Synthesis and Characterization of Biobased Carbon Nanoparticles from Lignin

by

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF BIOBASED CARBON NANOPARTICLES FROM LIGNIN

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Lignin is an undervalued product that does not yet provide economic returns. Finding value-added applications of lignin is needed to achieve economic sustainability. Carbon nanoparticles have great technological and industrial importance because of their enhanced physicochemical, electrical, thermal and mechanical properties. In this work a novel method has been explored to produce carbon nanoparticles from lignin. The objective of this work is to synthesize carbon nanoparticles with high surface area from lignin through the carbonization process. Lignin was dissolved in alkaline solutions with different weight ratios of lignin and potassium hydroxide. An intermediate sublimation process was adopted to reduce agglomeration of particles. The lignin was thermo-stabilized after the sublimation process in oxidizing atmosphere followed by the carbonization process in an inert atmosphere at 700°C using tubular furnace. The increase in glass transition temperature during thermo-stabilization process was confirmed by DSC analysis. The condensation reactions during thermo-stabilization process were confirmed by FTIR analysis. The formation of carbon nanoparticles was confirmed by transmission electron microscopy (TEM) analysis. Carbon nanoparticles with high specific surface area of 42 m²/g were produced. From the DLS particle size distribution it was found that 5 wt% KOH is the optimum concentration for synthesizing carbon nanoparticles from lignin.
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List of Abbreviations and Defined Terms

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<td>SEM</td>
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<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium Hydroxide</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>Inverse Centimetre</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<tr>
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<td>Energy Dispersive X-ray Spectroscopy</td>
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<tr>
<td>nm</td>
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<td>DC</td>
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<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<td>wt%</td>
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Chapter 1. Introduction

Nanomaterial is a material with at least one of its dimensions in the nanometre scale i.e. 1 to 100 nm [1]. The main advantages of these materials are unique thermal, mechanical, electronic, and biological properties which are not found in conventional materials [2]. Combining these unique properties with their remarkable recognition capabilities has resulted in systems with significantly improved performance and novel applications [2]. This phenomenon is the result of the limited number of their constituent particles or molecules [1]. For example elemental carbon is not strong and is a poor conductor of electricity; whereas two dimensional carbon is a semiconductor that has high charge mobility and obeys the laws of relativistic quantum mechanics rather than regular quantum mechanics, one dimensional carbon is 100 times stronger than steel, possessing either a conducting or semiconducting nature [3-4]. Apart from high mechanical strength most of the exceptional characteristics of nanomaterials are linked to their surface properties (area, roughness, energetic, and electron distributions) [4], which enable improved interactions. The principle factors that cause the properties of nanomaterials to significantly differ from bulk materials are increased relative surface area and quantum effects. These factors change or enhance the chemical reactivity and affect the optical, magnetic, mechanical, and electrical properties. The unique properties of the various types of nanomaterials can make them highly desirable for applications in commercial, medical, military and environmental sectors.
1.1 Carbon-based Nanomaterials

Carbon-based nanomaterials have been extensively used in a wide range of applications including hydrogen storage, water filtration, electronics, and energy applications. Different types of carbon-based nanomaterials are available including nanodiamonds, nanoions, nanofibres, nanorings, nanotubes, and fullerenes [5]. However, fullerenes and carbon nanotubes are receiving wide attention from the scientific community due to their high performance structure. In both cases, the basic structure is composed of a layer of sp$^2$ bonded carbon atoms, where each atom is connected to three other carbon atoms in the x–y plane and by a weakly delocalized $\pi$ electron cloud along the z-axis. This configuration, which resembles that of graphene is responsible for the higher electrical conductivity [5].

Carbon nanostructures have traditionally been produced by a wide variety of methods such as physical extrusion, chemical vapour deposition, arc discharge, laser vaporization, and porous silica template imprinting [6]. In general, these methods require carbon-based feedstock to build an underlying polymer. Ethylene gas, rayon, coal and oil pitches, polyvinyl alcohol, and polyacrylonitrile are commonly used as polymer precursors. However, these precursors are from fossil-based petroleum. Hence, there is a need to work on carbon from renewable feedstocks for synthesizing carbon-based nanomaterials.
1.2 Motivation

Currently, all carbon based nanomaterials are synthesized from petroleum resources. Depleting petroleum feedstock and environmental concerns have led to work in alternative resources for synthesizing carbon nanostructures. Within the wide range of bio-based feedstocks lignin looks promising due to its availability and high carbon content. Lignin is a by-product of paper and lignocellulosic ethanol industries. Lignin has approximately 40-60% carbon content [7]. Currently it is used as filler for polymeric components and industrial boiling. These two applications do not provide high economic returns. Hence there is a need to find high value-added applications such as carbon nanomaterials from lignin. Synthesis of carbon nanoparticles from lignin is receiving great scientific and technological interest because of its carbon rich structure.
Chapter 2. Literature Review

2.1 Allotropes of Carbon

Allotropes are the structural modifications of an element. Carbon is known to have several allotropes which includes diamond, amorphous carbon, graphite, fullerenes, carbon nanotubes, and graphene [8]. Structures of carbon allotropes are as shown in the Figure 2.1. The allotropes of carbon are briefly explained in the following sections.

Figure 2.1: Allotropes of carbon (a) Diamond lattice (b) Graphite structures (c) Graphene (d) Single wall carbon nanotube (e) Buckminster fullerene

2.1.1 Diamond

Diamond is an allotrope of carbon and it is the hardest naturally occurring mineral and ranks among the rarest materials known. Most natural diamonds are formed under high pressure and high temperature conditions in the earth mantle and are brought close to the surface through volcanic eruptions. Diamonds can also be produced synthetically by chemical vapour deposition [9-10]. In nature diamond is present in the cubic form, where all the atoms are bound to one another with tetrahedral sp³ coordination as shown in Figure 2.1(a). The cubic form of diamond is thermodynamically stable. Without use of any catalysts, graphite can be converted to diamond at pressures above 15 GPa and at high temperatures (>1000°C) [11].

2.1.2 Graphite

Graphite is composed of hexagonal planar layers of carbon atoms where electron orbitals are sp² hybridized. These hexagonal planar layers are held parallel to each other via van der Waals forces as shown in Figure 2.1(b). These carbon layers are known as graphene layers. In each hexagonal lattice, carbon atoms are separated by 0.142 nm, and the distance between planes is 0.335 nm. The chemical bonds within the layers are covalent with sp² hybridization [12-13]. Hexagonal and rhombohedral are the two different form arrangements found in graphene layer. Although these layers are arranged differently, they have similar physical properties. The thermodynamically stable form of graphite is hexagonal graphite with an ABAB stacking sequence of the graphene layers. The unit cell dimensions are a = 0.246 nm and c = 0.6708 nm [14]. Hexagonal graphite is thermodynamically stable below approximately 2600 K and 6 GPa [15]. The rhombohedral graphite is thermodynamically unstable with an ABCABC stacking sequence of the layers. The
unit cell constants are \( a = 0.2566 \text{ nm} \) and \( c = 1.0062 \text{ nm} \) [16]. This form has not been isolated in pure form. It is always mixed with the hexagonal form in variable amounts which can be increased up to 40% rhombohedral content. Progressive heating to above 1600 K transforms rhombohedral graphite to hexagonal graphite, which shows that the hexagonal phase is thermodynamically more stable [17].

### 2.1.3 Graphene

Graphene is a two dimensional monolayer of carbon atoms tightly packed in a honeycomb crystal lattice structure with a bond length of about 0.142 mm. This is the basic element for graphitic materials of all dimensionalities. It can be wrapped into 0D fullerenes or 1D nanotubes or stacked into 3D graphite as shown in Figure 2.2 [18].

![Graphene as a 2D building material for carbon materials of all other dimensionalities: 0D fullerenes, 1D nanotubes or 3D graphite](image)

*Figure 2.2:* Graphene as a 2D building material for carbon materials of all other dimensionalities: 0D fullerenes, 1D nanotubes or 3D graphite

Theoretically graphene has been studied for several years to describe various properties of carbon based materials [19-20]. It was believed that graphene was thermodynamically unstable and did not exist in free space until the experimental discovery of graphene and other free-standing 2D atomic crystals in 2004 [21-22]. Free standing graphene layers are difficult to obtain, as they have the tendency to roll and form scrolls with respect to the lower energy state of graphene [23]. Many efforts have been made to produce very thin films of graphite by mechanical exfoliation but nothing fewer than several hundreds of layers has been produced [24]. In 2004, Geim and Novoselov [21] obtained single atom thick graphene from bulk graphite by using a process called micromechanical cleavage. Many challenges have to be addressed in graphene synthesis for practical applications because of limited control on size and shape of graphene. Experimental results have shown graphene has remarkable electron mobility at room temperature [18]. A single layer of graphene has Young’s modulus of more than 1 TPa and is the stiffest known material [25]. Balandin et al. [26] measured thermal conductivity of single layer graphene. At room temperature the conductivity of graphene is \((4.84 \pm 0.44) \times 10^3\) to \((5.30 \pm 0.48) \times 10^3\) W/mK which is more than the conductivity of nanotubes and diamond [26].

### 2.1.4 Carbon Nanotubes

Carbon nanotubes were discovered by Iijima in 1991 [27] and since then, they have been extensively investigated using both experimental and theoretical studies. Initially, Iijima discovered carbon nanotubes consisting of multiple cylinders of layers known as multi-walled carbon nanotubes. Later, however, both Bethune et al. [28-29] and S. Iijima and T. Ichihashi [28-29] discovered that under specific synthesis conditions (cobalt as the catalyst in the arc discharge method) single wall nanotubes may be formed. Based on diffra-
tion studies and transmission electron microscopy studies, a carbon nanotube is proposed to consist of cylinders of pentagons and hexagons. These are members of the fullerene family made of \( \text{sp}^2 \) hybridized carbon atoms. The simplest way of visualizing carbon nanotubes (CNT) is to consider a graphene sheet rolled into the form of a cylinder with a diameter in the order of nanometres as shown in Figure 2.3 [30].

Carbon nanotubes are classified into two categories based on structure: single walled carbon nanotubes (SWCNT) which are made up of a single layer of graphene and multi-walled carbon nanotubes (MWCNT) which are made up of multi-layers of graphene [31]. MWCNT consists of two or more graphene sheets in the form of coaxial cylindrical shells, with a hollow interior. The distance between adjacent layers is nearly equal to that of the distance between graphite layers (0.335 nm). The typical diameter of a carbon nanotube ranges from 2 nm to 25 nm, while length can extend up to a few microns. In the case of SWCNT, the diameter usually ranges from 1-2 nm and the length generally extends to several microns.

Carbon nanotubes possess extraordinary properties. Nanotubes are predicted to have high mechanical strength and high flexibility because nanotubes are highly symmetric molecules which are linked by covalent bonds. Treacy, Ebbesen, and Gibson found that Young’s modulus of carbon nanotube is above 1 TPa [32]. Their high stiffness, coupled with their low density, implies that nanotubes might be useful as nano-scale fibres in strong, lightweight composite materials [32].

The electrical properties of carbon nanotubes depend on the exact arrangement of carbon atoms. The first electronic transport measurements revealed that at low temperatures, nanotubes act as single electron transistors [33]. After that, it was found that a semi-
conducting tube functions as a single molecule field effect transistor at room temperature. Carbon nanotubes are therefore ideal candidates for molecular electronics [33-35]. The cylindrical structure is built from a hexagonal honeycomb lattice of sp² bonded carbon with no dangling bonds.

