energy costs for regeneration. Chang et al. (2009) described the interactions between CO₂ and amine functional groups to produce ammonium carbамates under anhydrous conditions as follows [56]:

1. \( CO₂ + 2RNH₂ \rightarrow RNHCOO⁻ + RNH₃⁺ \)
2. \( CO₂ + 2R₂NH \rightarrow R₂NCOO⁻ + R₂NH₂⁺ \)

### 2.4.1 Activated carbons

Activated carbons are materials with a high degree of porosity and extended surface area (around 500-2000 m²g⁻¹), consisting 90% of the element carbon. The size of the pores determines how the adsorption takes place. Per the International Union of Pure and Applied Chemistry (IUPAC) recommendation, porous carbon materials can be classified into three types based on their pore sizes: microporous < 2 nm, mesoporous 2 nm < 50 nm, and macroporous > 50 nm. Activated carbons can be produced from all natural organic materials such as coal, peat, lignite, wood, nut shells, coconut shells and have been applied in the removal of a wide variety of
pollutants and gas separation. Activation can generally be grouped into two: 1) thermal activation or 2) chemical activation [57].

Thermal activation, also known as gaseous or physical activation involves two steps which usually succeed each other:

a. Carbonization: the raw material is heated in the absence of oxygen to temperatures lower than 1000 °C, usually in the range 400-900°C to remove the non-carbon elements.

b. Thermal activation: the already carbonized material is exposed to an oxidizing atmosphere consisting of gases such as steam, carbon dioxide, air or a combination of gases at temperatures between 500-1000°C which develops the porosity. Reactions of carbon and steam can be represented in three equations below:

\[
\begin{align*}
C + H_2O & \rightarrow CO + H_2 \\
C + 2H_2O & \rightarrow CO_2 + 2H_2 \\
C + CO_2 & \rightarrow 2 CO
\end{align*}
\]

Chemical activation on the other hand involves impregnating the raw material with strong oxidizing agents such as potassium hydroxide (KOH), zinc chloride (ZnCl₂), phosphoric acid before after which they are pyrolyzed at temperatures between 600-1200°C. These oxidizing agents act as dehydrating agents which influence the carbonization process by inhibiting the formation of tar and thereby enhancing char yield. The process gives rise to porous carbons with high specific surface areas of over 2000 m²g⁻¹ and large pore volumes consisting of micropores or mesopores [58].

Textural properties of activated carbons make them excellent materials for selective CO₂ removal [59]. Pore size distribution can easily be controlled by varying preparation and activation
conditions [60]. Sevilla and Fuertes [61] reported CO₂ uptake capacities of 3.2 mmolg⁻¹ at 25°C. Lee and Park [62] also reported CO₂ uptake of about 5.7 mmolg⁻¹ for activated carbons. In both instances, CO₂ adsorption was more dependent on the presence of micropores rather than the surface area or pore volume of activated carbons since they have a higher adsorption potential. Additionally, CO₂ adsorption can also be enhanced by the controlling the surface chemical functionalities of activated carbons [63,64]. Other studies have also aimed at increasing CO₂ adsorption capacity by incorporation of basic amine groups on to activated carbons [65].

2.4.2 Carbons from biomass and waste materials

Lignocellulosic biomass, its waste and by-products from crop and fruit production are considered attractive precursors for the preparation of carbons and/or activated carbons since they are cheap and easily available [66,67]. Common to all crop and biomass precursors is the basic chemical structure which comprises cellulose, hemicellulose and lignin. Activated carbons have been produced from wood, lignite, bones from animals. Similarly crops and waste materials such as cane sugar, maize stalks, pecan nut shell, coconut shell, bagasse, coir, etc. [68-71]. Untreated composition as well as activating agent used influence the morphology, micropore structure and adsorption properties of the final activated carbon [72]. Recent studies have however reported other biomass types and waste materials (e.g. egg shells) can be used as alternative and low cost activating agents for improving adsorption properties of activated carbons used in water purification [73].

Thermo-chemical processes used in the processing of biomass and its waste products into porous carbon materials have included pyrolysis, hydrothermal carbonization, microwave assisted irradiation [74,75].
2.5 Hydrothermal carbonization

To date, most carbon materials are synthesized from fossil fuel sources using relatively harsh conditions (direct pyrolysis, chemical vapor deposition, laser ablation), as such their accessibility and sustainability are somewhat limited [76]. Sustainability and environmental considerations for product development require a paradigm shift from petroleum to bio-based feedstocks with similar efficiency in the production of high performance carbon materials.

Hydrothermal carbonization (HTC) is an alternative attractive, sustainable, lower-cost technology for converting biomass and other organic waste streams to carbonaceous materials. Bergius was first to describe this process in 1913, when he noticed a transformation of cellulose into coal-like materials [77]. When temperature increases, water behaves like an organic solvent. Water is used as the reaction medium under relatively low-temperature (180 - 374°C) and low pressure (2000 psi) conditions in an autoclave [78].

The process is considered green and advantageous because the carbon materials are produced from cheap, readily available biomass sources and most often waste products of biological processes. Water is the solvent required for the process. A fraction of the carbon remains in the HTC carbon materials, as such HTC mitigates greenhouse gases. Untreated materials for HTC can be used wet, a huge savings in energy cost involved in drying compared to pyrolysis emissions [79,80]. Also at the same temperature, HTC carbons are better than dry torrefied carbons since they have a higher mass and energy density [80].

The focus of HTC has shifted from biofuel production to producing functional carbonaceous materials from biomass. However, it must be stated that these carbonaceous materials (over 60% carbon) still contain other elements such as oxygen and hydrogen when compared to carbon (consisting > 90% elemental carbon). HTC carbons have found many applications such as water
purification, sorption, soil amendment, chromatography, energy storage and catalysis. Factors affecting the use of these carbonaceous materials in those applications include their surface area (porosity), surface functionality, conductivity and chemical inertness [82].

2.5.1 Subcritical water (hydrothermal carbonization)

Water is an environmentally friendly and inexpensive solvent that exhibits a wide range of properties when heated, making it effective in solvating and decomposing moderately polar or non-polar compounds. Based on its critical point ($T_c = 374^\circ\text{C}$, $P_c = 22.1$ MPa), water can be described as sub-critical (below its critical point) or super-critical (above its critical point). Sub-critical water is hot water under enough pressure to maintain the liquid state (Fig. 2.6). Above the critical point, water exists in either liquid or gas-like with increasing temperature without any phase transition [83].

There are several properties of water which affect its use as a reaction media. These include miscibility, dielectric constant, ionic product, electrolytic solvent power, transport properties (viscosity, diffusion coefficients and ion mobility), hydrogen bonding, etc. These properties are strongly influenced by temperature and pressure changes. When water is heated, the H-bonding is dissociated into acidic hydronium ions ($\text{H}_3\text{O}^+$) and basic hydroxide ions (OH$^-\text{)}$). The effect is a decrease in the dielectric constant as temperatures approach the critical point making water behave like hydrocarbon solvent [84]. The ionic product ($K_w = [\text{H}^+] [\text{OH}^-]$) of water also increases with increasing temperature and is greater by 1 to 2 orders of magnitude compared to ambient temperatures (Fig. 2.7). Similarly, a rise in temperature also enhances the transport properties (high diffusion coefficient and thermal conductivity, low viscosity) causing more reaction rates [83].
The changes in the physical and chemical properties of water as it approaches its critical point can be utilized advantageously in the conversion of biomass into solid carbonaceous materials (bio-char), liquids (biofuels) and gases (methane, hydrogen) by varying the temperature and pressure (Fig. 2.6).
Figure 2.7 Physical and chemical properties of water with temperature [85].
2.6 References


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CHAPTER 3: HYDROTHERMAL CARBONIZATION OF LIGNIN: INFLUENCE OF TEMPERATURE ON YIELD, THERMAL AND PHYSICAL PROPERTIES OF CARBONACEOUS MATERIALS.

3.1 Abstract

In this study, hydrothermal carbonization (HTC) was used to upgrade a biorefinery waste lignin (HP-L\textsuperscript{TM}) at temperatures ranging from 200 to 350°C and a residence time of 60 minutes. The effect of temperature on yield was investigated and the thermal and physical properties of the produced carbonaceous materials (CMs) were also investigated. Yield was highest at the lowest processing temperature (200°C), and decreased when temperature increased. The thermal qualities of the CMs were significantly improved: with O/C and H/C ratios between 0.1-0.4 and 0.3-1.1 respectively compared to untreated lignin. An increased degree of carbonization in CMs was also confirmed with Raman spectroscopy and X-ray diffraction. Scanning electron micrographs showed both open and closed vesicles after hydrothermal carbonization. This study showed that HTC was a promising conversion process for producing carbonaceous materials from lignin.

3.2 Introduction

Lignin is a major waste stream from the emerging bio-refinery and the established pulp and paper industry. On weight basis, it represents approximately 30% of biomass and is the most abundant aromatic biopolymer. Yet, to-date, lignin remains heavily underutilized and large scale use is limited to as energy source heat. Valorizing lignin is a great opportunity to improve the economics of the bio-refinery process [1,2]. Increasingly, greater research effort is being made to develop value added products for lignin. Carbonaceous materials (CMs) derived from lignin are one such potential added-value products.
Recently, non-graphitic porous carbonaceous materials derived from renewable sustainable precursors have been described as “Green Carbons” [3]. The use of renewable precursors is attractive especially when compared to traditional precursors such as coal. The latter requires high energy processes such as pyrolysis, chemical vapor deposition (CVD), arc-discharge methods and laser ablation [3]. In contrast, hydrothermal carbonization (HTC) process, although not novel, is a facile, low-energy, low-cost and environmentally friendly route for manufacturing novel functionalized carbonaceous materials [4]. CMs produced by HTC exhibit well-controlled morphology, composition and structure with improved thermal properties [5].

The synthesis of such CMs notably from module compounds of simple and complex carbohydrates (glucose, xylose, fructose, cellulose, starch) have been reported in literature [6-8]. A major hurdle to the commercialization of the HTC process is the relative high cost and sustainability of these model compounds (glucose, cellulose, etc.) when used at the commercial scale as feedstocks. Consequently, bio-refinery waste-streams like lignin can be valorized and their environmental footprint also reduced.

Unlike carbohydrate precursors, only few studies on HTC of lignin have been reported [9,10]. Also, lignin is a more complex heterogeneous biopolymer consisting of three mono-lignols: p-coumaryl, coniferyl and sinapyl alcohol connected by various bonds [ether (β-O-4’, α-O-4’); carbon-carbon linkages (β-β’, β-5’, and 5-5’)] [11]. Structurally, lignin varies by species, subcellular location, plant tissue and methods of extraction. During extraction, new linkages such as enol ethers may be formed and quinone methide intermediates may produce additional C-C bonds [12,13]. Consequently, lignin derived from chemical and physical extraction processes are inherently heterogeneous, highly polydisperse and exhibit complex and variable functional groups [14]. These extracted lignins are often denoted as technical lignins and differ both physically and
chemically from native lignin. As result of the just mentioned significant differences in lignin structure, functionality, reactivity and heterogeneity, industrial utilization of this biopolymer presents significant challenges [15]. The knowledge of the effect of reaction temperature will be vital to the design and efficient operation of HTC reactors using different technical lignins.

