Microwave-assisted Production of Activated Carbon from Pulp Mill Sludge with White Liquor

By

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University of Toronto
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Chemical Engineering and Applied Chemistry
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Abstract

This work establishes the technical feasibility of producing a value added product, activated carbon, from a waste stream, pulp mill sludge, using white liquor as the activating agent and microwaves as the energy source. The work also demonstrates the potential of the sludge-derived activated carbon in removing bioactive compounds in pulp mill effluents that affect fish production. Readily available at kraft mills, white liquor is able to convert sludge into activated carbon with a specific surface area (SSA) of 650 $m^2/g$. While NaOH in white liquor creates pores in the carbon from sludge, other two components of white liquor, $Na_2S$ and $Na_2CO_3$, inhibit the activation process. Porosities of activated carbon produced with microwave oven and conventional furnace are comparable. The use of microwaves reduces the activation time from hours to minutes. However, strong microwave absorbers, such as NaOH and KOH, are needed for pyrolysis and activation, since pulp mill sludge and wood polymers are weak microwave absorbers with $\tan \delta < 0.1$. Adding 1 wt% of KOH to the dried sludge enables a uniform and complete pyrolysis. With microwaves, however, the retained carbon is 20% lower than that with conventional heating, likely due to the higher heating rate with microwaves.
NaOH is more effective than KOH in creating porosity in the carbon from pulp mill sludge. The SSA achieved from NaOH activation in both microwave oven and conventional furnace is consistently over 2000 m$^2$/g. Secondary sludge is more suitable than primary sludge as the raw material for activated carbon. A pressure-based temperature probe is designed, constructed and used to measure sample temperatures during microwave heating. Measured temperatures are in agreement with temperatures simulated with a 3-D model developed using COMSOL multiphysics 4.4. The model also reveals that microwave-heated samples lack uniformity in temperature.
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Nomenclature

P  Power dissipated
E_{rms}  Root mean square of the electrical field
H_{rms}  Root mean square of the magnetic field
D_p  Penetration depth
C  Specific heat capacity
C  Carbon
H  Hydrogen
O  Oxygen
S  Sulfur
N  Nitrogen
k  Thermal conductivity
T  Temperature
m  Mass
V  Volume
t  Time
W  Watt
P  Power
h  convection coefficient

Greek letters

\varepsilon^*  Complex permittivity
\varepsilon'  Dielectric constant
\varepsilon''  Electric loss factor
\varepsilon_0  Electric permittivity of free space
\varepsilon_{\text{eff}}  Effective dielectric loss factor
\mu_0  Magnetic permeability of free space
\mu_{\text{eff}}  Effective magnetic loss factor
\tan \delta  Loss tangent
\omega  Angular frequency
\alpha  Attenuation factor
\rho  Density
\pi  Mathematical constant
\phi  Porosity
\mu_r  Magnetic permeability
\sigma  Electric conductivity
k_0  Wave vector in free space
f  Frequency
Acronyms

BET  Brunauer Emmett Teller
TGA  Thermo Gravimetric Analysis
SEM  Scanning Electric Microscopy
SSA  Specific Surface Area
XRD  X-ray Diffraction
HSC  Thermodynamic software
FactSage  Software for thermodynamic calculations
UV-vis  Ultraviolet-visible spectroscopy
GC  Gas chromatography
MB  Methylene Blue
FTIR  Fourier Transform Infrared Spectroscopy
LIN  Linerboard recycled sludge
CM  Cow manure
NKS  News and kraft secondary sludge
NKP  News and kraft primary sludge
TMB  Tembec sludge
PS 50-50  Mixed sludge (50% primary - 50% secondary)
PS 70-30  Mixed sludge (70% primary - 30% secondary)
Overall yield (%)  Ratio of activated carbon weight to the dried sludge weight
Activation yield (%)  Ratio of activated carbon weight to the char weight
Carbonization yield (%)  Ratio of char weight to the dried raw material weight
Retained carbon (%)  Ratio of carbon percentage in the char to the raw material
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1 Overview

1.1 Introduction

Pulp mill sludge is a waste generated by both primary and secondary treatments in the pulp and paper industry. The Canadian pulp and paper industry produced 7.1 million tonnes of the dry sludge in 1995 (Mahmood & Elliott 2006) disposed by combustion or landfiling. The traditional waste disposal systems are no longer desirable and resulted in a demand for effective and environmental friendly options (Smith et al. 2009). The waste management cost in the pulp and paper industry is high due to the large quantity of the waste produced every day. Therefore transformation of the sludge materials into value added products would be a great benefit (Krigstin & Sain 2006).

Conversion of pulp mill sludge into activated carbon could potentially reduce the disposable sludge and capture contaminants at the mills with activated carbon. Currently the sludge is being burned in most pulp mills which causes environmental impacts and greenhouse gas emissions (GHGs) (Monte et al. 2009). The production of char from industrial or municipal wastes is possible (Khalili et al. 2000).

The production of activated carbon from wood and coconut shells is well studied; however, similar research on lignocellulosic wastes such as pulp-mill sludge is rather limited (Khalili et al. 2000). In particular, no systematic studies investigated the conversion of pulp mill sludge into activated carbon. In the production process of activated carbon from pulp mill sludge, the choice of activating agent, activation process, and suitable raw material control the economics of the process (Hoseinzadeh Hesas et al. 2013b). Among the popular activating agents, potassium hydroxide (KOH) is very effective in producing activated carbon with the high surface area (Díaz-Terán et al. 2003; Okada et al. 2003; Otowa et al. 1997).

In recent years, microwave radiation has been applied to many thermal processes because of its advantages of the shorter processing time and volumetric heating. It is expected that microwave heating of pulp mill sludge will reduces the processing time. Although the
temperature distribution inside the heated material needs to be investigated by experimental analyses and numerical modeling to improve the understanding of the complex microwave heating mechanism (Menéndez et al. 2010; Fernandez et al. 2011).

The conventional methods for production of activated carbon are time consuming (Smith et al. 2009). Production of activated carbon by microwave heating could be beneficial in terms of processing time. The properties of activated carbon produced with microwaves and a conventional furnace need to be analyzed and compared. In terms of activating agents, KOH and NaOH have been widely used for activation of the biomass with conventional heating methods, although their differences are not clearly understood. More research is needed to elucidate their effects on carbon activation with conventional furnace and microwaves.

There is a possibility of using white liquor (i.e., the cooking liquor that contains NaOH and Na$_2$S) as the activating agent for activated carbon production. The recovery process of white liquor, which is established at kraft pulp mills for many years, can possibly make the activated carbon production economical, because one of the major costs of activated carbon production is the cost of activating agent. The recovered white liquor contains Na$_2$CO$_3$, Na$_2$SO$_4$, Na$_2$SO$_3$, and Na$_2$S$_2$O$_3$ in addition to its main chemicals NaOH and Na$_2$S. No research has been done on the production of activated carbon with white liquor, but similar pure activating agents (i.e., NaOH and Na$_2$CO$_3$) have been used for the chemical activation.

Activated carbon has many potential applications in pulp mills. For instance, some of the pulp mill effluents affect fish reproduction. Studies demonstrated that the hormonal changes in fish caused the lower egg production capacity, smaller gonad size, delayed sexual maturity, and expression of secondary sex characteristics (Fentress et al. 2006; Hewitt et al. 2008). Although considerable effort has been made to address this issue, the sources and responsible compounds at some pulp mills remain unclear. Pulp mill effluents originating from wood, biodegradation products, and chemical products have been possibly involved in the endocrine disruption in fish. Either an additional effluent treatment step or modification in pulp mill processes could possibly eliminate the disruption effect of these compounds. The sources at the pulp mill are unknown;
therefore, the process modification option is not practically feasible. So far, there is not much work done on removal technologies of the compounds that affect fish reproduction. Activated carbon seems to be one of the possible options for removal of these compounds.

1.2 Objectives

The overall goal of this research is to analyze the technical feasibility of producing activated carbon from pulp mill sludge with microwaves as the energy source and white liquor as the activating agent. Specifically the objectives are as follow:

- Investigate the feasibility of activated carbon production from various pulp mill sludge samples by KOH-chemical activation;
- Analyze the feasibility of microwave pyrolysis and activation with KOH and NaOH;
- Compare the properties of char and activated carbon produced with the microwave oven and conventional furnace;
- Compare the temperature distribution of samples heated in a microwave oven and a conventional furnace;
- Analyze the activation of pulp mill sludge with white liquor and compare it with NaOH-activation; and
- Test the removal of the effluent compounds that affect fish reproduction.

1.3 Hypotheses

The four main hypotheses of this research are:

1. Pulp mill sludge can be converted into activated carbon by chemical activation.
2. Microwave radiation is more efficient than the conventional furnace in the production of activated carbon.
3. White liquor can be used as an activating agent for the production of activated carbon from pulp mill sludge and the properties of white liquor-activated carbon are comparable with that of NaOH-activated carbon.

4. Sludge-derived activated carbon can be used for removal of the effluent compounds that affect fish reproduction.

1.4 Thesis outline

As shown in Figure 1.1, the four key elements of this research are the sludge, microwaves, white liquor and bioactive compounds. The thesis addresses the challenges associated with the interactions of these elements in the production and application of the sludge-derived activated carbon. The thesis consists of nine chapters. The main chapters of the thesis are based on five papers, which are either published, submitted or to be submitted.

![Figure 1.1. The relationship of the key elements in this research](image)

Chapter 2 provides the fundamental knowledge and background information relevant to this study.
Chapter 3 includes the technical feasibility of activated carbon production from various pulp mill sludge samples and compares the quality of activated products.

Chapter 4 analyzes the char and activated carbon from microwave pyrolysis and activation and compares them with that of conventional furnace.

Chapter 5 investigates the temperature distribution of samples in microwave oven and conventional furnace with experiments and numerical modeling using COMSOL Multiphysics 4.4.

Chapter 6 describes the activation of pulp mill sludge using white liquor as the activating agent and compares it with NaOH-activation.

Chapter 7 discusses the utilization of produced activated carbon for the removal of the compounds that affect fish reproduction in pulp mill effluents.

Chapter 8 presents the overall conclusions and major findings.

Chapter 9 summarizes the recommendations for the future work, and implications of this research.
2 Literature Review

2.1 Pulp mill sludge

Generally, 35% of the raw materials that enter paper mills turn into residue (Scott & Smith 1995). There are two types of residues, the primary sludge and secondary sludge. Primary sludge, which is mainly composed of cellulose, hemicellulose and fillers, is the collected residues from the screens and filters of the primary settling tanks employed in wastewater treatment. Secondary sludge is generated in the secondary wastewater treatment process, where wastewater organic matter is broken down by means of the biodegradation. The main component of primary and secondary sludge is water. Sludge dewatering is often required prior to landfilling or incineration, hence dewatering is of utmost importance for pulp mills. The high woody organic material content of primary sludge makes the dewatering process easier compared to secondary sludge. Some pulp mills mix primary and secondary sludges together to improve the mechanical dewatering process; however, the high ratios of secondary sludge to primary one make the dewatering process challenging and expensive (Mahmood & Elliott 2006).

The four major types of sludge at the pulp mills are: (1) primary sludge, produced in the process of extracting virgin wood fiber; (2) de-inking paper sludge, produced in the process of removing inks from recycled paper; (3) secondary sludge, produced in the secondary biological wastewater treatment process; and (4) combined primary and secondary sludge. The mixed sludge from primary and secondary treatment is a muddy mass consisting of microorganisms, fibrous material, lignin, mineral components (limestone and phosphorous), clay, inert solids rejected during the recovery process, ash, and water (Monte et al. 2009). Table 2.1 shows the two examples of pulp mill sludge compositions.
Table 2.1. Compositions of pulp mill sludge (Kim et al. 2000)

<table>
<thead>
<tr>
<th>Pulp mill sludge source</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mead-Beit kraft mill, Columbus, GA</td>
<td>58</td>
<td>12</td>
<td>19</td>
</tr>
<tr>
<td>Australian newsprint mill</td>
<td>57</td>
<td>11</td>
<td>27</td>
</tr>
</tbody>
</table>

2.2 Kraft pulp mill process

The two main segments in a pulp mill are the fiber line and the chemical recovery process. In the fiber line, the main goal is removing lignin from the wood fibres by adding white liquor (Na$_2$S and NaOH). The fiber line process consists of wood digestion with white liquor, washing to remove lignin, and bleaching. White liquor is regenerated in the chemical recovery loop. In the chemical recovery process, weak black liquor is concentrated in a multi effect evaporation system to reach 60-70% solids, producing black liquor. Black liquor enters the recovery boiler, where the combustion of the liquor organics produces the energy for high pressure steam, recovers Na$_2$S from Na$_2$SO$_4$ by reduction reaction, and recovers Na$_2$CO$_3$. The molten salt is mixed with water in the smelt dissolving tank to produce green liquor (Na$_2$S, Na$_2$CO$_3$). Green liquor is sent to the clarifier, where the supernatant is taken to the causticizing reaction, in which the white liquor is recovered (Castro & Doyle 2004). The recovery of chemicals from the spent cooking liquor has the following steps (Smook, 1982):

1. Concentration of the residual liquor in multiple effect evaporators to form strong black liquor
2. Incineration of liquor in the recovery furnace
3. Dissolving smelt to form green liquor
4. Causticizing green liquor with lime to form white liquor
5. Burning lime mud to recover lime

The recovery cycle makes the pulp mill process economic.
Activated carbon

Activated carbon is a porous and adsorbent carbonaceous material, which has a large volume fraction of very small pores resulted in a large surface area. Due to the special characteristics as an adsorbent, catalyst, or catalyst support, activated carbon has found various applications in the industries dealing with separation or catalytic processes. Some of its most common applications include water treatment, decolorizing, recovery of gold and silver, manufacturing of protective filters, general air conditioning as well as gas purification. Activated carbon can be prepared in the form of a powder, granules, or shaped as briquettes and fibers depending on its specific applications (Linares-Solano A, 2007).

A suitable porous structure of activated carbons is critical for the adsorption of specific compounds. According to IUPAC, pores are categorized into three classes: micropores with pore diameter less than 2 nm, mesopores with pores between 2 and 50 nm, and macropores with pores greater than 50 nm (Sing et al, 1985). The efficiency of an adsorption process depends on the characteristics of adsorbent and adsorbate, as well as hydrophobic interactions (Moreno-Castilla 2004). Much research on activated carbon production from biomass has been carried out (Yu & Zhong 2006; Williams & Reed 2006). A common goal is to be able to produce a cost-effective

Figure 2.1. Schematic representation of the structure of activated carbon (Stoeckli 1990)
adsorbent for the removal of toxic substances from air or water. It has been shown that enhanced adsorption capacity toward specific pollutants depends on porous structure and surface chemistry of activated carbon (Tsang et al. 2007; Yeganeh et al. 2006). These characteristics are determined mainly by the raw material and activation conditions (Guo & Lua 1999; Lozano-Castello et al. 2001).

2.3.1 Raw materials for activated carbon production

Activated carbon can be produced from variety of biomass sources such as coconut shell, agricultural wastes (Girods et al. 2009; Yeganeh et al. 2006), coffee crops, etc. (Ahmad et al. 2007; Aci et al. 2008; Tay et al. 2009). In the past, available carbon sources such as wood, peat, and vegetable waste were used as the raw material. Today, many industrial and agricultural residues are investigated to be used as the raw material for activated carbon production. The most important factors in choosing a biomass as a precursor for activated carbon production are the availability, low inorganic content, price and chemical/physical properties (Nabais et al. 2008). The physical and chemical properties of activated carbon, such as surface area and bulk density, vary with the nature of the precursors and the production process (Bansal et al. 1988).

2.4 Pyrolysis

Pyrolysis produces bio-oil, gases, and a solid char. The yield of pyrolysis depends on the operating conditions and the equipment used (Dominguez et al. 2005). Primary and secondary pyrolysis are two possible stages of pyrolysis process. During primary pyrolysis, the thermal decomposition of the main components takes place and devolatilizes the material. This step mainly involves dehydration, dehydrogenation, decarboxylation or decarbonization reactions. During secondary pyrolysis, reactions between the volatiles release (homogeneous reactions), or between the volatiles and the carbonaceous residue (heterogeneous reactions) occur. The second step comprises processes such as cracking (thermal or catalytic). In cracking process, heavy compounds break into gases, and char is converted into the gases such as CO, CO₂, CH₄ and H₂. The reaction with gasifying agents, partial oxidation, polymerization and condensation reactions are involved in the cracking process (Dominguez et al. 2005).
Two important pyrolysis processes are: fast pyrolysis that yields high amounts of bio-oil and carbonization that produce the char. In fast pyrolysis, biomass is subjected to the heat by fast heating rates of the solid in moderate temperature ranges (500-600°C) and short residence times of the vapor-phase products to minimize the char production. The particle size reduction and pre-drying are necessary since biomass and char are poor heat transfer media and evaporation is an endothermic process (Conesa et al. 1998; Ciacci et al. 2010).

Pyrolysis is the first process in activated carbon production and involves heating the material at a high temperature (up to 800°C) in an inert environment, which removes nitrogen, oxygen, sulphur, and hydrogen in the form of volatile species. The remaining carbon atoms comprise 85-95% of the material’s mass and group themselves as graphitic crystallites with irregular forms. Carbonization results in the formation of interstitial voids which may become filled with tar or disorganized carbon. These pores will be developed during the activation step and result in a porous structure for an effective adsorption.

2.5 Activation reaction

There are, in principle, two methods for activation: physical and chemical activation. The physical activation method involves the carbonization of a precursor at elevated temperatures (500 – 800°C) under an inert atmosphere such as N₂, followed by the activation of the resulting material at high temperatures (800 – 1000°C), which promotes some reactions between the activating gas (CO₂ or steam) and carbon atoms of the char. The activating gas reaction with carbon is shown in Equation (2.1) and (2.2).

\[2C + O_2 \rightarrow 2CO\]  
\[\text{Equation 2.1}\]

\[C + H_2O \rightarrow CO + H_2\]  
\[\text{Equation 2.2}\]
In the chemical activation process, the precursor is impregnated with an activating agent and the impregnated material is heated under inert atmosphere at lower temperatures (400 – 700°C). In this method, the carbonization step and the activation step can occur simultaneously. Chemical agents are the dehydrating agents that influence the pyrolytic decomposition and consequently result in the high yield of activated carbon. Activation is followed by the washing and drying processes, which remove chemical agents from the final activated carbon.

Several advantages of the chemical activation method over the physical activation method include the high surface area, relatively higher yield and lower activation temperature. However, chemical activation methods also incorporate few disadvantages such as the corrosion and some environmental issues due to the chemicals used in the process.

Chemical activation is widely used to generate activated carbon from carbon-containing materials. Common chemical reagents for activation include ZnCl₂, H₂SO₄, H₃PO₄ (Arjmand et al. 2006; Solaimani & Kaghazchi, 2007), alkali metal hydroxides (KOH and NaOH), and alkali metal carbonates such as K₂CO₃ (Linares-Solano et al. 2006). KOH is often the choice for producing porous activated carbon (Guo & Lua 1999; Kawano et al. 2008). The overall reaction between a carbon-containing precursor and KOH is often given as follows (Hayashi 2000):

\[ 6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \]

**Equation 2.3**

The temperature at which activation begins and the degree of pore development depend not only on the activating agent but also on the nature of the precursor material (Tseng et al. 2007).

When activating by KOH, the development of surface area occurs through the two processes. First, the removal of carbon occurs by the reaction between KOH and carbon (Otowa et al. 1997; Mitani et al. 2004). Second, the removal of elemental K generated from KOH-C reaction and intercalated into the carbon matrix (Raymundo-Piñero et al. 2005). The weight loss
during activation is caused by the carbon removal, while the removal of elemental K does not significantly affect the weight loss. More pores are created by the removal of K.

2.6 Production of activated carbon from lignocellulosic wastes

Studies on activated carbon production from lignocellulosic wastes have been focused on various activating agents, carbonization temperature, and the effect of raw material composition on the produced activated carbon. It is necessary to gain the fundamental understanding of carbonization and activation process parameters for lignocellulosic materials in order to establish a suitable process for the conversion of pulp mill sludge into activated carbon (Cagnon et al. 2009).

2.6.1 Effect of the raw material characteristics

Chemical composition (cellulose, hemicellulose, and lignin) of lignocellulosic materials affect their thermal decomposition behavior. Thermal decomposition of lignocellulosic material demonstrated similar weight loss at 271 and 350°C which is related to hemicellulose and cellulose decompositions, respectively. Up to 400°C, depolymerization and chain scission through the ether and carbon-carbon bond control the decomposition. Lignin is thermally stable and decomposes slowly over a broad range of temperatures (150-900°C) (Reina et al. 1998). Lignin contributes to production of char more than cellulose and hemicellulose. Lignin has an aromatic cross-linked polymeric structure and total carbon atoms in its structure are higher than cellulose and hemicellulose which leads to a different pattern of weight loss during pyrolysis (Cagnon et al. 2009). Also its structure is similar to bitumen coal which makes lignin an ideal candidate for activated carbon production (Suhas et al. 2007).

Cagnon et al. (2009) investigated the contribution of lignocellulosic compositions on the produced activated carbon with steam activation. Their results indicated that high lignin content of the raw material is effective on the final product. All components, i.e. cellulose, hemicelluloses, and lignin, contributed to activated carbon porosity. Thermogravimetric analyses showed that the higher the hemicellulose and cellulose components are, the higher the mass loss of raw materials during carbonization will be. This could be due to the higher oxygen content of
cellulose and hemicelluloses compared to lignin (Cagnon et al. 2009). The elemental analysis of lignin, cellulose, and hemicellulose are reported in Table 2.2.

**Table 2.2. Elemental analysis of cellulose, hemicellulose, and lignin (Cagnon et al. 2009)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Carbon (%)</th>
<th>Oxygen (%)</th>
<th>Hydrogen (%)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>41.8</td>
<td>51</td>
<td>6.4</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>38.1</td>
<td>48</td>
<td>6</td>
<td>6.7</td>
</tr>
<tr>
<td>Lignin</td>
<td>58.6</td>
<td>30</td>
<td>5.7</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Gonzalez et al. (2009) demonstrated that activated carbon porosity is affected by the thermal decomposition rate of lignocellulosic materials. In their experiments, the almond tree pruning decomposed slowly during the first stage of pyrolysis and yielded activated carbon with a higher volume of meso and macropores. The results suggested that after pyrolysis at 600°C for 1 h, lignin mainly converted into char. While cellulose and hemicellulose mainly converted into a liquid. The composition of the sludge influences the development of porous surface during the carbonization and activation processes (Gonzalez et al. 2009). Also Yagmur et al. (2008) showed that a high lignin content of the waste tea (42%) compared to that of wood (20%) used in the production of activated carbon by H₃PO₄ activation resulted in a higher surface area (Yagmur et al. 2008).

The raw material reactivity has a crucial effect on the activation process. Lillo-Ródenas et al. (2007) showed that NaOH is more efficient for activation of highly reactive materials (i.e. almond shell and coconut shell), while KOH is a better choice for highly ordered materials (i.e. carbon fiber) (Smith et al. 2009). The lignocellulosic material structure affects the activated carbon porous texture but little is known about it. Zuo et al. (2009) studied H₃PO₄-activation of lignocellulosic materials (China wood, cotton, stalks, and corn cob) and suggested that the lower crystallinity in the structure of lignocellulosic materials caused a higher surface area due to the easier penetration and dispersion of H₃PO₄ (Lillo-Ródenas et al. 2007).

Several studies showed that blending and physical modifications of raw materials improve the activated carbon properties. Mixing of the sewage sludge with low ash materials increased the surface area of produced activated carbon. The specific polymers and metal-containing sludge
blended with sewage sludge produced activated carbon with up to 10 times higher surface area compared to pure sewage sludge (Smith et al. 2009a). Several physical modifications such as washing with acid or water increased the surface area of the produced activated carbon. Immersing the carbonized char into the water for 72h increased the surface area by 50%. The possible explanation is that the reaction between the surface oxides in the large pores and water molecules can create new micropores within large pores. Another possibility is the formation of new cavities by alkali components.

Another method to produce activated carbon with high surface areas is reducing the inorganic content of carbonaceous compounds in the raw materials. Ros et al. (2006) reported an increase in the surface area of a char obtained from sewage sludge from 13 to 188 m²/g by HCl washing. Also the ash content of the char decreased about 40% by acid washing, which induces a higher surface area (Ros et al. 2006). Bagreev et al.’s (2001) studies on pyrolysis of sewage sludge indicated that the acid washing could reduce the surface area of char, if the carbonization temperature (400°C) is not high enough to fully carbonize the organic matters. Acid washing increased the surface area of the sample carbonized at 800°C (Bagreev et al. 2001).