![Schematic diagram of the basic unit of a carbon nanotube](image)

**Figure 2.3:** Schematic diagram of the basic unit of a carbon nanotube


### 2.1.5 Fullerenes

Spherical fullerenes are zero-dimensional molecules as all dimensions are limited to nanoscale. Fullerenes are a unique class of spherical molecules containing a conjugated π electron system. Each fullerene represents a closed network of hexagons and pentagons [37]. The chemical formula of spherical fullerenes is \( C_n \), where \( n \) represents the number of atoms in the molecule. Among all \( C_n \) fullerenes isolated stable fullerenes are \( C_{60}, C_{70}, C_{76}, C_{80}, C_{84} \) and the series extends to gigantic fullerenes. The smallest stable, and at the same
time the most abundant, fullerene is the buckminsterfullerene $C_{60}$ [38-39]. It is also the smallest carbon molecule with pentagonal faces isolated from each other. Their average diameter is 0.683 nm. The arrangement of its 60 carbon atoms resembles truncated icosahedrons similar to a soccer ball. Fullerenes are chemically stable, but they are less dynamically stable than graphite. The $sp^2$ hybridized carbon atoms must be bent to form closed spheres in comparison to planar graphite in which the atoms are at their minimum energy level. Fullerenes have been used as the main material in various applications. Some examples are solar cells [40], photo detectors [41], field effect transistors [42], and additives in polymers [43].

2.2 Sources of Carbon Nanomaterials

Many efforts have been made in developing carbon nanomaterials some of the synthesis methods described in the section below. In general the disadvantages of these methods are high temperature processing, complicated to control, and use non-renewable materials. This is because most of the synthetic methods were based on the idea of obtaining adequately active carbon atomic species or clusters from carbon sources and assembling them into CNTs. The current industrial feedstock for carbon fibre includes petroleum and coal based pitches, polyacrylonitrile (PAN), ethylene gas, polyvinyl alcohol, and rayon.

2.3 Synthesis Methods of Carbon Nanomaterials

Laser ablation, arc discharge, and chemical vapour deposition (CVD) are the main techniques that have been developed to produce carbon nanomaterials. In the first two methods, a solid piece of graphite carbon is heated to a high temperature where carbon atoms are separated and reassembled on a cathode in the arc discharge method or on a cooled plate in the laser ablation method. During the reassembling process, highly ordered carbon
nanomaterials are formed. In CVD, instead of a solid piece of carbon, hydrocarbon gas is used as a feedstock which dissociates either thermally or in the presence of plasma.

2.3.1 Arc Discharge
An arc discharge device consists of a vacuum chamber in which two graphite electrodes are held at a short distance apart as shown in Figure 2.4. Inert gas is released through the deposition chamber at controlled pressure. DC voltage is applied between two graphite electrodes. The potential difference creates high temperature discharge between the two electrodes [44]. The position of the electrodes is adjustable. As the rods are brought closer together a discharge occurs resulting in the formation of plasma. This discharge vaporizes the surface of smaller carbon electrodes and forms a carbon deposit on the larger electrodes. This carbon deposit consists of a mixture of components of SWCNT, MWCNT as well as carbon nanoparticles [45]. Nanotubes synthesized by the arc discharge method exhibit high crystalline structure with a few structural defects which is due to the high temperature processing. In order to use these nanotubes, additional separation and purification steps are also required.
2.3.2 Laser Ablation

In the laser ablation method, similar to the arc discharge method, very high temperatures are reached during carbon nanomaterial production. A graphite target is placed in the deposition chamber and heated to approximately 1200°C by the tube furnace in an inert atmosphere. A high power laser is pointed at the target to generate vaporized material which is carried by gas into the cooled collector, where vaporized material condenses as shown in Figure 2.5 [47]. Highly ordered nanotubes can be produced using laser vaporization aligned along a common axis. The average diameter and size can be controlled by processing parameters, i.e. growth temperature, pressure inside the chamber, and gas flow rate. Thess et al. [47] synthesized SWCNT by using a target of graphite and metal catalyst
particles using the laser ablation method. The best yield is obtained by using a nickel and cobalt mixture at 1200°C. Along with the arc discharge method, the laser ablation method also has some drawbacks. First, additional steps are required for purifying carbon nano-materials. Second, this method consumes a large amount of energy and yields less [45, 48].

**Figure 2.5:** Schematic diagram of laser furnace apparatus


### 2.3.3 Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is the process in which solid material is deposited from the gaseous phase. In this method, precursor gas is delivered to the reaction chamber at ambient temperature containing one or more objects to be coated. Chemical reactions occur on and near the hot surfaces, resulting in deposition of solid phase material on the substrate. The temperature of the substrate is critical because it influences the reactions that take place. This method is accompanied with the production of chemical by-products that are exhausted out of the chamber along with the unreacted precursor [49-50]. The ba-
sic CVD apparatus consists of a quartz tube placed in a tube furnace connected to a gaseous carbon source as shown in Figure 2.6. Metal catalysts are deposited onto the substrate before synthesis. The purpose of depositing carbon nanomaterials is to create in-situ nanoscale catalyst particles during the growth process. Iron, nickel, and cobalt are the most studied catalysts for growing CNT. The most commonly used precursors are carbon monoxide and hydrocarbons such as methane, ethane, ethylene, and acetylene. The growth behaviour of CNT is related to catalyst preparation, temperature, source of carbon and feeding rate. In the typical growth process, the air in the tube is removed by purging the inert gas and the furnace is heated until the desired temperature is achieved by the substrate. Then carbon precursors are introduced into the system at a specific rate for a specific growth period. Finally the carbon source is turned off and the reactor is cooled down to room temperature in the presence of inert gas. The advantage of this method is a lower growth temperature unlike the arc discharge and laser ablation methods. The need to prepare the catalyst for deposit is a disadvantage [49-50].

![Figure 2.6: Schematic diagram of a CVD setup](image)

2.4 Renewable Resource-based Carbon Nanomaterials

Precursors used for carbon nanostructures play an important role in both structure and yield. At present, petroleum-based oil, gaseous hydrocarbons (methane and acetylene), and carbon rich polymers, i.e. polyacrylonitrile (PAN), are well known precursors for the development of carbon nanostructures. Depleting petroleum resources and greenhouse gas emissions motivated the researchers to investigate alternative renewable resources for the development of carbon nanostructures. Advantages of biomass are its low cost, availability in large amounts, it can be rapidly generated, and easily accessed and is environmentally friendly. Hence using biomass as a starting material for synthesis of carbonaceous material is a promising solution for reducing the carbon footprint. The different morphology as well as chemical structure of these renewable resources results in the formation of diversified carbon nanostructures. A wide range of renewable materials has been used for the synthesis of carbon nanostructures. Some of the methods developed for the synthesis of carbon nanostructures from renewable resources are discussed below.

2.4.1 Pyrolysis

Ma and Bao [51] prepared graphitic carbon nanostructures by microwave assisted pyrolysis from biomass precursors filled with conducting polymers and iron catalyst species. The biomass precursors used in their study were wood and cotton because of their special morphology, textural properties, and chemical structures. Ma and Bao [51] also reported that under microwave irradiation, biomass samples were converted into carbon nanostructures in the presence of the Fe catalyst.
2.4.2 Cyclic Oxidative Carbonization

Xie et al. [52] explained the stepwise formation of carbon nanostructures via carbonization of wood. Shafizadeh’s [53] studies showed that when cellulose is heated, it decomposes via two pathways. The first path involves the degree of polymerization reduction that dominates the reaction below 300°C. The major decomposition products are CO, CO₂, H₂O and solid carbon. The second path occurs above 300°C and involves cleavage of molecules and disproportionate reactions to produce a mixture of anhydro-tars and low molecular weight substances. Heating the wood in air at temperatures below 300°C promotes the first pathway for cellulose decomposition with increased char yield and reduces the production of tar. Therefore carbonizing wood in this manner retains the original cell wall structure of cellulose with a hemicellulose, cellulose and lignin matrix at the nanometre level. When wood fibre is heated in air at 250°C there are readily visible changes, such as the colour change to dark brown or black as it is carbonized. However, as reported above these changes can also occur at the nano-scale level. Heating wood and plant fibre in air at temperatures greater than 400°C can result in rapid ablation of the cellulose carbon derived from cellulose microfibrils. Under appropriate conditions, this can result in the formation of nanometre sized channels in the material. In this way, the stepwise carbonization process at low temperature produces nano-scale channels from ablation of residual cell wall microbials in the carbonized cell wall structure [52].

Kang et al. [54] obtained carbon nanotubes (CNT) from grass. Grass consists of many vascular bundles in stem, protein, fat and so on. The vascular bundles are a strand of conducting tissue extending lengthwise through the stem and roots of the plants. They have a similar structure to ferns, fern allies, gymnosperms, and angiosperms. They have tubular
structures, and the major compositions are also cellulose, hemicellulose and lignin. In this approach, during pre-treatment, the protein and fat were removed through heat treatment at approximately 250°C. Rapid heat treatment at approximately 600°C and the presence of oxygen cause the lignin oxidative delignification. At the same time the cellulose is dehydrated and converted into nanostructured carbon. The formation of carbon nanotubes has been explained as follows. First water that was absorbed by the cellulose is released followed by the release of water through β-elimination from the cellulose hydroxyls. This process makes the tubular structures contract which causes the formation of carbon-to-carbon double bonds. Simultaneously, oxygen makes the pyrolytic reactions of the vascular bundles more rapid. The complex chemistry of the C–O–H system of ligno-cellulosic materials helps in the synthesis of nano-structured carbon [54]. Goodell et al. [55] observed the formation of carbon nanotubes within fibre cell walls when unmodified wood undergoes oxidative carbonization at 250°C followed by a cyclic oxidation process at 400°C.

2.4.3 Hydrothermal Carbonization

Hydrothermal carbonization of ligno-cellulosic biomass is an environmental process where biomass is treated in hot compressed water. It is a convenient way to convert biomass into carbonaceous materials under moderate conditions. Titirici et al. [56] reported that they prepared the carbonaceous nanostructures using crude plant materials. They found that the presence of metal ions can effectively accelerate the hydrothermal carbonization process. They have also reported that from soft biomass hydropholic and water dispersible carbonaceous nanoparticles are formed in the range of 20-200 nm. These particles are in a spherical structure which indicates biomass is first liquefied and
then carbonized. The hydrothermal carbonization process not only produces carbonized materials from biomass but also forms useful nanostructures [56]. Hu et al. [57] synthesized carbon nanomaterials from crude plants and from carbohydrates through a direct and catalyzed hydrothermal process.

### 2.4.3.1 Direct Hydrothermal Carbonization

Hu et al. [57] reported that in direct hydrothermal carbonization biomass compounds were heated in sealed autoclaves in the presence of citric acid at 200°C for 16 hours. Interestingly they found two types of carbonaceous materials: soft plant tissues and hard plant tissues. Soft plant tissues were without extended crystalline cellulose scaffolds of spherical carbonaceous nanoparticles of a very small size and porosity. Hard plant tissues are with structural crystalline cellulose scaffolds, however, they can preserve the shape and large scale features on a macro and micro scale; as a result of considerable mass loss, there arises a significant structural change on a nano-scale resulting in a sponge like continuous carbon network with well-defined mesoporous structures [57].