In this study, several CMs were synthesized from a precursor bio-refinery lignin waste-stream, HP-L™ lignin under varying temperature conditions for 60 minutes. The quality of the carbonaceous products was evaluated by investigating their morphology, thermal and physical properties. HP-L™ lignin is a waste-stream produced by Lignol Innovations Inc. (Lignol) via a proprietary modified organosolv pretreatment method for lignocellulose biomass to produce cellulosic ethanol, purified lignin and furfural from hardwoods. It has high water-insolubility, high phenolic content, low molecular weight and relative purity (i.e. low carbohydrate content, ash and free of sulfur) [16].

3.3 Materials and methods

3.3.1 Materials

The lignin (HP-L™ lignin) used in this study (Fig. 3.1), was supplied by Lignol Innovations Inc. (Lignol Energy Corporation, Burnaby, BC, Canada). The precise composition of HP-L™ lignin (Fig. 3.1) material is provided in Table 3.1.

Figure 3.1 Sample of HP-L™ lignin.
Table 3.1 Composition of HP-L™ lignin

<table>
<thead>
<tr>
<th>Properties</th>
<th>HP-L™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>&lt; 0.5%</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>&lt; 0.5 ppm</td>
</tr>
<tr>
<td>Hildebrand solubility δ</td>
<td>~ 20</td>
</tr>
<tr>
<td>Polar solvent (e.g. acetone)</td>
<td>100%</td>
</tr>
<tr>
<td>Klason lignin <em>(determined in the lab)</em></td>
<td>99.47</td>
</tr>
</tbody>
</table>

3.3.2 Hydrothermal carbonization of untreated lignin

The study was conducted in two phases. Phase 1 was a preliminary study to screen HTC processing temperatures used in Phase 2, which was the main study. In phase 1 (limited data presented), the effect of six temperatures: 200, 250, 300, 315, 335 and 350°C, on yield was determined (Table 4.1). All experiments were independently triplicated (n = 3), except for L350 which was duplicated. For sample L350, the pressures inadvertently exceeded the maximum pressure of 3000 psi of the autoclave leading to the rupture of the pressure disc of the autoclave and most of the liquid content in the autoclave was lost. Therefore, some of the information for this sample is missing in Table 4.1. From the results, four processing temperatures: 200, 250, 300 and 350°C were selected for use in the main study. Samples are designated as L-temp, e.g. L-200 – lignin samples hydrothermally carbonized at 200°C. Differences between treatment means were tested using a One-way Anova. All statistical analysis of data was performed using Origin Pro version 16 statistical software.

HTC of HP-L™ untreated lignin was carried out in an autoclave (Parr Instruments, Model 4766), with a pyrex-glass liner. Temperature was controlled by varying the voltage applied to the
heater of the autoclave and the gauge pressure (psi) was recorded using an analog pressure meter connected to the interior of the autoclave by an air-tight feed through. Similarly, temperature was monitored with a thermocouple (and a digital meter) inserted through the feed through. Figure 3.2 shows the experimental set up used in these experiments. HTC was carried out per the following procedure. Approximately 5g of oven-dried lignin was dispersed in 70 mL distilled water and HTC was carried out at one of the experimental temperatures. The resulting solid products which are hereafter described as carbonaceous materials were recovered by filtration; dried overnight at 103 ± 3°C and weighed. The percentage yield was calculated as: Yield (%) = (Final weight / Initial weight) x100.

Figure 3.2 Basic components of the autoclave, power supply, temperature/pressure system used in HTC of lignin.

3.3.3 Elemental analysis

Carbon, hydrogen and nitrogen contents of the HP-L™ lignin untreated and CMs were determined using a Perkin Elmer 2400 analyzer as per ASTM- D5373 standard. Approximately 1-
3 mg of each sample was used for the measurement. Sulfur (S) was analyzed separately and oxygen (O) was calculated by difference.

**3.3.4 Thermo-gravimetric analysis**

The thermal stability of the treated and untreated lignins were measured by heating specimens at a rate of 7°C per minute in flowing nitrogen gas (Fig. 3.3). The weight of the specimen was monitored as a function of temperature using a TA Instruments Inc. (Model TA Q50). Typically, 10 to 30 mg of a sample was used in each experiment. The gaseous effluents during the experiment were not monitored or analyzed.

![Thermal gravimetric system (TA Model Q50) for thermal analysis.](image)

**3.3.5 Raman Spectroscopy**

Raman spectra was collected using a Renishaw Invia Raman microscope (Renishaw Inc., Chicago, IL) equipped with an excitation laser of a wavelength of 532 nm. The laser beam was focused on the sample with a 20X objective of the Raman microscope. For each sample, exposure
time was kept at 10 s while taking a total of 15 accumulations using a laser power of 10%. Extended scans of the samples were measured within a spectrum range of 1000–2000 cm⁻¹.

3.3.6 X-ray diffraction analysis

The crystallinity of HP- L™ lignin and the carbons derived from them were determined by X-ray diffraction (XRD). XRD of the specimens was acquired using a PAN analytical X’Pert system with Kα source (λ=0.154184 nm). The step size in the 2θ scans was 0.001 degrees. Powdered samples were loaded onto a special silicon plate with negligible background and absence of any Bragg peaks in the scanned range of 2θ=5° to 75°.

3.3.7 Morphology of lignin and CMs

The morphology of the lignin and their CMs were studied using a JEOL 7600 FE-SEM system (15 keV) scanning electron microscope (SEM).

3.4 Results and discussion

3.4.1 Hydrothermal carbonization of lignin

The changes in pressure and temperature with time for samples carbonized at 200, 250, 300 and 335°C are shown in Fig. 3.4. Also, maximum pressure vs temperature for the various treatments was compared with the pressure-temperature (P-T) phase diagram of water (Fig. 3.5). Data points from all treatments followed the phase diagram of water quite well, an indication that autogenic pressure recorded during hydrothermal carbonization of the untreated lignin was primarily due to the vapor pressure of water since very little gas is generated while the organics remain as or are transformed into solids [17,18].
Figure 3.4 Changes in pressure and temperature with time (lignin = 5g, time = 60 minutes).
Figure 3.5 Pressure-Temperature phase diagram of water (red dots) compared with the maximum P-T conditions of the HTC experiments.

### 3.4.2 Yield of CMs

Table 3.2 reports the yield (%) of HTC derived CMs as a function of temperature for all experiments (Phase 1). Differences in final mass (yield) between all temperature treatments was significantly different ($p$-value=1.03E-07<0.05). For L350, autogenic pressure during hydrothermal treatment exceeded the maximum 20 MPa limit of the autoclave resulting in a rupture of the pressure seal and partial loss of the products. The yield could not be determined accurately for this sample. A yield of nearly 90% for L200 suggested that only about 10% of the untreated lignin dissolved in the liquid compared to nearly 70% dissolution of microcrystalline cellulose under similar conditions [19]. Dissolution of the untreated material in water significantly affects carbon yield. A case in point, Falco et al. (2011), calculated yields of rye straw, cellulose, glucose and Alcell lignin [20]. Their results showed a 0% yield for glucose at low hydrothermal
process temperatures (160°C), because it readily dissolved in water. However, yield for treated cellulose, lignin and rye straw

Table 3.2 Process conditions and product yields of CMs obtained from the hydrothermal carbonization of lignin

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Mass (g)</th>
<th>Pressure (MPa)</th>
<th>Maximum Temp. (°C)</th>
<th>Process Time (mins)</th>
<th>Final mass (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L200</td>
<td>5</td>
<td>1.48</td>
<td>200</td>
<td>60</td>
<td>4.4</td>
<td>88</td>
</tr>
<tr>
<td>L250</td>
<td>5</td>
<td>4.41</td>
<td>250</td>
<td>60</td>
<td>4.4</td>
<td>88.6</td>
</tr>
<tr>
<td>L300</td>
<td>5</td>
<td>8.72</td>
<td>300</td>
<td>60</td>
<td>3.9</td>
<td>78.6</td>
</tr>
<tr>
<td>L315</td>
<td>5</td>
<td>10.44</td>
<td>315</td>
<td>60</td>
<td>3.3</td>
<td>66</td>
</tr>
<tr>
<td>L335</td>
<td>5</td>
<td>13.88</td>
<td>335</td>
<td>60</td>
<td>2.8</td>
<td>56.4</td>
</tr>
<tr>
<td>L350</td>
<td>5</td>
<td>20.78</td>
<td>&gt;350</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

precursors decreased from 100% due to increased liquefaction and gasification at higher temperatures. A two-phase lignin degradation mechanism was proposed by Bobleter and Concin [21]. To account for this observation in the hydrothermal treatment of lignin, the untreated is initially degraded into soluble fragments under pressurized water, and these fragments are re-arranged to form new compounds through re-condensation reactions. The major changes occurring during hydrothermal carbonization of lignin are cleavage of β-O-4 aryl ethers; demethylation of methoxyl functional groups and dehydroxylation reactions. Weaker ether bonds in the β-O-4 linkage are easily cleaved to form phenoxy and alkyl aromatic radicals which re-polymerize by crosslinking to form higher molecular weight carbonaceous materials [22,23]. However, at relatively lower hydrothermal temperatures (≤ 200°C), the benzene ring remains stable since such temperatures are considered low to effect any strong chemical modification of the lignin. The dissolution of a small fraction of the lignin is to be expected, but does not necessarily lead to a
modification of its elemental composition [24]. Also, HP-L™ lignin is highly water-insoluble, highly phenolic, low molecular weight and relatively pure (i.e. low in carbohydrates, ash and free of sulfur). The relatively higher yield for L200, can therefore be linked to the thermally unreactive nature of phenolic HP-L™ lignin at lower temperatures.

At 335°C, HTC yield decreased by 36%. Similar results have been reported for hydrothermal carbonization of lignin in subcritical water [10,23]. With increasing temperature and reaction time, demethoxylation and alkylation of phenolic compounds may occur to produce more alkyl phenols. A decrease in yield was attributed to cross-linking between reactive degradation fragments obtained from the depolymerization of lignin to produce fragments with higher molecular weights [23]. When biomass precursors other than lignin were used, this decrease in yield was associated with the degradation of high molecular weight intermediate products into oils and other volatile gases through deoxygenating reactions such as dehydration and decarboxylation [10]. Also, up to 25°C, mass yield remained constant (88%), but decreased to 56% when temperature reached 335°C. Results from the yield analysis showed that major structural transformations in the lignin untreated only occurred after 300°C, as reflected in the results of the elemental analysis below.