2.6.2 Effect of the activating agents

The activating agent is one of the important parameters that control the characteristics of produced activated carbon. The most popular activating agents are KOH, NaOH, ZnCl₂, K₂CO₃, and H₃PO₄. The most effective activating agents in biomass activation are KOH and NaOH. Ros et al. (2006) compared alkali hydroxides (KOH, NaOH) with H₃PO₄ and CO₂ physical activation of sewage sludge. The results indicated that H₃PO₄ and CO₂ activation is not very effective for the production of activated carbon. KOH and NaOH behaved similarly and produced activated carbon with the SSA of 1686 and 1224 m²/g, respectively, when the activating agent ratio to char was 3 (Ros et al. 2006). The highest surface area obtained from pulp mill sludge activation with KOH was 1002 m²/g (with no pretreatment) reported by Kang et al. (2006). The reason for achieving such a high surface area is that KOH and NaOH react with the carbon atoms while acidic reagents react with oxygen functional groups (Hsu & Tseng, 2000).
H$_3$PO$_4$ has been widely used as an activating agent, although it is not a suitable activating agent for sewage sludge activation since the highest obtained surface area was 289 m$^2$/g (Zheng et al. 2005). In the chemical activation of lignocellulosic materials with H$_3$PO$_4$, cross-linked structure formation reduces volatile matter releases, tar formation, and the formation of small pores. During pyrolysis, the volatiles derived from the thermal decomposition of lignocellulosic materials diffused out of the pyrolyzing materials. The volatiles underwent the cracking or polymerization within the formed char, due to the catalytic dehydration of phosphoric acid (Jibril et al. 2008). The polymerization of volatiles produced the additional char that is perhaps deposited on the surface of the char formed previously. Zuo et al. (2009) concluded that the mesoporous structure and the high char yield during phosphoric acid activation can be explained by the carbonization of volatiles.

For activation of pulp mill sludge, ZnCl$_2$ chemical activation combined with physical activation was used in several studies. They obtained a high surface area of 1294 m$^2$/g when using activating agent ratio of 2.5 (Littrell et al. 2002). Higher concentrations of ZnCl$_2$ blocked the micropores and resulted in the lower surface area. One of the limiting factors of using ZnCl$_2$ is its boiling point of 732$^\circ$C. Pores mainly formed during volatilization of ZnCl$_2$ and applying temperatures higher than the boiling point is beneficial. In the activation of pulp mill sludge, K$_2$S has been more effective than ZnCl$_2$ in terms of producing a higher SSA (Cho & Suzuki, 1980).

The other crucial factor in obtaining a high surface area is applying the two steps of carbonization and activation. Carbonization generates pores while the pore development occurs during activation. However, Lillo-Rodenas et al. (2007) studied the effect of coconut shell pyrolysis prior to activation with KOH and NaOH and indicated that pyrolysis at 350$^\circ$C lowered the SSA from 2000 to 1300 m$^2$/g when using NaOH.

It has been found that KOH is a better activating agent than NaOH due to its greater ionic radius (0.266 nm for K$^+$ compared to 0.190 nm for Na$^+$). The sewage sludge and coal tar pitch were used as precursors for the activation at 800$^\circ$C for 1.5 h with the activating agent concentration of 1 mol/L. The SSA, total pore volume, and pore size distribution of the products
from KOH and NaOH activation processes were 450 and 381 m²/g, 0.394 and 0.37 cm³/g, and 38.72 and 36.72 Å, respectively (Hwang et al. 2008). Macia-Agullo et al. (2007) found that Na and K reduced metals can be removed from the carbon matrix by evaporation, but they may partially intercalate in the carbon matrix, during the activation reaction. Moreover, Compared to Na, K metals produce more intercalation compounds. Therefore, during the hydroxide activation, K is more effective than Na. NaOH is reported to be more reactive with carbon causing a lower yield, while KOH generated a more selective porosity of microspores (Maciá-Agulló et al. 2007).

Jibril et al. (2008) investigated the effect of H₃PO₄ and KOH on the activated carbon produced from lignocellulosic material (stem of date palm). While using KOH, the oxidation occurred by increasing the temperature and resulted in a carbon layer separation and pore development. The highest surface area and pore volume obtained from H₃PO₄ activation were at 500°C, while the average pore diameter was higher for KOH activation. The KOH activation reaction consists of dehydration, dehydroxylation, and alkalide formation. When the activation temperature increases from 400 to 600°C, different pore sizes will be developed at different sites (Jibril et al. 2008).

One study found that K₂CO₃ is more effective than KOH as a chemical reagent at 800°C, in terms of both pore volume and yield of activated carbon. Tay et al. (2009) studied activated carbon production from the soybean oil cake with component analyses of 21% cellulose, 2% lignin, and 58% hemicellulose at 600 and 800 °C by chemical activation with K₂CO₃ and KOH. The SSA of K₂CO₃ activated samples increased from 614 to 1352 m²/g when the activation temperature increased from 600°C to 800°C, but the SSA of KOH-activated sample did not change significantly. The ash and sulphur content of the activated carbon obtained with chemical activation by K₂CO₃ was lower than those obtained by KOH (Tay et al. 2009).
2.7 Production of activated carbon by microwave radiation

2.7.1 Microwave radiation

Microwaves are electromagnetic waves with wavelengths between 1mm to 1m, which corresponds to the frequencies between 0.3 to 300 GHz. Domestic and commercial microwave applicator operates at 2.45 GHz with 12.25 cm wavelength. Microwaves have two components of electric and magnetic waves (Figure 2.2). The electric component of an electromagnetic field causes heating by two main mechanisms: dipolar polarization and ionic conduction (Kappe & Stadler 2005).

![Electric and magnetic field components of microwaves](image)

Figure 2.2. Electric and magnetic field components of microwaves (Kappe et al, 2009)

The interaction of the electric field component with the matrix is called the dipolar polarization mechanism. The ability of materials to be heated by microwaves depends on the dipole moment. The interaction of microwaves with molecular dipoles results in dipole rotation and dissipation of energy in the form of heat. The second major heating mechanism is ionic conduction. The dissolved ions oscillate back and forth under the influence of the microwave field. Their collisions with neighboring molecules cause agitation or motion, creating heat (Kappe et al, 2009).
2.7.2 Dielectric properties

Materials can be classified into three groups based on their interaction with microwave radiation. The first group is conductors, which reflect microwave radiation, such as metal and alloys. The second group is dielectrics, which absorbs microwave energy, such as aqueous solutions. The third group is insulators, which transmit microwave radiation, such as ceramics and Teflon. Figure 2.3 shows three groups of the material interactions with microwave radiation.

![Figure 2.3. Interaction of materials with microwave radiation (Yuen & Hameed 2009)](image)

Dielectric properties of material are important for their heating characteristic under microwave irradiation. The ability of a material to be heated in the presence of a microwave field is defined by its dielectric loss tangent:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

Equation 2.4

The dielectric loss tangent is composed of two parameters, the dielectric constant (or real permittivity), \(\varepsilon'\), and the dielectric loss factor (or imaginary permittivity), \(\varepsilon''\); i.e., \(\varepsilon = \varepsilon' - i\varepsilon''\), where \(\varepsilon\) is the complex permittivity (Kappe et al. 2009). The dielectric constant (\(\varepsilon'\)) represents the amount of reflected energy versus the amount of absorbed, while the dielectric loss factor (\(\varepsilon''\)) measures the dissipation of electric energy into heat within the material. For conversion of microwave energy into heat, a moderate value of \(\varepsilon'\) combined with high values of \(\varepsilon''\) is ideal and
consequently the high value of \( \tan \delta \) e.g. 0.1-20. Some materials are transparent to microwaves meaning that they do not have a sufficiently high loss factor to allow the dielectric heating. Other materials, such as some inorganic oxides and most carbon materials are good microwave absorbers (Kappe & Stadler 2005; Hameed et al. 2007; Menéndez et al. 2010). Table 2.3 shows the loss tangent of carbonaceous materials. The loss tangent of these materials are higher than 0.1 and they can easily absorb microwave radiation.

### Table 2.3. Dielectric loss tangent of carbonaceous materials (Menéndez et al. 2010)

<table>
<thead>
<tr>
<th>Material</th>
<th>( \tan \delta = \epsilon'' / \epsilon' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>0.2-0.08</td>
</tr>
<tr>
<td>Carbon foam</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Charcoal</td>
<td>0.11-0.29</td>
</tr>
<tr>
<td>Carbon black</td>
<td>0.35-0.83</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>0.57-0.8</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>0.25-1.14</td>
</tr>
<tr>
<td>Carbon nanofiber</td>
<td>0.58-1.00</td>
</tr>
</tbody>
</table>

Attenuation coefficient (\( \alpha \)) is the indicator of how easy the beam can penetrate into the material. The penetration depth (\( D_p \)) is the distance of adsorbed electric field into the material in which the power reaches \( (1/e) \) of the initial power and is given by (Campanone & Zaritzky 2005):

\[
\alpha = \frac{2\pi}{\lambda} \sqrt{\frac{\epsilon'(1 + \tan^2 \delta)^{1/2} - 1}{2}}
\]

**Equation 2.5**

\[
D_p = \frac{1}{2\alpha}
\]

**Equation 2.6**

where \( \lambda \) is the wavelength of the microwaves in free space. For the frequency of 2450 MHz, \( \lambda \) is 12.24 cm.
The power inside microwave heated samples can be explained by both Lambart’s law and Maxwell’s equations. Lambart’s law indicates that the power penetrates through the material with an exponential decay (Campanone & Zaritzky 2005).

\[ P = P_0 e^{-2\alpha y} \]

**Equation 2.7**

Efficiency of electricity conversion into microwave energy is around 95% and the conversion of the microwave energy into the heat inside the material is up to 85% if the material is a good microwave absorber (Thostenson & Chou 1999; Kappe & Stadler 2005).

### 2.8 Numerical simulation of the microwave heating process

#### 2.8.1 Maxwell’s Equations

The governing equation of the electromagnetic field is based on Maxwell’s equation. Microwaves penetrate and propagate inside the dielectric materials. They generate an internal electric field (E) that induces polarization and movement of charges. The resistance to the induced motions due to internal, elastic and frictional forces attenuates the electric field. These losses result in volumetric heating. The resulting electromagnetic power absorbed per unit volume \( P_{EM} \) \([\text{Wm}^{-3}]\) by a material is given by (Shukla et al. 2010):

\[ P_{EM} = 2\omega \{ \varepsilon_0 \varepsilon_r'' (T) |E_{\text{rms}}|^2 + \mu_0 \mu_r'' (T) |H_{\text{rms}}|^2 \} \]

**Equation 2.8**

where, \( \omega \) is the frequency of the microwave radiation (2.45 GHz), \( \varepsilon_0 \) is absolute permittivity in free space \((8.85\times10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2})\), \( \varepsilon_r'' \) is the relative imaginary component of the dielectric constant, \( \mu_0 \) is absolute permeability of free space \((4\pi\times10^{-7} \text{ NA}^{-2})\), \( \mu_r'' \) is relative imaginary component of permeability constant. \( E_{\text{rms}} \) and \( H_{\text{rms}} \) are root mean square values of electric and magnetic field, respectively.
At steady state and time harmonic electromagnetic field, the total volumetric power generation of microwave is (Thostenson & Chou 1999; Robinson et al. 2010):

\[ P = 2\pi f \varepsilon'' \varepsilon E^2 \]

**Equation 2.9**

\( f \) is the microwave frequency, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon'' \) is the dielectric loss factor and \( E \) is the magnitude of the dielectric field.

### 2.8.2 Heat transfer in microwaves

The heat transfer equation describes the space and time behavior of the temperature field:

\[ \rho C_p \frac{dT}{dt} = \nabla (\kappa \nabla T) + P_{abs} \]

**Equation 2.10**

where \( \rho_d, C_p, \) and \( \kappa \) show the material’s density, specific heat capacity and thermal conductivity, respectively. For solving the above equation \( \rho_d, C_p, \) and \( \kappa \) are usually considered to be independent of position, time and temperature. \( T = T(x,y,z,t) \) and \( P = P(x,y,z,t) \) in the electromagnetic power dissipated per unit volume. The mathematical model consists of the electromagnetic field equation and the heat transfer equation. \( P \) is determined by the electromagnetic power density calculation. The calculated power is used for temperature calculations in the heat transfer equation.

There are several numerical methods used for solving the Partial Differential Equation (PDE) such as Finite Differential Time Domain (FDTD) method, the Finite Element Method (FEM), and the Transmission Line Matrix (TLM) method, etc.
2.9 Advantages and challenges of microwave heating

![Image showing comparison between conventional and microwave heating]

Figure 2.4. Comparison of conventional and microwave heating (Kappe et al. 2009)

The main advantages of microwave heating compared to the conventional heating process would be volumetric heating, whereby the microwave radiation is dissipated in a dielectric material and the electromagnetic energy is converted directly into heat inside the sample (Figure 2.4). Microwaves transfer heat at the molecular level. Thus selective heating and consequently unique microstructure of the material could be created when using microwave (Thostenson & Chou 1999).

There are several factors for considering microwave processing. First, microwaves heat chemicals directly, minimize the temperature gradients in a single material, and enhance selectivity. The selective heating of mixtures, process simplicity, capital investment, power bill, and rapid start-up are the potential advantages of using microwaves in industrial applications for the materials that are good absorbers of microwave radiation. Before considering the microwave processing, dielectric constant and loss factor are necessary to be analyzed (Kuester 1994).

There are also some challenges associated with the microwave heating. Electromagnetic fields are not uniform and cause non-homogenous heating patterns when using microwaves. Physical and structural changes in materials during the heating affect their dielectric properties and consequently cause difficulties in process control and modeling. Microwave processing is complicated because of the chemical composition, size and shape of the materials, and the nature of microwave interaction with materials (Hoseinzadeh Hesas et al. 2013b).
“Thermal runaway” is the concentration of microwave energy in the microwave receptor, which leads to an exponential increase in heating rate due to high thermal adsorption of these materials. Thermal runaway is the result of the thermal instability inside the materials when they are heated with microwaves. This phenomenon happens because of the interaction between the material and electromagnetic waves. During thermal runaway, the temperature of the material continues to increase until the material is destroyed (Fernández et al. 2011).

Hotspots have been observed when heating with microwaves. The hot-spot phenomenon is the thermal instability due to nonlinear dependence of the electromagnetic and thermal properties of the material. The formation of standing waves in microwave cavity causes exposure of some regions to a higher energy level than others (Appleton et al. 2005).

The observed sparks during microwave pyrolysis could be considered as “microplasmas”. While the overall temperature corresponds to the one measured by the optical pyrometer, the temperature in these microplasmas must be extremely high (Menéndez et al. 2007). The formed microplasmas can be divided in two different types based on their shape and nature. The formation of quasi-spherical plasmas (ball lightning) can be observed, such as the one is shown in Figure 2.5a. These are relatively abundant during the experiments and do not depend on the temperature of the carbon bed. The electric arcs mainly occur at the higher temperatures (Figure 2.5b) (Fernández et al. 2011).

**Figure 2.5. Plasma formation during microwave heating of a biomass char: (a) ball lighting and (b) arc discharge (Fernández et al. 2011)**

During microwave pyrolysis, microplasmas favor heterogeneous reactions between the solid and the gases produced and consequently the reaction of CO₂ with C starts even at the low
bulk temperature of 500°C (Menéndez et al. 2007). In carbonaceous materials, microplasmas occur because the π-electrons are free to move in relatively broad regions. The kinetic energy of some electrons may enable them to jump out of the material, resulting in the ionization of the surrounding media (Menéndez et al. 2010).

In some cases, the microwave heating starts after a lag phase. “Waiting time” occurs due to the non-linear dependence of the electromagnetic and thermal properties of the material to temperature. Waiting time behavior is exhibited by materials that either responds to microwave heating only after a finite amount of time has passed, or the conventional heating is required before they can absorb microwave radiation (Fernández et al. 2011).

Dielectric loss factor ($\varepsilon''$) is the most important parameter that affects the thermal runaway because it controls the input power into the materials. Rousy et al. (1985) defined the term of “critical temperature” for the first time. They assumed the thermal loss is mainly by heat conduction. Based on their assumption, $\varepsilon''$ could be calculated by a quadratic function and it increases with temperature.

$$\varepsilon'' = \alpha_0 + \alpha_1 (T - T_0) + \alpha_2 (T - T_0)^2$$

Equation 2.11

where $T_0$ is the initial temperature and $\alpha_0$, $\alpha_1$, and $\alpha_2$ are constant parameters.

By applying Equation 2.11 to the heat transfer equation (Equation 2.10), three types of temperature profiles can be obtained. Figure 2.6 shows the possible temperature profiles versus time calculated by Rousy et al. (1985). If the dielectric loss factor ($\varepsilon''$) of a material is strongly depend on temperature, the material will become lossy by increasing the temperature ($\alpha_2 > h/4\alpha_0$). If $\alpha_2 \leq h/4\alpha_0$, the material can reach a plateau temperature. They calculated a critical temperature that represents the limit of thermal stability for a material.
Figure 2.6. Theoretical temperature response of the microwave irradiated granular materials versus time (Rousy et al. 1985)

In the case of thermal instability due to local temperature rise, the heat transfer equation can be written in the form of:

\[ \rho C_p \frac{dT}{dt} = P_{\text{loss}} - P_{\text{abs}} \]

Equation 2.12

\( P_{\text{loss}} \) is the heat loss by convection and radiation. \( P_{\text{abs}} \) shows the absorbed electromagnetic power per unit volume of the material (Wu, 2002).

2.10 Microwave pyrolysis

Microwave pyrolysis has some advantages over the conventional heating for some materials. In microwaves, the centre of the material is at the higher temperature than the surrounding area, however in conventional heating, the furnace should reach the operating temperature, before the heating of the material starts (Menéndez et al. 2007). Thus microwave heating favors the reactions in the solid materials (e.g. devolatilization or heterogeneous
reactions) and the conventional heating is appropriate for the reactions in surroundings, such as homogeneous reactions in the gas-phase. The lower temperature in the microwave cavity can be useful to prevent undesirable reactions and condensation of the final pyrolysis vapors in this area (Fernández et al. 2011, Zhang & Hayward 2006).

The highest temperature of a biomass in microwave heating depends on the dielectric properties of the receptor, while the heating rate is a function of the chemical composition of material and is slightly affected by the physical structure. The choice of microwave receptor affects the conductivity and permittivity of the biomass as well as the strength of the electric fields in the biomass and the power dissipated in it.

The efficiency of microwave processing depends on the properties of the material, e.g. its physical properties, such as structural arrangements, thermal conductivity, and specific heat and its chemical characteristics, such as organic and inorganic composition. In the primary phase, the microwave receptor components absorb microwaves and generate heat; gradually nearby particles of the materials are heated by the conventional methods (convection, conduction and radiation). By the time the volatiles have escaped, the remaining char bed is a good absorber of the microwave radiation. The uniform distribution of microwave receptor components in precursor improves the temperature uniformity and provides faster heating rates during pyrolysis (Fernández et al. 2011).

Several studies investigated the microwave pyrolysis of biomasses and divided it into four stages. First, the dielectric relaxation phenomenon of water molecules governs the heating of the biomass. Second, the temperature reaches a constant level before the pyrolysis temperature. The addition of the microwave receptor affects the temperature significantly. Third, the temperature rises rapidly corresponding to an acute loss of mass. Forth, thermal equilibrium is achieved (Zhao et al. 2010).

During microwave pyrolysis, the dielectric properties of the biomass change and make this process more complicated. Robinson et al. (2010) studied microwave pyrolysis of wood pellets. Their dielectric measurement results indicated that the dielectric loss factor is around
0.05 at 100°C for dried wood pellet and the only microwave absorbing phase is water up to 500°C. Above 500°C, wood is decomposed into the hydrocarbons and char, consequently, the dielectric loss factor increases to 1.2 at 700°C. The produced char had a higher loss tangent compared to the wood pellet due to the graphitization process.

2.11 Char production from biomass by microwave pyrolysis

Char is the product of both primary and secondary pyrolysis reactions. By increasing the temperature, the char yield initially decreased, due to the competition between the primary reaction of the char and the formation of volatiles. At the higher temperatures, the temperature gradient becomes small and consequently the char yield remains constant. Through the secondary pyrolysis reaction, the temperature controls the char yield by affecting residence time of the volatiles and volatiles release rate. The high external pressure and low heating rate helps in the creation of the secondary char on the primary char surface (Di Blasi 2009).

During secondary reactions, organic vapors decompose on the carbonaceous solids and create additional char. Tar compounds (organic vapors) decompose faster under pressure. Generally pressure and flow rate are the major parameters affecting the microwave pyrolysis. The high reaction temperature (>773K) cause the activity of secondary reactions for tar cracking. Therefore there is a linear relationship between the heat of pyrolysis reactions and char yields (Di Blasi 2008).

Several studies indicated that the formation of char depends on the exothermicity of pyrolysis. The main components of the forest residues are lignin and cellulose. Their decompositions are exothermic and endothermic, respectively. Studies showed that the char yield of lignin is higher than cellulose. During fast pyrolysis (under high heating rate) holocellulose (hemicelluloses and cellulose) convert into liquid while lignin produce char. On the contrary, at low temperature ranges, char and liquid formation are competing (Di Blasi 2008).
2.12 Production of activated carbon by microwaves

Carbonaceous materials are good absorbers of microwaves. Recently microwave radiation has been used for the production and regeneration of activated carbon. Activated carbon has been produced by chemical and physical activation using microwaves. Hesas et al. (2013) reviewed the chemical activation by microwaves when using KOH, K$_2$CO$_3$, H$_3$PO$_4$, ZnCl$_2$ and NaOH as the activating agent. These compounds are the main absorbers of microwave radiation at the initial stages of activation (Hoseinzadeh Hesas et al. 2013a). The SSA and activation condition of the produced activated carbon are summarized in Table 2.4. For the agricultural wastes, the SSA of activated carbon ranged between 700-2500 m$^2$/g using a microwave power of 600-700W. Chen and Hashisho (2012) produced activated carbon from oil sand coke by KOH activation. They obtained activated carbon with SSA of 1131 m$^2$/g after 10 min of activation (Chen & Hashisho 2012).

Table 2.4. Properties of activated carbon produced by microwave chemical activation of agricultural residues (Hoseinzadeh Hesas et al. 2013b)

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Agent</th>
<th>Microwave power (W)</th>
<th>Radiation time (min)</th>
<th>Impregnation ratio*</th>
<th>SSA (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pineapple peels</td>
<td>KOH</td>
<td>600</td>
<td>6</td>
<td>1:1.25</td>
<td>1006</td>
</tr>
<tr>
<td>Rice husks</td>
<td>KOH</td>
<td>600</td>
<td>7</td>
<td>1:1.075</td>
<td>752</td>
</tr>
<tr>
<td>Cotton stalks</td>
<td>KOH</td>
<td>660</td>
<td>10</td>
<td>0.6:1</td>
<td>729</td>
</tr>
<tr>
<td>Orange peels</td>
<td>K$_2$CO$_3$</td>
<td>600</td>
<td>6</td>
<td>1.25:1</td>
<td>1104</td>
</tr>
<tr>
<td>Sunflower seed oil residues</td>
<td>K$_2$CO$_3$</td>
<td>600</td>
<td>8</td>
<td>1:1.5</td>
<td>1411</td>
</tr>
<tr>
<td>Tobacco stem</td>
<td>K$_2$CO$_3$</td>
<td>700</td>
<td>30</td>
<td>1.5:1</td>
<td>2557</td>
</tr>
<tr>
<td>Pistachio nut shells</td>
<td>KOH</td>
<td>700</td>
<td>7</td>
<td>1.75:1</td>
<td>700</td>
</tr>
<tr>
<td>Oil palm fibers</td>
<td>KOH</td>
<td>360</td>
<td>5</td>
<td>0.5:1</td>
<td>707</td>
</tr>
<tr>
<td>Lotus stalks</td>
<td>H$_3$PO$_4$</td>
<td>700</td>
<td>15</td>
<td>2:1</td>
<td>1432</td>
</tr>
<tr>
<td>Pomelo skin</td>
<td>NaOH</td>
<td>500</td>
<td>5</td>
<td>1:1.25</td>
<td>1355</td>
</tr>
</tbody>
</table>

* (grams of agent: grams of precursor)

Nabais et al. (2008) studied the effect of microwave radiation on structural properties of activated carbon. They found that microwave heating is effective in surface chemistry modification of activated carbon (Nabais et al. 2008).
2.13 Estimate the cost of production using microwaves and conventional methods

The economic study of activated carbon production on the industrial scale is crucial to find out the major controlling factors of production process. Stavropoulos & Zabaniotou (2009) have studied the production cost analysis when using different raw materials. The activated carbon production price depends on the yield and activation process. Other parameters such as activating agent cost and plant size control the total investment cost for an activated carbon plant from woody material (Stavropoulos & Zabaniotou 2009).