### 2.4.3.2 Catalytic Hydrothermal Carbonization

In the catalytic hydrothermal carbonization process catalysts are used to accelerate the carbonization process. Recently, Yu et al. [58] reported that the presence of metal ions can effectively accelerate hydrothermal carbonization of starch, which reduces the reaction time but also directs the synthesis toward various metal-carbon nano-architectures such as carbon nanocables, nanofibres, and spheres. They also reported that iron ions and iron oxide nanoparticles were shown effectively to improve the hydrothermal process [56, 58].
2.5 Lignin: Origin, Source and Chemistry

Lignin is the second most abundant naturally occurring aromatic biopolymer on earth [59-60]. It acts as a binder and holds together the cellulose and hemicellulose microfibers in biomass through lignin-carbohydrate complexes and hydrogen bonding [61]. Depending on the type of biomass the amount of lignin present varies in the approximate range of 10-30%. It is an amorphous polyphenolic and highly polymerized substance. Lignin has a complex structure consisting primarily of phenylpropane units derived from three alcohols: p-coumaryl, coniferyl and sinapyl alcohols [62]. Figure 2.7 shows the structural units of lignin. The amount of lignin varies with different sources of plant biomass but generally lignin content is higher in wood than grasses. Based on the composition of structural units present in the lignin it has been classified into three categories, soft wood, hard wood, and grass lignin [62]. Softwood lignin is also called guaiacyl alcohol or coniferos lignin because it is made up of coniferyl alcohol units. Hardwood lignin is made up of sinapyl alcohol and coniferyl alcohol. Finally grass lignin is made up of p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [62]. The most common linkage types found in a lignin molecule are β-O-4, α-O-4, β-5, 5-5, 4-O-5, β-1, and β-β. Although numerous structures are found in lignin, the predominant linkage is the β-O-4 linkage [62]. Figure 2.8 shows the major types of inter-linkages between phenylpropane units observed in lignin. The proportion of linkages present in the hardwood and softwood lignins is presented in the Table 2.1. Table 2.1 clearly indicates that the majority of inter-linkages between phenylpropane units are β-O-4. The further polymerization of lignin involves monolignols with phenolic end groups or radicals, forming a large 3-dimensional branched polymer. Figure 2.9 shows the designed scheme of the softwood lignin.
Figure 2.7: The major building blocks of lignin

Figure 2.8: Characteristic linkages present in the lignin

Figure 2.9: Structure of soft wood lignin


Table 2.1: Different concentration of phenylpropane inter unit linkages present in the soft and hard wood lignins

<table>
<thead>
<tr>
<th>Linkage type</th>
<th>Percentage of total linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hardwood lignin</td>
</tr>
<tr>
<td>β-O-4</td>
<td>60</td>
</tr>
<tr>
<td>α-O-4</td>
<td>7</td>
</tr>
<tr>
<td>β-5</td>
<td>6</td>
</tr>
<tr>
<td>5-5</td>
<td>5</td>
</tr>
<tr>
<td>4-O-5</td>
<td>7</td>
</tr>
<tr>
<td>β-1</td>
<td>7</td>
</tr>
<tr>
<td>β-β</td>
<td>3</td>
</tr>
</tbody>
</table>

Generally, isolation of lignin from ligno-cellulosic materials is difficult due to condensation and oxidation reactions occurring during the isolation process [63]. In current pulping and bleaching processes, acids, alkalis, organic solvents or biological reagents are used to attack the lignin causing degradation and dissolution. Then cellulose fibres are separated from the lignin. The alkali process is the most widely used method and has two variations: kraft and soda processes. Acidic pulping by sulphate process uses a combination of sulphur dioxide and water at high temperature and pressure [64].

2.6 Lignin as a Carbon Source

Lignin is an industrial byproduct of cellulosic ethanol and the pulp and paper industries. The thermo-chemical conversion of lignin into value added products is of interest as a consequence of its huge availability and its potential to produce higher value products. Extensive research has been done to expand the use of lignin in various sectors. Currently the largest amount of lignin is burned to cover the energy needs. Other applications of lignin are adhesives and polymer composite applications [61]. Lignin has also been used as a precursor for synthesis of activated carbon and carbon fibre. Another possible application of lignin is its use as a precursor for the production of carbon nanoparticles. The ability to use a bio-derived, high-volume by-product as a source for carbon nanomaterials improves availability, decreases sensitivity to petroleum cost and reduces environmental impacts associated with carbon nanomaterials. The molecular structure of lignin confirms that it has high carbon content. Its high carbon content and huge availability motivated us to use lignin as a precursor for carbon nanoparticle synthesis. The synthesis of activated carbon and carbon fibre from lignin is explained in the following section.
2.6.1 Activated Carbon from Lignin

Activated carbons have a very high porous structure with a large internal surface area around 500-2000 m²/gm and have good adsorption capacities. It has application in removing a wide variety of pollutants including organic and inorganic substances from liquid or gas phase. There are two methods for the synthesis of activated carbon: (1) Physical activation and (2) Chemical activation.

2.6.1.1 Physical Activation

Physical activation is a process in which the precursor is developed into activated carbon using gases and it is generally carried out in two steps. Carbonization is the first step which involves conversion of the precursor into carbon, which is generally nonporous, by the pyrolysis process at 600 – 900°C. Activation is the second step and involves contacting char with oxidizing gases such as steam or CO₂ in the temperature range of 600 – 1200°C. During this reaction disordered carbon atoms are removed, which results in the formation of a well-developed micropore structure [65].

2.6.1.2 Chemical Activation

Chemical activation is a single step process for preparation of activated carbon where carbonization of the precursor in the presence of a chemical agent takes place. Chemical activation involves impregnation of the precursor with chemicals such as H₃PO₄, KOH, ZnCl₂, and NaOH followed by heating under inert atmosphere at temperatures in the range 450 – 900°C, depending on impregnation used. The activating agents function as dehydrating agents that influence the carbonization process by inhibiting tar formation and thereby enhancing carbon yield. This method leads to high micropore volumes and
wider micropore sizes. Therefore these materials are preferred for liquid phase applications [65-66].

2.6.2 Carbon Fibre from Lignin

Carbon fibre is generally produced from polyacrylonitrile (PAN) and pitch. Many researchers have synthesized carbon fibre from lignin. Lignin has several advantages over PAN and pitch for commercial production of carbon fibre. Lignin is readily available, relatively inexpensive and structurally rich in carbon content. However lignin possesses some disadvantages such as difficulty to recover in pure form.

Kadla et al. [67] produced carbon fibres from kraft lignin without any chemical modification by thermal spinning, followed by carbonization. They also investigated the use of lignin-polyethylene oxide (PEO) blends as the precursors for the production of carbon fibre. The addition of PEO to lignin produced a miscible blend which improved fibre spinning capability. With the addition of 3-5% PEO, the lignin-PEO blends could be readily converted into carbon fibre. The blends with more than 5% PEO added led to fibre fusing during the thermo-stabilization process.

Kubo and Kadla [68] produced carbon fibre from hardwood lignin and synthetic polymer blends. They reported on lignin blended with poly (ethylene terephthalate) (PET), polyethylene oxide (PEO) and polypropylene (PP). Fibre spinning strongly depended on the partner polymer and its thermal properties. They observed good fibre spinning for all blends. The lignin thermal stabilization process was also affected by polymer blending with PET and PP. Only lignin requires a slower heating rate for thermal stabilization, whereas higher heating rate resulted in fusion of lignin fibres. Blending with PET allowed for a higher heating rate and for thermal stabilization to be used. The tensile properties of
carbon fibres obtained from lignin/PET are comparable to commercial pitch based carbon fibres. Similarly, mechanical properties of lignin/PP based carbon fibres are less compared to lignin/PET based carbon fibres but comparable to commercially available activated carbon fibres [68].
Chapter 3. Research Problem Statement, Objectives and Hypothesis

3.1 Problem Statement

Lignin is an industrial co-product produced in pulp and paper and ligno-cellulosic ethanol industries. Finding the value-added applications of lignin is becoming a mandate for these industries in order to achieve economic and environmental sustainability. Carbon nanostructures synthesized from petroleum resources are expensive. Synthesis of carbon nanostructures from renewable resources decreases the cost as well as the carbon footprint. Synthesis of nanostructures from lignin as a renewable material is receiving great scientific and technological interest because of the carbon rich composition of lignin. Carbon nanostructures have great technological and industrial importance because of their enhanced physicochemical, electrical, thermal and mechanical properties. Such carbon nanostructures can find application in materials, energy storage, electronics, as well as in applied chemistry. The primary aim of this study is to synthesize carbon nanoparticles with higher surface area, higher yield than the conventional processes, and less impurities using lignin as a precursor.

The following are some problems associated with using lignin as a precursor for carbon nanoparticles.

i) The properties of lignin depend on the source and the extraction methods. Also all lignins will not be suitable as a precursor for synthesis of carbon nanoparticles because of variation in yields, impurities, and processing parameters. In order to use lignins as a precursor for synthesis of carbon nanoparticles the properties of lignins have to be studied first.
ii) Lignin consists of macroparticles. When lignin is carbonized it turns into carbon macroparticles instead of nanoparticles.

iii) Agglomeration of lignin particles during alkali treatment leads to formation of macroparticles.

iv) Also the glass transition temperature of lignin is in between 50°C and 150°C. When the temperature reaches above the glass transition temperature in the carbonization process, lignin fuses together and forms lumps.

3.2 Objectives and Hypothesis

Objective 1: The objective of the initial work is to identify lignin suitability and processing parameters for carbon nanoparticle synthesis with higher yield.

Hypothesis 1: Characterization of lignin from different resources using TGA, FTIR, and elemental analysis provides structural and thermal information that can be used to identify the suitability and processing parameters of lignin for carbon nanoparticles synthesis.

Objective 2: The second objective of this study is to prepare carbon nanoparticles with high surface area by decreasing the size of the original lignin macroparticles before the carbonization step.

Hypothesis 2: The specific surface area of lignin can be increased by dissolving in a suitable solvent and separating lignin from the solvent without agglomeration.
**Objective 3:** To eliminate agglomeration of lignin particles during alkali treatment which can help produce nano size particles.

**Hypothesis 3:** Agglomeration and particle size of lignin can be controlled by separating lignin polymer from solution by sublimation process.

**Objective 4:** To prevent the fusion property of lignin in order to obtain nanosize particles.

**Hypothesis 4:** Thermo-stabilization of lignin increases the molecular weight of lignin, which increases the glass transition temperature of lignin. This thermo-stabilization process converts the thermoplastic nature of lignin to thermosetting nature.
Chapter 4. Experimental Methods

4.1 Materials

Lignins were collected from different resources. Polybind 300 lignin was obtained from Northway chemicals, Canada. Protobind 2400 lignin was obtained from A L M India Pvt. Ltd. This lignin is a by-product of the paper industry. A hydrolyzate solid from pre-treated fibres (HSPF) lignin was obtained from Mascoma Canada. HSPF is a by-product from ligno-cellulosic ethanol industries. Lignins were used as received for further characterization. Protobind 2400 lignin was used for synthesis of carbon nanoparticles. Potassium hydroxide was used for chemical modification of lignin.