3.4.3 Elemental analysis of carbonaceous materials

The elemental composition (C, H and O) of the green carbons is presented in Table 3.3. By comparing the elemental composition of untreated lignin to CMS, it is possible to explain the effect of increased temperature on the carbonization process. Up to 300°C, majority of the hydrothermally treated samples contained lignin. The H content is almost constant, with a corresponding 7% increase in both O and C elements. However, significant modifications occurred after 350°C, with elemental C increasing up to 86%. Similarly, H and O also decreased to 3 and 11% respectively. This supports our conclusion that up to 300°C, HP-L™ lignin is resistant to
hydrothermal treatment and if any changes at all, is modest. HP-L\textsuperscript{TM} lignin was only partially carbonized at lower hydrothermal temperatures. Significant improvements occurring after 350°C suggest that, a greater degree of carbonization occurs at higher HTC temperatures due to deoxygenating reactions. Similarly, well condensed products resulting from dehydration and decarboxylation reactions have been reported for biomass in an HTC environment [4].

Table 3.3 Elemental composition of CMs with increasing temperature.

<table>
<thead>
<tr>
<th>LIGNIN</th>
<th>Treatment temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HP-L\textsuperscript{TM} 200</td>
</tr>
<tr>
<td>C</td>
<td>64</td>
</tr>
<tr>
<td>H</td>
<td>6</td>
</tr>
<tr>
<td>O</td>
<td>31</td>
</tr>
<tr>
<td>Higher heating value (MJkg\textsuperscript{-1})</td>
<td>24</td>
</tr>
</tbody>
</table>

From the elemental analysis data, H/C and O/C molar ratios were calculated. The results were plotted in a Van Krevelen diagram [25] to illustrate the hydrothermal carbonization process (Fig. 3.6). The O/C and H/C ratios of solid wood and torrefied wood at 250 and 300°C have also been included for comparison [26]. The effect of temperature on chemical reactions and composition of the final product in a hydrothermal environment is clearly seen. At more severe HTC conditions, both H/C and O/C ratios linearly moved from upper right to lower left, an indication that dehydration and decarboxylation reactions have occurred and the results are a more aromatic, hydrophobic carbonaceous material. Apart from HP-L\textsuperscript{TM} lignin treated at 350°C, which had an H/C ratio of 0.37, the H/C ratio of the remaining samples varied between 0.8 and 1.1. L350 had an O/C ratio ≤ 2, while HP-L\textsuperscript{TM} lignin and HTC derived CMs had O/C range between 0.2-0.4. H/C ratios around 0.3 have been associated with very highly condensed aromatic structures, whereas
H/C ratios ≥ 0.7 indicate no condensed aromatic structures. Below 300°C, the CMs resembled lignite, whereas at 350°C they had more coal-like features [26]. The conversion of the organic material into aromatic C structures was highest at 350°C, resulting in low O/C and H/C ratios [25,26]. When compared with wood and torrefied wood, the HTC produced CMs were more carbonized. Also, lower O/C and H/C ratios for CMs indicated early stages of carbonization, characterized by chemical structures such methoxyl and hydroxyl functional groups.

Figure 3.6 Van Krevelen diagram of CMs after hydrothermal carbonization
3.4.4 Thermo-gravimetric Analysis (TGA)

The thermal decomposition pattern for HP-L\textsuperscript{TM} untreated lignin and their CMs are presented in Fig. 3.7. For the CMs, mass loss decreased and the residual weight increased with increasing temperature (Fig. 3.8). Peak thermal decomposition temperature was between 200-600°C for all samples. Between 300°C and 450°C, less than 10% mass of L350 was lost compared to nearly 50% mass loss for the untreated lignin. Thermal decomposition of lignin is affected by its nature, reaction temperature, heating rate as well as degradation atmosphere. Unlike cellulose or hemicellulose, lignin decomposes over a broader temperature range (200-500°C), because

![Figure 3.7 Comparison weight loss (%) with temperature (°C) for HTC of HP-L\textsuperscript{TM} lignin.](image-url)
Figure 3.8 Residual weight at peak temperatures for hydrothermally treated HP-L™ lignin

Various oxygen functional groups on its structure have different thermal stabilities, their cleavage occurring at different temperatures [27]. At higher temperatures, there is a complete rearrangement of the lignin backbone leading to a 30-50% weight char and release of volatile products. Simultaneously, aryl-ether linkages are cleaved to form highly reactive and unstable free radicals which can further react to form products with increased stability [28]. Increased degradation temperatures of the hydrothermally produced CMs can be linked to the increasing fixed carbon content and relative stability of the products formed by condensation reactions at higher hydrothermal temperatures.
3.4.5 X-ray diffraction analysis of untreated lignin and CMs

The X-ray diffraction (XRD) spectra of the untreated lignin (Fig. 3.9) shows a broad peak near $\theta = 21.4^\circ$ corresponding to $d = 0.415$ nm and a weaker peak near $\theta = 42^\circ$. The increase in the X-ray intensity below $\theta = 10$ degrees could be due to the porous structure. These observations are characteristic of carbons since similar observations have been reported in activated carbons and coal based carbons. These results showed that some carbonization of the lignin takes place during HTC process.

Figure 3.9 X-ray diffraction (XRD) patterns of untreated lignin and CMS
Based on the graphitic structure, the apparent crystallite size along the c and a direction are written as [29,30].

\[ L_c = \frac{(0.91)\lambda}{\beta \cos \theta}, \quad L_a = \frac{(1.84)\lambda}{\beta \cos \theta} \quad \text{(1).} \]

Here \( \beta \) is the instrument-corrected full-width at half maximum (FWHM) of the (002) line near \( 2\Theta \approx 22^\circ \) whereas the (101) or (112) peaks near \( 2\Theta \approx 44^\circ \) can be used for determining \( L_a \).

### 3.4.6 Raman spectroscopy analysis of CMs

The Raman spectra of untreated lignin, L300 and L350 are shown in Fig. 3.10. The spectra for all the samples are qualitatively similar in that two broad overlapping peaks are observed for Raman shifts between 1000 cm\(^{-1}\) and 2000 cm\(^{-1}\), with the center of the peaks near 1350 cm\(^{-1}\) (D-band) and 1600 cm\(^{-1}\) (G-band), like the observations reported in other carbons. The vibration mode of the D peak corresponds to a disordered graphitic lattice (graphene layer edges), whilst the G peak corresponds to an ideal graphitic lattice [31,32]. For perfect graphite (Fig. 3.11), there is only one band at about 1580 cm\(^{-1}\) corresponding to stretching vibration mode with \( E_{2g} \) symmetry in the aromatic layers of the graphite crystalline [33,34]. The presence of both peaks in all samples is an indication of Csp\(^2\) atoms in benzene or condensed benzene rings in amorphous (partially hydrogenated) carbon, indicating the presence of small aromatic clusters in all samples [34].
Figure 3.10 Raman spectra of untreated Lignin, L300 and L350

Figure 3.11 Raman spectra of graphene sample showing well separated D and G bands
Ferrari and Robertson [34], discussed a three-stage model of amorphization of carbon starting with graphite. In the first stage of graphite to nanocrystalline graphite with no change in sp^2 bonding, D mode appears and G mode shifts from its position from 1580 cm\(^{-1}\) to about 1600 cm\(^{-1}\) mainly due to the appearance of D mode at 1620 cm\(^{-1}\). In stage two, transition from nanocrystalline graphite to amorphous carbon takes place primarily through disorder in bond angle and bond bending resulting in the formation of sp^2 rings and chains and introduction of sp^3 sites. Experimentally, the position of the G peak may shift from 1600 to about 1510 cm\(^{-1}\), and the intensity ratio \(I_{(D)}/I_{(G)}\) decreases. In the third stage of going from amorphous carbon to tetrahedral amorphous carbon, the sp^3 content increases from about 10 -20% to about 85 % and sp^2 sites change from rings to chains. Experimentally, the ratios \(I_{(D)}/I_{(G)}\) decreases towards zero and the position of the G band shifts from 1510 cm\(^{-1}\) in stage 2 to about 1570 cm\(^{-1}\) in stage 3.

Additionally, Raman spectra was de-convoluted into D and G bands (Fig. 3.12) for representative samples of untreated lignin and L350. Variations in D and G positions, full widths at half-maximum (FWHM) and intensity ratios of D and G modes of all samples are presented in Table 3.4. The variation in the position of the G band among different samples is quite small, between 1595 cm\(^{-1}\) and 1599 cm\(^{-1}\), and its FWHM varies from 92 cm\(^{-1}\) for precursor lignin to 81 cm\(^{-1}\) for L335 and 74 cm\(^{-1}\) for L350. The intensity ratio \([I_{(D)}/I_{(G)}]\), does not have a systematic variation for different samples, varying between 1.29 for precursor lignin to 1.72 for the L350.
Figure 3.12 Deconvoluted D and G bands of lignin and L350

Table 3.4 Position of G and D modes, Full-widths at half-maximum at the G and D modes and ratio of the integrated intensities of the D and G modes for lignin and CMs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position (D)</th>
<th>Position (G)</th>
<th>FWHM (D)</th>
<th>FWHM (G)</th>
<th>I(D)/I(G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>1372.0</td>
<td>1595.0</td>
<td>231.6</td>
<td>91.9</td>
<td>1.3</td>
</tr>
<tr>
<td>L200</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>L250</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>L300</td>
<td>1379.5</td>
<td>1595.9</td>
<td>283.3</td>
<td>85.0</td>
<td>1.7</td>
</tr>
<tr>
<td>L350</td>
<td>1370.2</td>
<td>1599.1</td>
<td>289.1</td>
<td>74.4</td>
<td>1.7</td>
</tr>
</tbody>
</table>
3.4.7 Morphology of untreated lignin and CMs

Scanning Electron micrographs of untreated lignin and CMs are shown in Fig. 3.13. The untreated lignin showed agglomerated structures with some vesicles on its surface. Between 200-250°C, the lignin was converted into a mass of vesicles with increased agglomeration. The CMs exhibited both closed and open vesicles throughout the entire hydrothermal temperature range although lesser vesicles with increased open pores were found at 350°C like the results reported by Sharma et al. [35]. The presence of large openings in these agglomerated vesicles have been linked to the formation of secondary products at elevated temperatures and evolution of volatiles [35,36].
Figure 3.13 SEM images of (A) untreated lignin with scale bar 10 µm (1µm) for inset, HTC lignins at (B) 200°C with scale bar 10 µm (1µm) for inset (C) 250°C with scale bar 1 µm (100 nm) for inset (D) 300°C with scale bar 100µm (1µm) for inset and (E) 350°C with scale bar 100µm (100 nm).
3.5 Conclusions

In this study, a bio-refinery waste-stream, HP-L\textsuperscript{TM} lignin, was hydrothermally carbonized at four processing temperatures: 200, 250, 300, and 350°C. After the HTC process, the yield of CMs was highest at the lowest processing temperature (200°C) and decreased with increasing temperature. The fixed carbon content and thermal decomposition properties of the CMs were enhanced. This was supported by Raman and X-ray diffraction analysis. In addition, a decrease in the O and H content of the CMs was observed. A Van Krevelen diagram revealed that L350 had features similar to coal. Finally, SEM analysis showed that HP-L\textsuperscript{TM} lignin untreated exhibited agglomerated structures with some vesicles at elevated temperatures.
3.6 References


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32. Fuertes, A. B.; Arbestain, M. C.; Sevilla, M.; Maciá-Agulló, J. A.; Fiol, S.; López, R.; Smernik, R. J.; Aitkenhead, W. P.; Arce, F.; Macias, F. Chemical and structural properties...