Table 2.5. Economic analyses of production of activated carbon by conventional method

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon production yield %</td>
<td>14</td>
<td>22</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Raw material (tonnes per day)</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Production cost</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed operating cost % /year</td>
<td>47</td>
<td>39</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Variable operating cost % /year</td>
<td>36</td>
<td>42</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>General expenses %</td>
<td>15</td>
<td>19</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Activated carbon (tonnes per day)</td>
<td>1.4</td>
<td>6.6</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Production cost of activated carbon $/kg</td>
<td>2.72</td>
<td>1.3</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>ROI</td>
<td>NA</td>
<td>18.2</td>
<td>27.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5 compares three economic analyses of activated carbon production from pecan shell, bamboo and waste tires.

The general sale price of activated carbon can range from US$ 1–3/kg, depending on the quality and origin of the activated carbon. In Table 2.5 the selling price of the active carbon produced from Bamboo and waste tire is set at $ 1.93, which is close to the price of carbon used in the water treatment industry (Rural Industries Research and Development Corporation, 2001).
Production of activated carbon by microwaves has not been analyzed. The capital cost of a microwave power generator is around $1500-5500 per kW depending on the power system. The maintenance cost of the industrial microwave system is constant. Magnetron, the microwave generator, usually lasts for longer than 5000h (Hasna 2011).

2.14 Removal of the pulp mill effluent compounds that affect fish reproduction

It is well known that some pulp mill effluents affect fish reproduction (Kovacs & Martel 2006; Hewitt et al. 2008; Hall et al. 2009). Natural wood components possibly have adverse effect on fish reproduction. Extractives are in wood tissues to protect trees by their biologically active nature. Some natural bark components such as stilbene, glucoside, tannins and astringins are inherently bioactive to protect trees. Natural wood components that are responsible for adverse effect of effluent on fish are tannins, fatty acids, resins, and phytosterols (Dube et al. 2000). Some of the reported compounds include bisphenol, phytosterols, and diethylphthalate (Kazner et al. 2008). Phytosterols are a group of hormonally active compounds and the major phytosterols in pulp mill effluent are b-sitostrol and stigmasterol (R. Orrego et al., 2009).

Phytosterols were found in thermal mechanical pulp (TMP) and kraft pulp mill effluent as a by-product of the digestion process (Conner et al. 1976). The chemical structure of phytosterols is similar to the steroid hormones and may affect the reproduction systems in biota by mimicking hormones. The identified phytosterols include stigmasterol, β-sitosterol, camposterol and b-sitostanol. Figure 2.7 illustrates the structure of different phytosterols. Stilbenes, lignans and plant sterols, particularly sitosterol, can be present in effluent discharges and exhibit estrogenic activity in laboratory studies (MacLatchy et al. 1995; Van Der Kraak et al. 1998). The effect of phytosterol on fish is controversial in laboratory and field studies probably because of environmental conditions, age, and duration of exposure. Analysis of pulp mill effluents in 22 mills is the US indicated that β-sitostrol is the major sterols fraction. The total sterols concentration varied between 70-535 µg/L in the effluent of these mills. Studies illustrated that recycling fiber in mills may reduce sterols discharge. However, sterols reported
to be biodegradable; products of sterols degradation and transformation by aerobic microorganisms disrupt the endocrine system and cause morphological problems (Conner et al. 1976).

Figure 2.7. Different plant sterols in the pulp mill effluent

The analyses on the suspected compounds were necessary to identify the sources at pulp mills. Burnison et al. (1996) studied the active substances in the HPLC isolations of pulp mill effluent. The results indicated that these compounds were present in a relatively non-polar region of the chromatographic separation, with a logarithmic octanol/water partition coefficient ($K_{ow}$) of 4.6–5.1. Effluent constituents such as β-sitosterol (MacLatchy & Van Der Kraak, 1995; Tremblay & Van Der Kraak, 1999), abietic acid, pinosylvin, and betulin (Mellanen et al. 1996) have the potential to affect fish reproduction when tested individually, but the cause and effect relationships is not well understood due to the differences in species response patterns between laboratory tests and wild fish, the mechanisms of action uncertainties (Van Der Kraak et al. 1998), and the complexity of effluent.

To identify the suspected stream at the mill, a reverse osmosis (RO) treatment was installed in a mill in Saint John to remove the condensates stream from evaporators, used to concentrate the black liquor. The results indicated that RO could remove the potential of the condensate to depress plasma testosterone in Mummichog fish. The responsible compounds in the condensate for steroid depression were identified to be diterpenoids, sesquiterpenoids, and
stilbenes. Similar experiments on different mill extracts support the hypothesis that similar chemicals may produce hormonal effects, in spite of the different wood furnished (Belknap et al. 2006; Hewitt et al. 2008). Based on their results, handling of condensates, spill control, and appropriate biotreatment can improve the effluent quality. However, the effect of specific modification (RO) for removal of suspected compounds is difficult to analyze, because mills apply multiple process changes at a time (Orrego et al. 2009). Dube and MacLatchy (2001) exposed Mummichog fish to the condensates with the concentration of (1% v/v) for 21 days and their experiments support that the recovery condensate stream is the major contributor of the hormonally active waste stream.

After the identification of the condensate as a source of the compounds that affect fish reproduction, solid phase extraction (SPE) was applied to isolate the condensate components in the Saint John mill. GC/MS analyses demonstrated that the sources of these compounds are in the kraft lignin processes (Hewitt et al. 2002). This hypothesis was supported by other studies that showed that lignin degradation products were the main source of the bioactivity in the digest wood, black liquor, and bleaching stream (Dube & McLatchy, 2001).

Individual effluent extractives such as resin acids (e.g. abietic acid), pinosylvin, betulin genistein, isoflavonoid, and phytosterols (sitosterol and stigmasterol) may interfere in the natural fish reproductive system, because they are similar to endogenous steroids in fish (mellanen et al. 1996; Kiparissis et al. 2001). Figure 2.7 illustrates the chemical structure of the bioactive compounds in pulp mill effluent. In another study, 68 wood extractives from monoterpenes, phenolics, fatty acids, resin acids, resin acid neutrals and sterols were identified by GC-MS analysis of a pulp mill effluent in Canada, Quebec (Wartman et al. 2009). Table 2.6 shows the compound name and concentrations.
Table 2.6. Organic wood extractive concentrations (µg/L) in the pulp and paper effluent (Wartman et al. 2009)

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Compound concentration µg/L</th>
<th>Compound name</th>
<th>Compound concentration µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guaiacol</td>
<td>0.5</td>
<td>Isopimaric acid</td>
<td>125.5</td>
</tr>
<tr>
<td>Vanillin</td>
<td>17.8</td>
<td>Dehydroabietic acid</td>
<td>303.7</td>
</tr>
<tr>
<td>Acetovanillone</td>
<td>20.5</td>
<td>Abietic acid</td>
<td>1949</td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>0.7</td>
<td>13-Abietenic acid</td>
<td>48.1</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>6.5</td>
<td>Seco-1-dehydroabietic acid</td>
<td>39.9</td>
</tr>
<tr>
<td>Docosanoic acid</td>
<td>8.4</td>
<td>Seco-2-dehydroabietic acid</td>
<td>42.7</td>
</tr>
<tr>
<td>Tetracosanoic acid</td>
<td>7.6</td>
<td>Cholesterol</td>
<td>83.0</td>
</tr>
<tr>
<td>Methyldehydroabietin</td>
<td>21.3</td>
<td>Campesterol</td>
<td>226.0</td>
</tr>
<tr>
<td>Pimmaric acid</td>
<td>81.9</td>
<td>Stigmasterol</td>
<td>161.5</td>
</tr>
<tr>
<td>Sandaracopimaric acid</td>
<td>45.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the toxicity evaluations, goldfish and Mummichog were exposed to 13 wastewater streams at the mills with different processes. The results showed that condensates, generated from the weak black liquor evaporation during chemical recovery, can depress steroids. The exposure to acid stream (24% of the final effluent flow) lowered the egg production. Condensates also contain the chemicals that depressed steroid in Mummichog (Hewitt et al. 2008). Endocrine disrupting compounds in pulp mill effluent could be polar or non-polar, water soluble or not soluble, and they can act as ligands for estrogen and androgen receptors.

Several worldwide experiments have been conducted to find out which operation condition affects fish reproduction. Long term exposure of fish was examined in Pearl River near the Bogalusa pulp mill, which manufactures linerboard paper by the unbleached kraft process. Male fish appear to be unaffected, but female fish were affected when the kraft mill effluent was greater than or equal to 1% of river flow. Similar research demonstrated that the same process can cause reproduction effect in one mill, while did not in the others. Therefore, the relationship of the experiment in vitro, in vivo and in wild fish remains complex until the identification of the sources of compounds at the mills.
2.15 Significance of the research

Currently the disposal of pulp mill sludge is an issue, economically and environmentally. The best potential approach to solve this problem is the conversion of sludge into the value added products. This work aims to develop a process for the production of activated carbon from pulp mill sludge. KOH has been widely used for the production of activated carbon. KOH-activation of pulp mill sludge will be studied to understand the feasibility of activated carbon production and to analyze the effect of operating parameters i.e. KOH:C ratio, activation time, and temperature on the activated carbon properties.

In recent years, applying microwave radiation has been reported to improve many chemical processes. There are possible benefits in using microwaves for pyrolysis and activation. Literature on the microwave activation of biomass is scarce. This work will investigate the effect of microwave pyrolysis and activation of pulp mill sludge.

Many researches indicated that non-uniformity of the heating inside microwave oven causes non-homogenous products. One of the challenges of this work is to study the temperature distribution when heating with microwaves.

With the purpose of using available resources at the pulp mills for activation of the sludge, white liquor will be used as the activating agent. White liquor is mainly composed of NaOH, Na$_2$CO$_3$ and Na$_2$S. NaOH is reported as a good activating agent. Using white liquor might improve the process of activated carbon production economically, because the recycling process of white liquor is available at the pulp mills.

The applicability of activated carbon will be tested with the treatment of pulp mill effluents. A group of compounds in the pulp mill effluent affect fish reproduction for many years. The removal of these compounds became complicated because of the unknown nature of these compounds. To address this issue, the produced activated carbon will be used for removal of these compounds.
Production and Characterization of Lignocellulosic Biomass-derived Activated carbon

Abstract

The goal of this chapter is to establish the technical feasibility of producing activated carbon from pulp mill sludges. KOH chemical activation of six lignocellulosic biomass materials, four sludges from pulp mills, one sludge for a linerboard mill, and cow manure, were investigated experimentally, with a focus on the effects of KOH:C ratio (1:1, 1.5:1 and 2:1), activation temperature (400-600°C) and activation time (1 to 2 h) on the development of porosity. The activation products were characterized for their physical and chemical properties using a surface area analyzer, scanning electron microscopy and Fourier transform infrared spectroscopy. Experiments were carried out to establish the effectiveness of the lignocellulosic biomass-derived activated carbon in removing methylene blue (MB), a surrogate of large organic molecules. The results show that the activated carbon is highly porous with specific surface area greater than 500 m²/g. The yield of activated carbon was greater than the percent of fixed carbon in the dry sludge, suggesting that the activation process was able to capture a substantial amount of carbon from the organic matter in the sludge. While 400°C was too low, 600°C was high enough to sustain a substantial rate of activation for linerboard sludge. The KOH:C ratio, activation temperature and time all play important roles in pore development and yield control, allowing optimization of the activation process. Methylene blue adsorption followed a Langmuir isotherm for all four activated carbon, although the adsorption capacity of news and kraft primary sludge-derived activated carbon was considerably lower than the rest, consistent with its lower specific surface area.

1 Based on the following article:

3.1 Introduction

Activated carbon is versatile adsorbent that can be used in many applications such as the removal of contaminants from air and water. It can be produced from variety of biomass sources such as coconut shell, agricultural wastes (Yeganeh et al. 2006), coffee crops (Schröder, 2007). Today, many industrial and agricultural residues are used as raw material for activated carbon production. The most important factors in choosing a biomass as a precursor for activated carbon production is its availability, price and chemical/physical properties (Nabais et al. 2008; Girod et al. 2009).

As one of North America’s largest industries, pulp and paper mills produce considerable amounts of lignocellulosic biomass such as sludge which requires disposal (Pokhrel & Viraraghavan 2004; Lacorte et al. 2003). In comparison to burning the lignocellulosic biomass as fuel, producing activated carbon from the lignocellulosic biomass could potentially add value to the waste and benefit the environment via waste abatement, water/air purification and greenhouse gas emission reduction.

Chemical activation is widely used to generate activated carbon from carbon-containing materials. Common chemical reagents for activation include ZnCl₂, H₂SO₄, H₃PO₄ (Arimand et al. 2006; Solaimani & Kaghazchi 2007), alkali metal hydroxides (KOH and NaOH), and alkali metal carbonates such as K₂CO₃ and Na₂CO₃ (Linares-Solano et al. 2006). KOH is often the choice for producing highly porous activated carbon (Guo & Lua 1999; Kawano et al. 2008). The overall reaction between a carbon-containing precursor and KOH is often given as (Hayashi 2000):

\[6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3\]

Equation 3.1

Upon reacting with KOH, some carbon is oxidized and converted to carbonate. Since potassium carbonate is water soluble and reacts with acid, during the washing step much of the carbonate is dissolved in water. HCl will then react with dissolved carbonate and produce CO₂.
During activation, the formation of CO and CO$_2$ is also possible. The temperature at which activation begins and the degree of pore development depend not only on the activating agent but also the nature of the precursor material (Tseng et al. 2007). In order to determine the optimum conditions for the best porous structure and surface area, a set of experiments should be conducted on each specific raw material since activated carbon properties depend on the activation conditions and raw material characteristics.

A suitable porous structure of activated carbon is critical to the efficiency of a process in which the rate limiting step is mass transfer within the porous media. According to IUPAC, pores are categorized into three classes: micropores with pore diameter less than 2 nm, mesopores with pores between 2 and 50 nm, and macropores with pores greater than 50 nm (Zhu et al. 2007). The efficiency of an adsorption process depends on the characteristics of adsorbent and adsorbate, as well as hydrophobic interactions (Moreno-Castilla, 2004). Much research on activated carbon production from biomass has been carried out (Yu & Zhong 2006; Williams & Reed 2006).

A common goal is to be able to produce a cost-effective adsorbent for removal of toxic substances from air or water. It has been shown that enhanced adsorption capacity toward specific pollutants depends on activated carbon porous structure and surface chemistry (Tsang et al. 2007; Yeganeh et al. 2006). These characteristics are determined mainly by the raw material and activation conditions (Guo & Lua 1999; Lozano-Castello et al. 2001). The production of activated carbon from wood and coconut shells is well studied (Lozano-Castello et al. 2001); similar research on other lignocellulosic biomass materials, such as pulp-mill sludge, is rather limited. In particular, there is a lack of information on the effects of activation conditions on final product characteristics.

In this work, chemical activation of pulp-mill sludge and another lignocellulosic biomass-cow manure was investigated. The activation process, consisting of pyrolysis and KOH activation, was investigated under different conditions. The goal was to study the technical
feasibility of activated carbon production from these lignocellulosic biomass materials and their characterization for environmental applications.

3.2 Material and methods

3.2.1 Materials

All six raw materials used in this research were biomass wastes. The first one is a mixed sludge produced by a recycled linerboard mill in Ontario, Canada; the second and third ones are primary and secondary sludges from a pulp mill in Ontario, Canada, while the fourth raw material is the mixture of 70% secondary and 30% primary sludge from a mill in Northern Ontario. The fifth biomass waste is the residue of the bioprocessed wood chips provided by FPInnovations research center. This residue was from the hardwood and contains 54% lignin and 1% protein. Lignin has been reported as the major component that contributes to the char production. Therefore, high lignin content raw materials are expected to be a good option for production of activated carbon. The sixth raw material was cow manure from a farm in Ontario. The cow manure was chosen since it is a large waste biomass stream that is available locally. It is inherently different from the other three and adds another dimension in understanding the effect of raw materials on activated carbon. All of the pulp mill sludges were collected from daily discharges of the mills, transferred to the lab, and stored at \(-4^\circ\text{C}\) prior to experiments.

The total ash, volatile matter, and fixed carbon of the raw materials were measured according to ASTM methods (ASTM D3174-04 for ash analysis and ASTM D3175-89a for volatiles). To measure ash content, the dry sludge samples were heated in a muffle furnace to 800\(^\circ\text{C}\), which took 3 hours, and kept at the same temperature for 12 hours. Volatile matter content was measured by pyrolyzing dry samples at 850\(^\circ\text{C}\) for 8 min without oxygen. Total fixed carbon was the dry sludge weight subtracting ash and volatile matter contents.

Differential Scanning Calorimetric- Thermogravimetric Analysis (DSC-TGA) was conducted by a thermogravimetric analyzer SDT Q600. Approximately 20 mg of sample was heated from room temperature to 800\(^\circ\text{C}\) in nitrogen atmosphere. The instrument was set to
increase temperature at the rate of 10°C/min, under nitrogen atmosphere with a flow rate of 100 mL/min.

3.2.2 Activation procedure

Figure 3.1 is a representation of the activation procedure. For each activated carbon produced, the raw material was dried at 110°C overnight and then, under nitrogen, pyrolyzed at 400°C for four hours and then cooled down to room-temperature. Char formation required removal of oxygen and hydrogen. The product of the carbonization step is carbon and ash. Basically, carbonization yield depends on the amount of carbon that is removed by O and H. The next step is activation, in which the ratio of KOH:C, activation temperature and activation time were varied in order to study which conditions are more effective in producing activated carbon.

The activation temperature was varied from 400 to 600°C and the heating time was set to 1 or 2 h. The KOH:C mass ratio was varied from 1 to 2. To remove activating agent derivatives and impurities, the product was washed with de-ionized water until the pH value of the washing solution became neutral. The activated carbon products were labeled based on their respective activation conditions and raw material. The first number is the KOH:C ratio, followed by an abbreviation relating to the raw material, then activation time and activation temperature. For example, 1Lin2-600 means the activated carbon was produced with KOH:C =1 from Linerboard sludge. The activation process took 2 hours at 600°C. The carbon yield after activation was calculated by weighing the product of each step. Yield, \( Y \), is an indicator of activation process efficiency and is given by (Marsh & Rodriguez-Reinoso 2006):

\[
Y = \frac{\text{Mass of activated carbon produced}}{\text{Mass of dried raw material}} \times 100
\]

\text{Equation 3.2}

In these experiments, the production of activated carbon experiments was duplicated to ensure the accuracy of the results.
With the aim of comparing physical and chemical activation of the pulp mill residues, lignin waste was converted into activated carbon using physical and chemical activation. For the physical activation, the lignin waste samples were carbonized for 4h at 400°C under nitrogen atmosphere under similar conditions applied to chemical activation analyses. Produce chars were activated by CO$_2$ flow of 300ml/min for 2h under various activation temperatures (600-1000°C). While for chemical activation, produced char was mixed with KOH (with the mass ratio of 1 or 2) and activated under various temperature of 600-1000°C.

### 3.2.3 Analytical techniques

#### 3.2.3.1 Surface area measurement

In order to characterize the activated carbon products, nitrogen adsorption isotherm data were obtained. The samples were degassed at 200°C for 2 hours prior to the measurements. The BET, t-plot, and BJH pore size distribution methods were used to interpret the isotherms (Brunauer et al. 1983).

![Activated carbon production procedure diagram](image)

**Figure 3.1. Activated carbon production procedure**
3.2.3.2 FTIR Spectroscopy analysis

The surface functional groups on the activated carbon from the different activation conditions were detected by Fourier transform infrared (FTIR) spectroscopy (FTIR-2000, PerkinElmer). This technique was used to obtain quantitative information about the surface functional groups, thus helping to understand the effect of activation conditions. The frequency range used was from 400 to 4000 cm\(^{-1}\). Spectra of activated carbon were obtained using finely powdered KBr as reference in a KBr/AC mixture (200:1 mass ratio).

3.2.4 Adsorption experiments

Methylene blue (MB) was chosen as the adsorbate in this study as it is widely used to test large organic molecule adsorption capacity of activated carbon. Adsorption tests were performed in a set of 250 mL Erlenmeyer flasks in which 100 mL of MB solutions with initial concentrations of 50–350 mg/l were placed. 0.1g of the activated carbon was added to each flask and kept in a water bath shaker at 120 rpm for 20 hours to allow the equilibrium to be reached. All samples were centrifuged prior to analysis in order to separate the activated carbon particles from the solution. The concentration of MB in the supernatant solution before and after adsorption were determined using a double beam UV–vis spectrophotometer (UV-1601, Shimadzu) at 668 nm, which is the maximum wavelength of the MB used. Each experiment was duplicated under the same conditions.

The amount of MB adsorbed at equilibrium, \(q_e\) (mg/g), was calculated by:

\[
q_e = \frac{C_e - C_0}{W}
\]

\textbf{Equation 3.3}

where \(C_0\) and \(C_e\) (mg/l) are the concentrations of MB at initial and equilibrium point, respectively, \(V\) is the volume of the solution (L) and \(W\) is the mass of dry activated carbon used (g).
The kinetics of adsorption was assessed with 0.05 g activated carbon in 250 mL flasks with 100 mL of MB solution with initial concentration of 100 mg/l. The procedure for the kinetics tests was similar to that of equilibrium tests. The aqueous samples were taken at different time intervals and the concentrations of MB were analyzed using the same UV-vis spectrophotometer. The amount of MB adsorbed at time t, $q_t$ (mg/g), was calculated by:

$$q_t = \frac{C_t - C_0}{W}$$

Equation 3.4

where $C_t$ (mg/L) is the concentration of the dye at a given time t.

3.3 Results and discussion

3.3.1 Characterization of raw materials

Table 3.1 shows the ultimate analysis of the six raw materials. All the analyses are triplicate and similar results obtained. The moisture content (%) of samples was related to their treatment process. Low moisture content of linerboard sludge was attributed to the recycling process applied by the mill. The primary sludge mainly contains wood fibers; while the secondary sludge was undergone the biological treatment. The fixed carbon is the potential of the sludges to convert into activated carbon. However the volatile matter has carbon content bonded to other molecules, which can be captured by appropriate activation process. Lignin waste had the highest carbon content and low ash content which makes it a desirable candidate for activated carbon production, based on the literature.
Table 3.1. Characteristics of the six raw materials

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Moisture content (wt %)</th>
<th>Dry sludge composition</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ash content (wt %)</td>
<td>Fixed carbon (wt %)</td>
<td>Volatile matter (wt %)</td>
</tr>
<tr>
<td>Linerboard mill sludge</td>
<td>6±1</td>
<td>18</td>
<td>9±1</td>
<td>73±2</td>
</tr>
<tr>
<td>News and kraft primary sludge</td>
<td>54±1</td>
<td>25±1</td>
<td>11±2</td>
<td>64</td>
</tr>
<tr>
<td>News and kraft secondary sludge</td>
<td>56±2</td>
<td>25</td>
<td>5</td>
<td>70±1</td>
</tr>
<tr>
<td>Mixed sludge</td>
<td>16±1</td>
<td>4±1</td>
<td>18±1</td>
<td>77±2</td>
</tr>
<tr>
<td>Cow manure</td>
<td>69±1</td>
<td>6±2</td>
<td>72±1</td>
<td>22±1</td>
</tr>
<tr>
<td>Lignin waste</td>
<td>40±1</td>
<td>2±1</td>
<td>18±2</td>
<td>80±3</td>
</tr>
</tbody>
</table>

3.3.2 DSC-TGA analyses

Figure 3.2 shows the weight loss behavior of the Linerboard sludge, News and kraft primary and secondary sludges under the heating rate of 10°C/min in nitrogen atmosphere. The major weight loss occurs between 200 and 300 °C. The remained char for Linerboard, primary and secondary sludges are around 20, 12, and 5% at 700°C. Based on the obtained heat flow, the pyrolysis process for sludge is exothermic at 400 °C.