4.2 Methods

4.2.1 Freeze Drying

Freeze-drying is a proven technique to improve the long-term stability of nanoparticles and preserving the original particle size in the solution [69-70]. Hence, in this work freeze drying has been used to separate lignin from lignin solution after chemical treatment. SAVANT-MODULYO (Model no: B1576) freeze dryer was used to separate lignin from alkaline solution. The chamber of the dryer has to be vacuum tightened. To dry the material first, it has to be frozen so water is separated from the material as ice crystals. Then a vacuum is created in the chamber to decrease the boiling point of frozen water. During this process heat is going into the frozen product, while the vacuum promotes a process known as sublimation in which water comes out as a vapour without melting. This process leads to overall drying of all the materials. When vapour comes out of the material it is attracted towards the colder areas of the freeze drying machine and condensed back to ice.
4.2.2 Tube Furnace

Sentro Tech tube furnace has been used in this study to carry out thermo-stabilization and carbonization. This furnace has a 16-segment digital microprocessor temperature controller with an advanced self-tuning feature. This self-tuning automatically sets the best parameter values to control the furnace operation. The Sentro Tech tube furnace can be used to maintain a constant temperature in the range between room temperature and 1100°C. Figure 4.1 is a schematic diagram illustrating the furnace which was used in the thermo-stabilization and carbonization experiments. A ceramic boat was used to hold the samples during the carbonization processes. The ceramic boat was mounted in a ceramic tube equipped with rubber stoppers to preclude air from entering the ceramic tube.

![Schematic diagram of tube furnace](image)

Figure 4.1: Schematic diagram of tube furnace

4.2.3 Thermo-stabilization and Carbonization

Lignin samples were placed in the ceramic boat and positioned in the central constant temperature zone of the horizontal tube furnace. The reactor consists of a 10 cm diameter alumina tube. The samples were heated to 250°C in the presence of air in the thermo-stabilization process. A low heating rate of 1°C/min was used. The samples were carbonized at 700°C in the presence of nitrogen for two hours. A slower heating rate of 5°C/min
was used as suggested by Sudo and Shimizu [71] when they synthesized carbon fibre from lignin. Slower heating rates increase the probability of cross linking, crystallization of decomposing polymers and reduce the volatilization of organic molecules resulting in higher yield [72-73]. After that the samples were cooled to room temperature by maintaining a nitrogen atmosphere.

4.3 Characterization Techniques

4.3.1 Elemental Analysis
The LECO SC444 is used to measure the total carbon and sulphur content in soil, plant, waste and other samples. Inorganic carbon can be determined by ashing the sample at 475°C for three hours prior to LECO SC444 use. Organic carbon is calculated from the subtraction of the inorganic carbon result from the total carbon result. The LECO SC-444 method of carbon and sulphur determination is based on the combustion and oxidation of C and S to form CO₂ and SO₂ by burning the sample at 1350°C or 1450°C in a stream of purified O₂. The amount of evolved CO₂ and SO₂ is measured by infrared detection and used to calculate the percentages of C and S in the sample.

Total carbon present in the lignin was measured by the LECO SC-444 method according to Nelson and Sommer [74]. In our studies the total carbon, nitrogen, and sulphur contents of lignin were evaluated using the LECO combustion method at the Laboratory Services Division at the University of Guelph. This is based on the Dumas Method, and is routinely used by Sandia National Laboratories for the analysis of total nitrogen in plant and soil samples. Samples were dried, and ground or sieved prior to analysis. The samples were combusted in a sealed system. Nitrogen compounds released were reduced to N₂ gas, which was measured by a thermal conductivity cell using the LECO FP428 [75].
4.3.2 Determination of Moisture and Dry Matter Content

The moisture content of the lignin samples was measured according to ASTM E871-82 (2006). Approximately 50 grams of each lignin sample were placed in glass beakers and the initial weights of samples were measured. These samples were kept in an oven to maintain the temperature at 103 ± 1°C for 16 hours. After 16 hours, samples were removed from the oven and the weights were measured. Samples were returned back to the oven for 2 hours at 103 ± 1°C. Again weights of the samples were measured. This process was repeated until the total weight change varied less than 0.2 %; that was recorded as the final weight. The percentage of total moisture and dry content of lignin was calculated as follows:

\[
\% \text{ of moisture} = \frac{(W_i - W_f)}{W_i} \times 100
\]

Where \( W_i \) = Initial weight of the sample

\( W_f \) = Final weight of the sample

\( \% \text{ of dry content} = 100 - \% \text{ of moisture} \)

4.3.3 Determination of Bulk Density

The lignin samples were kept in a measuring beaker and the volume of the sample was measured. The weight of the samples with beaker and without beaker was measured. The density of lignin samples was calculated as follows:

\[
\text{Density} = \frac{(\text{Weight of the beaker + sample} \ - \ \text{weight of the beaker})}{\text{Volume of the sample}}
\]
4.3.4 pH Measurement

pH of the material is defined as: \( \log_{10} \frac{1}{[H^+]} \). Where \([H^+]\) is the number of moles of hydrogen ions in one cubic decimetre of a solution. Measuring the pH of a material gives an idea about its acid content. In this study, about 1.00 gram of the lignin sample was ground, and poured into 100 ml of distilled water. After one hour the pH was measured using pH paper.

4.3.5 Energy Dispersive X-ray Spectroscopy (EDS)

Energy dispersive X-ray spectroscopy is a micro-chemical analysis technique used along with scanning electron microscopy (SEM). In this technique, X-rays emitted from the materials are analyzed when the sample is bombarded with electrons. When the sample is bombarded with electrons, the electrons are ejected from the atom contained in the surface of the sample. These electron vacancies are filled by higher energy state electrons; the X-rays are emitted to balance the energy difference between the two energy states. The X-ray energy is characteristic of the element from which it was emitted. The EDS X-ray detector measures the relative abundance of emitted X-rays versus their energy [76]. Quantitative results can be obtained from the relative x-ray count at the characteristic energy levels for the sample constituents. Total elemental composition of lignin was evaluated through energy dispersive X-ray analysis (EDS) in combination with a scanning electron microscope (SEM) at the Laboratory Services Division at the University of Guelph.
4.3.6 Thermogravimetric Analysis (TGA)

Thermogravimetry is a technique for measuring the change in mass of the sample as a function of temperature and/or time in a controlled atmosphere. These measurements are used to study the thermal stabilities and compositional properties of the materials. These TGA measurements can be used to select the material for certain end use applications, predict the performance and improve the product quality [77]. TGA was used to study thermal degradation kinetics of lignin. The analysis of lignin samples was carried out using TA-Thermogravimetric Analyzer Q500 instruments. 5 to 10 mg of lignin samples were heated at 20°C/min ramp rate in nitrogen atmosphere (flow rate 60:40 CC/min). TGA (weight loss as a function of temperature) and its derivative (DTG) curves were recorded from room temperature to 700°C.

4.3.7 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is used to study the surface functional groups in molecules. Surface functionality of lignin was investigated by FTIR using Thermo Scientific Nicolet TM 6700 FT-IR Spectrometer, USA. Attenuated total reflection infrared (ATR-IR) mode was used to obtain the spectra of the lignin samples. ATR-IR spectroscopy of the surface of the materials was conducted with a resolution of 4 cm\(^{-1}\) and 32 scans per sample. The spectral outputs were recorded in transmittance mode as a function of wavenumber (cm\(^{-1}\)).

4.3.8 Differential Scanning Calorimetry (DSC)

DSC measures the heat flow to or from a sample as a function of temperature and time. A small portion of the sample is placed in an aluminum pan and heated or cooled at controlled rates. A reference material (usually an empty aluminum pan) simultaneously un-
dergoes the same programmed temperature routine. The difference in the amount of heat energy added to both cells is measured as temperature for both the sample and reference are kept the same. The amount of energy absorbed (endotherm) or released (exotherm) as the sample undergoes physical or chemical changes is measured in calories as a function of the temperature change. DSC can provide information regarding a polymer material including: melting temperature, heat of fusion, glass transition temperature, curing temperature and heat of reaction. DSC is ideal for studying reversible reactions of thermoplastics such as melting-crystallization points and glass transition temperature. It is also used in the study of the kinetics of thermoset curing reactions, purity, heat capacities and the effects of additives [76].

In our study we measured the glass transition temperature of lignin by following the procedure suggested by Baker, Gallego, and Baker [78]. The glass transition temperature of lignin was measured by using DSC TA instruments Q-200 Apparatus. 3 to 5 mg of lignin samples were placed in a standard aluminum pan with a lid and heated in a nitrogen atmosphere to 80°C and held for 30 minutes to expel any remaining moisture in the sample. Then the sample was cooled to 0°C and equilibrated. A second DSC trace was obtained by heating the sample to 250°C at 20°C/min ramp rate in nitrogen atmosphere.

4.3.9 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) can be used for qualitative surface topography analysis, primarily based on the fact that SEM allows excellent visualization. Possible magnification levels were from less than 100X up to 100,000X. This means that the image range can either be on the order of 1 mm² or just 1 μm². SEM is in fact a multi-scale technique. At high magnification, the ultimate resolution is as good as about 2 nm on conduc-
tive surfaces. SEM metrology is not limited by light diffraction. Such high resolving power can only be achieved by scanning probe microscopes that, on the other hand, are limited in terms of the measurable range. In a SEM, features lying at different depths can be kept simultaneously in focus. Lignin samples were analyzed using Scanning electron microscope FEI inspect S50 Netherlands. Cressington sputter coater 108 auto was used to coat gold on the samples. The current and time used for sputter coating were 30 mA, 30 seconds. Images of the samples were taken at different magnification and different locations.

4.3.10 Transmission Electron Microscopy (TEM)

During the synthesis of nano-scale materials, different dimensional limits in 1-D, 2-D, and 3-D are formed. TEM is suitable to observe these nano-scale materials because of their limited dimensions. For example single layers such as graphene sheets, carbon nanotubes, nanowires, quantum dots, nanoparticles, and catalyst particles can be observed precisely by TEM. We can observe all these types of materials in TEM without any modifications [79]. Samples for TEM analysis were prepared by grinding to a powder and successive ultrasonic treatment in acetone for 1 minute. A drop of the suspension was dried on the standard TEM sample grid covered with material film [80]. Acetone was used in preparing samples for TEM analysis because it evaporates easily. Carbon nanoparticles synthesized from lignin were analyzed using JEOL 2010F FEG TEM/STEM. The operating voltage used was 200 kV.

4.3.11 BET Surface Area Analysis

The surface of a material is the dividing line between solid and its surroundings, liquid, gas or another solid. We can anticipate therefore, that the amount of surface, or surface
area, is an important factor in the behaviour of a solid. Whenever solid matter is divided into smaller particles new surfaces are created thereby increasing the surface area. Similarly, when pores are created within the particle interior (by dissolution, decomposition or some other physical or chemical means) surface area is also increased.

Brunauer-Emmet-Teller (BET) surface areas of the lignin samples and carbon nanoparticles synthesized from lignin were measured in nitrogen gas sorption analysis at 77.3 K using NOVA station-C, Quantachrome Instruments. Helium was used as a calibration gas. Before the analysis the samples were degassed by passing nitrogen gas at 55°C for 8-16 hours to remove the volatiles. Degassing times varied based on the time necessary to reach a stable surface area measurement. BET surface areas were taken from a multipoint plot over a P/Po range of 0.05-0.35. In this experiment nitrogen is used as an adsorbent gas because it is readily available in high purity, and the interaction of nitrogen with solid substances is strong.