CHAPTER 4: HYDROTHERMAL CARBON FROM LIGNIN: STRUCTURAL CHARACTERIZATION OF CARBONACEOUS MATERIALS VIA $^{13}$C SOLID STATE NMR

4.1 Abstract

In this study, the chemical transformations occurring during hydrothermal carbonization of lignin was investigated. The experiments were examined at 200 to 350°C with a residence time of 60 minutes. With a small amount of gases produced, analysis was focused on the solid carbonaceous products. Higher reaction temperatures enhanced the breakage of lignin into fragments, followed by aromatization and re-polymerization reactions to form the solid carbonaceous materials. Overall, major structural changes in the HP-LTM lignin only occurred after 300°C. Fourier transform infrared (FTIR) analysis and x-ray photoelectron spectroscopy (XPS) analysis showed that bands due to lignin functionalities disappeared at 350°C. Deconvolution and peak analysis using nuclear magnetic resonance (NMR) revealed the evolution of a more condensed structure characterized by aromatic C when temperature reached 350°C. Unlike carbohydrates and other biomass types which can easily be hydrothermally treated at temperatures 160-220°C, our results showed that lignin remains relatively unchanged up until 350°C where significant aromatization occurs. 350°C is therefore the desired temperature for the hydrothermal treatment of HP-LTM lignin.

4.2 Introduction

Lignin is a heterogeneous, amorphous, cross-linked phenolic polymer biosynthesized from three mono-lignols: coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. The proportions of these monolignols will depend on variations within and between plant species. These monolignols undergo polymerization to form lignin-inter unit linkages such as β-O aryl ether (β -O-4), resinol
(β - β), phenylcoumaran (β -5), biphenyl (5-5) and 1,2-diarylpropane (β -1’) [1-3]. Structurally, lignin varies by species, subcellular location, plant tissue and method of extraction [4,5]. Consequently, lignin derived from chemical and physical extraction processes are inherently heterogeneous, highly polydisperse and exhibit complex and variable functional groups [6]. These extracted lignins which are often denoted as technical lignins, differ both physically and chemically from native lignin. The differences in lignin structure, functionality, reactivity and heterogeneity, present significant challenges to the industrial utilization of this biopolymer [7].

Hydrothermal carbonization (HTC), is thermochemical conversion process to convert lignocellulosic biomass into value added products. This process has been shown to produce carbonaceous materials from wet waste biomass, municipal solid waste, sludge etc. [8-11]. HTC occurs at relatively low temperature under autogenous pressures in hot compressed water to yield gases, a liquid phase and a carbon rich residue [13,14]. During the hydrothermal treatment of lignin, the major reactions occurring are depolymerization by cleavage of β-O-4’ linkages and ester bonds and repolymerization by acid-catalyzed condensation. There are also some other linkages such as α-ether and β-aryl ether linkages which are broken [15-17]. The cleavage of β-O-4 linkages lead to a more condensed lignin with a high average molecular weight, while polymerization of water soluble phenolic compounds leads to the formation of a phenolic rich char [18,19]. Also, non-dissolved lignin compounds may undergo heterogeneous pyrolysis to form polyaromatic carbons [20]. Depolymerization and repolymerization of lignin results in both morphological and structural changes [21-23]. Majority of the literature on mechanism of lignin HTC have focused on the liquid fraction or from model lignin compounds [17,24,25]. So far, literature on the hydrothermal carbonization of lignin provide a rather inconsistent picture and only
few have provided on the chemistry of the solid reaction products (carbonaceous materials) and how that is influenced by the severity of the reaction temperature.

Therefore, the main goal of this study was to gain insights into the mechanisms underlying mechanisms during HTC. The study focused on the reaction of an organosolv (HP-L™) lignin the chemical and structural properties of its carbonaceous products. The resulting CMS were characterized by Fourier transform infra-red spectroscopy (FTIR), nuclear magnetic resonance (NMR) and x-ray photoelectron spectroscopy (XPS).

4.3 Materials and methods

4.3.1 Hydrothermal carbonization

The procedure for the hydrothermal carbonization of untreated lignins has been detailed in the materials and methods of Chapter 3.

4.3.2 FTIR analysis

FTIR spectra were acquired (700 to 4000 cm\(^{-1}\) range) using Diffuse Reflectance Spectroscopy (Perkin Elmer Spectrum 400).

4.3.3 \(^{13}\)C solid state NMR spectroscopy

Solid state NMR spectra was acquired using a Bruker DSX300 solid-state NMR spectrometer. High resolution solid state \(^{13}\)C spectra with signal enhancement by variable amplitude cross-polarization (VACP) and direct polarization (DP) at a spinning speed of 10 KHz were measured using a MAS probe suitable for the use with 4 mm OD rotors (Bruker). According to the experience of the authors, the chosen parameter sets provided reliable data for a great variety of carbonized and cellulosic materials: DP experiments consisted of a single 90-degree pulse at the \(^{13}\)C frequency (75 MHz) followed by high power \(^1\)H decoupling. The relaxation delay between individual scans
was set to 4 seconds, which can be considered sufficiently long to allow the quantitative evaluation of spectra through integration/deconvolution of peaks. $^{13}$C varying amplitude cross polarization (VACP) experiments consisted of a 90-degree excitation pulse at the $^1$H frequency (300 MHz) followed by a cross polarization period consisting of a square-rf pulse for the $^{13}$C channel and a ramp-shaped pulse for $^1$H. The amplitude of the ramp ranged from 85% and 100% and its overall magnitude was optimized using a reference compound (adamantane). The length of the contact time was 2 ms. Repetition time between individual scans was 4 seconds. While CP experiments usually do not provide spectra which can be analyzed by quantitative peak analysis, they have the advantage that they usually provide a better signal to noise than DP spectra acquired in a comparable amount of time. However, when a short to medium length contact time is used, they also provide complimentary information to DP spectra in the sense that the cross-polarization effect is most effective for sites, which are rich in $^1$H.

### 4.3.4 X-ray photoelectron (XPS) analysis

The surface functionalities (oxygen groups) of the CMs were determined using a Physical Electronics VersaProbe 5000 X-ray Photoelectron Spectroscope with a monochromatic Aluminum Kα X-ray source (Chanhassen, MI, USA). The base pressure in the high vacuum analysis chamber was around 2 x10⁻⁶ Pa. An Aluminum X-ray source of 1486.6 eV was used for photoelectron excitation with X-ray power of 25 W and anode voltage of 15 kV. Pass energies of 117.4 eV for survey scan and 23.5 eV for detail scan were used for the data acquisition with energy steps of 0.5 eV for survey scan and 0.05 eV for detail scan, respectively. PHI MultiPak software was used for element identification and peak fitting. The C1s peak at a binding energy of 284.8 eV was used as the internal reference. A Shirley-type background was subtracted from the spectra and Gauss–Lorentz curves were used to fit the spectra.
4.4 Results and Discussion

4.4.1 Infra-red spectroscopy analysis

FTIR analysis was performed to characterize what type of functional groups were enhanced or weakened (Fig. 4.1). The untreated lignin showed patterns typical of lignin such as the band at 1697 cm$^{-1}$ which corresponded to stretching of unconjugated carbonyls from aldehyde/ketone groups and aromatic ring vibrations at 1600 cm$^{-1}$ and 1512 cm$^{-1}$. Other bands were assigned to

![Figure 4.1 IR spectra of HP-L$^{TM}$ lignin and their HTC-derived CMs](image-url)
bending of methyl and methylene groups (1456 cm\(^{-1}\)), C-H deformation (1421), ring breathing of syringyl (1324 cm\(^{-1}\)) and guaiacyl (1211 cm\(^{-1}\)) units. Moreover, the bands at 1027 cm\(^{-1}\) and 822 cm\(^{-1}\) corresponded to C-O stretching in primary alcohols and C-H bending in syringyl respectively [26]. Up to 300°C, IR spectra of hydrothermally produced CMs showed similarities with the untreated lignin. When temperatures reached 350°C, bands due to the various functional groups disappeared, a clear indication that at temperatures below 300°C, no significant chemical transformation occurred in the hydrothermal carbonization of HP-L\(^{\text{TM}}\) lignin.

**4.4.2 Nuclear magnetic resonance analysis**

NMR provided complimentary functional group information to FTIR and the ability to quantify and compare integration areas between spectra. \(^{13}\)C cross polarization (CP) NMR spectra for HP-L\(^{\text{TM}}\) lignin as well as CMs treated lignin at 200 and 350°C are depicted in Fig. 4.2a. The absence of signals between 90-102 ppm is indicative of little or no carbohydrates in the sample [27]. This observation agrees with results of the Klason lignin analysis which showed that 99.47% of the parent material was lignin. Signals at 209 and 173 ppm were attributed to the presence of ketones and unconjugated carboxylic acid functional groups. The signals in the 125–130 ppm region correspond to fused aromatic rings and those in the 150-ppm region correspond to oxygenated
Figure 4.2 a. $^{13}$C CP and b. $^{13}$C DP solid state NMR of HP-L$^{TM}$ lignin and their HTC-derived CMs
aromatic groups. Lastly, peaks around 55 ppm depicted methoxyl groups [28,29]. CMs showed a gradual decrease in amounts of oxygenated aromatics, methoxyl and aliphatic substructures with increasing temperature. At 350°C, the Ar-O decreased significantly and carboxyl structures disappeared, resulting in increased intensity in the aromatic region (δ =128 ppm). Increased aromaticity with a consequent reduction in aliphatics was evidence of deoxygenation and dehydration reactions with increased treatment temperatures [28]. The disappearance of carboxyl and ketone groups with carbonization contrasts with their rather significant amounts in carbonized carbohydrates. This is to be expected since the number of available free hydroxyl groups in lignin is much less than in carbohydrates.