The major weight loss for hemicellulose, cellulose and lignin occur at 295,345, and 375 °C, respectively. Lignin has higher carbon content compared to cellulose and hemicellulose. During pyrolysis, the rate of volatile loss is slower when the lignin and wax content are higher in the biomass. While a sharper weight loss in the range of 300-350°C is because of the higher cellulose and hemicellulose contents of a biomass (Suhas et al.2007).
(A) Linerboard sludge

(B) News and kraft primary sludge
Figure 3.2. DSC-TGA analyses of (A) Linerboard pulp mill sludge (B) News and kraft primary Sludge (C) News and kraft secondary sludge

3.3.3 SEM micrographs

The morphology of the activated carbon products was investigated using scanning electron microscopy (SEM). Hitachi S-5200 Scanning Electron Microscope was used to obtain the micrographs. Figure 3.3 (A-D) illustrates the change of morphology after activation, showing the development of a porous structure in activated sludges and cow manure. The activated carbon derived from pulp-mill sludge appears to have thicker pore walls than the one from cow manure. It should be noted that pulp mill sludge is highly heterogeneous in its morphology while cow manure is more homogeneous. These pictures are chosen to demonstrate the formation of porous structures of nanometer scales.

3.3.4 Specific surface area and yields of lignocellulosic biomass-derived activated carbon

The volatiles consist of carbon-containing species such as carboxylic acid and phenol. Under activation conditions, however, carboxylic acid and phenol can undergo
polymerization and additional carbon is retained as char, result a yield that is greater than the fixed carbon (Jain et al. 1989; McKay 1982; Zuo et al. 2009). It was reported that lignocellulosic materials may lose 50-80% volatiles during activation at 500°C. The char obtained from woody material pyrolysis was reported to be between 23-50% of dry raw material (Gonzalez et al. 2009). The reported yield values range from 5 to 30% (Tay et al. 2009; Gonzales et al. 2009)

Few researchers used pulp mill sludge as a raw material for production of activated carbon. Shimada et al. (1990) produced activated carbon from newsprint paper at 850 °C and under CO₂ atmosphere. The obtained yield and surface area were 40% and 1000 m²/g, respectively. Khalili et al. (2002) activated pulp mill sludge with ZnCl₂, UV light and steam, and achieved a specific surface area of 1020 – 1700 m²/g.

In this work, the range of the specific surface area and yield (%) of activated carbon produced under various conditions from the six biomass wastes were between 23-770 m²/g and 20-40%, respectively. The highest specific surface area is obtained from the news and kraft secondary sludge, mixed sludge, and lignin waste with activation condition of 600°C, KOH:C of 2, and 2h. While the lower range of surface area obtained from news and kraft primary sludge under various activation conditions. Given their similar compositions from the ultimate analyses, this difference is somewhat unexpected. Clearly, there are other factors that affect activation that need further investigation. The yield varied from about 20 to 40%. The yield, in some cases, is higher than the total % of fixed carbon and ash (Table 1), which suggests that some of the carbon measured as volatile matter (e.g. organics) had been converted into activated carbon. Interestingly, although cow manure had the highest fixed carbon content, its yield was rather low. Yield is determined by the raw material and activation conditions. Cow manure is highly reactive raw material and the conclusion at this stage is that the carbonization and activation condition was not ideal for cow manure probably lower carbonization time and temperature may increase the yield.
Figure 3.3. SEM micrographs of (A) raw secondary sludge, (B) activated carbon produced from secondary sludge, (C) activated carbon produced from primary sludge and (D) activated carbon produced from cow manure (600°C, 2h, KOH:C=2)

3.3.5 Effects of activation conditions on specific surface area (SSA)

The parameters affecting the specific surface area of activated carbon included activation temperature, KOH:C ratio and activation time, all of which were studied by a set of experiments on the Linerboard sludge.

Figure 3.4 (A-D) illustrated the effect of temperature on the SSA. The comparison of A, B, C, and D implied that the rates of activation at 400 and 600°C were very different and that the final SSA achieved at the higher temperature was controlled by the amount of KOH available (Figure 3.4-A vs. 3.4-B and 3.4-C vs. 3.4-D). This result is expected since the rate of activation reaction increases with temperature. There should be a minimal temperature at which the rate of activation reaction becomes substantial. Interestingly, the increase in activation time from 1 to 2 h did not have much effect on the final SSA (Figure 3.4-C vs. 3.4-A). Based on figure 3.4-B vs. 3.4-D, with a constant KOH:C ratio of 2, the surface area
increased from lower than 50 m²/g to over 500 m²/g with an increase in activation temperature from 400 to 600°C.

It appears that an increase in temperature can increase the SSA of activated carbon, provided that KOH:C is 2 or more. In other words, if the temperature is high enough to ensure a substantial rate of activation, with enough activation time, the final SSA should be determined by the amount of KOH available. The high SSA obtained at 400°C (Figure 3.4-A) however it is unexpected.

This dependence of SSA on temperature was also observed when the KOH:C ratio was 1 but only for the one hour activation (Figure 3.5-A). After two hours, the final SSA at 600°C did not change (Figure 3.5-A vs. 3.5-D), supporting the conclusion that the final SSA was controlled by the amount of KOH.

Comparison of figure 3.6-A vs. 3.6-B illustrated the effect of activation time on SSA. Apparently, at 600°C, the rate of activation reaction was high enough for all of the KOH to be consumed within one hour. Consequently, no additional surface area was created after the first hour. Similar observations were made for the other three lignocellulosic biomass materials (data not shown). The yield (%) under all applied activation condition is higher than fixed carbon of linerboard sludge (9%), suggesting that the carbon of volatiles has been captured during activation process.
Figure 3.4. Effect of activation temperature on SSA

Figure 3.5. Effect of KOH:C ratio on SSA
Pore size distribution analysis of activated carbon

Pore size distribution (PSD), a very important property of adsorbents, determines the fraction of the total pore volume accessible to molecules of a given size and shape. Figure 3.7A indicated that increasing activation temperature resulted in an increase in micro- and mesopore volume (< 50 nm), while longer times led to a greater volume of meso and macropores (> 20 nm). By increasing the KOH:C ratio, the pore volume increased significantly, consistent with the SSA results. The increase was particularly substantial for mesopores and macropores with pore diameter of 25-100 nm.
3.3.7 FTIR analysis of the produced activated carbon

To better understand the surface chemistry of the activated carbon and how it is affected by activation conditions, the products were analyzed by FTIR. The FTIR spectra of the linerboard activated carbon displayed the following bands: 3400 cm\(^{-1}\) (O–H stretching vibrations), 2995 cm\(^{-1}\) (aliphatic groups stretching vibrations), 1700 cm\(^{-1}\) (carbonyl groups), 1559 cm\(^{-1}\) (C=C stretching vibration in aromatic rings, which shows the existence of phenolic groups), 1236 cm\(^{-1}\) (C–O–C stretching vibrations in ethers), and 1086 cm\(^{-1}\) (C–OH stretching vibrations in carboxylic acids, alcohols and phenols) (Yagmur et al. 2008; Guo &
Rockstraw 2007; Jiang et al. 2008). Figure 3.8 shows the changes in the surface chemistry which resulted from modifying KOH:C ratio, activation temperature, and activation time.

From Figure 3.8 (A), it is evident that longer activation time increases carbonyl and C-OH groups, while causing no changes in the cyclic groups. This may suggest that the creation of carbonyl and C-OH groups is closely associated with activation reaction and requires time. According to Figure 3.8 (B), higher activation temperature breaks cyclic surface groups and creates more C-OH groups at the surface, likely due to the high thermal stability of the C-OH group. Based on Figure 3.8 (C), a higher KOH:C ratio in the activation process breaks cyclic, C-OH and carbonyl groups; this result is in agreement with the results of other researchers (Yagmur et al. 2008). The main reason for breakage of these bonds is the capture of carbon from substances measured as volatile matter causing decreases in bands at the wavelengths of 1086, 1559 and 1700 cm$^{-1}$. 
3.3.8 Adsorption experiments of methylene blue

a) Kinetics Adsorption experiments were performed with 100 mL MB solutions with an initial concentration of 100 mg/l using 0.05 g of activated carbon. The four activated carbon used in this set of experiments were produced under the same activation conditions, but with different raw materials of linerboard recycled, news and kraft primary and secondary and cow manure sludge samples. As shown in Figure 3.9, all sludges reached equilibrium in
about 300 minutes and the linerboard, NKS and cow manure-derived activated carbon had similar initial rates of adsorption which were greater than that of the NKP sludge-derived activated carbon. The error bars showed the standard deviation of obtained results when repeating the experiments.

**b) Isotherms** The isotherm data were fitted to the Langmuir and Freundlich models. The Langmuir isotherm is defined as follows:

\[
q_e = \frac{QK C_e}{1 + K C_e}
\]

*Equation 3.5*

where \(C_e\) is the equilibrium concentration of the adsorbate (mg/l), \(q_e\) is the amount of adsorbate per unit mass of adsorbent (mg/g), and \(Q\) and \(K\) are Langmuir constants related to adsorption capacity and equilibrium constant, respectively (Marsh & Rodriguez-Reinoso, 2006). Equilibrium isotherms provide information pertaining to the amount and type of adsorption. In Figure 3.9, apparently, the linerboard, NKS, and cow manure activated carbon fit the Langmuir model better than the NKP. The \(R^2\) value is smallest for the NKP in Table 3.2. Interestingly, although the NKP and secondary sludge-derived activated carbon had very different BET-SSA, their adsorption capacity was very similar when normalized with surface area.

On the other hand, while they had the same SSA, the NKS and cow manure-derived activated carbon had different normalized capacity values, 0.231 vs. 0.340 mg/m\(^2\). The linerboard sludge activated carbon gave the highest normalized capacity at 0.500 mg/m\(^2\). It is expected that the normalized adsorption capacity is controlled by surface chemistry and porous structure of activated carbon.

Previous research has shown that meso- and macroporosity in activated carbon derived from lignocellulosic materials are dependent on the precursor (Gonzalez *et al.* 1995). Kang *et al.* (2006) obtained activated carbon with SSA of 1000m\(^2\)/g from pulp mill sludge
with KOH chemical activation at 700°C for 1.5h, under nitrogen atmosphere. The MB adsorption capacity of this activated carbon was reported to be 152 mg/g, which is lower than the result obtained in this work. Given the size of MB molecule, 1.43 nm × 0.61 nm × 0.4 nm (Costas & Snoeyink 2000), meso- and macropores are expected to be accessible while some of the micropores may not be useful to MB adsorption. An understanding of the effects of surface chemistry and pore size requires further study.

Table 3.3 showed a comparison of this work with other works on MB adsorption by activated carbon produced from biomass. It can be seen that the adsorption capacity values of activated carbon produced in this work are within the range reported by other works summarized in Table 3.3, suggesting that our material can be useful for many of the applications using commercial activated carbon.

Figure 3.9. Adsorption kinetic of MB by four selected activated carbon. Error bars indicate plus/minus one standard deviation.
Figure 3.10. Langmuir isotherm of MB adsorption by Linerboard activated carbon, cow manure activated carbon, NKS activated carbon, and NKP activated carbon

Table 3.2. MB adsorption isotherm coefficients

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Surface area (m²/g)</th>
<th>Langmuir</th>
<th>Normal Q* (mg/m²)</th>
<th>K (L/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linerboard</td>
<td>571</td>
<td>0.99</td>
<td>286</td>
<td>0.500</td>
</tr>
<tr>
<td>NKP</td>
<td>250</td>
<td>0.94</td>
<td>58</td>
<td>0.232</td>
</tr>
<tr>
<td>NKS</td>
<td>770</td>
<td>0.99</td>
<td>178</td>
<td>0.231</td>
</tr>
<tr>
<td>Cow Manure</td>
<td>770</td>
<td>0.99</td>
<td>262</td>
<td>0.340</td>
</tr>
</tbody>
</table>

*Normal Q= Q/SSA
Table 3.3. Comparison of MB adsorption by various activated carbons from literature

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>sunflower oil cake</td>
<td>Apricot</td>
<td>pistachio Shells</td>
<td>fir wood</td>
<td>biomass</td>
</tr>
<tr>
<td>Activation Temperature (°C)</td>
<td>600</td>
<td>800</td>
<td>500</td>
<td>N/A</td>
<td>600</td>
</tr>
<tr>
<td>Activating agent</td>
<td>H₂SO₄</td>
<td>ZnCl₂</td>
<td>H₃PO₄</td>
<td>NaOH</td>
<td>KOH</td>
</tr>
<tr>
<td>Ratio of activating agent</td>
<td>1.9</td>
<td>6</td>
<td>N/A</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>114</td>
<td>774</td>
<td>1436</td>
<td>380</td>
<td>250-770</td>
</tr>
<tr>
<td>MB adsorption capacity (mg/g)</td>
<td>16.4</td>
<td>8.82</td>
<td>129</td>
<td>484</td>
<td>58-286</td>
</tr>
<tr>
<td>Normalized capacity (mg/m²)</td>
<td>0.142</td>
<td>0.011</td>
<td>0.090</td>
<td>1.27</td>
<td>0.231-0.5</td>
</tr>
</tbody>
</table>

Table 3.4 shows the comparison of the raw materials used in this research for the production of activated carbon and produced activated carbon properties. The SSA of activated carbon was compared at 600 °C, 2h and KOH:C ratio of 2, because it was the optimum condition for all of the studied raw materials. The yield and SSA of activated carbon by KOH-chemical activation produced from secondary sludge, mixed sludge and lignin waste were similar. Cow manure-activated carbon also had similar SSA to the mixed sludge, lignin waste and mixed sludge. The lowest SSA and yield obtained from the primary sludge activated carbon.
Table 3.4. Properties of the raw materials and produced activated carbon

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Carbon (%) in raw material</th>
<th>Ash (wt%)</th>
<th>Carbonization yield (wt%) (4h,400°C)</th>
<th>Overall yield (wt%)</th>
<th>Overall yield SSA (m²/g)</th>
<th>600°C, 2h, KOH:C of 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recycled sludge</td>
<td>36</td>
<td>18</td>
<td>42</td>
<td>24</td>
<td>24</td>
<td>571</td>
</tr>
<tr>
<td>News and kraft</td>
<td>32</td>
<td>25</td>
<td>50</td>
<td>18</td>
<td>18</td>
<td>250</td>
</tr>
<tr>
<td>Primary sludge</td>
<td>39</td>
<td>25</td>
<td>59</td>
<td>23</td>
<td>23</td>
<td>770</td>
</tr>
<tr>
<td>News and kraft</td>
<td>50</td>
<td>4</td>
<td>26</td>
<td>25</td>
<td>25</td>
<td>700</td>
</tr>
<tr>
<td>Secondary sludge</td>
<td>75</td>
<td>6</td>
<td>60</td>
<td>18</td>
<td>18</td>
<td>770</td>
</tr>
<tr>
<td>Mixed sludge</td>
<td>65</td>
<td>2</td>
<td>35</td>
<td>26</td>
<td>26</td>
<td>770</td>
</tr>
<tr>
<td>Cow manure</td>
<td>85</td>
<td>4</td>
<td>40</td>
<td>25</td>
<td>25</td>
<td>770</td>
</tr>
<tr>
<td>Lignin waste</td>
<td>65</td>
<td>2</td>
<td>35</td>
<td>26</td>
<td>26</td>
<td>770</td>
</tr>
</tbody>
</table>

3.3.9 Comparison of physical and chemical activation of lignin waste

To compare the physical and chemical activation, activated carbon was produced with both methods at similar temperature ranges. Table 3.5 shows the yield%, pore size distribution, pore volume, and SSA of produced activated carbon. The yield was decreased to half, by increasing the temperature from 800°C to 1000°C. However, the highest surface area was obtained at 1000°C. Physical activation of lignin waste generated microporous activated carbon.

Table 3.5. Properties of activated carbon produced by CO₂ physical activation

<table>
<thead>
<tr>
<th>Activation conditions</th>
<th>Overall yield%</th>
<th>Micropores volume cc/g</th>
<th>Mesopores volume cc/g</th>
<th>Macropores volume cc/g</th>
<th>Pore volume cc/g</th>
<th>SSA m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C, 2h,</td>
<td>33</td>
<td>0</td>
<td>0.05</td>
<td>0.014</td>
<td>0.156</td>
<td>293</td>
</tr>
<tr>
<td>800°C, 2h,</td>
<td>30</td>
<td>0.148</td>
<td>0.049</td>
<td>0.027</td>
<td>0.17</td>
<td>321</td>
</tr>
<tr>
<td>1000°C, 2h,</td>
<td>15</td>
<td>0.251</td>
<td>0.04</td>
<td>0.005</td>
<td>0.28</td>
<td>587</td>
</tr>
</tbody>
</table>

Table 3.6 summarized the properties of activated carbon produced by KOH-activation. The highest SSA is 1721 m²/g, obtained at 800°C after 2 hours with a KOH:C ratio of 2. It is particularly interesting that the activated products are microporous. The comparison of the activated carbon produced by physical and chemical activation showed that KOH-chemical activation creates more pores under similar operating conditions.
Table 3.6. Properties of activated carbon produced by KOH- chemical activation

<table>
<thead>
<tr>
<th>Activation conditions</th>
<th>Overall yield%</th>
<th>Micropores volume cc/g</th>
<th>Mesopores volume cc/g</th>
<th>Macropores volume cc/g</th>
<th>Pore volume cc/g</th>
<th>SSA m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C,2h, KOH:C=2:1</td>
<td>26</td>
<td>0.93</td>
<td>0.090</td>
<td>0.014</td>
<td>.94</td>
<td>1721</td>
</tr>
<tr>
<td>800°C,1h, KOH:C=2:1</td>
<td>26</td>
<td>0.64</td>
<td>0.093</td>
<td>0.011</td>
<td>0.73</td>
<td>1210</td>
</tr>
<tr>
<td>800°C,2h, KOH:C=1:1</td>
<td>28</td>
<td>0.32</td>
<td>0.026</td>
<td>0.004</td>
<td>0.34</td>
<td>599</td>
</tr>
<tr>
<td>600°C,2h, KOH:C=2:1</td>
<td>30</td>
<td>0.40</td>
<td>0.039</td>
<td>0.007</td>
<td>0.44</td>
<td>770</td>
</tr>
</tbody>
</table>

3.4 Conclusions

Activation temperature, time and KOH:C ratio all affect the activation process and properties of the activated products. The highest BET-SSA was 770m²/g obtained from the News and kraft secondary sludge, lignin waste and cow manure, which is in the range of commercial activated carbon. For the linerboard mill sludge, at 600°C, the rate of activation reaction was high enough for all KOH to be consumed within one hour, while 400°C seemed too low to sustain a substantial rate of activation. The NKP sludge is not promising for activated carbon production.

Activation parameters analyses indicated that the most dominant parameter is activation temperature. The yield of activated carbon varied from about 20 to 40%, depending on activation conditions. When the temperature is 600°C and the activation time is 2h the yield will be less than 25% but when the activation time is 1h the yield would be higher than 25%. Thus to get higher yield activation time is important. The yield was often higher than the total percentage of fixed carbon and ash, suggesting that the KOH activation process was able to capture some carbon measured as volatile matter. Despite their similar fixed carbon, volatile and ash contents, the NKS sludge-derived activated carbon had a much higher SSA than that of the NKP sludge-derived one. This attributed to the fact that cellullosic content of pulp mill sludges can control properties of activated carbon. Pore size distribution
analyses indicated that 600°C, and 2h activation with KOH:C=2 is a favorable condition to get high pore volume especially mesopores to increase the adsorption of large molecules.

The results of methylene blue adsorption experiments show a Langmuir isotherm for all four activated carbon, although the adsorption capacity of NKP sludge-derived activated carbon was considerably lower than the rest, consistent with its lower SSA value. Overall, the activated carbon produced in this work from pulp mill solids have properties similar to other common types of activated carbon in surface area and pore volume. Further research is needed to better understand the effects of surface chemistry and porous structure on the adsorption.

In this work, the technological feasibility of producing activated carbon from pulp mill sludge was established; there is clearly a need to make this process economic. Since KOH is an expensive chemical for activation, other activating agents should be studied. To that end, a chemical that is readily available at pulp mill would be a sensible target.
4 Microwave-assisted Pyrolysis and Activation of Pulp Mill Sludge Using Alkali Hydroxides

Abstract

The aim of this chapter is to understand the effects of microwaves versus conventional heating on the pyrolysis and activation products from a lignocellulosic biomass. The pyrolysis and activation of pulp mill sludge samples were carried out in a microwave oven operating at 2450 MHz with a power input of 1200 W. The properties of the chars were compared with the ones produced by conventional furnace. The microwave heating method shortened the pyrolysis time by more than 50%. The primary and secondary contents of the sludge samples affected the retained carbon of the chars. Addition of a microwave absorber (i.e. KOH) accelerated the pyrolysis reaction and assisted in the uniformity of pyrolysis by increasing thermal diffusivity. The effects of alkali activating agents (NaOH and KOH) on the SSA and yield (%) were studied for both microwave and conventional activation. In microwave assisted activation, the activation yields for NaOH and KOH activation were in the range of 40-70 wt% and 60-80 wt%, respectively. The NaOH-activation takes 1.5 h in furnace to fabricate an activated carbon with the SSA of 2300 m$^2$/g; however in microwave activation, a five min activation under medium power results in activated carbon with a similar SSA. The activation yield is mainly controlled by activation temperature for both furnace and microwave assisted activation. Given the dual roles of the alkali metal hydroxides as an activating agent and a microwave absorber, the pyrolysis and activation process can be combined. Although the SSA of the combined pyrolysis and activation (500 m$^2$/g) is lower than that of the two steps process.

2 Based on the following article: A. Namazi, C.Q. Jia, D.G. Allen (2014) Microwave Assisted Pyrolysis and Activation of Pulp Mill Sludge Using Alkali Hydroxides, to be submitted to biomass and bioenergy journal
4.1 Introduction

Pulp mill sludge is a waste generated by both primary and secondary treatments in the pulp and paper industry. The Canadian pulp and paper industry produced 7.1 million tonnes of the dry sludge in 1995 disposed by the combustion or landfilling (Mahmood & Elliott 2006). The traditional waste disposal systems are no longer applicable and there is a demand for effective and environmental friendly alternatives (Smith et al. 2009). The waste management cost in the pulp and paper industry is an economic issue due to the large quantity of the waste produced every day. Transformation of the sludge materials into value added products would be a great benefit in terms of reducing the amount of disposable wastes (Krigstin & Sain 2006). Pulp mill sludge can be converted into activated carbon through a process with two steps of pyrolysis and chemical activation. In addition, it can be used at the pulp mills for the treatment of effluents.

Pyrolysis is a thermo-chemical conversion process of biomass in an oxygen free environment. Microwave assisted pyrolysis of biomass is an alternative technology that has received increasing attention in recent years. Research activities have been more focused on the production of biofuels from biomass pyrolysis and less on the char production. In general, residues such as organic wastes, sewage sludge, tires (Appleton et al. 2005), and oil shales are poor absorbers of microwave radiation. Microwave receptors such as carbon and metal oxides can be mixed with the biomass to achieve the complete pyrolysis (Menéndez et al. 2002). The control of product yield is still the challenging aspects of the process, although various efforts have been made to improve pyrolysis (Yin 2012). Also, the lack of the dielectric properties of the biomass, the uncertainty of the actual cost, the need for establishing the pilot test unit prevented the microwave technology from being widely used (Fernandez et al. 2011).

Activated carbon was produced from several biomass sources through chemical activation with the conventional furnace (Mameli et al. 2004; Amaya et al. 2007; Altenor et al. 2009; Demirbas 2009). The pore development in alkali hydroxide activation occurs through three steps. First, the disorganized carbon atoms are removed from the carbon matrix.
Second, carbon atoms are converted into carbonate. Third, the metal atoms created through the reduction of hydroxide and intercalated between the graphene layers of the char (Linares-Solano A. et al. 2007). The hydroxide activation reaction occurs through the following reaction (Lillo-Ródenas et al. 2003).

\[
6\text{MOH} + 2\text{C} \rightarrow 2\text{M} + 3\text{H}_2 + 2\text{M}_2\text{CO}_3 \quad \text{where M=Na, K}
\]

Equation 4.1

Many studies reported KOH as a better activating agent compared to NaOH in the porosity development because of the higher production of intercalation compounds during activation (Maciá-Agulló et al. 2007; Hwang et al. 2008). However, Lillo-Ródenas et al. (2004) showed that the reactions between alkali hydroxides and carbon material begin with the hydrogen evolution that relates to the raw material reactivity. They defined a $T_{20}$ as the indicator of the temperature for 20% of the raw material weight loss. The lower the $T_{20}$ was, the higher was the reactivity of the raw material in chemical activation reaction (Lillo-Ródenas et al. 2004). Therefore it is necessary to study the effect of NaOH and KOH on the activation mechanism of a specific biomass.