**4.3.12 Dynamic Light Scattering (DLS) Particle Size Analysis**

Dynamic light scattering particle size analyzers are used to measure the size of very small particles (0.6 nm to 6 um) in solution. This class of particle size analyzer interprets particle sizes from the fluctuations in the scattered laser light created by the Brownian motion of the particle. Dynamic light scattering analysis is used in medical, biological research and materials science applications, and is also known as photon correlation spectroscopy or quasi-electron light scattering. In our study the average diameter distribution was measured using Brookhaven Zeta Plus Particle Size Analyzer – 35MM solid state 657 nm laser at 90° scattering angle.
Chapter 5. Characterization of Lignin from Different Resources

Lignins obtained from different resources were characterized to identify their suitability and processing parameters as a precursor for synthesizing carbon nanoparticles. Elemental and chemical composition, thermal stability and degradation kinetics of lignin were studied using EDS, FTIR and TGA respectively. Also carbon, nitrogen and sulphur were identified by the Leco combustion method. In this work, three different types of lignin were used: (1) Polybind 300 from Northway chemicals, ON, Canada, (2) Protobind 2400 from ALM Private Limited, Hoshiarpur, Punjab, India, which was obtained from the paper industry, (3) Hydrolyzate solids from pre-treated fibres (HSPF) lignin obtained from Mascoma Canada Inc, which was the by-product of cellulosic ethanol production.

5.1 Physico-chemical Properties of Lignin

Figure 5.1 shows the three different types of lignin used in this work. Physical appearance, moisture content, dry content, density and pH of lignin samples were measured and are presented in Table 5.1.

Figure 5.1: Polybind 300, Protobind 2400, and HSPF Lignin
Table 5.1: Physico-chemical properties of lignins

<table>
<thead>
<tr>
<th>Properties</th>
<th>Polybind 300</th>
<th>Protobind 2400</th>
<th>HSPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical appearance</td>
<td>High viscous liquid</td>
<td>Solid powder</td>
<td>Solid powder</td>
</tr>
<tr>
<td>Colour</td>
<td>Black</td>
<td>Brown</td>
<td>Brown</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>53.31</td>
<td>3.24</td>
<td>41.6</td>
</tr>
<tr>
<td>Dry content (%)</td>
<td>46.69</td>
<td>96.76</td>
<td>59.40</td>
</tr>
<tr>
<td>Density (gm/cc)</td>
<td>1.262</td>
<td>0.55</td>
<td>0.95-1.1</td>
</tr>
<tr>
<td>pH</td>
<td>8.5-9.5</td>
<td>4-5</td>
<td>4-6</td>
</tr>
<tr>
<td>Solubility</td>
<td>Water</td>
<td>Alkaline solution</td>
<td>Dimethylformamide (DMF)</td>
</tr>
</tbody>
</table>

It can be seen that the moisture content in the lignin studied were ranked as Polybind 300 > HSPF > Protobind 2400. Also it is worth noting that HSPF is a solid that has approximately 41.6% of moisture compared to 3.24% in solid Protobind 2400. This may be due to the different processes used in obtaining these lignins.

5.2 Thermal Degradation Behaviour of Lignin

Thermal analysis of dried lignin was carried out using TGA from room temperature to 700°C. Thermal degradation behaviour of lignin is shown in Figure 5.2. The initial weight loss that occurred from room temperature to 105°C is due to the departure of residual moisture present in lignin. The phases of degradation of lignin materials were observed between 150 and 630°C. The TG curve of Polybind 300 and Protobind 2400 shows two stages of degradation of constituents, whereas single stage degradation was observed for hydrolyzate solids from the pretreated fibres (HSPF). Sahoo et al. [7] reported the same
phenomenon when they characterized various lignins for industrial uses. The different stages of degradation of Polybind 300, Protobind 2400, hydrolyzate solids from pretreated fibres (HSPF) are presented in Tables 5.2, 5.3, and 5.4.

### Table 5.2: Stages of degradation of Polybind 300 lignin

<table>
<thead>
<tr>
<th>Stages of degradation</th>
<th>Temperature range</th>
<th>Maximum peak</th>
<th>Loss of mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; stage</td>
<td>170 – 380°C</td>
<td>260°C</td>
<td>29.8%</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; stage</td>
<td>380 – 570°C</td>
<td>460°C</td>
<td>17.3%</td>
</tr>
</tbody>
</table>

### Table 5.3: Stages of degradation of Protobind 2400 lignin

<table>
<thead>
<tr>
<th>Stages of degradation</th>
<th>Temperature range</th>
<th>Maximum peak</th>
<th>Loss of mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; stage</td>
<td>150 – 290°C</td>
<td>260°C</td>
<td>15.4%</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; stage</td>
<td>290 – 630°C</td>
<td>380°C</td>
<td>49.9%</td>
</tr>
</tbody>
</table>

### Table 5.4: Stages of degradation of hydrolyzate solids from pretreated fibres (HSPF)

<table>
<thead>
<tr>
<th>Stages of degradation</th>
<th>Temperature range</th>
<th>Maximum peak</th>
<th>Loss of mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; stage</td>
<td>160 – 570°C</td>
<td>353°C</td>
<td>73.4%</td>
</tr>
</tbody>
</table>
Figure 5.2: TG curves of Polybind 300, Protobind 2400 and HSPF lignins
5.2.1 Weigh Loss Analysis

The temperature parameters used for carbonization of lignin were determined from TG and DTG curves as shown in Figure 5.3. The initial weight loss may be due to the residual moisture present in the sample [81]. Percentage of degradation between 150 to 600°C was taken to compare degradation behaviour. In the temperature range between 150 to 600°C, HSPF showed the highest weight loss of 7% and Polybind 300 showed the lowest weight loss of 50%. The weight loss in the case of Protobind 2400 was 65%. Degradation of lignin is a complex mechanism. Dehydration is one of the main mechanisms that leads to the formation of lateral unsaturated chains, carbon monoxide, carbon dioxide and methane.
The degradation of lignin may be due to the disintegration of methyl - aryl ether (β-
O-4) bonds, which has been reported by Babel and Jurewicz [83]. As a result small mole-
cules will be formed corresponding to mono and oligomers [83]. Varied –OH groups in
lignin have different thermal stabilities. As a result, water is a major degradation product -
originating from various types of hydroxyl groups - and derivative curves appear to be
different. Decomposition of aromatic rings present in lignin occur above 400°C [84]. Fur-
ther continuous heating leads to saturation of aromatic rings, C-C bond cleavage of lignin
as well as the release of H₂O, CO and CO₂. Above 500°C, the degradation process slows
down and decreases the rate of weight loss. This reduced rate of weight loss indicates
gradual restructuring of carbon in the degraded material [83]. From the previous men-
tioned study it can be seen there is a mechanism of conversion of high molecular weight
fragments to low molecular weight fragments up to the critical temperature. After this
stage there is a gradual decrease in weight loss, which shows restructuring of carbon. The
critical temperature was different for the different lignins used. Critical temperatures for
Polybind 300, Protobind 2400, HSPF are 500°C, 450°C, 400°C respectively. Hence, it can
be concluded that, the minimum temperature required for carbonization of lignin should
be higher than the critical temperature as observed in these studies.
5.3 FTIR Analysis of Lignins

FTIR spectra of lignin used in this study are interpreted in Figure 5.4. It can be seen that spectra of all lignin are very similar to each other. This may be due to the fact that many different bonds are contributing to the multiplicity of absorptions. Every lignin has a strong wide band between 3500 - 3100 cm\(^{-1}\) assigned to O-H stretching vibrations. This band is caused by the presence of alcoholic and phenolic hydroxyl groups involved in hydrogen bonding [85]. The small peak at 2920 cm\(^{-1}\) is due to C-H stretching vibrations of aromatic methoxyl groups and in methyl and methylene groups of side chains [86]. Spectra of lignin show no absorption bands in the range of 2800 - 1800 cm\(^{-1}\). The peak at 1706 cm\(^{-1}\) in Protobind 2400 is due to the stretching vibrations of C=O present in the carbonyl and carboxyl groups which is absent in HSPF and Polybind 300 [87]. The absorption bands at 1626 - 1608 cm\(^{-1}\) and the low intensity of the band 950 cm\(^{-1}\) indicates that lignin
has a small number of C=C double bonds [86]. The absorption bands present at 1600 - 1500 cm\(^{-1}\) are related to the vibration of aromatic rings present in the lignin [85-86]. The peaks at 1560 cm\(^{-1}\) in Polybind 300 lignin, 1594 cm\(^{-1}\) and 1508 cm\(^{-1}\) in Protobind 2400, and 1593 cm\(^{-1}\) and 1505 cm\(^{-1}\) in HSPF are due to aromatic ring vibrations present in the lignins and are very similar for all lignins. The absorption band present at 1406 cm\(^{-1}\) in Polybind 300, 1456 cm\(^{-1}\), 1422 cm\(^{-1}\) in Protobind 2400 and 1455 cm\(^{-1}\) in HSPF are due to the C-H deformations and aromatic C-H in-plane deformation with an aromatic ring stretching. The small peak at 1325 cm\(^{-1}\) present in the Protobind 2400 is due C-O of the syringyl ring. The C-O stretching for methoxyl groups show similar bands in Protobind 2400 and HSPF lignins (1212 cm\(^{-1}\)) although it is absent in Polybind 300. The peaks at 1041 cm\(^{-1}\) in Polybind 300, 1030 cm\(^{-1}\) in Protobind 2400 and 1029 cm\(^{-1}\) in HSPF are due to alkyl ether vibrations (β-O-4).

5.4 Carbon (C), Nitrogen (N), and Sulphur (S) Analysis

Elemental composition of lignin in terms of carbon, nitrogen and sulphur content was analyzed. From Table 5.5, it can be seen that very low carbon content (39%) was observed in Polybind 300 and very high carbon content (60.3%) was observed in Protobind 2400 followed by hydrolyzate solids of pretreated fibers (HSPF) lignin. Nitrogen content also varied from lignin to lignin, which may be due to different source material and different extraction techniques. Nitrogen content observed in Polybind 300, Protobind 2400, and HSPF was 0.28%, 0.62%, and 0.34% respectively. A very low content of sulphur (0.03% in Polybind 300 and 0.08% HSPF lignin) was observed. Protobind 2400 has the highest sulphur content 0.61%. Carbon content values are very close to the values found in existing literature, which are reported by Sahoo et al. [7]. They reported the carbon content in
Polybind 300, Protobind 2400 and hydrolyzate solids of pretreated fibres (HSPF) to be 37.2%, 62.6%, 56.4% respectively [7].