$^{13}$C direct polarization (DP) NMR spectra for HP-L$^{\text{TM}}$ and HTC lignins are presented in Fig. 4.2b. This was consistent with $^{13}$C CP spectra except a more enhanced aromatic region for lignin treated at 350°C was revealed. Evolution of aromaticity with increasing hydrothermal temperature was measured by the quantification of the aromatic signal in the 100-160 ppm region [30,31]. This was done by deconvoluting the DP spectra into peaks associated with the three prominent functionalities (aromatics, methoxyl and aliphatics) present in the samples (Figs. 4.3a,b,c). Results of relative percentages of these functional groups are presented in Table 4.2. Less than half of untreated lignin and L200 is aromatic (25 and 34% respectively), based on the DP spectra. However, the proportion of aromatic C reached 77% when hydrothermal temperatures reached 350°C. Similarly, there was a corresponding reduction in methoxyl groups (from 41 to 9%), as well as aliphatics (34 to 14%) when hydrothermal temperatures reached 350°C. This agrees with both data from infra-red and elemental analysis that only little modifications occurred in HP-L$^{\text{TM}}$ lignin treated at 200°C. The ratio of aromatics to methoxy, which is an indication of aromatics to lignin was also shown. There was very little increase from 0.61 to 1.36 when lignin was subjected
to HTC temperature of 200°C. However, this increased sharply to 11, which is about 94% increase from the starting material. Therefore, results from the NMR

![Graph](image1)

**Figure 4.3a**: HP-L™ lignin DP spectrum and fitted peaks from deconvolution

![Graph](image2)

**Figure 4.3b**: L200 DP spectrum and fitted peaks from deconvolution
Figure 4.3c: L350 DP spectrum and fitted peaks from deconvolution

Table 4.2 Composition of functional groups (%) in hydrothermally treated lignin obtained by quantitative DP/NMR analyses

<table>
<thead>
<tr>
<th>Samples</th>
<th>ppm</th>
<th>150-100</th>
<th>90-50</th>
<th>45-0</th>
<th>Aromatic (%)</th>
<th>Methoxy (%)</th>
<th>Aliphatic (%)</th>
<th>Aromatic: Methoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td></td>
<td>25</td>
<td>41</td>
<td>34</td>
<td>25</td>
<td>41</td>
<td>34</td>
<td>0.61</td>
</tr>
<tr>
<td>L200</td>
<td>34</td>
<td>25</td>
<td>41</td>
<td></td>
<td>34</td>
<td>41</td>
<td>11</td>
<td>1.36</td>
</tr>
<tr>
<td>L350</td>
<td>77</td>
<td>9</td>
<td>14</td>
<td></td>
<td>11</td>
<td>9</td>
<td>77</td>
<td>11.00</td>
</tr>
</tbody>
</table>
analysis showed that the hydrothermal treatment of HP-LTM lignin enhances the carbonization process towards more aromatic carbons with graphitic domains already at a treatment temperature of 350°C. This further emphasizes the fact that 350°C is the desired temperature for the hydrothermal treatment of HP-LTM lignin.

4.4.3 Surface chemistry analysis by X-ray photoelectron spectroscopy

The C1s peak at a binding energy of 284.8 eV was used as the internal reference. C1s deconvolved peaks were assigned to the following known chemical shifts: Peak 1 (C–C/C–H; BE=284.8 eV) sp2 graphitized carbon, Peak 2 (BE=285.75) sp3 graphitic carbon, Peak 3 with a chemical shift of ΔE=1.8 eV (C–O, BE=286) carbon in phenolic, alcohol or ether groups and Peak 4 (288.8 – 289.2 eV) corresponding to carbon in carboxyl or ester groups [32]. Similarly, deconvolution of O1s spectra yielded the following: Peak 1 (BE = 531-531.9 eV) carbonyl oxygen in quinines, Peak 2 (BE = 532.2 eV) carbonyl oxygen in besters, anhydrides and oxygen atoms in hydroxyl groups and Peak 3 (533.1-533.8 eV) phenolic OH, oxygen atoms in esters and anhydrides [32,33]. Figure 4.4 shows XPS spectra of untreated lignin and hydrothermally produced CMs together with their fitted C1s and O1s peaks. The relative contents of functional groups in C1s and O1s and their relative atomic concentrations are also presented in Table 4.3. The atomic percentage of carbon detected by the XPS were significantly higher than those calculated by elemental analysis (Table 3.3). With increasing temperature, C1s atomic percentage increased while O1s decreased. After hydrothermal treatment, the band at 284.80 eV remained present as previously shown by the 13C solid states NMR experiments, suggesting that part of the parent lignin materials remains unchanged. The most significant change occurred in L350 which presented a major C1s component at 285.75 eV corresponding to sp3 graphitic carbon and a weak component at 289.29 eV indicative of extended aromatic features.
Figure 4.4 XPS detail scans showing changes in C1s (a) and O1s (b) of hydrothermally treated HP-L™ lignin.
Table 4.3 Relative contents of functional groups in C1s and O1s and their relative atomic concentrations for XPS data

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s-wt (%)</th>
<th>O1s-wt (%)</th>
<th>Atomic conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak 1</td>
<td>Peak 2</td>
<td>Peak 3</td>
</tr>
<tr>
<td>Lignin</td>
<td>50.93</td>
<td>37.75</td>
<td>11.33</td>
</tr>
<tr>
<td>L250</td>
<td>68.18</td>
<td>30.85</td>
<td>0.97</td>
</tr>
<tr>
<td>L300</td>
<td>67.65</td>
<td>32.18</td>
<td>0.17</td>
</tr>
<tr>
<td>L350</td>
<td>53.49</td>
<td>42.94</td>
<td>3.56</td>
</tr>
</tbody>
</table>

4.4.4 Mechanism for formation of carbonaceous material

Clarifying the exact mechanism for the degradation of lignin under hydrothermal treatment still remains a challenge due to the more complex and varying nature of lignin when compared to hemicellulose or cellulose. It is suggested that a free radical reaction forms the most mechanism involved in lignin degradation [34-36]. Free radical formation starts with the breakage of β-O-4 bonds (Fig. 4.5). These radicals can capture protons of other species with weak C-H or O-H bonds to form other decomposed products. With time the radicals are passed to other species for further reaction forming longer chains. The chain reactions cease when two radicals collide with each other to form stable compounds [37]. Kang et al. (2012) described a mechanism of dissolved lignin fragments decomposing into phenolics and repolymerization into phenolic chars [20].
4.5 Conclusions

HTC had a remarkable effect on the chemical structure of carbonaceous materials obtained from the hydrothermal treatment of lignin at elevated temperatures. FTIR and $^{13}$C NMR analysis clearly showed decreased aliphatic carbons and enhancement of both aromatic and carbonyl-type carbons in the CMS. Increasing the HTC temperature can enhance the aromatization, repolymerization, polycondensation reactions occurring through treatment. Unlike carbohydrates and other biomass types which can easily be hydrothermally carbonized at temperatures (160-220°C), HP-L$^{10}$ lignin remains relatively unchanged up until 350°C where significant aromatization has occurred. 350°C is therefore the desired temperature for the hydrothermal treatment of HP-L$^{10}$ lignin.
4.6 References


https://doi.org/10.1007/s12155-013-9314-7
CHAPTER 5: CARBON DIOXIDE CAPTURE USING AMINE FUNCTIONALIZED HYDROTHERMAL CARBONS FROM LIGNIN

5.1 Abstract

CO₂ sorbents were synthesized from the hydrothermal carbonization of a biorefinery waste lignin. Lignin was treated at 350°C (L350), and the resulting carbonaceous materials activated with potassium hydroxide (KOH) at 800°C to improve its textural properties. Activated samples were further functionalized with polyethylenimine (PEI) at different loadings to evaluate their synergistic effect on capturing CO₂. Activation improved surface area from 2.8 m²/g to 1341 m²/g. Activated samples attained the highest CO₂ uptake at 30°C due to improved textural properties. CO₂ uptake improved at a 5% PEI loading after which it began to decrease with increasing PEI loading. This was ascribed to blockage of the micropores in the activated samples at high PEI impregnation. Also, activated samples showed faster adsorption kinetics compared with PEI functionalized activated samples. This study showed that improving textural properties of hydrothermally treated lignins, followed by lower loadings of PEI proved more favorable for CO₂ uptake.

5.2 Introduction

The last decade has seen an increase in carbon dioxide (CO₂) capture research technologies due to rising atmospheric CO₂ levels. Post-combustion capture of CO₂ from point sources such as coal and gas-fired plants is particularly interesting since these technologies can easily be retrofitted into existing plants. Typically, liquid based amine (monoethanolamine) scrubbers have been used for this purpose. These liquid based processes suffer high energy costs during the regeneration part, corrosion of the tanks and their degradation products are volatile resulting in additional pollutant emissions [1-4]. Although membrane CO₂ capture technologies have been reported, they
require a high cost module, not durable and not suitable for treating large volumes of emission
gases [5,6].

Recently, CO₂ capture using solid sorbents have received intense attention from both research
and industrial fields [7,8]. Unlike liquid sorbents, solid sorbents can be used over a wider
temperature range from ambient to 700°C, yielding less waste during cycling, and the spent
sorbents can be regenerated or disposed without causing harm to the environment [9]. For solid
sorbents to be competitive, they must be: i) low cost and highly available ii) high CO₂ uptake and
sorption rate iii) good selectivity and iv) easy regeneration [10]. Bio-based or biomass based
derived precursors will serve as suitable alternatives for solid sorbents since they are readily
available, renewable and leave no environmental foot prints [10].

Hydrothermal carbonization (HTC) is an alternative thermochemical conversion process for
biomass and biomass derived waste into carbonaceous materials (CMs) or precursors for several
value-added products. Using HTC as a treatment, several biomass precursors such as Kraft lignin,
cellulose, hydrolysis lignin, birchwood and sawdust have been employed as carbon materials for
CO₂ adsorption [11,12]. More recently, potassium hydroxide (KOH) activated carbons produced
from the hydrothermal treatment of lignin could achieve high CO₂ uptake up to 4.6 mmol/g at 1bar
and 25°C, 17.3 mmol/g at 20 bar and 25°C. Activation at KOH/carbon 1:4 could generate carbons
with surface area and pore volume of up to 3235 m²g⁻¹ and 1.77 cm³g⁻¹ respectively [13].

Also, modifying the surface chemistry of activated carbons can further enhance their
adsorption performance. Nitrogen (amine) functional groups increase the basicity of these
sorbents, favoring the adsorption of an acidic gas such as CO₂. The most widely used surface
modification technique is incorporating amine groups either by impregnation or by grafting.
Amine functionalities have been impregnated into the pores of activated carbons using liquid
amine polymers such as polyethylenimine (PEI), tetraethylenepentamine (TEPA) or diethanolamine [14,15]. Grafting is similar except grafted amines are more stable and not easily desorbed during regeneration. The choice of amino functional group for grafting is affected by the porosity and type of functional groups present on the surface of the adsorbent. The most researched amines grafted on carbons include ethylenediamine, diethylene triamine, tris (-2-aminooethyl) amine and (3-aminopropyl) triethoxysilane [16-18]. For instance, Jang et al. (2011), reported CO₂ adsorption capacities as high as 43.8 cm³/g for tris (-2-aminooethyl) amine grafted activated carbons [16]. They explained enhanced capacity was due to the presence of isolated amine groups in the amine grafted carbons. The activated carbons alone showed less CO₂ uptake.