Recently, microwave radiation has been used for the production of activated carbon from the char. KOH, K$_2$CO$_3$, H$_3$PO$_4$, ZnCl$_2$, and NaOH were used as the activating agents for microwave assisted activation of agricultural wastes. These compounds are the main absorbers of microwave radiation at the initial stages of activation. The SSA of produced activated carbon ranges between 700-2500 m$^2$/g using the microwave powers between 600-700W. KOH chemical activation of rice husk and cotton stalk chars resulted in activated carbon with SSA of 750 m$^2$/g (Foo & Hameed 2011; Hui et al. 2011). Ji et al. (2007) produced activated carbon by KOH activation of coal tar pitch char using microwaves. The produced activated carbon had SSA values between 2500 and 4100 m$^2$/g depending on the KOH:biomass ratios in the range of 5 to 8. NaOH microwave activation of pomelo skin produced an activated carbon with SSA value of 1335m$^2$/g (Foo & Hameed 2011).
The objectives of this study were to investigate the use of microwave radiation for pyrolysis and activation of pulp mill sludge and to compare it with the conventional furnace method. This paper presents the effect of the controlling factors on microwave pyrolysis and activation of lingocellulosic materials.

4.2 Materials and methods

4.2.1 Characterization of two sludge samples

4.2.1.1 Proximate and ultimate analyses

The total ash, volatile matter, and fixed carbon of the raw materials were measured according to ASTM methods (ASTM D3174-04 for ash analysis and ASTM D3175-89a for volatiles). To measure ash content, the dry sludge samples were heated in a muffle furnace to 800°C, which took 3 h, and kept at the same temperature for 12 h. Volatile matter content was measured with pyrolyzing dry samples at 850°C for 8 min without oxygen. Total fixed carbon content was calculated by subtracting measured ash and volatile matter contents from the dry sludge weight.

Total carbon, hydrogen, nitrogen, and oxygen elemental content of the pyrolyzed sludge were determined using an Exeter Analytical CE-440 Elemental analyzer. Through quantitative high temperature decomposition, solid substances undergo sublimation to form gaseous mixtures. A 0.02 g sample was burned at 1000°C and the released gases were separated into their components. The composition was determined with a precision and accuracy of up to 0.1%.

4.2.1.2 Extractives, carbohydrates, lignin, and protein measurements

The extractive content was measured based on the procedure presented in the TAPPI Standard T 264 (TAPPI 1996). Two soxhlet extraction stages using a 1:2 mixture of 95% ethanol and analytical grade toluene and 95% ethanol were followed by pure water digestion for 4 h. The residual material was used to determine the percentage of cellulose, hemicellulose and lignin constituents in the following steps.
The cellulose and hemicellulose contents of the extractive-free sludge were determined by a procedure developed by Zobel and McElwee (Zobel and McElwee, 1958). In this method, 0.7 g of extractive free sample was treated with 10 mL of glacial acetic acid, 20 g sodium hydroxide, and 1 mL chlorite solution. The samples were placed in a 70°C hot water bath for 4 h. The remaining solids were washed with acetic acid and acetone to remove the moisture. The dried samples were weighted to determine the final percentage of holocelluloses (cellulose and hemicelluloses).

Klason lignin was measured by following the TAPPI standard T 222 om-88 method (TAPPI 1996), which is based on acidic digestion of polysaccharides in sample. Total protein in sludge samples were measured using the Kjeldahl method (Kyllonen et al. 1988).

4.2.2 Microwave pyrolysis set-up

Microwave pyrolysis was carried out in a commercial microwave oven Panasonic NE1257 with the power of 1200 W and the microwave frequency of 2450 MHz with top and bottom magnetrons. Figure 4.1 shows the microwave pyrolysis set-up. The brass hole, with the outer diameter (OD) of 3.17 cm, was created on the cavity of the oven for inlet and outlet of gas flow. Since the hole is smaller than 1/3 of the radiation wavelength (12 cm), the microwave radiation is not expected to leak. The microwave was located in the fume hood and purged with nitrogen gas 2 min prior to the pyrolysis to create an oxygen free environment for the experiments. In every experiment, the quartz reactor was packed with 30 g of dried sludge, placed inside the microwave oven, and connected to the gas outlet. Samples of pulp mill sludge were pyrolyzed in the quartz reactor under various conditions, time (3-10 min) and power level (medium = 600 and high = 1200 W). The char was cooled to room temperature before weighting.
Figure 4.1. Microwave pyrolysis set up 1- Microwave cavity 2- Quartz reactor 3- Capillary column 4- brass hole 5- Pressure gauge 6- outlet for gases 7- Magnetron

\[ \text{Pyrolysis Yield (\%)} = \frac{\text{Mass of char (carbon+ash)}}{\text{Mass of dried raw material}} \times 100 \]  
\text{Equation 4.2}

\[ \text{Retained carbon (\%)} = \frac{\text{Pyrolysis yield(\%)} \times \text{carbon content(\%)}}{\text{Raw material carbon content (\%)}} \]  
\text{Equation 4.3}

The two most important factors in analyzing pyrolysis effectiveness are carbon content of the char and pyrolysis yield. The total retained carbon is defined as the percentage of carbon in the char after pyrolysis divided by the percentage of carbon in the raw material. For comparative purposes, sludge samples were pyrolyzed in a conventional electric furnace as well.

Microwave pyrolysis experiments were designed to test the effect of biomass composition, density, and microwave absorber ratio on the char products and compare the results with the experimental data from the furnace. It has been shown by many researchers
that the interior of the sample is hotter than surroundings when heating by microwaves. This phenomenon causes quenching of the primary volatiles on the surface of biomass samples. To test this hypothesis, the powdered samples were pressed into small cylindrical pellets. The 2 g pellets of sludge, lignin and cellulose were made with the diameter of 1 cm and height of 0.4 cm. The retained carbon percentages from the pyrolysis of the pellet and powder forms were compared.

4.2.3 Microwave activation set-up

Figure 4.2 shows the microwave activation set-up. Since the alkali hydroxides caused breakage of the quartz reactor when heated at high temperatures, the ceramic crucibles were used for chemical activation. The crucibles were covered by a Pyrex shield that has an inlet and outlet for Nitrogen and the gases, respectively. A 5 g sample of furnace pyrolysed sludge was homogenously mixed with ground NaOH and KOH. The activation was performed under the condition of activating agent mass ratio to carbon of 1, 2, and 3; power levels of medium = 600 W and high = 1200 W; and activation times of 3 and 5 minutes. The powder mixture of char and alkali hydroxide was packed into the crucible and placed at the center of the microwave. To create an oxygen free environment, the crucible was covered by a Pyrex shield with an inlet for nitrogen and outlet for the activation gases. To avoid thermal runway inside the sample, the microwave oven was stopped for five seconds after every 30 seconds.
of heating. After activation and cooling, the produced activated carbon was washed by water and 10% HCl solution until neutralized and then dried at 110°C. The SSA and activation yield of the produced activated carbon were measured.

Surface morphology of the sample was studied using an Scanning Electron Microscopy system Hitachi S570.

4.2.4 Specific surface area measurement

The SSA was measured by N₂ adsorption at 77K using a Quantachrome Autosorb-1-C. The samples were degassed at 200°C for 2 hours prior to the measurements. The BET, t-plot, and BJH pore size distribution methods were used to interpret the isotherms (Brunauer et al. 1983).

4.2.5 Comparison of microwave and furnace activation

Activated carbon samples were produced by KOH and NaOH-chemical activation using conventional furnace, as well. A 5 g sample of the pyrolyzed char was used in each activation experiment. The chemical activation was investigated with a focus on activating agent mass ratio to carbon 1, 2, and 3; activation time 1 or 2 h; and activation temperatures of 800 and 1000°C. The chemical activation procedure was explained by Namazi et al. (2010). The activated carbon samples produced by furnace and microwave assisted activation were compared.

4.3 Results and discussion

4.3.1 Characterization of the biomasses

Two pulp mill sludge samples from a northern Ontario mill with 50-50% and 70-30% ratio of primary-secondary sludge were used in this work. The reason for using two sludge samples was to understand the effect of sludge composition variations on the pyrolysis. Table 4.1 shows the wood polymers contents of two samples named sludge PS50-50 and PS70-30. The carbohydrates show the hemicelluloses and cellulose contents of the samples. PS50-50 and PS70-30 samples were very similar in their constituents except for their protein content.
PS70-30 contained less protein compared to PS50-50 due to the lower secondary sludge percentage. Primary sludge mainly contains wood fibers and fillers and secondary sludge is composed of the microbial cells, wood fiber and ash.

Table 4.1. Wood polymers contents of the sludge samples

<table>
<thead>
<tr>
<th>Properties</th>
<th>Protein (%)</th>
<th>Carbohydrates (%)</th>
<th>Lignin (%)</th>
<th>Extractives (%)</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 50-50 50% primary-50% secondary</td>
<td>20</td>
<td>45±5</td>
<td>15±4</td>
<td>16±5</td>
<td>4</td>
</tr>
<tr>
<td>PS70-30 70% primary-30% secondary</td>
<td>8</td>
<td>48±3</td>
<td>23±2</td>
<td>18±4</td>
<td>4±1</td>
</tr>
</tbody>
</table>

Table 4.2 shows the proximate and ultimate analyses of the dried sludge samples. Proximate analysis shows the composition of the biomass in terms of gross components i.e. fixed carbon, volatile matter, and ash contents, while the ultimate analysis shows the elemental compositions of the biomass. Volatile matter content of a biomass is the condensable and non-condensable vapors released when the dried biomass is heated to 850°C for 7min. The solid remaining from this process is the sum of the fixed carbon and ash. The fixed carbon is the carbon in the solid form and it is different from the elemental carbon of ultimate analysis. PS50-50 had the higher elemental carbon content of 51%, the higher volatile matter content but lower fixed carbon content compared to that of PS70-30. Thus it is expected to get a higher yield from PS70-30 because of its higher fixed carbon content. Both sludge samples had low ash content of 4% which is favorable for carbon production.

Table 4.2. Characteristics of dried pulp mill sludge samples

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Proximate analyses (%)</th>
<th>Ultimate analyses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed carbon</td>
<td>Volatile matter</td>
</tr>
<tr>
<td>PS 50-50</td>
<td>13±1</td>
<td>82±1</td>
</tr>
<tr>
<td>PS70-30</td>
<td>18±1</td>
<td>77±2</td>
</tr>
</tbody>
</table>

4.3.2 The uniform heating of lignocellulosic biomasses with microwave pyrolysis

Sludge, cellulose and lignin were not pyrolyzed in microwave oven probably due to their low microwave absorbability. These compounds are long chain polymers in nature and
cannot easily reorientate in the microwave electric field. To overcome the challenge, they were mixed with KOH which had the high microwave absorbability. The uniformity of the pyrolysis is expected to depend on the KOH:biomass ratio.

Microwave pyrolysis of powdered sludge and pellets were investigated. As can be seen in Figure 4.3, non-uniformity of pyrolysis of the sludge pellets mixed with 1 wt% KOH was observed for a 3 min pyrolysis time. The biomasses with a higher density have a lower thermal diffusivity and this leads to a decrease in the uniformity of the pyrolysis. During the microwave heating, the microwave absorber (KOH) readily absorbs microwave radiation leading to a faster heating, while the biomass particles are heated by a slower conduction mechanism. In order to obtain uniform chars from microwave pyrolysis, the sludge was ground and mixed with 5 wt% KOH.

![Figure 4.3. Pellet (A) and powder (B) of the pulp mill sludge after addition of KOH and three min microwave pyrolysis](image)

### 4.3.3 Effect of the density of the biomass samples on retained carbon content

The pulp mill sludge samples contain high amounts of volatile matter, which are released in the early stages of pyrolysis. To increase the contact time between the solid carbon and volatiles, the samples were pressed into small size cylindrical pellets. Figure 4.4 shows the retained carbon (%) of cellulose, lignin, and sludge after microwave pyrolysis for the pellet and powdered samples, when 5 wt% KOH was added. The pellets had a density of two times greater than the powder samples to compare the effect of powder and pellet forms on carbon retention during pyrolysis. For sludge, lignin and cellulose, the form did not affect
the carbon retention, significantly. Among all, lignin was a better precursor for the char production based on the retained carbon % for 5 min pyrolysis, as shown in Figure 4.4.

Even with the addition of 5 wt% KOH, the pellet form pyrolysis resulted in a non-uniform char for all of the biomasses compared to the powdered form. The large error bars for lignin and cellulose pyrolysis can be explained by their low microwave absorbability and consequently the non-homogenous chars produced from these biomass samples.

![Graph A: Sludge](image)

![Graph B: Lignin](image)
The pellet and powdered forms of the samples were also tested with furnace pyrolysis. Figure 4.5 shows the retained carbon from the furnace pyrolysis of cellulose, lignin and sludge in furnace for the powdered and pellet forms. The char obtained from the powdered sludge had more carbon compared to the pellet one. The reason could be the creation of the high pressure inside pellets due to the high volatile matter content of the sludge. The pressure may cause faster release of gases and lower contact time between gas phase and char bed which leads to the lower carbon retention from the gas phase. Similar behavior was observed and reported by Dominguez et al. (2005). Lignin and cellulose contain less volatile matter compared to the sludge. For lignin, the pellet form retained more carbon during furnace pyrolysis especially at the temperatures lower than 600°C. For cellulose, the retained carbon for both powdered and pellet were comparable.
(A) Sludge

(B) Lignin
Figure 4.5. Effect of temperature on retained carbon content of the (A) sludge, (B) lignin and (C) cellulose in conventional furnace

4.3.4 SEM micrograph of microwave pyrolyzed and activated sludge

The morphology of the produced activated carbon was investigated using scanning electron microscopy (SEM) Hitachi S-5200. Figure 4.6 A and B illustrates the formation of porous structures on the char and activated carbon after microwave pyrolysis and activation, respectively. Pores in the produced char were on the micrometer scale and they were in nanometer scale for activated carbon produced with microwave activation.
4.3.5 Effect of microwave oven and furnace pyrolysis on retained carbon of sludge

PS50-50 and PS70-30 were mixed with 1% KOH in powdered form and were pyrolyzed in an inert atmosphere and power of 1200 W. The effect of pyrolysis time on retained carbon content for experiments between 3 and 10 min are shown in Figure 4.7. The total carbon content of the PS50-50 and sludge PS70-30 were 51 and 46%, respectively. During the first three minutes of pyrolysis, the mass of the sludge reduced rapidly due to the release of volatiles. After 3 min of pyrolysis, the retained carbon content of PS50-50 and PS70-30 was 42% and 35%, respectively. By increasing the pyrolysis time from 3 min to 5 and 10 min, the retained carbon content did not change significantly at the 95% confidence level.
Figure 4.7. Effect of pyrolysis time on retained carbon (%) for PS50-50 and sludge PS70-30 (error bars are standard deviation)

Figure 4.8 illustrates the retained carbon for pyrolysis time of 1 to 4 h at 400°C, when using a conventional furnace for pyrolysis. The retained carbon for PS50-50 was 70% after 4 h of carbonization while the highest retained carbon (58%) for PS70-30 was at 2 h of carbonization. The higher retained carbon content in the char from PS50-50 was not expected. It had a higher volatile matter content compared to PS70-30 and a lower fixed carbon content. Probably the higher percentage of secondary sludge and elemental carbon content in the PS50-50 was the reason of its high retained carbon content. In this case, the carbon content of volatiles contributed in the char formation showing the fixed carbon was not the only source for the char content.
In the microwave pyrolysis, the addition of KOH as the microwave absorber, the residence time of volatiles in the reactor, and the heating rate were the factors that affect retained carbon content. The addition of KOH as the microwave absorber causes carbon loss, since the carbon reacts with KOH until complete consumption of KOH, which could be one of the reasons of the lower retained carbon in microwave pyrolysis compared to the furnace pyrolysis. Also the faster rate of the volatile release during microwave pyrolysis reduced the chance of carbon quenching on the char bed which leads to a lower retained carbon content. Microwave and conventional pyrolysces are inherently different processes. This work showed that retained carbon content strongly depend on the type of the pyrolysis process.

To analyze the amount of carbon loss due to the addition of KOH to the sludge samples, the retained carbon (%) was measured for various KOH additions in the samples. Figure 4.9 shows the effect of added KOH, as a microwave absorber, on the retained carbon after 7 min pyrolysis of PS50-50 and PS70-30. KOH addition had no significant effect on the retained carbon content for both sludge samples.
4.3.6 Microwave activation of pulp mill sludge

The need for a microwave absorber during pyrolysis leads into the activation of pulp mill sludge in one step. Pulp mill sludge was directly mixed with the ground NaOH with the mass ratio of 1:1 and subjected into microwave radiation. Figure 4.10 shows the SSA values obtained from NaOH activation without prior pyrolysis. This process was named as one step process. The results show that a surface area of 500 m$^2$/g can be obtained by only 5 min activation with microwaves. By increasing the NaOH:C ratio from 1 to 2, the SSA increased from 500 to 700 m$^2$/g.

In microwaves, the overall yield of activated carbon produced with 5 min activation and without pyrolysis was 20%, which is lower than the one produced with pyrolysis and activation (24%). Although sludge activation without pyrolysis produced activated carbon with a reasonable surface area, pyrolysis prior to activation is expected to have a positive effect on both yield and surface area of activated carbon.
To systematically analyze the effect of microwave activation on the final product, KOH and NaOH microwave assisted activation were investigated. Another reason of using both KOH and NaOH was to understand the differences in the produced activated carbon properties.

4.3.6.1 KOH-microwave activation by two step process

KOH_ chemical activation was achieved by two step process of carbonization and activation. Figure 4.11 shows the effect of KOH:C ratio, activation time and activation power on the SSA and activation yield. By increasing KOH:C mass ratio from 1:1 to 2:1, the SSA decreased from 700 to 300 m$^2$/g and the reduction was statistically significant (p value = 0.003). However, the activation yield remained constant at approximately 60% (p value = 0.055). Further increase of KOH:C ratio did not significantly affect the SSA and yield ( p value= 0.43 and p value= 1). It should be noted that increasing the added KOH was considered as both an increase in activating agent ratio and activation temperature, since KOH is a good absorber of microwave radiation. The SSA was in the range of 300-700 m$^2$/g and the activation yield (%) was in the range of 60-76% for all of the studied conditions.
(A) 5 min activation, medium power level

(B) KOH:C mass ratio of 2:1, medium power level
(C) 3 min activation, KOH:C mass ratio of 3:1

Figure 4.11. Effect of (A) KOH:C mass ratio, (B) activation time and (C) power level on the activation yield (%) (gray bars) and SSA (black bars) of the produced activated carbon using microwaves (5 gr char was used for each experiment)

4.3.6.2 NaOH–microwave activation by two step process

To our knowledge, this work is the first systematic study on NaOH-microwave activation. Figure 4.12 shows the effect of NaOH microwave activation on the SSA and activation yield. By increasing the NaOH:C mass ratio from 1:1 to 2:1 and 3:1, the SSA increased from 400 to 1400, and 2000 m²/g. The increase in SSA value was statistically significant (p value is 1.2×10⁻⁵). The activation yield decreased from 50 to 40% (p value is 0.0065). This observation suggests that carbon loss contributes to surface area development and the activation reaction is not limited by NaOH. The higher ratio of NaOH not only increases the rate of the activation reaction but also increases the activation temperature due to the high absorbability of microwave radiation by NaOH.

Figure 4.12 (B) shows that increasing the activation time from 3 to 5 min did not significantly affect the SSA and activation yield (p values were 0.0780 and 0.3086, respectively).
(A) 5 min activation, high power level

(B) NaOH:C mass ratio 2:1, high power level
The operating power level of the microwave oven affects the SSA of the activated carbon. Changing the power level from medium to high, significantly lowered both the SSA from 1900 to 1400 m$^2$/g and activation yield (%) from 67 to 45%, when the NaOH:C mass ratio is 2:1 (p values were 0.0001 and 0.0014 respectively). In contrast, when the NaOH:C is 1:1, the high power level did not affect the SSA but lowered the activation yield (p values are 0.1774 and 0.0004). This results suggest that when the NaOH:C is 1:1, the NaOH supply is not enough to maintain the activation reaction and develop the surface area as the carbon is consumed. When the NaOH:C is 2:1, the surface area is well developed at medium power and by increasing the power both the SSA and activation yield are reduced. This observation can be explained by the very high activation temperature caused from both the high power and the higher NaOH:C ratio.

Using NaOH seems more promising for generating high surface area, compared to KOH produced activated carbon. The SSA of NaOH microwave activated carbon was in the range of 400-2000 m$^2$/g and activation yield was between 40 to 70%, depending on the activation conditions. The NaOH:C mass ratio was the most important factor in the surface

Figure 4.12. Effect of (A) NaOH:C mass ratio, (B) activation time and (C) power level on the activation yield (gray bars) and SSA (black bars) of the produced activated carbon with microwaves (5 gr char was used in each experiment)
area development. Microwave activation, using KOH, produced activated carbon with the SSA in the range of 300-700 m$^2$/g and activation yield of 60-75%.

One of the possible explanations for the higher SSA obtained by NaOH activation is the higher molar ratio of NaOH available for reaction with carbon. Based on the equation Equation 4.1, for 0.8 mol carbon activation, 2.4 mol activating agent is needed. In this work, when the activating agent :C ratio is 2:1, 0.8 mol carbon was added to 0.5 and 0.35 mol of NaOH and KOH, respectively. In the case of activating agent :C ratio of 3:1, 0.75 and 0.53 mol of NaOH and KOH were used. In both cases, the molar ratio of the added KOH was 30% lower than NaOH which could be considered as one of the reasons of the lower SSA obtained by KOH activation.

### 4.3.7 Conventional furnace activation

Microwave activation is different from the conventional furnace activation in three ways. First, the temperature is controlled by both microwave power and activating agent ratio. Second, the activation temperature during the time is not constant due to the consumption of the activating agent and carbon loss. Third, the rate of the activation reaction was much higher when heating with microwaves.

Microwave activation indicated that NaOH is a better activating agent for pulp mill sludge activation. This finding was in contrary to the common practice that found KOH as a better activating agent to obtain high surface area. Considering the differences between the microwaves and the conventional method, conventional activation of pulp mill sludge was investigated using KOH and NaOH at the temperature range of (600-1000˚C) to further analyze their differences.

#### 4.3.7.1 KOH furnace activation

Figure 4.13 shows the effect of temperature; KOH:C ratio and activation time on the activation yield (%) and specific surface area of the activated carbon produced by KOH activation. The temperatures lower than 600˚C were insufficient to develop a surface with a high porosity level, based on the previous work by this group (Namazi et al. 2010).
(A) KOH:C mass ratio 2:1, activation temperature 800°C

(B) Activation time=2 h, activation temperature=800°C
Figure 4.13. Effect of activation conditions (activation time, KOH ratio and temperature) on the activation yield (%) (gray bars) and SSA (black bars) of the produced activated carbon with furnace

Figure 4.13(A) shows that by increasing the activation time from 1 to 2 h the SSA increased from 1100 to 1800 m$^2$/g, while the activation yield (%) remained constant. The porosity development was mainly based on the creation of more mesopores (2-50 nm). By increasing the KOH ratio from 1:1 to 2:1, the SSA increased four times due to the reaction between the KOH and char. By further increase of KOH ratio to 3:1 the SSA and activation yield (%) did not change probably because the reactive carbon was not sufficient and limited the reaction (Figure 4.13B). The reactive carbon is the carbon that participates in activation reaction. Therefore, the highest SSA can be obtained at 800°C, 2 h and KOH:C mass ratio of 2:1. The porosity analysis showed that micropore enlargement was responsible for the porosity development rather than a pore creation mechanism (Appendix F). In Figure 4.13 (C), activation yield (%) remained constant at 51% by increasing the temperature from 600 to 800°C and then lowered to 10%, when the temperature increased to 1000°C. It shows that by increasing the temperature from 600 to 800°C, more micro and meso-pores were created and then they were destroyed at 1000°C. Therefore, the controlling parameters for pore development were KOH ratio and activation temperature. The error bars in Figure 4.13 (A)
present the repeatability of the surface area and yield measurements. The furnace activation results are assumed to be reproducible.