Table 5.5: C, N, S analysis of lignin

<table>
<thead>
<tr>
<th>Name of Lignin</th>
<th>Industries</th>
<th>C (wt %)</th>
<th>N (wt %)</th>
<th>S (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybind 300</td>
<td>Northway chemicals, Canada</td>
<td>39</td>
<td>0.28</td>
<td>0.08</td>
</tr>
<tr>
<td>Protobind 2400</td>
<td>ALM Pvt. Ltd., Punjab, India</td>
<td>60.3</td>
<td>0.62</td>
<td>0.61</td>
</tr>
<tr>
<td>HSPF</td>
<td>Mascoma, Canada</td>
<td>57.0</td>
<td>0.34</td>
<td>0.03</td>
</tr>
</tbody>
</table>

5.5 Energy Dispersive X-Ray Spectrometer (EDS) Analysis

Elemental composition of the industrial lignin used in this study in terms of carbon, oxygen and other elements was analyzed using EDS. The EDS spectra of lignin are shown in Figure 5.5. The relative abundance of elements observed by EDS analysis is given in Table 5.6. From Table 5.6, it can be observed that very low carbon content was observed in Polybind 300 and very high carbon content was observed in Protobind 2400 followed by hydrolyzate solids of pretreated fibres (HSPF). This study showed comparable data obtained in the C, N, and S analysis. The key observation was that Polybind 300 lignin contained a very high amount of sodium (Na) approximately 13.13 wt%.
Figure 5.5: EDS spectra of Polybind 300, Protobind 2400 and HSPF lignins
Table 5.6: Elemental composition of lignins studied by EDS analysis

<table>
<thead>
<tr>
<th>Composition</th>
<th>Polybind 300</th>
<th>Protobind 2400</th>
<th>HSPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>39.11</td>
<td>63.32</td>
<td>55.73</td>
</tr>
<tr>
<td>O</td>
<td>46.93</td>
<td>35.14</td>
<td>43.76</td>
</tr>
<tr>
<td>Mg</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ca</td>
<td>0.07</td>
<td>0</td>
<td>0.19</td>
</tr>
<tr>
<td>Na</td>
<td>13.13</td>
<td>0.50</td>
<td>0.27</td>
</tr>
<tr>
<td>Al</td>
<td>0.07</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Si</td>
<td>0</td>
<td>0.19</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>0.07</td>
<td>0.85</td>
<td>0.05</td>
</tr>
<tr>
<td>K</td>
<td>0.46</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

5.6 Carbonization Yield of Lignin

Lignin was carbonized in nitrogen atmosphere using a tube furnace. The samples were positioned in a central constant heating zone in the tube furnace using ceramic boats. A 5°C/min heating rate was used. The samples were dried before carbonization to remove residual moisture. The weight of the samples was measured before and after carbonization. The carbonization yields were calculated based on dry content. The yields of carbonization of Polybind 300, Protobind 2400, and HSPF were 48 wt%, 37 wt%, and 15 wt% respectively.
5.7 Summary

From the analysis of the physico-chemical properties of lignin, it was found that the dry content of Protobind 2400 is very high at approximately 96 wt%, whereas the dry content of Polybind 300 and HSPF were 46 wt% and 59 wt% respectively. Also it was found that Polybind 300 is soluble in water, Protobind 2400 is soluble in alkali medium, and HSPF is soluble in dimethylformamide (DMF). The solubility of lignin plays a key role in our study because carbon nanoparticles were prepared by a bottom up approach. From the TGA analysis it was found that the initial degradation temperatures for Polybind 300, Protobind 2400, and HSPF were 170°C, 150°C, and 160°C respectively. This initial degradation temperature is the minimum temperature for conversion in a thermo-stabilization process. Also it was observed that the critical temperature was different for different lignin. Critical temperatures for Polybind 300, Protobind 2400, HSPF are 500°C, 450°C, 400°C respectively. Hence, it can be concluded that the minimum temperature required for the carbonization process must be above the critical temperature. From EDS of lignin it was observed that Polybind 300 has a high amount of Na metal content (approximately 13.13 wt %). From C N S analysis and EDS analysis it was found that the carbon content of Protobind 2400 lignin is high compared to the other two lignins. Although HSPF lignin has a high carbon content, the carbonization yield is only 15 wt%, which is very low, compared to other lignins. From basic characterization of lignin we concluded that from the three sampled lignins Protobind 2400 was a suitable precursor for the synthesis of carbon nanoparticles with higher yield and purity.
Chapter 6. Synthesis of Carbon Nanoparticles from Lignin

Based on the characterization of lignin it has been concluded that Protobind 2400 is the most suitable for synthesis of carbon nanoparticles as compared to other two lignins. Protobind 2400 has high carbon content, low impurities as well as generating high yield during the carbonization process.

The conversion of lignin to carbon nanoparticles involves two steps: 1. Surface area improvement of lignin by sublimation process, 2. Thermo-stabilization and carbonization of sublimated lignin.

(1) Surface Area Improvement of Lignin by Sublimation Process

Protobind 2400 lignin is in powder form with particles in the micrometre size range. If this lignin is carbonized directly, the resulting carbon particles will also be on the micrometre size. In order to obtain carbon particles in nanometre size, the size of the lignin particles should be decreased before carbonization process. The objective of this step is to reduce particle size and improve the surface area of lignin without agglomeration. In order to reduce the particle size the lignin has to be solubilized in a suitable solvent and separated without agglomeration. The improvement of surface area of lignin involved two steps. In the first step, lignin was dissolved in aqueous alkaline solution with varying weight ratio of KOH and lignin. This was followed by separation of lignin polymer using the sublimation process. The sublimation process was conducted by freeze drying. The morphology of freeze dried lignin and effect of KOH was studied using scanning electron microscope (SEM) and BET surface area analyzer.
(2) Thermo-stabilization and Carbonization of Sublimated Lignin

The conversion process of lignin to carbon nanoparticles consists of two steps. First, thermo-stabilization of sublimated lignin was completed by heating the lignin up to 250°C in an oxidizing atmosphere. This was followed by carbonization in an inert atmosphere at 700°C. During these two processes the sample undergoes changes in its physical structure and properties. The objective of this chapter is to discuss the thermo-stabilization and carbonization process of lignin. Finally the morphology of carbonized lignin was studied using transmission electron microscope (TEM) and surface area was measured using the BET surface area analyzer. Figure 6.1 shows the systematic steps involved in synthesis of carbon nanoparticles from lignin.

6.1 Materials

From the characterization study it was found that Protobind 2400 has high carbon content and low impurities. This lignin was chosen for further study in the synthesis of carbon nanoparticles. Potassium hydroxide (KOH) was used to dissolve the Protobind 2400 lignin in water and for chemical modification.

6.2 Methods

Synthesis of carbon nanoparticles from lignin involved two steps: 1. Surface area improvement of lignin by sublimation process, 2. Thermo-stabilization and Carbonization of sublimated lignin. The systematic procedure of carbon nanoparticles synthesis from lignin is shown in Figure 6.1.
Figure 6.1: Method of carbon nanoparticles synthesis from lignin
6.2.1 Surface Area Improvement of Lignin

From the characterization studies of lignin it was found that Protobind 2400 lignin is soluble in aqueous alkaline solution (Table 5.1). Potassium hydroxide (KOH) has been used to dissolve the lignin in water. 2 grams of lignin with 0 wt%, 5 wt%, 10 wt%, and 15 wt% of potassium hydroxide (KOH) was added to 500 ml of water. This solution was sonicated to dissolve lignin in KOH solution. The sonication process reduced the time needed to dissolve lignin. Lignin which was dissolved in alkaline solution was transferred to a steel beaker. This solution was solidified using liquid nitrogen. Then this frozen material was transferred to a freeze dry chamber to separate the lignin polymer by sublimation without any agglomeration. As shown in Figure 6.1 Protobind 2400 lignin was dissolved in alkaline solution then transferred to the freeze dryer chamber. Water in the lignin solution was removed by maintaining a vacuum. This technique separated lignin from the lignin solution. The process of removing water from frozen material is called sublimation and is explained below. The materials obtained after the sublimation process were examined with SEM and BET surface area analyzer.

6.2.2 Freeze Drying

The freeze drying process involved three steps: freezing (solidification), primary drying (ice sublimation) and secondary drying (desorption of unfrozen water). Freezing is an important step and involves an aqueous solution or liquid being frozen to solid state. This freezing can also be carried out using liquid nitrogen. The freezing rate can influence subsequent sublimation process and quality of the final product. The general statement is that a slow freezing rate would shorten the sublimation period because large pores are developed in large crystals [88]. The fast freezing rate is suitable to avoid aggregation and re-
combination of particles [88]. In primary drying the frozen solvent is sublimated. This sublimation can be achieved by reducing pressure to a value below the triple point. The secondary drying involves removal of the bound water or solvent that was not frozen [69, 88]. Fast freezing with super cooling improves the stability of particles. High super cooling leads to the formation of small ice crystals and decreases mechanical stress on particles, avoiding their aggregation.

6.2.3 Thermo-stabilization of Lignin after Freeze Drying

(1) Protobind 2400 (2) Protobind 2400 + 5 wt% KOH (3) Protobind 2400 + 10 wt% KOH (4) Protobind 2400 + 15 wt% KOH are the four lignin samples obtained after freeze drying as discussed in section 6.2.2 above. These samples were first thermo-stabilized then carbonized. To convert the lignin polymer obtained from the sublimation process into carbon nanoparticles a thermo-stabilization step is necessary to prevent fusing of the lignin. The thermo-stabilization process involves oxidation of lignin. The reactions occurring during thermo-stabilization increases $T_g$ of lignin. As a result the thermoplastic nature of lignin is changed to thermosetting during the thermo-stabilization process, enabling the lignin to maintain its structure during the subsequent carbonization. Heating of lignin materials for thermo-stabilization was performed in air at 250°C by using Sentro Tech tubular furnace. The samples were heated at 1°C/min up to 250°C and this temperature was maintained for two hours. As discussed in section 5.2, TGA of lignin samples showed that Protobind 2400 lignin degraded above 200°C. In this study, the thermo-stabilization process was carried out at 250°C which is little bit higher than the degradation temperature of the sample lignin. The purpose of carrying out thermo-stabilization process above its degradation temperature is that when the temperature of lignin reaches above the deg-
radiation temperature, the material starts to convert to carbon instead of fusing. Temperature versus time profile of the thermo-stabilization process is shown in Figure 6.2. The materials obtained after thermo-stabilization process were examined by DSC, FTIR, and SEM.