In this chapter, the adsorption properties of HTC lignin treated at 350°C was investigated. The effect of KOH activation, followed by PEI surface functionalization on CO₂ sorption capacity is also evaluated.

5.3 Materials and methods

5.3.1 Hydrothermal carbonization

CMs were prepared at 350°C by using previously reported procedure (Chapter 3). In experiments using NaOH as a catalyst, the lignin was dissolved in 70 mL of either 0.1 M or 0.5 M NaOH solution. Reaction conditions were similar to reported HTC procedures (Chapter 3).

5.3.2 KOH activation

Oven-dried carbonaceous samples from the HTC process were mixed with potassium hydroxide (KOH) in the ratio of 1:4 (weight basis). This was then heated in a horizontal tube furnace at 10°C/min to 800°C and held at that temperature for two hours in a nitrogen atmosphere. After cooling the activated samples was washed in 0.1M hydrochloric acid and later washed in
deionized water until the pH reached neutral. The collected activated samples were oven dried and stored till use.

5.3.3 PEI impregnation

CM samples were impregnated with polyethylenimine (PEI, Sigma Aldrich, average Mw = 1300) via wet impregnation. The desired amount of PEI was dissolved in 10g methanol and 1g CM was added under stirring. The mixture was stirred for 24 hours and the methanol removed via rotary evaporation at room temperature. The resulting powder was dried at 80°C overnight and then stored under ambient conditions until use.

5.3.4 FTIR analysis

Mid-Infrared spectra of the samples before and after PEI impregnation were recorded from 4000 to 650 cm\(^{-1}\) using a Perkin Elmer Spectrum model 400 (Perkin Elmer Co., Waltham, MA) combined with a single Attenuated Total Reflectance (ATR) sampling unit. All samples were scanned 32 times at a resolution of 4 cm\(^{-1}\) at room temperature and averaged.

5.3.5 TGA analysis

The thermal stability of samples was measured by heating specimens at a rate of 10°C per minute in flowing nitrogen gas up 800°C and held isothermal for 2 hours. The weight of the specimen was monitored as a function of temperature.

5.3.6 CO\(_2\) adsorption measurements.

The kinetics of CO\(_2\) adsorption on the activated and adsorbents were studied using a TA Instruments (Model TA Q50) thermogravimetric analyzer at atmospheric pressure. Before each kinetic measurement, the adsorbent sample (approximately 10 mg) was pretreated under a 50-mL min\(^{-1}\) flow of pure nitrogen at 120°C for 1 h to guarantee the removal of moisture and other dissolved gases. The temperature was decreased to the desired temperature (selected temperatures
ranging from 30 to 60°C), and the nitrogen gas was then changed to pure CO₂ at the same flow rate. The sample was maintained at the final temperature under a constant flow of CO₂ and held isothermally for 60 mins. The adsorption capacity of the adsorbent was expressed in moles of CO₂ per gram or mg/CO₂/g of adsorbent and is determined from the weight change of the sample after the introduction of CO₂.

5.3.6 Surface area and pore size analysis

Surface area was estimated by nitrogen sorption isotherms measured at 77.36 K. Specific surface area of the materials was computed from the sorption isotherm via the Brunauer-Emmet-Teller (BET) method using Micrometrics Model Autochem II 2920. The pore size distribution was determined by BJH (Barrett-Joyner-Halenda) model. Samples were degassed at 200°C for 45 minutes before surface area analysis began.

5.4 Results and discussion

5.4.1 FTIR analysis

The activated carbon materials before and after PEI impregnation were characterized using (FTIR) spectroscopy (Fig. 5.1). In the spectrum of the PEI loaded carbons, the emerging bands at 1650 cm⁻¹ was assigned to the bending of secondary amines (-N(R)H) in PEI [19,20]. With increasing PEI loading, the peaks increased. The existence of band at 1590 cm⁻¹ indicates the presence of oxygenated functionalities in non-conjugated and conjugated systems [21]. The broad band at 978–1210 cm⁻¹ is attributed to vinyl group (= C–H) in-plane and out-of-plane vibration, and maybe related to (C–O) and (C–N) bonds [22]. These non-carbon elements and functional groups enhances the adsorption of gases [23].
**5.4.2 Thermogravimetric analysis**

Additional proof for the presence of the impregnated material on the surface of the carbonaceous materials was also obtained by the thermogravimetric analysis (TGA) performed under nitrogen flow. Fig. 5.2 shows the TGA of activated L350 sample loaded with different amounts of PEI (top), and the accompanying differential thermal gravimetric analysis (DTGA) results also included (bottom). Clearly, differences exist among the samples. Decomposition occurred in three regions. Mass loss below 100°C is attributed to physio-sorbed water and CO₂ within the samples. For PEI impregnated samples, mass loss around 300°C, which intensified for activated L350 with PEI loading rate of 25%, is attributed to the decomposition of amine groups bonded to the carbon matrix. The last stage of decomposition for all samples (between 600-700°C) is caused by the aromatization of the structural network [24-26]. TGA also revealed that the sorbents are thermally stable within an acceptable temperature range, since the sorption-desorption temperature range for CO₂ is 30–100°C.
Figure 5.2 TGA (top) and DTGA spectra of Activated L350 samples with different PEI loading rates
5.4.3 Surface area and pore characteristics

The nitrogen adsorption-desorption isotherms of L350 and KOH activated L350 is shown in Fig. 5.3. The isotherms (top) belonged to a mix type (isotherms II and IV) of IUPAC classification. A type II isotherm (L350) is associated with non-porous or macro porous materials where unrestricted monolayer-multilayer adsorption can occur, while type IV (activated L350) indicates a mixture of microporous and mesoporous materials. The BET surface area of L350 was 2.8 m²/g. Improvements in the surface area and porosity of hydrothermal carbons are therefore necessary if they should be utilized as adsorbents or energy storage. When chemically activated with KOH, surface area reached 1341 m²/g. Significant increases in surface area of KOH activated hydrothermal carbons have been reported in literature [28,29]. The presence of hydroxyl group on the carbon surfaces act as the oxidizer for the C-KOH reaction, resulting in the consumption of carbon and the formation of pores within the internal carbon structures. The pore size distributions were obtained by the BJH method (bottom). After activation, L350 had a narrow pore size distribution with a significant range less than 20 Å which is indicative of the presence of micropores in the activated sample. Predominantly micropores and some mesopores are formed during the activation process thereby increasing the surface area of the activated carbon [30].
Figure 5.3 Nitrogen sorption isotherms (top) and BJH pore size distribution (bottom) of L350 and activated L350
5.4.3 Adsorption of carbon dioxide

Using a TGA, the CO$_2$ adsorption process can be divided into three stages. At stage 1, the sample was preheated at 120°C for 60 minutes under nitrogen gas. In stage 2 the sample is cooled to the required CO$_2$ adsorption test temperature (30°C) and held isothermally for 30 minutes. There is a slight CO$_2$ weight gain caused by N$_2$ adsorption on the sample. After the sample temperature was stable (stage 3), the gas was switched to CO$_2$ and the associated weight gain was assumed to be due to the adsorbed CO$_2$. Representative TGA curves of CO$_2$ adsorption capacity for the samples are shown in Fig. 5.4 – Fig. 5.8. The sorption rate is very rapid, with a sharp curve for the non-impregnated activated L350 sample. This indicated a low mass-transfer resistance for the activated only sorbent, which can be explained by the large pore volume and well developed pore structure of the sample which gave easy access to the sorption sites and minimized the distance of internal diffusion [31]. With the addition of PEI, the sharpness of the curve reduced and decreased further with increased PEI loadings. Although the higher amine loadings may be achieved by impregnation, a large diffusion resistance also occurs [32]. This was attributed to pore blockage by the PEI, a phenomenon which has been described several times in literature [33-35].

The CO$_2$ sorption capacities of the samples are summarized in Table 5.1. Carbon dioxide adsorption capacities among the different treatments were significantly different ($p=0.0003 <0.05$). Activated L350 had a CO$_2$ capture capacity of 1.5 mmol g$^{-1}$ at (30°C). The high surface area and pore size distribution of the activated sample proved beneficial for effective CO$_2$ adsorption. Several studies have indicated that the presence of amine groups in carbonized-activated carbons can improve their performance for CO$_2$ capture [36]. PEI loading content affected the adsorption capacity in two respects: (1) increasing PEI leads to increased amine
content, potentially increasing the number of CO₂ capture sites. (2) the increase in PEI content will also lead to pore

![Graph showing CO₂ uptake of activated L350](image)

Figure 5.4 CO₂ uptake of activated L350
Figure 5.4 CO$_2$ uptake of activated L350 with 5% PEI loading

Figure 5.4 CO$_2$ uptake of activated L350 with 10% PEI loading
Figure 5.4 CO₂ uptake of activated L350 with 25% PEI loading

Table 5.1 CO₂ adsorption capacity of PEI modified activated hydrothermal carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ uptake (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated L350</td>
<td>1.50</td>
</tr>
<tr>
<td>Activated L350 PEI 5%</td>
<td>2.0</td>
</tr>
<tr>
<td>Activated L350 PEI 10%</td>
<td>1.53</td>
</tr>
<tr>
<td>Activated L350 PEI 25%</td>
<td>0.57</td>
</tr>
</tbody>
</table>

blockage of sorbents and aggregation of PEI molecules, reducing the opportunities of CO₂ capture. After impregnation, the sorption capacity increased to 2.0 mmolg⁻¹ at 5% PEI loading, which was the largest saturation sorption for this study. This was comparable to 2.03 mmolg⁻¹ PEI impregnated MCM-41 [37] or even better than PEI impregnated PIM-1[33]. For practical applications in the field, a CO₂ adsorption capacity of 2 mmolg⁻¹ is needed. The observed effect of
5% PEI blending can be explained in terms of the role of amine and hydroxyl groups on the sample. Amine groups can directly capture CO$_2$ by forming N–C covalent bonds and act as a proton acceptor:

$$2R^1R^2NH + CO_2 = R^1R^2NCOO^- + R^1R^2NH_2^+,$$

where $R^1R^2NH$ represents a primary or secondary amine [31,33]. Additional increases in PEI loading decreased the CO$_2$ sorption capacity of the sorbents. It was assumed at a sorption capacity of 0.57 mmolg$^{-1}$, most of the porosity of the sorbent was filled and most PEI became inaccessible, resulting in a great degradation of sorptive properties.