4.3.7.2 **NaOH-furnace activation**

Figure 4.14 shows the effect of activation time, NaOH:C mass ratio, and activation temperature on the SSA and activation yield (%) of the activated carbon. Similar to KOH activation, increasing the activation time for NaOH-activation did not affect the activation yield (%), but it increased the SSA. The porosity development was controlled by both micropore enlargement, and mesopore and macropore creation. The SSA remained constant at ~2000 m²/g by increasing temperature from 600 to 800°C and decreased to 600 m²/g at 1000°C. At 1000°C, both meso and micropores were reduced. As shown in Figure 13 (B), by increasing NaOH:C mass ratio from 1:1 to 2:1, the SSA increased from 500 to 2000 m²/g and activation yield decreased due to an increase in activation reaction rates. Further increases of NaOH:C ratio to 3:1 did not have a considerable effect on the SSA. Similar to the KOH activation, The controlling parameters in NaOH activation were the NaOH:C ratio and temperature. In both cases of NaOH and KOH activation, the temperature of 1000 °C is too high to obtain a high SSA, while the alkali:C of 1:1 is too low to develop the SSA.

![Graph](image)

(A) Activation temperature 800 °C and NaOH:C mass ratio is 2:1
Figure 4.14. Effect of activation conditions (NaOH:C mass ratio, activation time and activation temperature) on activation yield (%) (gray bars) and SSA (black bars) of the produced activated carbon with furnace.

The activation yield (%) for NaOH-activation was between 45-55%. In KOH-activation, the yield (%) was between 50-55% except for two cases of activation temperature of 1000°C and KOH:C of 1:1, which had the activation yield of 10 and 70%, respectively.
When the temperature increases to 1000°C, more carbon loss and less mesoporous reduction occurred in KOH activation compared to NaOH (pore size distribution data in Appendix F).

Comparison of KOH and NaOH furnace activation results showed that NaOH is a better activating agent for production of activated carbon from pulp mill sludge because it creates higher SSA of 2000 m$^2$/g and the surface area is well developed even at a moderate activation temperature of 600°C. When using NaOH, the porous structure was developed in a shorter period of time (1.5 h) via meso and macropore creation mechanism. In KOH activation, mesopores were created after 2 h. The activating agent ratio of 2 was sufficient to obtain high SSA for both NaOH and KOH at 800°C. For both KOH and NaOH activation, the higher activating agent mass ratio of 3:1 did not cause significant increase in SSA, because of the moderate carbon content of 60% available for the reaction.

The reason that NaOH is better than KOH cannot be only explained by the addition of 30% higher molar ratio of NaOH in the activation compared to KOH-activation. The results showed that the activation with a higher molar ratio of KOH did not increase the SSA significantly. It is possible that the properties of the precursor affect the SSA and yield of activation by KOH and NaOH. Lillo-Rodenas et al. (2007) demonstrated that as the reactivity of a precursor increases, NaOH-activated carbon will have a higher surface area compared to that of KOH–activated carbon (Lillo-Ródenas et al. 2007a; Hoseinzadeh Hesas et al. 2013).

Several researchers have studied the activation of carbon using KOH and NaOH with results summarized in Table 4.3. Mitani et al. (2004) produced activated carbon from coal by KOH and NaOH with an activating agent ratio of 4:1 at 800°C. The KOH-activated carbon had the SSA of 2300 m$^2$/g, while the NaOH activated carbon had the surface area of 730 m$^2$/g. However, in this work, NaOH-activated carbon had a higher SSA value compared to that of KOH-activated carbon. It shows that there is a relationship between the reactivity of the raw material and activating agent.

The comparison of the summarized results in Table 4.3 confirms that the high reactivity of the precursor is directly linked to the higher SSA of NaOH-activated carbon.
versus KOH-activated carbon. The major weight loss of the pulp mill sludge, Mango seeds, Eucaluptus wood and pitch based carbon fiber occurred in the temperature range of 250-500°C, which make them reactive precursors.

**Table 4.3. NaOH and KOH conventional furnace activation comparison with literature values**

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Activation condition</th>
<th>This work</th>
<th>(Moreno-Piraján &amp; Giraldo 2012)</th>
<th>(Lillo-Ródenas et al. 2001)</th>
<th>(Lillo-Ródenas et al. 2007b)</th>
<th>(Maciá-Agulló et al. 2004)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp mill sludge</td>
<td>Ratio 2, 800°C</td>
<td>Pulp mill sludge</td>
<td>Seeds Mango</td>
<td>Spanish antheracite</td>
<td>Eucaluptus wood</td>
<td>Pitch base carbon fibre</td>
</tr>
<tr>
<td>Seeds Mango</td>
<td>Ratio 2, 3,850°C, 1h soaking time</td>
<td>1950</td>
<td>1594</td>
<td>3100</td>
<td>1130</td>
<td>730</td>
</tr>
<tr>
<td>Spanish antheracite</td>
<td>Ratio 2, 730°C, 1h, 750°C</td>
<td>2300</td>
<td>1938</td>
<td>2000</td>
<td>1090</td>
<td>2320</td>
</tr>
<tr>
<td>Eucaluptus wood</td>
<td>Ratio 3, 750°C</td>
<td>1960</td>
<td>1500</td>
<td>1938</td>
<td>2000</td>
<td>1090</td>
</tr>
<tr>
<td>Pitch base carbon fibre</td>
<td>Ratio 4, 750°C, 1h</td>
<td>21</td>
<td>N/A</td>
<td>79</td>
<td>4</td>
<td>78</td>
</tr>
<tr>
<td>coke</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Yield (%)</td>
<td></td>
<td>26</td>
<td>N/A</td>
<td>66</td>
<td>2</td>
<td>71</td>
</tr>
<tr>
<td>Overall Yield (%)</td>
<td></td>
<td>1960</td>
<td>1500</td>
<td>79</td>
<td>4</td>
<td>78</td>
</tr>
<tr>
<td>SSA- NaOH (m²/g)</td>
<td></td>
<td>2300</td>
<td>1960</td>
<td>1500</td>
<td>1938</td>
<td>2000</td>
</tr>
<tr>
<td>Overall Yield (%)</td>
<td></td>
<td>21</td>
<td>N/A</td>
<td>79</td>
<td>4</td>
<td>78</td>
</tr>
<tr>
<td>SSA-KOH (m²/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be concluded that the SSA values and activation yields for both microwave and conventional activation are in the similar ranges. However, the microwave activation was achieved in a very shorter time period. It can be explained by the higher reaction rate which is a well-known benefit of using microwaves. Some researchers justify it with the "microwave thermal effect". They suggest that the dielectric heating causes an increase in the temperature of reaction and kinetic differences are not expected between reactions heated by microwaves and classical heating. However others believe in "microwave non-thermal effects" originated from many examples that cannot be explained by microwave thermal effects. They believe
that microwaves increase the molecular mobility and affect the reaction kinetics. Consequently, the activation energy is reduced or the pre-exponential factor in the Arrhenius equation is increased, which leads to a higher activation rate (De La Hoz et al. 2005, Gude et al. 2012).

In this work, the microwave activation increased the reaction rate by 15 times when compared to the furnace activation. Considering that the temperature of microwave activation experiments was in the range of 600-1000°C, the observed results cannot be explained only by thermal effects. Microwaves are expected to affect the kinetic parameters of activation reactions by alkali hydroxides. This effect was more evident in the case of NaOH microwave activation probably because it is a more reactive compound compared to KOH.

4.4 Conclusions

Microwave pyrolysis of pulp mill sludge is not possible without the addition of a microwave absorber such as KOH. Using a well-dispersed alkali metal hydroxide in the sludge improves the uniformity of pyrolysis and activation products, due to the improved thermal diffusivity. Generally, the retained carbon of microwave pyrolysis was lower than conventional pyrolysis which might be due to the faster release of volatiles.

The sludge PS50-50 with higher protein content had 10% higher retained carbon from both microwave and conventional pyrolysis. Between the two tested wood polymers, lignin had 20% higher retained carbon from both microwave and conventional pyrolysis.

A pellet form of the biomasses i.e. sludge, lignin, and cellulose did not improve carbon retention in microwave and conventional pyrolysis which was not expected. The pellet form of sludge-KOH mixture resulted in a drop in the product uniformity compared to the powdered form even with KOH addition probably due to their higher density. The pellets are not recommended for the microwave pyrolysis.

Given the dual roles of the alkali metal hydroxides as activating agent and microwave absorber (heat source), the activating agent to carbon ratio can be adjusted according to the
desired product properties. Combining pyrolysis with activation is recommended considering the need to add a microwave absorbing agent during pyrolysis.

Activated carbon was able to be produced from pulp mill sludge using microwaves. The activation yields for NaOH or KOH activation were in the range of 40-70 wt% or 60-80 wt%, respectively. The lower yields of NaOH activation suggests that the reaction had a higher rate compared to KOH activation. The highest SSA achieved was 2300 m$^2$/g from NaOH-microwave activation.

Activated carbon produced with microwave oven and conventional furnace had similar properties in terms of SSA and yield. NaOH was found to be a more effective activating agent than KOH for pore development in both microwave oven and conventional furnace. For both NaOH and KOH activation, the conventional furnace activation yield was in the range of 40-50 wt% except for the two cases of KOH-activation at 1000°C and activating agent to carbon ratio of 1:1.

Both microwave pyrolysis and activation were performed in a shorter time with a higher reaction rate compared to the conventional methods. For example, the NaOH-activation takes 1.5 h in furnace to fabricate an activated carbon with the SSA of 2300 m$^2$/g; however in microwave activation 5 min activation under medium power results in activated carbon with a similar SSA. Microwaves are expected to have "non-thermal effects" on the kinetic parameters of activation reactions with alkali hydroxides.
5 Temperature Distribution in Microwave Heating of Biomass Materials

Abstract

This work analyzes the temperature distribution inside the microwave-heated lignocellulosic samples through experiments and finite element modeling. Dielectric properties of the samples were measured using a coaxial probe technique. The results showed that the biomasses were weak absorbers of microwave radiation with a low loss tangent of less than 0.1, suggesting the need of adding strong microwave-absorbing agent. To measure temperature during microwave heating, pressure-based temperature probes were designed, built, calibrated and used. With added strong absorber of microwave (KOH), the temperature at the center of the sample was found to reach a plateau between 600 to 800°C after about 4 minutes. Using COMSOL multiphysics, a 3-D model was developed to simulate the temperature distribution in microwave-heated samples and its change with time. The model yielded a time-dependence of temperature that was similar to one measured with the probe. The model was used to determine temperature distribution in the sample at a given time. Microwave pyrolysis was resulted in a non-uniform temperature distribution even after reaching the plateau temperature, which is different from heating in a conventional furnace. The degree of non-uniformity changes with thermal properties of samples, such as heat conductivity and capacity, as well as the sample location in the microwave oven.

5.1 Introduction

Microwave heating has been implemented in many industrial applications in recent years because of its advantages of volumetric heating, selective heating and low processing time compared to conventional methods of heating. Two major differences between microwave and conventional heating are the inverse temperature profile inside microwave-

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3 To be submitted to the journal of analytical and applied pyrolysis
heated samples and the non-uniform power distribution in the volume of the samples. The non-uniformity of the power is the result of the both non-homogenous electric field strength and microwave absorbability of the material (Kappe et al. 2009).

As a dielectric material is heated by microwave radiation, internal bond charges are redistributed causing polarization of the material (Bykov et al. 2001). The degree to which this will occur is defined by the material’s dielectric loss tangent, \( \tan \delta = \frac{\varepsilon''}{\varepsilon'} \), which is composed of two parameters: the dielectric constant (or real permittivity), \( \varepsilon' \) (F/m), and the dielectric loss factor (or imaginary permittivity), \( \varepsilon'' \) (F/m). The absorption properties of different materials vary greatly with radiation frequency, physical structure, and chemical bonding, which consequently change the depth of microwave penetration. For most materials, microwave absorption increases sharply at high temperatures, which can cause a thermal runaway in some cases (Bykov et al. 2001). Overcoming this situation is a particular challenge for materials with high inherent microwave absorbability (\( \tan \delta > 10^{-1} \)). In contrast, materials with low microwave absorbability (\( \tan \delta < 10^{-3} \)) may require the addition of heat sources in the form of microwave absorbers (susceptors) in order to help overcome the inadequate heat transfer.

Although microwaves are widely used to heat materials, there is a limited understanding of the physics of the heating process. The non-uniform temperature distribution and the inaccuracy of common temperature measurement devices are an ongoing issue for studies of microwave heating processes. A thermocouple measures localized temperature at the point of the junction, while a pyrometer measures only the surface temperature of a material which is often quite different from the bulk temperature. In addition to experimental studies, numerical models can assist in analyzing the complex microwave heating process. A thorough understanding of the temperature distribution and analysis of its controlling parameters presents an opportunity to better control microwave heating processes.

Several studies have investigated the temperature distribution inside microwave heated materials using mathematical modeling methods. Farang et al. (2011) used Lambert’s Law to describe the microwave power dissipation within a wood block sample and simulated the internal temperature profile. Dutta et al. (2013) studied the dielectric properties of biochar and
used them to simulate and predict the product yield of the microwave pyrolysis process. Two well-established numerical methods that can be used to simulate microwave heating are Finite Element Method (FEM) and Finite Differential Time Domain (FDTD) methods (Zhao et al. 2011). Whichever method is employed, the numerical models of microwave heating obey two governing partial differential equations (PDEs): the heat transfer equation and Maxwell’s Equation. The two equations are coupled by the heat source (Q) in the heat transfer equation, which is provided by the microwave dissipation power term in Maxwell’s Equation. There are well established numerical methods, such as Finite Element Method (FEM) and Finite Differential Time Domain (FDTD) methods that can be used to simulate microwave heating (Zhao et al. 2011).

There is currently a poor understanding of the effect of electromagnetic non-uniformity on the microwave heating of complex materials such as biomass. This study is intended to improve this understanding through numerical simulation of the temperature distribution inside different biomass materials during the heating process. Experimental measurements are also carried out to compare with the simulation results. This work is expected to provide valuable insights that will allow better control and improved throughput of relevant processes such as microwave pyrolysis of biomass materials.

5.2 Material and methods

5.2.1 Materials

Two pulp mill sludge samples from a northern Ontario mill with 50-50% and 70-30% ratio of primary-secondary sludge were used in this work. The properties of sludge samples were described in previous chapter.

5.2.2 Measurement of dielectric constant of biomass materials

To determine the microwave absorption capacities of the precursor materials used in this study, values of $\varepsilon'$ and $\varepsilon''$ were measured by the “open-ended coaxial probe” method at a frequency of 2.45 GHz at room temperature. The biomass materials were ground to a fine consistency with a coffee grinder then pressed into pellets of 2 mm thickness. The coaxial probe was placed against each sample and the complex reflection coefficient related to the
permittivity and conductivity of the material was measured with a network analyser. Values of \( \varepsilon' \) and \( \varepsilon'' \) were measured for the pulp mill sludge samples, wood polymers and wood polymer mixture. The wood polymer mixture was assumed to have the composition of 40 wt.% cellulose, 30 wt.% lignin, and 30 wt.% hemicelluloses based on the pulp mill sludge wood polymer contents.

### 5.2.3 Measurement of temperature inside the microwave oven

A quartz reactor of 12 cm height and 5 cm inner diameter was constructed for this study. The mouth of the reactor was fitted with a ground glass joint for which a quartz adapter was built – this adapter consisted of two, parallel, 10 cm tubes merged together near the ground glass joint. A microwave with an inner chamber of \( 30 \times 30 \times 18 \) cm was retrofitted with a brass 2 cm ID access tube on its side through which the adapter could fit. After loading the sample to the reactor, the adapter and reactor were joined and sealed with high-temperature vacuum grease.

Thermocouples interact with microwaves and cannot be used to measure temperature during microwave heating. Pressure-based probes consisting of quartz capillary tubes connected to a pressure gauge were therefore designed to measure sample temperatures during microwave heating. Three designs were used: a capillary column with no bulb (OD = 2 mm, H = 40 cm, and vol = 1.19 cm\(^3\)); a capillary tube with a small bulb (bulb OD = 1 cm, H = 2 cm, vol. = 2.09 cm\(^3\)); and a capillary column with a large bulb (bulb OD = 1.4 cm, bulb H = 3 cm, vol. = 5.08 cm\(^3\)). To measure the temperature, the probe was inserted into the sludge sample inside the quartz reactor through one of the adapter tubes – this same tube also vented gases from the reactor. Pure nitrogen gas was flushed through the other adapter tube to prevent the sample from burning. Figure 5.1 and 5.2 show the three capillaries and their position inside the reactor and microwave oven, respectively.

The relationship between pressure and temperature was determined by heating each of the three probes inside a conventional furnace and measuring the pressure at different temperatures. Temperature of the microwave-heated samples was determined based on the calibration curves obtained from these conventional furnace experiments.
5.2.4 Simulation of temperature profile with COMSOL 4.4

COMSOL multiphysics is a software that can be used to simulate any physic-based system. In this work, it was used to analyze the temperature distribution in the biomass when heating with microwaves. The electromagnetic waves and heat transfer equations were applied for the microwave oven geometry dimensions of $30 \times 30 \times 18$ cm and microwave power of 1200 W. Copper and quartz were selected as the construction materials for the microwave cavity and reactor, respectively. The quartz reactor was assumed to have the height of 12 cm and inner diameter of 5 cm and was filled with nitrogen gas. The thickness of the reactor walls and bottom was assumed to be 2 mm. It was assumed that the microwave oven was filled with air during heating.
5.2.4.1 Microwave module of COMSOL multi-physics 4.4

- Theory

The microwave creates electromagnetic waves during heating. The power has two components of electric and magnetic fields governed by Maxwell’s equations.

The following equation governs the electromagnetic waves:

\[ \nabla \times \mu_r^{-1} (\nabla \times E) + k_0^2 \left( \varepsilon_r - \frac{j\sigma}{\omega \varepsilon_0} \right) E = 0 \]

*Equation 5.1*

where \( E \) is the electric field, \( \mu_r \) is the magnetic permeability, \( \sigma \) is the electric conductivity, and \( k_0 \) is the wave vector in free space.

The microwave power density, \( P \) (W/m\(^3\)) that is absorbed by a material can be expressed by:

\[ P = [ (\sigma + \omega \varepsilon'') E^2 + \omega \mu'' H^2 ] \]

*Equation 5.2*

where \( \sigma, \varepsilon'', \omega, \) and \( \mu'' \) are electric conductivity, dielectric loss factor, angular velocity, and magnetic permeability, respectively. For non-magnetic materials, the magnetic part is assumed to be zero (\( H = 0 \)).

In a steady state and time harmonic electromagnetic field, the total volumetric power generation in a microwave field is:

\[ P = \varepsilon_0 \omega \varepsilon'' E^2 \]

*Equation 5.3*
Coupling the absorbed electromagnetic power with the thermal energy, the temperature distribution in the material can be modeled based on the three dimensional heat transfer equation:

\[ \rho C_p \frac{dT}{dt} = \nabla (\kappa \nabla T) + Q_{abs} \]

Equation 5.4

where \( \rho, C_p \) and \( \kappa \) are density, heat capacity, and thermal conductivity of the material, respectively. The internal heat generation due to the microwave heating is represented by \( Q_{abs} \).

In this work, a 3-D Finite Element Model (FEM) was developed to simulate biomass heating in a domestic microwave oven with the frequency of 2.45GHz. Microwave radiation was transmitted through a rectangular waveguide (WR340) with the cross section area of 4.3 x 8.6 cm\(^2\).

The following assumptions were made:

- All materials are assumed to be non-magnetic;
- Variation in volume, physical, and chemical properties are not considered; and
- Chemical reactions during heating are not considered.

Boundary conditions were set as follows:

Electromagnetic boundary condition \( E(x,y,z,0) = 0 \)

The boundary and initial condition for the heat transfer equation are:

(1) Natural convection on the reactor walls; and

(2) At \( t=0 \) \( T(x,y,z,t) \) \( t=0 = T_{\text{initial}} (x,y,z,0) = 25^\circ\text{C} \).
5.3 Results and discussion

5.3.1 Characterization of the biomasses

The sludge samples from a pulp mill in Northern Ontario were investigated. They had a 50-50% and 70-30% ratio of primary-secondary sludge, respectively. The wood polymers contents of the two sludge samples are shown in Table 5.1. They were named as sludge PS50-50 and PS70-30.

Table 5.1. Wood polymers contents of the sludge samples

<table>
<thead>
<tr>
<th>Properties</th>
<th>Protein (%)</th>
<th>Carbohydrates (%)</th>
<th>Lignin (%)</th>
<th>Extractives (%)</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS50-50 50%Primary-50%Secondary</td>
<td>20</td>
<td>45±5</td>
<td>15±4</td>
<td>16±5</td>
<td>4</td>
</tr>
<tr>
<td>PS70-30 70%Primary-30%Secondary</td>
<td>8</td>
<td>48±3</td>
<td>23±2</td>
<td>18±4</td>
<td>4±1</td>
</tr>
</tbody>
</table>

Sludge PS70-30 contains less protein compared to PS 50-50 due to a lower secondary sludge percentage. Primary sludge mainly contains wood fibers and fillers and secondary sludge is composed of microbial cells, wood fiber, and ash.

Table 5.1 shows the proximate and ultimate analyses of the sludge samples. PS 50-50 has a higher elemental carbon content of 51%, a higher volatile matter content but a lower fixed carbon content compared to that of PS 70-30. Both sludge samples have the low ash contents of approximately 4% which is desirable for char production.

Table 5.2. Characteristics of pulp mill sludge samples

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Fixed carbon (%)</th>
<th>Volatile matter (%)</th>
<th>Ash (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 50-50</td>
<td>13±1</td>
<td>82±1</td>
<td>4</td>
<td>51±2</td>
<td>6±1</td>
<td>3</td>
<td>39</td>
</tr>
<tr>
<td>PS 70-30</td>
<td>18±1</td>
<td>77±2</td>
<td>4±1</td>
<td>46</td>
<td>6</td>
<td>8</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 5.3 summarizes the dielectric properties, and penetration depth of the two sludge samples, wood polymers, and a mixture of wood polymers. The wood polymer mixture was assumed to have the composition of 40 wt.% cellulose, 30 wt.% lignin, and 30 wt.% hemicelluloses, based on the sludge wood polymer content. Among all wood polymers,
hemicelluloses had the highest loss tangent, which is an indicator of high microwave absorbability.

All of the waste biomasses were poor absorbers of microwave radiation and they had a tan δ of lower than 0.1. Among all of the samples, PS 50-50 had the highest microwave absorption capacity. The dielectric properties were related to the composition of the mixture. PS 50-50 had higher loss tangent compared to that of PS 70-30, the former had 20% protein while the latter had only 8%. It is likely that protein affected the adsorption of microwaves radiation because it has the dielectric loss factor of 0.33. It is important to note that the dielectric properties of the tested biomass materials were not temperature dependent in the range of 25 to 250 °C.

Microwave penetration depth indicates the adsorbed electric field into the material and depends on the loss tangent (tan δ) and dielectric constant (ε'). It is defined as the depth that the microwave power reaches to the half of the surface dissipated power. The wood polymer mixture had the highest penetration depth of 1.13 cm, while hemicellulose had the lowest penetration depth of 0.58 cm (Table 5.3). The penetration depths for PS 70-30 and acid washed PS 70-30 were the same, because of their similar components and texture. This result suggests that the ash and minerals do not affect the penetration depth of microwave radiation into the biomass sample. It was also found that after acid washing, the dielectric constant was not affected. Therefore, the presence of inorganic compounds does not affect the polarization of the polymers but it does assist in the dissipation of electric energy in the form of heat inside the sample. The dielectric properties of mixed wood polymers were not expected, considering that the sample was the mixture of lignin, cellulose and hemicelluloses.
Table 5.3. Dielectric properties of the sludge samples and wood polymers

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Dielectric constant ($\varepsilon'$)</th>
<th>Dielectric loss factor ($\varepsilon''$)</th>
<th>Tangent delta (tanδ)</th>
<th>Penetration depth (Dp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 50-50</td>
<td>5.5±0.2</td>
<td>0.4±0.05</td>
<td>0.084</td>
<td>0.64</td>
</tr>
<tr>
<td>PS 70-30</td>
<td>3.5±0.2</td>
<td>0.12±0.03</td>
<td>0.035</td>
<td>0.86</td>
</tr>
<tr>
<td>Acid washed PS 70-30</td>
<td>3.5±0.2</td>
<td>0.07±0.01</td>
<td>0.019</td>
<td>0.86</td>
</tr>
<tr>
<td>Lignin</td>
<td>2.6±0.2</td>
<td>0.05±0.01</td>
<td>0.052</td>
<td>1.08</td>
</tr>
<tr>
<td>Cellulose</td>
<td>4.5±0.1</td>
<td>0.16±0.02</td>
<td>0.035</td>
<td>0.73</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>6.4±0.1</td>
<td>0.4±0.03</td>
<td>0.062</td>
<td>0.58</td>
</tr>
<tr>
<td>Mixed wood polymers</td>
<td>2.4±0.2</td>
<td>0.07±0.01</td>
<td>0.03</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Table 5.4 shows the comparison of the dielectric properties of pulp mills sludge with other similar biomass materials, carbon and activated carbon. Pulp mill sludge had a lower dielectric constant and dielectric loss tangent and its properties were comparable with the oil palm fiber sample. Carbon is usually added to improve the microwave absorbability of poor microwave absorber materials. Activated carbon had the highest dielectric constant of 8 and dielectric loss tangent of 0.62.