6.2.4 Carbonization of Lignin

After the thermo-stabilization process, thermo-stabilized lignin was carbonized at 700°C in nitrogen atmosphere. The samples were heated from room temperature to 700°C at the rate of 5°C/min as suggested by Sudo and Shimizu [71] when they synthesized carbon fibre from lignin. Once the temperature reached the maximum temperature of 700°C, the sample was maintained at that temperature for 2 hours. After the carbonization step temperature of the tube furnace was reduced and the sample was allowed to cool to room temperature. The purpose of carbonization is to eliminate all elements except carbon in order to generate a graphite-like structure with a high carbon content. To reach this goal oxygen present in the reactor is excluded during the carbonization process to prevent combustion of lignin and carbon. The temperature versus time profile of carbonization process is shown in Figure 6.2. The materials obtained after the carbonization process have been examined with TEM, BET surface area analyzer, and DLS particle size distributor.
Figure 6.2: Temperature and time profiles of thermo-stabilization and carbonization

6.3 Results

6.3.1 Freeze Drying

Figure 6.3 shows SEM micrographs of lignin after sublimation process. Figure 6.3-A shows pure Protobind 2400 lignin in which the particle size of lignin was found to be around 100 μm. Figures 6.3 B, C, and D show SEM micrographs of lignin modified with 5 wt%, 10 wt%, and 15 wt% KOH respectively. From Figure 6.3 it was observed that with increases in KOH content lignin is separated into small parts. Specific surface area of the lignin that was measured by BET analyzer also supported this result. The specific surface areas of lignins after sublimation process were presented in Table 6.1. The surface areas of lignins from which water has been removed by oven drying are also presented in the Table 6.1. From the Table 6.1 it was observed that the surface area of lignin without sub-
limation process is approximately 0.5 m²/g. In the case of sublimated lignin, the surface area has increased with increase in percentage of KOH. The surface area of pure lignin (Protobind 2400) is 1.079 m²/g. The specific surface areas of lignin modified with 5 wt%, 10 wt%, and 15 wt% are 11.88 m²/g, 42.7 m²/g, 62.32 m²/g respectively. From the Table 6.1, it can be seen that when lignin was not modified with KOH the surface area for sublimation process has increased from 0.5 to 1. But with KOH modification, the incremental gain in surface area is very high compared to that of conventional drying. This clearly indicates that KOH has dissociated the lignin into the smaller fragments. Conventional oven drying removes water from material and leads to lump formation. Whereas in the sublimation process lignin has been separated without lump formation and maintained a high surface area. Hence, this study emphasizes that the sublimation process is necessary to obtain lignin particles with high surface area.
Figure 6.3: Scanning electron micrographs of sublimated lignins

A- Protobind 2400, B-Protobind 2400 + 5 wt% KOH
C- Protobind 2400 + 10 wt% KOH, D-Protobind 2400 + 15 wt% KOH
Table 6.1: Effect of freeze drying on BET surface area of lignin

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>BET Surface area (m²/g)</th>
<th>Oven Drying</th>
<th>Freeze Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protobind 2400</td>
<td>0.512 ± 0.02</td>
<td>1.079 ± 0.018</td>
<td></td>
</tr>
<tr>
<td>Protobind 2400 + 5 wt% KOH</td>
<td>0.94 ± 0.01</td>
<td>11.884 ± 2.75</td>
<td></td>
</tr>
<tr>
<td>Protobind 2400 + 10 wt% KOH</td>
<td>0.56 ± 0.01</td>
<td>42.73 ± 4.05</td>
<td></td>
</tr>
<tr>
<td>Protobind 2400 + 15 wt% KOH</td>
<td>0.48 ± 0.03</td>
<td>62.32 ± 5.1</td>
<td></td>
</tr>
</tbody>
</table>

6.3.2 Thermo-stabilization of Lignin after Freeze Drying

Figures 6.4 and 6.5 show the lignin samples before and after thermo-stabilization processes. The colour of the pure lignin (Protobind 2400) and the modified lignins are found to be brown as shown in Figures 6.4 and 6.5. After the thermo-stabilization process the pure lignin changed to black whereas KOH modified lignins did not show much colour change. It clearly indicates that KOH plays a vital role in the thermo-stabilization process.

Glass transition temperature (T<sub>g</sub>) of lignin Protobind 2400 is approximately 89°C. In the carbonization process as the temperature of lignin approached its T<sub>g</sub>, fusing occurred. This is due to the lignin softening phenomenon. In order to prevent the fusing of lignin during the carbonization process T<sub>g</sub> has to be increased to above the degradation temperature of lignin. This is achieved with the thermo-stabilization process.

Figures 6.6 and 6.7 show DSC curves of Protobind 2400 lignin and Protobind 2400 lignin modified with KOH. The glass transition temperatures of lignin Protobind 2400 and modified with 5 wt% KOH, 10 wt% KOH and 15 wt% KOH are 89°C, 107°C, 111°C, and
121°C respectively. Figures 6.8 and 6.9 show the DSC curves of thermo-stabilized lignin. It can be observed that after the thermo-stabilization process lignin did not show glass transition temperatures up to 250°C indicating the shift in $T_g$ to higher temperatures. The phenomenon of an increase in glass transition temperature of lignin after thermo-stabilization is explained below.

Thermo-stabilization is the process in which glass transition temperature is increased to maintain the glassy state of lignin. Kadla and co-workers [67] used thermo-stabilization in synthesizing lignin based carbon fibres and explained the process as follows: In thermo-stabilization lignin is heated in the presence of an air atmosphere at slower heating rates. Oxidation reactions take place during thermal stabilization. Air oxidation is cost effective and a simple method of thermo-stabilization. The reactions occurring during thermo-stabilization increase $T_g$ of lignin. Previous oxidative studies of pitch have shown that $T_g$ increases due to both cross-linking and incorporation of oxidized groups [89]. As the temperature increases at a slower heating rate $T_g$ increases faster than the temperature of the material ($T_g > T$), and the resulting material is maintained in a glassy state. Thus the thermoplastic nature of lignin is changed to thermosetting. These slower heating rates are favourable for the formation of crosslink precursors [89-90]. In higher heating rates thermo-stabilization reactions are not able to maintain $T > T_g$ and material transforms into a rubbery state which leads to fusing [67]. Therefore slower heating rates are preferred in the thermo-stabilization process. Wisanrakkit and Gillham explained such phenomenon with thermosetting system in continuous heat transferring systems [91].

It was observed that, there was weight loss in the thermo-stabilization process. This weight loss may be due to an increase in molecular weight along due to the condensation
and dehydration reactions. Uraki et al. [92] reported that condensation reactions take place during thermo-stabilization of lignin. This condensation reaction may be due to the contribution of oxygen present in air and in the molecule in the formation of cross linking during thermo-stabilization process. Nakamura et al. [93] studied the condensation reactions of lignin related compounds in air at 250°C. It is well known that the glass transition temperature of a polymer substance is influenced by its physical properties such as molecular weight, branching and degree of cross-linking. The value of the $T_g$ increases as the molecular weight (M) of the polymeric material increases. The value of the $T_g$ can be correlated by an equation as given below.

$$T_g = T_g^\infty - \frac{K}{M} \quad (1)$$

Where

$T_g^\infty =$ Glass transition temperature of polymer of infinite molecular weight

$T_g =$ Glass transition temperature of polymer of molecular weight M

K = Constant

M = Molecular weight of the polymer

As the molecular weight increases the glass transition temperature of the polymer approaches the value at infinite molecular weight $T_g^\infty$ [94].

As shown in Figure 6.6 the glass transition temperature of Protobind 2400 lignin is approximately 89°C. After the thermo-stabilization process lignin does not show a glass transition temperature. The reaction which occurred during thermo-stabilization increased the glass transition temperature of lignin. In the thermo-stabilization process a condensation reaction of lignin has taken place.
The occurrence of condensation reactions was confirmed by FTIR analysis. The condensation reaction of lignin, the molecular weight, and increased cross linking of lignin led to the rise of $T_g$ as according to the equation 1. The thermoplastic nature of lignin was changed to thermosetting. Figures 6.10, 6.11, 6.12, and 6.13 show FTIR of lignin before and after thermo-stabilization process. From the FTIR of lignin, higher intensity of aromatic skeletal vibration at 1590 cm$^{-1}$ and 1500 cm$^{-1}$ can be observed after thermo-stabilization. This is because of the splitting of aliphatic side chains in lignin and condensation of lignin during the thermo-stabilization process [95]. The existence of condensed structures is confirmed by the appearance of higher intensity peaks at 1330 cm$^{-1}$ as well as the shift of 1245–1220 cm$^{-1}$ according to Elisabeth [96]. The peak at 1590 cm$^{-1}$ corresponds to aromatic skeletal vibrations and C=O stretching. The intensity of this peak is increasing with increasing percentage of KOH treatment. This means that more condensation reactions have taken place with increasing KOH treatment. These condensation reactions of lignin, followed by a cross linking mechanism resulted in the shift of $T_g$ to higher values as explained by equation 1.
Figure 6.4: Lignin samples before thermo-stabilization
Figure 6.5: Lignin samples after thermo-stabilization
Figure 6.6: DSC curves of sublimated Protobind 2400 and Protobind 2400 + 5 wt% KOH

Figure 6.7: DSC curves of sublimated Protobind 2400 + 10 wt% KOH and Protobind 2400 + 15 wt% KOH
Figure 6.8: DSC curves of thermo-stabilized Protobind 2400 and Protobind 2400 + 5 wt% KOH

Figure 6.9: DSC curves of thermo-stabilized Protobind 2400 + 10 wt% KOH and Protobind 2400 + 15 wt% KOH
Figure 6.10: FTIR spectra of Protobind 2400 and Thermo-stabilized Protobind 2400
Figure 6.11: FTIR spectra of Protobind 2400 + 5 wt% KOH and Thermo-stabilized Protobind 2400 + 5 wt% KOH
Figure 6.12: FTIR spectra of Protobind 2400 + 10 wt% KOH and Thermo-stabilized Protobind 2400 + 10 wt% KOH
Figure 6.13: FTIR spectra of Protobind 2400 + 15 wt% KOH and Thermo-stabilized Protobind 2400 + 15 wt% KOH
Figure 6.14: Scanning electron micrographs of non thermo-stabilized lignin after sublimation

A - Protobind 2400, B - Protobind 2400 + 5 wt% KOH
C - Protobind 2400 + 10 wt% KOH, D - Protobind 2400 + 15 wt% KOH
Figure 6.15: Scanning electron micrographs of thermo-stabilized lignin after sublimation

A- Protobind 2400, B - Protobind 2400 + 5 wt% KOH
C- Protobind 2400 + 10 wt% KOH, D - Protobind 2400 + 15 wt% KOH
Figure 6.14 shows SEM micrographs of lignins which were rapidly heated to 250°C in air atmosphere. Figure 6.15 shows SEM micrographs of lignins which were heated to 250°C in air atmosphere at 1°C/min. From these figures it can be observed that Protobind 2400 lignin fused and formed lumps in both cases. Whereas KOH modified lignins did not fuse in the thermo-stabilized lignin. Small lumps were observed in the case of non-thermo-stabilized lignin modified with KOH. This clearly indicates that addition of KOH changed the lignin properties. In the case of pure lignin (Protobind 2400) the condition $T_g > T$ was not satisfied. But in the case of KOH treated lignin $T_g > T$ condition was satisfied in the thermo-stabilization process. This may be due to changes in the chemical structure of lignin. According to equation 1 (page no. 61) the value of $K$ depends on the chemical structure. Therefore it can be concluded that KOH treatment of lignin helped in the thermo-stabilization process by maintaining the condition $T_g > T$.

### 6.3.3 Carbonization

Due to the low glass temperature of lignin it fuses together during the carbonization process. In order to prevent this fusing property, the glass transition temperature of lignin has to be increased to above its degradation temperature. The glass transition temperature of lignin has been increased using the thermo-stabilization process as discussed in the above section. After thermo-stabilization lignin was carbonized at 700°C in a tube furnace as described in section 6.2.4. Carbon nanoparticles obtained after carbonization process were analyzed using BET surface area analyzer and transmission electron microscope. During the carbonization there was a significant loss in weight. The purpose of this carbonization is to produce turbostatic graphene layers with higher carbon content. In carbonization lignin has been converted into carbon. It has been observed that pure lignin without any
modification with KOH fused and formed lumps during thermo-stabilization. Lignin modified with KOH did not fuse together. The carbon obtained from untreated pure lignin was grinded using a mortar before characterization. TEM electron micrographs of lignin are as shown in Figure 6.16. From TEM micrographs it was observed that carbon particles obtained from unmodified lignin were in the micrometer size while carbon particles obtained from KOH modified lignin are very small and in the nanometer size range. These particles are found to be around 100-150 nm in size. BET surface areas of carbon nanoparticles obtained from lignin were measured. Table 6.2 shows the specific surface areas of the carbonized lignins. From this table it can be observe that BET surface area of carbon nanoparticles increased with KOH modification at 5 wt% and 10 wt%. But when KOH increased to 15 wt%, the specific surface area decreased.