**5.5 Conclusions**

PEI impregnated activated carbons demonstrated improved CO$_2$ adsorption. Activated carbon materials were produced from lignin hydrothermally treated at 350°C. The experimental results illustrated significant improvements in the specific surface area SBET and CO$_2$ capture after PEI impregnation. Optimal PEI loading for CO$_2$ capture at 30°C was determined to be 5% and at higher loading, sorptive sites were increasingly blocked. The results suggest that low loadings of PEI on activated carbon sorbents had a good potential for CO$_2$ capture in the future.
5.6 References


CHAPTER 6: COMPARATIVE STUDY ON THE HYDROTHERMAL CONVERSION OF THREE COMMERCIAL LIGNINS

6.1 Abstract

Commercial lignin is a by-product of pulping and the emerging bio-refinery industries. The hydrothermal treatment (HTT) or carbonization (HTC) of three commercial types of lignin to carbonaceous materials was investigated. HTC of lignin was carried out in an autoclave in the presence of water at temperature and pressure of approximately 300°C and 1000 psi respectively. Morphological, physical and chemical properties of untreated lignins and their hydrothermally derived carbonaceous materials were characterized by x-ray diffraction, scanning electron microscopy (SEM), thermogravimetric analysis, elemental composition, Fourier-transform infrared (FTIR) and Raman spectroscopies. This study demonstrated differences in the morphology of carbons from the three lignin types. SEM analysis showed that hydrothermally derived carbonaceous materials from Mascoma lignin contained spherical particles with diameters ranging from 50 to 250 nm whereas that from ammonium and sodium ligno-sulfonate lignins contained similar particles but were highly agglomerated. The better characteristics of the post-HTT Mascoma carbon vis-à-vis post-HTT ammonium and sodium carbons are also evident in the results obtained from XRD, TGA and FTIR analysis. It is possible to produce carbonaceous materials from low-value commercial lignins via HTT and their properties are influenced by the type of lignin.

6.2 Introduction

Hydrothermal treatment (HTT) or carbonization (HTC) process dates back to the 20th century when Bergius and Specht first used it to carbonize polysaccharides such as cellulose [1]. The
process is exothermic, reduces hydrogen and oxygen content of the solid product, and occurs at relatively low temperatures of 200–350°C. The underlying mechanism of this process is complex and includes hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization. Initially, HTT was used as a low temperature, low-cost process to produce liquefied biomass product and very little attention was paid to the ‘‘solid by-product’’. However, recent studies have identified the solid by-product as carbonaceous material with interesting specific properties such as shape, size and chemical functionalities [1,2].

The HTT process is tunable such that, it is capable of producing carbon microspheres of specific size range [3]. HTT also represents a cheap, easy and green method for the production of carbon spheres having a hydrophobic core with a surface populated by functional groups emanating from the precursor [4]. Additionally, the physical and chemical properties of these particles are influenced by the chemistry of the precursor. HTT carbons have several applications such as electrodes in electrochemical storage battery systems, support for catalysts, water purification, carbon-assisted water electrolysis to produce energy-efficient hydrogen, carbon dots and fillers for nano-composites [3,5].

Sustainable and renewable materials such as lignocellulose biomass, and its major biopolymers and process waste-by-products, represent an alternative resource for the production of carbonaceous materials [6]. Lignin, a major biopolymer of lignocellulose bio- mass, is second to cellulose in terms of quantity and availability. It is a phenyl-propane-based bio-polymer whose chemistry is source and species dependent. Commercially, different technologies are used to pulp or bio-refine biomass resulting in the production of lignin with different chemistries [7,8]. To-date, this commercial waste/by-pro- duct has a low-market value and is burnt in pulp mills to generate heat for the plant. Additionally, lignin is also produced as a by-product of the emerging bio refinery
industry where it is recognized that the development of a technology to convert lignin to a higher-value added product is important to its economic viability.

In this chapter, the effect of temperature and pressure on the yield and morphology of carbonaceous materials produced from three commercial lignin samples are presented. Ammonium and sodium lignins were obtained from a commercial Kraft pulping process. The third sample from Mascoma Corporation, was produced by a proprietary consolidated bio-processing (CPB) which utilizes genetically modified yeasts and other microorganisms. The primary interest of this work was to characterize the solid carbonaceous material produced from these three lignins having different chemistries.

6.3 Materials and Methods

Samples of the sodium and ammonium lignosulfonate used were provided by the Dallas Group of America Inc. (Whitehouse, NJ). The second sample of lignin was provided by the Mascoma Corp. (Waltham, MA). All lignin samples were used as received. Deionized water was used for the HTC process.

6.3.1 Hydrothermal carbonization

HTC process has been described in detail elsewhere in chapter 3. The percent recovery of the solid product from the Mascoma, ammonium, and sodium lignin was 20.8, 15.4 and 14.9 % respectively. The brown residual liquid was not investigated further in this work.

6.3.2 Physical and chemical characterization

The as-received samples and the dried carbonaceous materials obtained after HTT of the three lignins were analyzed by X-ray powder diffraction (XRD) using Rigaku D-Max diffractometer (CuKα source, λ = 0.15418 nm). Secondary electron images of the samples were acquired by
scanning electron microscopy (SEM) using a JEOL 7600 FE-SEM. The Thermo-gravimetric analysis (TGA) of the samples was done in flowing nitrogen gas at a heating rate of 10°C per minute using the system acquired from TA Instruments (Model TA Q50). Carbon, hydrogen and oxygen contents were determined by elemental analysis. Functional group chemistry of the samples was determined using Fourier Transform infrared spectroscopy (FT-IR) and Raman microscopy. Mid-Infrared spectra of the as-received and HTT lignin samples were recorded from 4000 to 650 cm\(^{-1}\) using a Perkin Elmer Spectrum model 400 (Perkin Elmer Co., Waltham, MA) combined with a single Attenuated Total Reflectance (ATR) sampling unit. All samples were scanned 32 times at a resolution of 4 cm\(^{-1}\) at room temperature and averaged. For comparison and analysis, spectra of all three lignin samples were base-line corrected using Perkin-Elmer Spectrum Version 10.03.07 software. Raman spectra of the carbon samples were collected using a Renishaw Invia Raman microscope (Renishaw Inc., Chicago, IL) equipped with an excitation laser of a wavelength of 532 nm. The laser beam was focused on the sample with a 20X objective of the Raman microscope. For each sample, exposure time was kept at 10 seconds while taking a total of 15 accumulations using a laser power of 10%. Extended scans of the samples were measured within a spectrum range of 1000 cm\(^{-1}\) and 2000 cm\(^{-1}\) since the most intense of Raman bands for carbon are found within this range. The WIRE 3.2 software was initially utilized in processing of the scans for baseline shifts.

6.4 Results and discussion

6.4.1 Pressure and temperature conditions

The experimentally measured changes in pressure and temperature vs. treatment time for the three lignin samples are shown in Fig. 6.1. When compared with similar experiments with microcrystalline cellulose, the measured pressures of about 7.58 MPa are relatively higher,
although the temperature did not exceed 300°C [5]. These higher pressures likely correspond to water vapor pressure around 300°C (8.5MPa). However, these conditions are still sub-critical in that the conditions for super-critical water are: PC = 22.1 MPa and TC = 374°C.

Figure 6.1 Changes in the measured pressure (psi) and temperature (°C) inside the autoclave vs. time during hydrothermal treatment of the lignin samples.

6.4.2 X-Ray diffraction

X-ray diffraction patterns of the three untreated lignins are shown in Fig. 6.2. All three samples have broad (002) graphite-peak centered near 2θ ≈ 22.5° with the Mascoma lignin also having a second peak around 2θ ≈ 15° along with some sharp Bragg peaks due to crystalline impurities. After HTT, the XRD patterns (Fig. 6.3) were similar to those reported for other carbonaceous
Figure 6.2 X-ray diffraction patterns of untreated lignin samples

Figure 6.3 Comparison of ambient temperature X-ray diffraction patterns of the post-HTT samples.
materials [9-12]. Exception is the post- HTT Mascoma sample which had a hint of a very broad (101) peak. It was also evident that the sharp peaks due to minerals present in the untreated Mascoma sample were absent after HTT. On the other hand, for the ammonium and sodium lignin, the sharp Bragg peaks were absent in the parent samples but present HTT. Thus, the XRD characteristics of the Mascoma lignin is quite different from that of ammonium and sodium lignosulfonate after hydrothermal treatment. The interlayer d-spacing calculated from the $2\theta \approx 22.5^\circ$ in HTT-Mascoma in Fig. 6.3 equal 0.393 nm. This magnitude is characteristic of activated carbons whereas for highly ordered graphite, d (002) = 0.336 nm is known [12-14].

6.4.3 Thermal stability

TGA investigations of the untreated and post-HTT samples were carried out using a TA Q50 system at a heating rate of 10°C/minute. The system was constantly flushed with nitrogen gas and the temperature range covered was from ambient to 700°C. For the untreated samples, percent (%) changes in weight vs. temperature are shown in Fig. 6.4. The weight loss near 100°C in the three samples is identified with the loss of adsorbed moisture. For the sodium and the ammonium lignin samples, more rapid weight loss begins near 150°C and continues till approximately 350°C at which point nearly half the weight is lost. With further increase in temperature, rate of weight loss decreases somewhat, accelerating again at temperatures above 550°C. By 700°C, approximately 80% of the weight is lost. For the Mascoma lignin, the weight loss vs. temperature behavior is significantly different in that the rapid weight loss begins only above 300°C. It can be concluded that the untreated sodium and ammonium lignins contain significant amounts of hemi cellulosic components known to decompose near 150°C [5]. The higher yield of about 20% from the Mascoma lignin obtained under post-HTT products versus 15 % yield from the sodium and
ammonium lignin can thus be understood in terms of the contents of their untreated counterparts (Fig. 6.5). After HTT, significant weight loss started at temperatures above about 350°C for all

Figure 6.4 Percentage changes in weight vs. temperature for untreated lignin samples

Figure 6.5 Percentage changes in weight vs. temperature for the post-HTT samples
samples. This is understandable since after HTT, the hemi-cellulosic and cellulosic components have been removed and the lignin component has been likely converted into a carbonaceous material as discussed later.

6.4.4 Morphology

Representative images for post-HTT samples are shown in Fig. 6.6. The length of white scale bar in each case is 100 nm. After HTT, Mascoma particles resembled near spherical well-separated nanostructured carbonaceous materials (NSCM) with diameter of about 50 to 250 nm. Similar, Ammonia and sodium lignins showed NSCM but they were agglomerated. The agglomeration was

Figure 6.6 SEM images of post-HTT Mascoma lignin in (A), Sodium lignin (C) and Ammonium lignin in (D) with the length of scale bar in each case being 100 nm. The size distribution of HTT-Mascoma is shown in (B).
severe for the post-HTT ammonium lignin resulting in a glob whereas in the post-HTT sodium lignin, the particles are joined by rods. Thus, the three lignin samples prepared under similar HTT conditions yielded slightly different products as also evident from the results from XRD and TGA.