Table 5.4. Comparison of dielectric properties of several biomasses and char

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Reference</th>
<th>Dielectric constant ($\varepsilon'$)</th>
<th>Tangent delta (tanδ)</th>
<th>delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp mill sludge</td>
<td>This work</td>
<td>5.5</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Oil palm shell</td>
<td>(Appleton et al. 2005)</td>
<td>2.7</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Oil palm fiber</td>
<td>(Salema et al. 2013)</td>
<td>2</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>(Salema et al. 2013)</td>
<td>7</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Pine wood</td>
<td>(Vos et al. 2003)</td>
<td>2.7</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>(Ramasamy &amp; Moghtaderi 2010)</td>
<td>8</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>Biochar</td>
<td>(Peng et al. 2011)</td>
<td>5</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>
5.3.2 Measurement of sample temperature during microwave heating with pressure probe

5.3.2.1 Calibration of pressure probes

The sample’s temperature in the microwave oven was measured by the pressure probes. In order to calibrate the capillary pressure probe, it was inserted into the heating zone of an electric furnace. For a given furnace temperature, the pressure was recorded with the three probes. Figure 5.3 shows the linear relationship between the temperature and pressure measured with three probes. As expected, the probe with a large bulb at the end had a smallest slope and was the most sensitive one to the temperature changes. Therefore, it is the most accurate one.

![Figure 5.3. Relationship between temperature and pressure in conventional furnace measured with three pressure probes (calibration curves) for 20 gr dried sludge](image)

The three pressure probes were used to measure the pressure during microwave pyrolysis. The pressure was converted into temperature based on calibration curves (Figure 5.3). This temperature is referred as “measured temperature”. Measured temperature changes during microwave pyrolysis were shown in Figure 5.4. As expected the temperature changes
measured with the three pressure probes were similar. However, the one that was measured by the pressure probe with a large bulb at the end was the most reliable.

The energy balance for microwave pyrolysis consists of the input energy (dissipated microwave power) while the output energy includes the energy for the pyrolysis reaction, the convection loss through gas release, conduction to the reactor walls, and residual carbon sensible heat. Pulp mill sludge pyrolysis was overall an endothermic process that became exothermic between the temperatures of 300 to 500°C (Figure 3.2). During the temperature rise to 500°C, the gas evolution occurs. At 500°C, the major part of the gases was released, the properties of the remained char were stable in terms of its weight and its microwave absorbability, consequently the dissipated microwave power was stabilized. At 500°C, the convection and conduction losses were become constant. It causes the stabilization of the output energy of pyrolysis as well. Therefore, the output temperature of the char reached into a plateau temperature. The size of error bars in the temperature measurement with the pressure probes depends on the dispersion of microwave absorber and the sludge composition.

![Figure 5.4. Temperature profiles of sludge pyrolysis in microwave oven measured by three pressure probes (no bulb, small bulb, and large bulb capillaries were used with medium power and 5 wt% KOH added for 20 gr dried sludge)](image-url)
Figure 5.5. Effect of capillary type on the plateau temperature measured with the three pressure probes for 20 gr dried sludge

Figure 5.5 shows the comparison of the temperature measured by the three pressure probes. In all three cases the measured plateau temperatures were very similar. Therefore, the three probes were able to measure the temperature accurately. Among all, the large bulb had the highest precision in measurement.

In order to test the stability of the plateau temperature, the microwave oven was turned off after certain times. Figure 5.6 shows the temperature profile of the sludge inside the microwave oven, with various turn off times at 6, 8, and 18 min. Gas release began at approximately 3 min and continued until 6 minutes, at which point the power was cut for 1 minute. During this interval, temperature did not decrease significantly. At 9 minutes, the microwave was powered off for 3 minutes and the temperature dropped to 320°C. When microwave power was restored, the temperature reached a plateau of 600°C. After 18 minutes, microwave power was again shut off for 1 minute. The plateau temperature was seen to be constant at 600°C.
Figure 5.6. Temperature profile of sludge pyrolysis in microwave with on and off after 6, 8, and 18 minutes for 20 gr dried sludge

5.3.2.2 Effect of microwave operating conditions on measured temperature

The temperature of the sludge during pyrolysis is affected by the microwave power level, the amount of microwave absorber added, and the microwave absorbability of biomass. Figure 5.7 shows the temperature profiles for a power level of medium (600 W) and high (1200 W). The temperature rises to 600 and 800˚C, respectively, after four minutes and then it remained constant.
Figure 5.7. Temperature profiles of PS 50-50 for the power level of medium (600 W) and high (1200 W) during pyrolysis (5% KOH, 20 gr dried sludge)

Also, the addition of a strong microwave absorber (KOH) affects the temperature. Figure 5.8 shows the effect of microwave absorber on the temperature of sludge during pyrolysis. The temperature reaches to 500, 600 and 700 ºC after adding 1, 5, and 10 wt. % KOH, respectively. This suggests that even very small amounts of KOH can initiate the pyrolysis of the sludge during microwave heating.
Figure 5.8. Temperature profiles of PS 50-50 by adding 1 wt.%, 5 wt.% and 10 wt.% KOH during pyrolysis (medium power, 20 gr dried sludge)

Figure 5.9. Temperature profiles of the PS 50-50 (solid line) and PS 70-30 (dash line) during heating with a microwave for 8 min (5% KOH, 20 gr dried sludge)
Figure 5.9 shows the effect of sludge type on adsorption of microwave radiation. PS 50-50 and PS 70-30 had a similar temperature trend when heating using microwave radiation. They both reached a temperature of 600°C after 5 min of heating. Although PS 50-50 and PS 70-30 had different composition of wood polymers, both had similar ash content and they obtained similar plateau temperature when heating with microwaves. This result was not expected considering the dielectric properties of the sludge samples from Table 5.3. PS50-50, having a higher tanδ, would be expected to exhibit a higher temperature during microwave heating. One possible explanation for this discrepancy is the higher fixed carbon content of PS 70-30.

5.3.3 Simulation of temperature profile during microwave heating

The configuration and material properties were defined in the COMSOL multiphysics 4.4 environment using the dimensions of the experimental apparatus and the properties of the biomass. Of this configuration, the selected element was given the characteristics that are shown in Figure 5.10. The microwave magnetrons are placed at the top and bottom of the microwave oven and set to provide a power of 600 W each. The magnetron ports are assumed to have a rectangular shape with the Transverse Electric (TE) mode type and using a mode number of 10 (similar to household microwave ovens). The cavity and waveguide were filled with air (εᵣ = 1). The frequency domain solver was selected to model the electromagnetic field and the time dependent solver for heat transfer was selected to solve the partial differential equations using a finite element method.
Figure 5.10. (A) The electric field norm distribution inside microwave P=1200 W

(B) The electric field norm on the yz surface of the reactor center

Figure 5.10 (A) shows the electric field distribution inside microwave oven. Figure 5.10 (B) is a cross-sectional image situated at the centre of Figure 5.10 (A) and viewed along the x-axis. The rectangular silhouette in Figure 5.10 (B) is a cross-section of illustrates the
position of the reactor inside microwave oven. The simulated temperature of the sample inside the reactor is referred to as the “predicted temperature”.

Table 5.5. Properties of the materials used in the model

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant</th>
<th>Dielectric loss factor</th>
<th>Thermal conductivity W/mK</th>
<th>Density kg/m³</th>
<th>Heat capacity J/kgK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwave oven walls</td>
<td>Copper</td>
<td>-</td>
<td>400</td>
<td>8700</td>
<td>385</td>
</tr>
<tr>
<td>Reactor</td>
<td>Quartz</td>
<td>4</td>
<td>0.005</td>
<td>2600</td>
<td>820</td>
</tr>
<tr>
<td>Sample</td>
<td>Sludge</td>
<td>Table 5.3</td>
<td>Table 5.3</td>
<td>850</td>
<td>500</td>
</tr>
<tr>
<td>Sample</td>
<td>Carbon</td>
<td>7</td>
<td>2</td>
<td>380</td>
<td>930</td>
</tr>
</tbody>
</table>

Table 5.5 shows the properties of materials used in the modeling. The microwave oven was filled with air and its walls were made of copper, while the reactor was made of quartz. The sludge properties were used for the temperature profile analyses. The carbon sample properties are from the literature data measured by Dutta et al. (2013).

5.3.3.1 Physical model

![Figure 5.11. Physical model of the reactor (the center line in black and center diameter in red line inside the reactor were selected for temperature distribution studies)](image-url)

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Figure 5.11 shows a physical model for the reactor. The reactor walls are in contact to the surrounding air inside the microwave oven. Convective heat transfer occurs between the reactor walls and the surrounding air with the convective heat transfer coefficient (h) of 50 W/m².K. The sludge is shown in blue and is assumed to be in contact with the reactor walls. The heat is transferred by conduction between the sludge and the reactor walls. All of the samples were assumed to have 15% porosity which was filled with air. The heat consumed by the pyrolysis reaction was assumed to be negligible. The temperature variation versus time at the center of the sample was analyzed. The effects of boundary conditions, sample size, porosity, and sludge properties (thermal conductivity and heat capacity) on the temperature profile were analyzed. The uniformity of the temperature distribution along the length of the reactor (black line in Figure 5.11) and the sludge (red line in Figure 5.11) were studied for sludge, carbon, and wood polymers.

5.3.3.2 Effect of the sludge and carbon samples on the predicted temperature

After four minutes of pyrolysis experiment, the sludge was mainly converted into carbon. The properties of the sample (i.e. thermal conductivity, density, dielectric properties, and heat capacity) were changed. In order to simulate the temperature profile of pyrolysis with the model, the properties of two sludge samples and carbon were used. Figure 5.12 shows the predicted temperature change with time at the center of carbon and the two sludge samples. For carbon, the temperature reached the plateau at 770°C after 6 min of heating. The two sludge samples had low dielectric loss factors of 0.08 and 0.03 and they reached the plateau temperatures of 560 and 460°C after 10 min of heating, respectively. The experiments showed that the PS 70-30 temperature reaches a plateau at 400°C after five minutes when 1% KOH was added (Figure 5.8).

The temperature of the pyrolysis product is expected to be in a range between the temperatures of carbon and sludge i.e. between 460 and 770°C. In the initial stage of pyrolysis the sample properties are similar to those of the sludge. After the release of the volatiles, the remaining char properties are similar to carbon.
5.3.3.3 Effect of boundary condition on the predicted temperature

Figure 5.13 shows the temperature profiles for the three different cases regarding the boundary conditions. The tested cases were either natural convection, constant wall temperature, or thermally insulated. In the case using constant reactor wall temperature, the plateau temperature was achieved after ~3 min. This case is very similar to the observed results with the experimental measurements. If convection occurs on the outer surface of the reactor walls, the temperature reaches a plateau at 10 min of the heating. In the case of thermal insulation, the temperature continuously increases with time since heat cannot escape the system.
5.3.3.4   Effect of material properties on the predicted temperature

5.3.3.4.1   Sample size

During the pyrolysis experiment, the height of the sludge sample inside the reactor was reduced from 0.12 to 0.06 m in y direction due to the release of the volatiles. As a result of this process, the sludge is converted into carbon. The carbon sample’s surface was mainly in contact with nitrogen gas. In the simulation, the gas was assumed to be nitrogen. Figure 5.14 shows the predicted temperature profile when the volume of the carbon sample is reduced to half. The smaller volume of carbon (117.5 cm³) attained a plateau temperature of approximately 1800°C after about 7 minutes. This temperature was not observe during the experiment due to the excess heat loss from the volatile matters.
Figure 5.14. Effect of the carbon volume on the predicted temperature profiles at the center of the samples with volumes of 235 cm$^3$ and 117.5 cm$^3$

5.3.3.4.2 Effect of sludge thermal conductivity

Thermal conductivity of lignocellulosic biomass materials is in the range of 0.1 to 1 W/m.K. In order to analyze the effect of thermal conductivity on the temperature profile, the properties of PS70-30 was used to predict temperature at the center of sludge with two thermal conductivities of 0.1 and 0.8 W/m.K. Figure 5.15 shows the predicted temperature distribution of the sludge sample using a thermal conductivity of 0.1 W/m.K in comparison with the actual sludge conductivity of 0.8 W/m.K. The comparison shows that a higher temperature of 1200°C can be obtained in a longer period of time (60 min) if the thermal conductivity of sludge was 0.1 W/m.K.
5.3.3.4.3 Effect of sludge heat capacity

Heat capacity of the lignocellulosic biomass materials is in the range of 0.5 to 1.2 kJ/kg.K. In order to analyze the effect of heat capacity on the sludge temperature, the sludge with the heat capacities of 0.5 and 1 kJ/kg.K were compared. Figure 5.16 shows the effect of using a higher heat capacity of 1 kJ/kg.K on the temperature distribution of the sludge. It takes 20 min to reach the plateau temperature (460°C) when the material has a higher heat capacity of 1 kJ/kg.K.
5.3.3.4.4 Effect of sludge porosity

As the pyrolysis reaction started, the top surface of the sludge would become in contact with nitrogen gas due to the reduction of sludge volume to 0.1 m in the y direction. More pores were also created because of the release of volatiles; the pores were assumed to be filled with nitrogen gas. Figure 5.17 shows the effect of sludge porosity on the plateau temperature at a constant sample volume, when the sludge top surface is in contact with nitrogen gas. At a constant porosity of 15%, the predicted plateau temperature for sludge was reduced from 450 to 250°C when the top surface of sludge is in contact with nitrogen due to the convective heat transfer. A higher pore volume of 50% increases the temperature to 450 °C at the heating time of 7 min.
Figure 5.17. Effect of the sludge porosity on the predicted temperature profiles at the center of the sample (with the 15 and 50% porosity when the top surface is in contact with the air)

5.3.3.5 Uniformity of the temperature distribution of samples

Temperature distributions along the reactor center line and diameter for PS70-30, carbon, and wood polymers (i.e. cellulose, hemicelluloses, lignin) were simulated with the aim of analyzing the temperature uniformity inside microwave heated samples. Values of $\varepsilon''$ and $\varepsilon'$ from Table 5.3 were used for the modeling, since the dielectric properties of the material were found not to be temperature dependent.

Figure 5.18 shows the predicted temperature distribution by COMSOL multiphysics 4.4 for carbon and PS 70-30 after 8 min of heating. The temperature distributions were not uniform along the reactor center line and center disc. The temperature distribution along the center line of the sample was more affected by non-uniformity in the electric field, resulting in the temperature gradient of 200°C in PS 70-30. However, the temperature gradient between the center and the walls was 50°C in the disc line of the sample. The material interacts with the microwaves causing a non-uniform temperature distribution. The interaction of a material with
the electromagnetic field depends on several factors such as the dielectric properties of the material, position of the reactor, the microwave oven geometry, and the waveguide dimensions.

The level of non-uniformity shows the normalized temperature gradient along a certain length of the sample. The levels of non-uniformity along the reactor length and reactor diameter were ~72% and 37%, respectively, for sludge and carbon. It shows that the smaller dimension had a more uniform temperature distribution.

\[
\text{Level of non-uniformity} = \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}}} \times 100
\]

**Equation 5.5**

(A) Along the reactor length
Along the reactor diameter

Figure 5.18. Predicted temperature distributions of sludge and carbon along the reactor center line and center diameter after 8 min of heating

Figure 5.19 shows the temperature profiles of wood polymers along the reactor after 8 min of heating with microwaves. The properties of wood polymers in Table 5.6 were applied as the material properties for simulation. In all three cases, the temperature distributions were non uniform. Cellulose had the most non uniform heating pattern. Its level of non-uniformity was 89%, while lignin and hemicelluloses had the levels of non-uniformity of 54 and 64%, respectively. The non-uniformity of temperature distribution of various wood polymers was directly related to their dielectric loss tangents that are reported in Table 5.3. The temperature at the center of the diameter of hemicelluloses and cellulose samples were predicted to be lower which can be explained by their lower penetration depths of 0.58 and 0.73 cm, respectively.

The temperature rise of wood polymers at a certain time depends on the dielectric loss factor. Lignin had the lowest dielectric loss factor of (0.052) and the predicted temperature after 8 min of heating was only 200°C. The predicted temperature for hemicelluloses was higher compared to the other wood polymers because of its higher loss factor of 0.4.

![Diagram of temperature distribution](image.png)
### Table 5.6. The properties of wood polymers used for the simulation

<table>
<thead>
<tr>
<th>Wood polymer</th>
<th>Density (kg/m$^3$)</th>
<th>Heat capacity (kJ/kgK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>630</td>
<td>2.10</td>
</tr>
<tr>
<td>Cellulose</td>
<td>1300</td>
<td>1.55</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>1500</td>
<td>1.8</td>
</tr>
</tbody>
</table>

![Graph showing temperature distribution along reactor length](image)

(A) Along the reactor length
Along the reactor diameter

Figure 5.19. Predicted temperature profiles of the pure lignin, cellulose, and hemicelluloses along the reactor center line and diameter after 8 min heating with microwaves

5.3.3.5.1 Effect of reactor position inside microwave oven

In all of the previous simulations, the reactor position was in the horizontal direction, which is similar to the experimental design of the microwave oven. The position of the reactor was changed to the vertical position to study its effect on the temperature distribution, and the resulting cross-sectional electric field distribution is shown in Figure 5.20. The electric field inside the reactor varies in the order of $10^4$, which leads to a non-uniform heating. The level of electric field non-uniformity inside the sludge in vertical position is higher than the horizontal position.
The electric field distribution resulted in the non-uniform heating in the sample. Figure 5.21 shows the effect of reactor orientation on the temperature distribution of sludge in vertical and horizontal reactor orientations. After 8 min of heating, two hotspots at the 0.04 and 0.09 m of the reactor length were observed. A higher temperature of 1100°C for sludge was achieved with the vertical reactor in comparison to the temperature of 450°C for the horizontal orientation. The level of non-uniformity along the center line of the sludge was about 73% for both vertical and horizontal orientations. Along the diameter of the reactor, the level of non-uniformity was 55 and 37% for the vertical and horizontal reactor orientations, respectively. It can be concluded that the vertical reactor has a higher level of non-uniformity along its diameter in comparison to the horizontal reactor; although a higher temperature of 1100°C can be obtained in this orientation.
Figure 5.21. Effect of reactor orientation on temperature distributions of sludge, the vertical and horizontal reactor after 8 min of heating
5.3.3.6 Temperature distribution in furnace

The temperature distribution in the furnace heated sample was analyzed. The dimensions of the reactor were assumed to be similar to the real furnace. The vertical furnace was heated through the walls. The sample holder has a radius of 0.03 m and height of 0.2 m. By using the heat transfer equation and known values of $\rho$, $C_p$, and $\kappa$, the temperature distribution was simulated considering the following initial and boundary conditions.

- Initial Condition: $T_0=25^\circ$C

- Boundary Condition: Thermal insulation on the walls of the reactor

(A) 3-D temperature distribution in the furnace after 7 min of heating
(B) 2-D temperature distribution along the center diameter of the furnace at various times

Figure 5.22. Temperature distribution in the furnace (A) 3-D temperature distribution after 7 min of heating (B) 2-D temperature distribution in the center diameter of the reactor during 1 to 20 min (60-1200 s) of heating

Figure 5.22 shows the temperature distribution along the diameter of the reactor in furnace. The walls had a constant temperature of 800°C and the center temperature was increased from 25 to 800°C during 12 min of heating. After the heating for 12 min, the temperature distribution was completely uniform. The level of non-uniformity at 8 min of heating in furnace was only 9%. It shows that microwave heating of the biomass is 8 times more non-uniform compared to the furnace.

5.4 Conclusions

Pulp mill sludge and wood polymers are weak microwave absorber and have tan δ of lower than 0.1. Among all wood polymers, hemicellulose is the best absorber of microwave radiation. Secondary pulp mill sludge has a larger tan δ and is more effective at absorbing microwave radiation compared to the primary sludge due to its protein content. The tan δ of pure protein is approximately 0.33.
The pressure-based temperature probe with a larger bulb is better than the ones without a bulb and with a smaller bulb in term of repeatability. Under the conditions that were studied, the temperature at the center of the sample reaches a plateau, between 600 to 800 °C within about 4 minutes. The plateau temperature is controllable by adjusting the microwave power level and the amount of strong microwave absorber, such as KOH.

COMSOL multiphysics 4.4 was used to develop a 3-D model to simulate the temperature distribution in the microwave-heated sample and its time dependence. The effects of heat capacity (Cp), thermal conductivity (k) of samples, and position of the reactor inside the microwave oven were studied. Thermal conductivity was found to affect the uniformity of heating and the plateau temperature, while the heat capacity only affected the time to reach the plateau temperature. In addition, simulation results demonstrated the importance of the mode of heat transfer between the reactor and its surrounding, sample porosity and volume in determining plateau temperature.

The modelling results demonstrated that a continuing microwave radiation would result in a non-uniform temperature distribution even after reaching the plateau, which is very different from heating in a conventional furnace. The degree of non-uniformity changes with thermal properties of samples, such as heat conductivity and capacity, as well as sample location in the microwave oven.
Effect of Chemical Components in White Liquor on Carbon Activation

Abstract

Conversion of pulp mill sludge into activated carbon is an alternative solution for waste management at pulp mills. In this study, the use of white liquor as an activating agent with the aim of applying an available source at the pulp mills was investigated. White liquor is the cooking solution of the kraft pulp mills that mainly contains NaOH and Na$_2$S. The specific surface area (SSA) and activation yield (%) of the produced activated carbon were measured for various operating conditions and compared with the pure NaOH activation results. The SSA value of 650 m$^2$/g and an activation yield of 61% were achieved with synthetic white liquor at 600°C and 2 h. The SSA values obtained with white liquor were ~60% lower than that with NaOH alone. To understand the effect of white liquor compounds on the carbon activation, the thermodynamic equilibrium of the four activation reaction systems were analyzed using FactSage and HSC. X-ray diffraction (XRD) and elemental analyses were used to investigate the activation reaction products. It was found that sodium sulfide was inert and unable to participate in reactions with carbon in white liquor activation. Also Na$_2$CO$_3$, a key component of white liquor and a main product of NaOH activation, affected the equilibrium and hindered the development of pores during NaOH activation. Both Na$_2$S and Na$_2$CO$_3$ make NaOH less reactive and less available for the activation reaction with carbon.

4 To be submitted to the journal of industrial and engineering chemistry research
6.1 Introduction

The pulp and paper industry is one of the major producers of the solid waste in Canada (Statistic Canada, 2000). In 1999, the total pulp production of Canada was 31.2 million tons per year. One ton of sludge was generated for 40-50 kg of dry pulp production (Krigstin & Sain 2006, Monte et al. 2009). Landfilling and incineration, which are common practices for sludge disposal, have their own drawbacks, such as the leakage of hazardous substances to the environment and the high cost of the land. Therefore, conversion of pulp mill sludge into a value added product is an alternative (Mahmood & Elliott 2006; Monte et al. 2009; Ochoa de Alda 2008; Arrougé et al. 1999; Arrouge et al. 1998; Scott & Smith 1995). Our previous research has shown that one possible product from pulp mill sludge is activated carbon(Namazi et al. 2010).