Table 6.2: BET surface area of carbon nanoparticles

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>BET Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protobind 2400</td>
<td>0</td>
</tr>
<tr>
<td>Protobind 2400 + 5 wt% KOH</td>
<td>42.65 ± 2</td>
</tr>
<tr>
<td>Protobind 2400 + 10 wt% KOH</td>
<td>46.95 ± 1.14</td>
</tr>
<tr>
<td>Protobind 2400 + 15 wt% KOH</td>
<td>22.60 ± 2.11</td>
</tr>
</tbody>
</table>
**Figure 6.16:** Transmission electron micrographs of carbonized lignin

A- Protobind 2400, B - Protobind 2400 + 5 wt% KOH  
C- Protobind 2400 + 10 wt% KOH, D - Protobind 2400 + 15 wt% KOH
Figure 6.17: DLS particle size distribution of carbonized Protobind 2400 + 5 wt% KOH

Figure 6.18: DLS particle size distribution of carbonized Protobind 2400 + 10 wt% KOH
6.3.4 Particle Size Distribution of Carbon Nanoparticles

Figures 6.17, 6.18, and 6.19 represent the particle size distribution of carbon nanoparticles prepared from 5 wt% KOH, 10 wt% KOH and 15 wt% KOH respectively. The particles size shown on the X-axis of the graphs is the average diameter of the particles. This is the radius of gyration of the particles. In these studies the radius of gyration of carbon nanoparticles was measured using DLS particle size distribution. Even though the carbon nanoparticles prepared in our studies are not spherical, we have measured the radius of gyration for comparison. From Figures 6.17, 6.18, and 6.19 it can be seen that carbon particles prepared by 5 wt% KOH treatment are smaller in size compared to the particles prepared by using 10 wt% KOH and 15 wt% KOH treatment.

Figure 6.19: DLS Particle size distribution of carbonized Protobind 2400 + 15 wt% KOH
6.3.5 Yield of Thermo-stabilization and Carbonization of Lignin

The transformation of precursor materials into the final product is an important aspect in the production of carbon nanomaterials. Higher weight loss in the lignin during heat treatment leads to lower yields resulting in higher production cost. The conversion yields of lignin into carbon nanoparticleless during thermo-stabilization and carbonization were measured using equations 2, 3 and 4. Thermo-stabilization yield fraction ($Y_{TS}$) is the ratio of mass of lignin present after thermo-stabilization ($m_{TS}$) to mass of lignin before thermo-stabilization process ($m_{TS}^0$). Similarly carbonization yield fraction ($Y_C$) is the ratio of mass of carbonized material ($m_C$) to mass of material present before carbonization process ($m_{TS}$). Overall yield is the product of the Yields of thermo-stabilization ($Y_{TS}$) and the carbonization ($Y_C$).

$$Y_{TS} = \frac{m_{TS}}{m_{TS}^0} \quad \text{------------------- (2)}$$

$$Y_C = \frac{m_C}{m_{TS}} \quad \text{------------------- (3)}$$

$$Y_T = (Y_{TS}) \times (Y_C) = \left(\frac{m_{TS}}{m_{TS}^0}\right) \times \left(\frac{m_C}{m_{TS}}\right) = \left(\frac{m_C}{m_{TS}^0}\right) \quad \text{------------------- (4)}$$

Table 6.3 summarizes the yield of carbon nanoparticles from thermo-stabilization and carbonization of lignin. Table 6.3 also included overall production yields of lignin. Table 6.3 also summarizes the effect of chemical modification on yields of thermo-stabilization and carbonization.

The weight loss during thermo-stabilization of unmodified lignin is less than lignin modified with KOH. This weight loss is accompanied by an increase in molecular weight, the result of condensation and dehydration of lignin macromolecules as explained in earlier sections.
Table 6.3: Yields of thermo-stabilization and carbonization of lignin

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Yield of Thermo-stabilization (Y_{TS} %)</th>
<th>Yield of Carbonization (Y_{C} %)</th>
<th>Overall Yield (Y_{T} %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protobind 2400</td>
<td>92.88 ± 1.3</td>
<td>52.847 ± 1.11</td>
<td>49.08</td>
</tr>
<tr>
<td>Protobind 2400 + 5 wt% KOH</td>
<td>88.46 ± 2.5</td>
<td>55.072 ± 1.9</td>
<td>48.71</td>
</tr>
<tr>
<td>Protobind 2400 + 10 wt% KOH</td>
<td>75.97 ± 3.1</td>
<td>56.7 ± 2.1</td>
<td>43.07</td>
</tr>
<tr>
<td>Protobind 2400 + 15 wt% KOH</td>
<td>66.82 ± 3.5</td>
<td>57.8 ± 2.5</td>
<td>38.61</td>
</tr>
</tbody>
</table>

The yield values were approximately 70% for the various thermo-stabilized Protobind 2400 lignins prepared by chemical modification with KOH. The yield of thermo-stabilized lignin is slightly less than those reported in the literature. Kadla et al. [67] reported thermo-stabilization yields of Alcell lignin and hard wood Kraft lignin at 97% and 94%. In our study the thermo-stabilization yield for Protobind 2400 lignin was 92.8% which is comparable. In the case of chemically treated Protobind 2400 lignin, yield is decreasing with increases of KOH. This weight loss is accompanied by an increase in molecular weight which is the result of condensation and dehydration reactions of lignin macromolecules. But these results are opposite to that of oxidative thermo-stabilization of pitch fibres, in which weight increases [97]. In pitch, the formation of infused oxygen bridging and cross linking occurs analogous to lignin. However these reactions require alkyl components of pitch to be first oxidized before dehydrogenation and cyclization reactions, thus weight increases. But in the case of lignin side chains are already highly oxidized, and condensation reactions release water and decrease weight. Although the yield
is decreasing in thermo-stabilization process it provides the cross linking facilitated by radical reactions via lignin based oxygen [98].

The majority of weight loss occurred during the carbonization step. The yield of the carbonization process varied between 44% and 53% depending upon the precursor material. Low carbonization yields were expected because the lignin samples were heated to 700°C and carbon content of lignin was about 60% which was measured by elemental analysis. The purpose of carbonization is to produce turbostatic graphene layers with higher carbon content. The yield observed in carbonization is comparable to yield of lignin carbonization found in literature. From Kadla et al. 2002 [67] in which they synthesized lignin based carbon fibres, they reported carbonization yields of Alcell lignin and hard wood Kraft lignin to be 46.% and 51.6%.

Therefore the overall yield of carbon nanoparticles was about 37% to 43% for both thermo-stabilization and carbonization. The overall yield is controlled by the yield of the carbonization process, since it has a considerably lower yield than yield in the thermo-stabilization step. The initial carbon content in Protobind 2400 lignin is about 60% which was confirmed by elemental analysis. But the final yield is 37% to 43% because of additional losses in thermo-stabilization and carbonization.

6.4 Summary

Alkali solution has been identified as a suitable solvent to dissolve Protobind 2400. KOH has been used in preparing alkaline solution. Lignin has been successfully separated without agglomeration from the alkaline solution by sublimation. Scanning electron microscope analysis and BET surface area analysis confirmed the separation and removal of agglomeration of lignin during the sublimation process. The surface area of oven dried
lignin is approximately 0.5 m²/g. The specific surface area of pure sublimated lignin was 1.079 m²/g. Surface areas for sublimated lignin modified with 5 wt%, 10 wt%, and 15 wt% of KOH are 11.88 m²/g, 42.73 m²/g, and 62.32 m²/g respectively.

In a second step the fusing property of lignin was prevented by thermo-stabilization. The increase in glass transition temperature of lignin was confirmed by DSC analysis. The condensation reactions taking place during thermo-stabilization process were confirmed by FTIR analysis. Formation of carbon nanoparticles from lignin after the carbonization process was confirmed by TEM analysis. From DLS of particle size distribution of carbonized lignin and specific surface areas, it was observed that lignin modified with 5 wt% KOH was better than modifications with 10 wt% KOH and 15 wt% KOH.
Chapter 7. Future Studies and Recommendations

(1) Studying of lignins from different sources as a precursor for synthesis of carbon nanoparticles. A comparison can be made with ligno-cellulosic ethanol lignin and paper-based lignin in terms of morphology, purity and yield.

(2) Studying the morphology effects developed during sublimation on the final structure of carbon nanoparticles will help in controlling the morphology of the final particles through an intermediate step.

(3) Effect of other chemicals on the morphology and yield on nanoparticles from lignin can be studied using NMR, Raman and other advanced analytical techniques in order to understand the carbon nanoparticles synthesis.

(4) Thermo-stabilizing process can be studied in detail by varying the heating rates in order to understand the kinetics of the morphology changes.

(5) Carbonization and its dependency on temperature and intermediate steps can be studied in detail in order to obtain the desired morphology in the final nanoparticles.

(6) TGA-FTIR studies can be utilized to understand the chemical and structural changes in lignin during thermo-stabilization.

(7) Potassium and other impurities present in the final carbon nanoparticles can be studied using EDS studies.
Chapter 8. Conclusions

In this work, three lignins from different sources and carbon content were analyzed for their suitability as precursors for producing carbon nanoparticles. Protobind 2400, Polybind 300 were obtained from paper industries whereas HSPF was obtained from lignocellulosic ethanol industries. Thermogravimetric analysis revealed that the initial degradation temperatures for Polybind 300, Protobind 2400, and HSPF were 170°C, 150°C, and 160°C respectively, which is the minimum temperature required for thermo-stabilization process of these lignins. Critical temperature which is the starting temperature in the plateau region of the final weight loss curve of the thermo-gravimetric analysis is found to be 500°C, 450°C, and 400°C for Polybind 300, Protobind 2400, and HSPF respectively. This is the minimum temperature required for the carbonization of these lignins to obtain carbon nanoparticles. Our studies revealed that Protobind 2400 is a suitable candidate for synthesizing carbon nanoparticles from the three lignins studied. This conclusion is based on the carbon yield and elemental composition. Hence, Protobind 2400 was used to synthesize the carbon nanoparticles.

A two step procedure was adopted for synthesizing the carbon nanoparticles from lignin. First lignin was chemically modified using KOH and freeze dried to improve the surface area. This was followed by slow heating to thermally stabilize the lignin which was then carbonized at 700°C in nitrogen atmosphere. Lignin was modified using 5 wt%, 10 wt%, 15 wt% KOH in the chemical modification step. FTIR studies revealed that the condensation reactions were taking place during the thermo-stabilization process. DSC studies showed that the glass transition temperature of lignin increased and prevented the fusing
of lignin. TEM micrographs showed that the carbon particles had a particle size of 100-500 nm. Carbon nanoparticles were synthesized using Protobind 2400 as a precursor, and had a surface area of approximately 42 m²/gm. Based on the particle size and surface area 5 wt% KOH modified lignin yielded carbon nanoparticles with optimum surface area and size.
References


75. *LECO instruction/operations manual for the FP-428 Nitrogen and Protein Determinator* (Version 2.4.).