### 6.4.5 Elemental analysis

Elemental analysis of the three post-HTT samples was also carried out and the results are shown in Table 6.1. After HTT, Mascoma has the highest amount of carbon (74.5%), followed by ammonium (69.7%) and sodium (61.7%) lignin. Both treated sodium and ammonium samples also contained significant amounts (≈5%) of nitrogen and sulfur because they are by-products of a sulfur-based pulping process (Kraft pulping). The % of nitrogen and sulfur are comparatively quite negligible in the Mascoma sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon (%)</th>
<th>Nitrogen (%)</th>
<th>Hydrogen (%)</th>
<th>Oxygen (%)</th>
<th>Sulfur (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mascoma</td>
<td>74.5</td>
<td>0.65</td>
<td>5.1</td>
<td>19.75</td>
<td>0.03</td>
</tr>
<tr>
<td>Sodium Lignin</td>
<td>61</td>
<td>5.25</td>
<td>4.24</td>
<td>29.51</td>
<td>4.52</td>
</tr>
<tr>
<td>Ammonium Lignin</td>
<td>69.4</td>
<td>6.57</td>
<td>4.13</td>
<td>19.9</td>
<td>4.62</td>
</tr>
</tbody>
</table>

### 6.4.6 Mid Infra-red spectroscopy

The assignments of various peaks based on a search of literature for all the six samples (three untreated and the three post-HTT lignins) are summarized in Table 6.2. Irrespective of lignin type and conditions used, spectra contained the same IR bands indicating they have similar chemical make. All three lignin samples showed broad peaks occurring around 3300 cm⁻¹, however, this
Table 6.2 Assignments of the major IR bands in cm\(^{-1}\) observed in the untreated and post-HTT samples

<table>
<thead>
<tr>
<th>Mascoma lignin</th>
<th>HTT Sodium</th>
<th>Sodium lignin</th>
<th>HTT Ammonium</th>
<th>Ammonium lignin</th>
<th>HTT Ammonium</th>
<th>Band Origin</th>
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<tr>
<td>3335</td>
<td>3376</td>
<td>3217</td>
<td>3384</td>
<td>3204</td>
<td>3147</td>
<td>O-H stretch</td>
</tr>
<tr>
<td>2937</td>
<td>2935</td>
<td>2935</td>
<td>2935</td>
<td>2941</td>
<td>2934</td>
<td>C-H stretching</td>
</tr>
<tr>
<td>2845</td>
<td>2840</td>
<td>2840</td>
<td></td>
<td>1704</td>
<td>C=O</td>
<td>C=O stretch (Unconjugated)</td>
</tr>
<tr>
<td>1599</td>
<td>1600</td>
<td>1593</td>
<td>1600</td>
<td>1598</td>
<td>1591</td>
<td>C=C vibration stretching in lignin</td>
</tr>
<tr>
<td>1514</td>
<td>1514</td>
<td>1519</td>
<td>1514</td>
<td>1517</td>
<td>1515</td>
<td>C=C vibration stretching</td>
</tr>
<tr>
<td>1456</td>
<td>1455</td>
<td>1453</td>
<td></td>
<td>1448</td>
<td>Asymmetric CH(_3) bending in lignin</td>
<td></td>
</tr>
<tr>
<td>1322</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C-O vibration in syringyl ring</td>
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</tr>
<tr>
<td>1213</td>
<td>1210</td>
<td>1209</td>
<td></td>
<td>1208</td>
<td>Aromatic C-H in-plane deformation, C-O guaiacyl ring</td>
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<td>1112</td>
<td>1109</td>
<td>1115</td>
<td>1110</td>
<td>1115</td>
<td>Aromatic C-H in-plane deformation typical for syringyl units</td>
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<tr>
<td>1059</td>
<td>1083</td>
<td>1080</td>
<td></td>
<td></td>
<td>C-O of secondary alcohols</td>
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<tr>
<td>912</td>
<td>912</td>
<td>914</td>
<td></td>
<td></td>
<td>C-H out of plane</td>
<td></td>
</tr>
<tr>
<td>873</td>
<td>897</td>
<td>896</td>
<td></td>
<td></td>
<td>C-H out of plane</td>
<td></td>
</tr>
</tbody>
</table>
was most intense in Mascoma lignin. These bands are attributed to the hydroxyl (O-H) groups resulting from the adsorption of water and presence of hydroxyl groups (O-H) in lignin. The bands occurring around 2930 cm$^{-1}$ are known to arise from C-H stretching in aromatic methoxyl groups and in methyl and methylene groups. The bands at 1513 cm$^{-1}$ can be attributed to C=C vibration stretching. Since lignin is derived from lignocelluloses, the region (fingerprint) covering 1800 to 900 cm$^{-1}$ showed many different sharp peaks which were the result of various vibrations modes in carbohydrates and lignin [16-18]. In lignocelluloses, lignin is associated with carbohydrates to form lignin-carbohydrates complexes. Thus, most extracted lignin is associated with carbohydrates.

The most characteristic peaks for lignin in all three samples (parent and post-HTT) occurred between 1600 cm$^{-1}$ and 1500 cm$^{-1}$ representing lignin C=C aromatic skeletal vibrations. This indicates that all three samples have the same main lignin structural backbone. In other words, although sodium and ammonium lignosulfonates were different from Mascoma lignin in terms of their preparation, that did not affect the main lignin structure in all three lignin samples. Also, sulfate ions show a strong band around 1100 cm$^{-1}$ composed mainly of S-O stretch. However, it is difficult to assign these bands since these peaks can easily be overlapped by similar peaks from organic molecules. This could possibly explain why Mascoma lignin, which is not a lignosulfonate, still showed peaks occurring around 1100 cm$^{-1}$.

Infrared spectra of the post-HTT carbons were compared with those from their untreated counterparts to establish the effect of hydrothermal treatment on the structure of the lignins. Spectra for the parent and HTT lignins are shown in Fig. 6.7. After HTT of Mascoma lignin, the bands at 1322 cm$^{-1}$, 1059 cm$^{-1}$ and 873 cm$^{-1}$ disappear. In both sodium and ammonium lignosulfonates, the bands occurring around 1080 and 1158 cm$^{-1}$ from vibrations of C-O bonds in
primary and secondary alcohols disappear after HTT. Similarly, in the region from 900 to 800 cm\(^{-1}\), absorption bands caused by deformation vibrations of C-H bonds on the benzene ring are also lost after HTT. In sodium lignosulfonate, HTT resulted in the appearance of two absorption bands occurring at 2840 and 1700 cm\(^{-1}\) representing C-H stretching vibrations of methoxyl groups and C=O stretch (unconjugated) respectively. In both HTT lignosulfonates (sodium and ammonium), CH3 vibrations of acetyl groups appear at 1450 cm\(^{-1}\) with another band also appearing at 1209 cm\(^{-1}\) corresponding to aromatic C-H in plane deformation.

Figure 6.7 FTIR spectra of untreated and HTT lignins

**6.4.7 Raman spectroscopy**

Raman spectra of the three post-HTT samples are shown in Fig. 6.8. In all three cases, two well defined peaks near 1360 cm\(^{-1}\) (D band) and 1580 cm\(^{-1}\) (G band) are observed, similar to the observations reported in other carbonaceous materials [10,19,20]. There is no significant
difference in the position of the D and G bands in the three carbons although the ratios of the
intensity of the D and G in the four cases are certainly different.

Since the D-band is absent in highly-ordered-pyrolytic-graphite (HOPG), it has been common to
associate the intensity of the D-band to the degree of disorder relative to the perfect graphitic
structure [21,22]. On that basis, the comparatively lower intensity of D-band and the lower half-
width of the G-band in the post-HTT Mascoma carbon would suggest the presence of relatively
higher degree of graphitic-like order in this carbon. However, in recent years it has been suggested
that the disorder can result from a number of defects such as lack of symmetry in the hexagonal
layer, point defects, multiple vacancy defects, nitrogen or oxygen in the layers or at the edges
[23,24]. Thus the D-band is due to the scattering from such defects which breaks the basic
symmetry of the graphene sheet and is present in $sp^2$-carbons containing vacancies, impurities or
other symmetry breaking defects. The source of the G band is assigned to the Raman-allowed
optical mode E_{2g} of the 2D graphite by two-zone folding of the 2D graphene Brouillon zone and
is associated with vibrations in $sp^2$ carbons [24]. From the results presented here it is not possible
to identify the kind of defects that are present in the three carbons.
6.5 Conclusions

Structural characterization of the carbons produced by the hydrothermal treatment of three lignin samples indicates it is dependent on lignin type. The results of this study showed that the nanostructured carbonaceous materials nanoparticles produced from the HTT of Mascoma lignin has somewhat higher degree of graphitic-like order. XRD patterns of the HTT lignins were similar to those reported for other carbonaceous materials suggesting the lignins have been converted to carbonaceous materials after the hydrothermal treatment. With the exception of the disappearance of C-O and C-H bonds after HTT, analysis of the FTIR spectra showed little changes in the chemical structure for all three lignins after hydrothermal treatment. Future studies will evaluate improvements of these carbonaceous materials from low value lignin into high value carbons for specific applications such as adsorbents, water purification, energy storage etc.
6.6 References


CHAPTER 7: RECOMMENDATIONS FOR FUTURE RESEARCH

Lignin is a variable material with different chemistries owing to its origin, method of separation etc. A large quantity of lignin waste is generated via industrial pulp and paper technologies or through the forest bio-refinery process. Upgrading technical lignins into useful precursors for value added products is therefore needed. Hydrothermal carbonization is a low cost, low energy and environmentally friendly method of converting lignin into carbon materials which upon activation can be used for CO\textsubscript{2} capture. Future research should focus on: determine the molecular weight distribution of precursor lignins before and after hydrothermal carbonization.

1. Determine the chemical composition of the liquid fraction of hydrothermal carbonization in order to elucidate the underlying mechanism.

2. Determine the mass balance of HTC conversion of lignin to carbonaceous materials to further assist the above step.

3. Determine the effect of HTC temperatures on differently commercially available technical lignins

4. A preliminary investigation using sodium hydroxide (NaOH) as a catalyst produced spherical carbons. A detailed experiment investigating the combined effect of temperature and catalyst concentration will prove useful.

5. Determine the effect varying effects of temperature and varying KOH concentrations on the textural properties of the carbons.

6. Determine the effect of loadings of lower molecular weight PEI on pore properties of activated carbons.

7. Determine the selective adsorption of CO\textsubscript{2} (to mimic flue gases produced by power plants.)
8. Determine the effect of \( \text{CO}_2 \) concentration, temperature and pressure on its adsorption on CM solid sorbent.

9. Determine the regenerability of CM sorbents.
APPENDIX

Effect of temperature on final mass of lignin after hydrothermal carbonization

Anova: Single Factor

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Effect of PEI loadings on adsorption capacity of activated hydrothermal carbons

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