One of the common methods to produce activated carbon is chemical activation, using alkali hydroxides. Lillo-Ródenas analyzed chemical reactions that take place for activation of the coal with sodium hydroxide. The proposed reaction for sodium hydroxide activation of carbon in the temperature range of (600-900˚C) is (Lillo-Ródenas et al. 2003, Yuan et al. 2012):

$$6\text{NaOH} + 2\text{C} \rightarrow 2\text{Na}_2\text{CO}_3 + 2\text{Na} + 3\text{H}_2$$

**Equation 6.1**

The kraft process is the major pulping process currently used in the pulp and paper industry. White liquor is the cooking liquor of this process and mainly contains NaOH and Na₂S. Black liquor is the remaining solution of the cooking step and it contains dissolved organic and inorganic substances from pulping. The chemical recovery process has been used to recycle pulping chemicals (NaOH and Na₂S) at the pulp mills for many years (Tran and Vakkilainen 2008). Black liquor enters to a recovery boiler for recovering energy and recycling pulp mill chemicals. The composition of white liquor after the recovery process is shown in Table 6.1. White liquor could be a possible candidate to be used as an activating agent because of its high sodium hydroxide content of 53 wt%.
Table 6.1. White liquor composition after recovery process at pulp mills

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaOH</th>
<th>Na₂S</th>
<th>Na₂CO₃</th>
<th>Na₂SO₃</th>
<th>Na₂SO₄</th>
<th>Na₂S₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td>53</td>
<td>21</td>
<td>15</td>
<td>3</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

The major components of recycled white liquor are NaOH, Na₂S and Na₂CO₃. These chemicals have been individually used in the production or modification of activated carbon. For example, NaOH has been previously used as an activating agent. It was shown that Na₂CO₃ can also be used for activation of biomass by microwave radiation (Li et al. 2010). Lillo-Rodenas (2003) studied the reaction of NaOH and Na₂CO₃ with carbon and showed that the reaction of NaOH with carbon produces Na₂CO₃, but pure sodium carbonate cannot be used as an activating agent at operating temperatures below 760°C (Lillo-Ródenas et al. 2007). Their thermodynamic analyses showed that the activation temperature needs to be above 760°C to decompose Na₂CO₃, physically activate carbonaceous material, and produce Na₂O. Another example is the use of Na₂S as an additive for increasing the capacity of activated carbon for adsorption of specific compounds (Meena et al. 2010).

The choice of activating agent and raw materials both affect the produced activated carbon properties and price (Altenor et al. 2009). The major cost associated with activated carbon production from the waste biomass is the cost of activating agent (Stavropoulos and Zabaniotou 2009). Using white liquor as an activating agent and recycling it through the pulp mill recovery process is expected to be beneficial. The main objective of this work is to study the chemical activation of pulp mill sludge with NaOH and white liquor in the temperature ranges of (600-1000°C). In order to better understand activation mechanisms, the effects of major components of white liquor on activation were investigated through experiments and thermodynamic simulation.
6.2 Material and methods

6.2.1 Materials

Pulp mill sludge was collected from a pulp mill in Northern Ontario, Canada. The sludge was a dried mixture of the primary and secondary sludge. Table 6.2 shows the proximate and ultimate analyses of the dried pulp mill sludge used as the raw material for activated carbon production. The proximate analysis provides the weight percentage of fixed carbon, volatile matter, and ash. While ultimate analysis indicates the elemental composition of a biomass.

Table 6.2. Proximate and ultimate analyses of pulp mill sludge

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Proximate analyses (%)</th>
<th>Ultimate analyses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed carbon</td>
<td>Volatile matter</td>
</tr>
<tr>
<td>Sludge</td>
<td>18±1</td>
<td>77±2</td>
</tr>
</tbody>
</table>

A dry synthetic white liquor was prepared by grinding and mixing the dry chemical grade reagents consists of NaOH, Na₂CO₃ and Na₂S·9H₂O, Na₂SO₄, Na₂SO₃ and Na₂S₂O₃ (Sigma-Aldrich) homogenously with the weight ratio given in Table 6.1.
6.2.2 Analytical techniques and procedures

Figure 6.1. Production of activated carbon process

The activated carbon was produced by the procedure illustrated in Figure 6.1. Dry NaOH and synthetic white liquor were ground, mixed with produced char, and activated under various conditions of temperature and time. The chemical activation was performed under the conditions of activation temperatures of 600, 800, and 1000°C; activation times of 1 and 2 h; and NaOH:C mass ratios of 1:1 to 3:1. The activating agent: C mass ratios of 2:1 and 4:1 were applied to make the white liquor (contains 53% NaOH) activation comparable to the NaOH one with the ratios of 1:1 and 2:1. The SSA and activation yield (%) were measured for the produced activated carbon.

\[
\text{Activation yield (\%)} = \frac{\text{Activated carbon weight (g)}}{\text{Char weight (g)}} \times 100
\]

Equation 6.2
The total elemental contents of the samples before and after the washing step were determined using an Exeter Analytical CE-440 Elemental Analyzer. This device is based on a combustion technique and some forms of sulfur, such as inorganic sulfates and pyrites were not taken into account, depending on the decomposition temperatures. The sulfur content determined by this method is only combustible sulfur.

The activated carbon sample was analyzed prior to washing by X-ray diffraction (XRD) to determine the sulfur form in the crystalline structure of white liquor–activated carbon. The samples were ground to create a fine and uniform particle size. The X-ray diffraction was performed at room temperature and 2θ was set for 22° to 50° at 0.01°/sec and the XRD peaks were obtained.

6.2.3 FactSage software for thermodynamic simulation

The thermodynamics of the carbon activation reaction with white liquor were investigated to find the equilibrium compositions. Thermodynamic simulations were performed using FactSage software, a commercial thermodynamic software package which predicts the products by minimizing the Gibbs free energy. The reaction was studied for the activating agent:C mass ratio of 2:1 under a helium atmosphere. For a comprehensive understanding of white liquor chemical effects on carbon activation, various mixtures of white liquor chemicals were used as activating agents. The ratios of activating agent chemicals were the same as their ratio in the white liquor composition. The carbon reactions with five activating agents were analyzed with FactSage simulations. The activating agent names and molar compositions are summarized in Table 6.3. In each case, the reaction of activating agent and 8.33 moles of carbon was simulated. Thermodynamic simulations assume unlimited time for the reactions to happen. The relevant compounds in the gaseous and solid phase were selected from the FactSage data base and are summarized in Table 6.4.
Table 6.3. Five activating agents used for thermodynamic simulations

<table>
<thead>
<tr>
<th>Activating agent compositions (moles)</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) 2.6 NaOH</td>
<td>Hydroxide</td>
</tr>
<tr>
<td>(B) 0.28Na₂CO₃-2.6NaOH</td>
<td>Carbonate and hydroxide</td>
</tr>
<tr>
<td>(C) 0.54Na₂S-2.6NaOH</td>
<td>Sulfide and hydroxide</td>
</tr>
<tr>
<td>(D) 0.54Na₂S-0.28Na₂CO₃-2.6NaOH</td>
<td>Carbonate, sulfide, and</td>
</tr>
<tr>
<td>(E) 0.07Na₂SO₄-0.047Na₂SO₃-0.54Na₂S-</td>
<td>hydroxide</td>
</tr>
<tr>
<td>0.282Na₂CO₃-2.6NaOH</td>
<td>White liquor</td>
</tr>
</tbody>
</table>

The products were used to predict the equilibrium compositions using a thermodynamic software package HSC (enthalpy (H), entropy (S), and heat capacity (C)). HSC does not take into account the kinetics of the chemical reaction and non-ideality of the solutions.

Table 6.4. List of the components considered for FactSage modeling

<table>
<thead>
<tr>
<th>Groups</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen-containing gaseous</td>
<td>O₂, OH, H₂O, HO₂, H₂O₂, CO, CO₂, HCO, CH₃OH,</td>
</tr>
<tr>
<td>compounds</td>
<td>C₂H₄O, CH₃COOH,</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>CH₃, CH₄, C₂H₂, C₂H₃, C₂H₆</td>
</tr>
<tr>
<td>Sulfur containing compounds</td>
<td>S, S₂, HS, H₂S, CS, CS₂, SO, SO₂, SO₃, COS</td>
</tr>
<tr>
<td>Sodium compounds</td>
<td>Na, NaH, NaO, Na₂O, Na₂CO₃</td>
</tr>
<tr>
<td>Oxides</td>
<td>Na₂O, SO₃</td>
</tr>
<tr>
<td>Sulfur containing species</td>
<td>Na₂SO₃, Na₂SO₄, Na₂S</td>
</tr>
<tr>
<td>Hydroxides</td>
<td>NaOH</td>
</tr>
<tr>
<td>Solid species</td>
<td>C (graphite)</td>
</tr>
</tbody>
</table>

6.3 Results and discussion

6.3.1 Surface area and activation yield (%) analyses

6.3.1.1 NaOH Activation

Figure 6.2 shows the effect of activation time, NaOH:C mass ratio, and activation temperature on the SSA and activation yield (%) of the activated carbon. The main controlling parameters in NaOH activation were the NaOH:C mass ratio and activation temperature. The highest surface area of 2500 m²/g was obtained at 800°C, 1.5 h activation and NaOH:C mass ratio of 2:1. The activation yield (%) did not change significantly with activation temperature, activation time (1 to 2 h), and NaOH:C mass ratio and was in the
range of 45-54%. Figure 6.2 (B) shows that the SSA remained constant at ~2000 m$^2$/g for temperatures of 600 to 800˚C and decreased to 600 m$^2$/g at 1000˚C. By increasing the NaOH:C mass ratio from 1:1 to 2:1, the SSA increased from 500 m$^2$/g to 2000 (Figure 6.2 (C)). Further increases in the NaOH:C mass ratio to 3:1 did not have a significant effect on SSA. The obtained SSA values were relatively high compared to the literature values for the produced activated carbon from biomass (Dias et al., 2007; Mohamad Nor et al., 2013; Tay et al., 2009).

The porosity analyses of activated carbon indicated that the majority of the pores were mesoporous and no macropores were created when activating by NaOH. By increasing temperature from 600 to 800˚C mesoporous volume increased, while the micropore volume remained constant, showing that the dominant mechanism in surface area development was pore creation. Additional heating to 1000˚C destroyed both mesopores and micropores (Figure is not shown).

(A) Activation temperature of 800˚C; NaOH:C mass ratio is 2:1
6.3.1.2 White liquor activation

Since white liquor contains approximately 53 wt% NaOH, the white liquor:C mass ratio of 2:1 or 4:1 was expected to be comparable with NaOH-activation results for the ratio of 1:1 or 2:1.
(A) Activation temperature is 1000˚C, white liquor:C mass ratio is 4:1

(B) Activation time is 2h, white liquor:C mass ratio is 4:1
(C) Activation temperature is 800˚C; activation time is 2h

Figure 6.3. Effect of activation conditions (A) activation time (B) activation temperature, and (C) white liquor:C mass ratio on the SSA (black bars) and activation yield (%) (grey bars) of white liquor derived activated carbon

In all studied cases, the SSA of white liquor activated carbon was lower than the NaOH activated carbon. At 1000˚C, the surface area increased from 109 to 650 m$^2$/g when the activation time increased from 1 to 2 h (Figure 6.3A). However, at the temperatures of 600 and 800˚C, an increase in the SSA with activation time was not observed (data not shown). Thus there appears to be a hindering effect on the activation reaction, which was reduced after 2 h of heating at 1000 ˚C. The activation yield for white liquor activation was 20% lower than that for NaOH activation, suggesting carbon did not participate in the activation reaction.

Figure 6.3 (B) shows the effect of temperature on the SSA and activation yield of the activated carbon. Unlike NaOH activation, for white liquor, the SSA remained approximately constant at 600 m$^2$/g, when the temperature increased from 600 to 1000˚C. Also the activation yield (%) decreased from 61 to 33%. This result suggests that carbon is lost and does not contribute to surface area development, leading to a lower activation yield and lower SSA.
By increasing the white liquor:C mass ratio from 2:1 to 4:1, the SSA increased from 300 to 600 m$^2$/g (Figure 6.3C). The white liquor contains 53% NaOH and it is expected that the surface area development would be similar to NaOH-activated carbon. The reason of the low surface area of white liquor could be due to the limited contact between NaOH and char caused by the other chemicals in the white liquor.

During the activation by either NaOH or white liquor, the surface area is developed from the consumption of NaOH. The effectiveness of activation is attributed to the ability of Na to produce the intercalation compounds with carbon. For the NaOH:C ratios of 1:1, 2:1, and 3:1, NaOH was the limiting component in the activation reaction. The highest theoretical activation yields (%) were calculated as 90, 80, and 70%, respectively, based on the activation reaction in Equation 6.1. In this work, the obtained activation yields for NaOH-activation of sludge samples were 52, 48, and 45%, respectively. In the case of white liquor activation, the actual activation yields were 61 and 54% for white liquor:C mass ratio of 2:1 and 4:1. This suggests that less carbon is consumed in the activation reaction and consequently fewer pores are developed when using white liquor. Also, it is hypothesized that NaOH is less effective in creating porosity in the presence of the other chemicals in white liquor.

### 6.3.2 Thermodynamic analyses of white liquor-carbon reaction using FactSage and HSC

To analyze the effect of white liquor chemicals on carbon activation, five reaction systems of (A) hydroxide-C, (B) carbonate and hydroxide, (C) sulfide and hydroxide, (D) carbonate, sulfide and hydroxide, and (E) white liquor-C were analyzed by FactSage. The amounts of compounds were similar to the white liquor composition. In each reaction system, the effect of chemicals on carbon activation was analyzed. The thermodynamic analyses provided more information on reactions and inhibitory effects of the compounds present in white liquor. The predicted concentrations of reaction products at equilibrium are summarized in Table 6.5. The main solid products anticipated by FactSage were carbon, Na$_2$S and Na$_2$CO$_3$, and the major gas products were H$_2$, CH$_4$, Na, and NaH. The analysis showed that Na$_2$CO$_3$ is one of the products of NaOH activation and Na$_2$S does not participate.
in the reaction with carbon. Na$_2$S has a melting point of 1170°C which could be the reason for staying unreacted during the activation reaction, although experimental analysis of the sulfur content is necessary to confirm its form during the reaction. Other sulfur compounds in the white liquor i.e. Na$_2$SO$_4$, Na$_2$S$_2$O$_3$ and Na$_2$SO$_3$ were not stable and converted into Na$_2$S.

Table 6.5. The amount of the compounds at equilibrium predicted by FactSage for five reaction systems of hydroxide, carbonate and hydroxide, sulfide and hydroxide, carbonate, sulfide and hydroxide and white liquor-C

<table>
<thead>
<tr>
<th>Moles</th>
<th>(A) Hydroxide-C</th>
<th>(B) Carbonate and hydroxide-C</th>
<th>(C) Sulphide and hydroxide-C</th>
<th>(D) Carbonate and sulfide and hydroxide-C</th>
<th>(E) White liquor-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$(g)</td>
<td>1.04</td>
<td>1.04</td>
<td>1.04</td>
<td>1.04</td>
<td>1.01</td>
</tr>
<tr>
<td>Na (g)</td>
<td>0.86</td>
<td>0.86</td>
<td>0.86</td>
<td>0.86</td>
<td>0.38</td>
</tr>
<tr>
<td>NaH (g)</td>
<td>2.19x10$^{-3}$</td>
<td>4.3x10$^{-3}$</td>
<td>4.3x10$^{-3}$</td>
<td>4.3x10$^{-3}$</td>
<td>2.1x10$^{-3}$</td>
</tr>
<tr>
<td>CO (g)</td>
<td>3.99x10$^{-3}$</td>
<td>4.73x10$^{-3}$</td>
<td>3.99x10$^{-3}$</td>
<td>4.16x10$^{-3}$</td>
<td>4.12x10$^{-3}$</td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.152</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>4.6x10$^{-6}$</td>
<td>8.8x10$^{-6}$</td>
<td>8.8x10$^{-6}$</td>
<td>8.8x10$^{-6}$</td>
<td>1.22x10$^{-5}$</td>
</tr>
<tr>
<td>Graphite (s)</td>
<td>7.33</td>
<td>7.33</td>
<td>7.43</td>
<td>7.53</td>
<td>7.12</td>
</tr>
<tr>
<td>Na$_2$S (S)</td>
<td>0</td>
<td>0</td>
<td>0.54</td>
<td>0.54</td>
<td>0.76</td>
</tr>
<tr>
<td>Na$_2$CO$_3$(S)</td>
<td>0.86</td>
<td>1.4</td>
<td>0.86</td>
<td>1.14</td>
<td>1.33</td>
</tr>
</tbody>
</table>

*Initial amount of the compounds (A) 2.6 NaOH-8.33 C (B) 2.6NaOH-0.28Na$_2$CO$_3$-8.33C (C) 2.6NaOH-0.54Na$_2$S-8.33C (D) 2.6NaOH-0.54Na$_2$S-0.28Na$_2$CO$_3$-8.33C (E) 0.05 Na$_2$S$_2$O$_3$-0.07Na$_2$SO$_4$-0.047Na$_2$SO$_3$-0.54Na$_2$S-0.282Na$_2$CO$_3$-2.6NaOH-8.33C
(B) Carbonate and hydroxide-C

(C) Sulfide and hydroxide-C
Figure 6.4. HSC predicted production of Na$_2$CO$_3$ versus NaOH consumption when the temperature increased from 0 to 1000 °C for four activating agents of (A) hydroxide-C, (B) hydroxide and carbonate-C, (C) hydroxide and sulfide-C, and (D) hydroxide, carbonate and sulfide-C

Na$_2$CO$_3$ is one of the major products of the NaOH-activation reaction. Figure 6.4 shows the HSC predicted production of Na$_2$CO$_3$ from NaOH and carbon reaction for four activating agents of (A) hydroxide, (B) hydroxide and carbonate, (C) hydroxide and sulfide, and (D) hydroxide, carbonate and sulfide. Figure 6.4 (A) shows that NaOH activation produces 0.1 mol of sodium carbonate at 1000°C. In Figure 6.4. (B), from the reaction of 0.3 mol NaOH, 0.04 mole sodium carbonate is produced at the temperature of 1000°C. The comparison indicates that, in the latter case, a higher NaOH consumption occurred; however, the amount of the product is lower. It suggests that NaOH is less available for carbon activation and consequently less pore development is expected. The maximum amount of sodium carbonate was produced from the pure NaOH reaction with carbon in the absence of all other chemicals. This result is consistent with the experiments.

The comparison of Figures 6.4 (A) and (C) shows that the amount of Na$_2$CO$_3$ produced over the range of temperatures is very similar for these activating agents. Based on this simulation, Na$_2$S is not expected to affect NaOH activation, although this needs to be
verified with experiments. In Figure 6.4.D), both the production of Na$_2$CO$_3$ and the consumption of NaOH were low compared to the other three activating agents. It confirms the existence of the barrier to the reaction of NaOH and char. More investigations are required to analyze the causes of the barrier.

### 6.3.3 Experimental comparison of white liquor, Na$_2$S-NaOH, Na$_2$CO$_3$–NaOH and NaOH as the activating agent

To further understand the effect of Na$_2$S and Na$_2$CO$_3$ on NaOH activation individually, activated carbon was produced at 800°C and 2 h activation using NaOH, NaOH-Na$_2$CO$_3$, and NaOH-Na$_2$S as activating agents, while keeping the mass ratio of NaOH:C at 3:1. The results are summarized in Table 6.6.

<table>
<thead>
<tr>
<th>Activating agents</th>
<th>SSA (m$^2$/g)</th>
<th>Activation Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3NaOH:C</td>
<td>2310</td>
<td>46</td>
</tr>
<tr>
<td>3NaOH-Na$_2$CO$_3$:C</td>
<td>1784</td>
<td>46</td>
</tr>
<tr>
<td>3NaOH-Na$_2$S:C</td>
<td>1153</td>
<td>50</td>
</tr>
</tbody>
</table>

The surface area of NaOH-Na$_2$CO$_3$ activated carbon was lower than NaOH activated carbon, while the yields were similar. This suggests that Na$_2$CO$_3$ did not affect the reactivity of NaOH but hindered the development of pores. The surface area of NaOH-Na$_2$S activated carbon is half that of the NaOH-activated carbon. This confirms the strong inhibitory effect of Na$_2$S on the pore development. The high yield suggests the lower consumption of carbon in the activation reaction which can be due to a hindering effect of Na$_2$S on the reactivity of NaOH.

### 6.3.4 NaOH-Na$_2$CO$_3$-Na$_2$S Phase diagram

To further understand the difference between Na$_2$S and Na$_2$CO$_3$ in their ability to affect NaOH activation, the Na$_2$CO$_3$-Na$_2$S-NaOH phase diagram was analyzed. As shown in Figure 6.5, this system has a eutectic point at 280°C at the molar composition of 7% Na$_2$S and 7% Na$_2$CO$_3$ and 86% NaOH. NaOH and Na$_2$S form two inter-molecular compounds: Na$_2$S.NaOH and Na$_2$S.2NaOH. Both compounds have a high melting or decomposition point (875 and 675°C). As the white liquor has a molar composition of 75% NaOH, 16% Na$_2$S, and
9% Na$_2$CO$_3$, it is located in the region near Na$_2$S.2NaOH and between the 500 and 735°C tie lines in the phase diagram. The presence of the high-melting point inter-molecular compound could make NaOH less available for carbon activation reaction, which explains the observed high yield with Na$_2$S addition. On the other hand, inter-molecular compounds did not exist between Na$_2$CO$_3$ and NaOH, consistent with the same carbon yield (46%) of NaOH and NaOH-Na$_2$CO$_3$ systems.

![Phase diagram](image)

**Figure 6.5. The Na$_2$CO$_3$-Na$_2$S-NaOH phase diagram (Anderson et al. 1982)**

### 6.3.5 Elemental analyses of the white liquor-activated carbon

To determine the chemical changes during white liquor activation, elemental analyses were carried out for white liquor-activated carbon samples produced at different temperatures, before and after washing. The initial amount of sulfur in the white-liquor and char mixture was about 10 wt%. As shown in Figure 6.6.A, after activation at 600 and 1000°C, the sulfur content dropped from 7.2 to 5.9 wt%, respectively, suggesting the loss of sulfur. This loss in sulfur may be attributed to the formation of H$_2$S gas. It should be pointed out that the elemental analyzer can only detect sulfur that can be oxidized—such as sulfide and that can release SO$_2$ and/or SO$_3$ upon heating to over 1000°C. Na$_2$S is detectable with the
elemental analyzer. After washing the activated carbon samples with water, the sulfur content further dropped to 2% due to the removal of Na$_2$S with washing. Most of the activation by-products, e.g. Na$_2$CO$_3$, were removed from activated carbon by washing.

As discussed previously, at 1000°C, the SSA value increased 4 times with the increasing of the activation time from 1 to 2 h. The elements were measured before and after washing (Figure 6.6.B) to investigate the reason. After washing, the sample obtained with 1 h activation contained less carbon, showing that some of the carbon was not reacted with NaOH and lost in the form of water soluble compounds.

(A) Effect of temperature, 2h activation
Figure 6.6. Effect of the activation temperature (A) and activation time (B) on the elemental contents of activated carbon before and after washing (in legend %C: Carbon, %S: Sulfur, %N: Nitrogen, %R: other compounds)

6.3.6 XRD analyses of activated carbon produced by NaOH and white liquor activation

To identify the activation products, X-ray Diffraction (XRD) analyses of the unwashed activated carbon samples produced from NaOH and white liquor at 1000°C were conducted. The peaks were matched using the XRD database of compounds. As shown in Figure 6.7 and Figure 6.8, in both cases, the main product was Na$_2$CO$_3$. In the case of white liquor activation, Na$_2$S also existed in activated carbon sample before washing. Na$_2$S did not participate in the reactions, consistent with the thermodynamic simulation results.

Figure 6.9 shows the result of XRD analysis for carbon activated with white liquor at 600°C, revealing the presence of Na$_2$S and NaOH and the absence of Na$_2$CO$_3$. The result is expected since at 600°C the rate of NaOH activation reaction would be lower compared to the activation at 1000°C.
Figure 6.7. XRD analysis of unwashed activated carbon with NaOH:C mass ratio of 2:1, 1000 °C

Figure 6.8. XRD analysis of the unwashed activated carbon white liquor: C mass ratio of 4:1, 1000°C
To solve the issues associated with the sludge disposal at the pulp mills, utilizing white liquor as the activating agent was proposed by this work. Providing the activating agent inside kraft mills could improve the economy of the activated carbon production process. However, a large amount of white liquor is needed for the production of activated carbon. Two tonnes of dried white liquor are consumed for the conversion of 1 tonne of the dried pulp mill sludge into activated carbon. This process is anticipated to produce 500kg of activated carbon. The produced activated carbon can be used for the effluent treatment at the pulp mills. One potential option is utilizing activated carbon for the removal of a group of compounds that affect fish reproduction.

6.4 Conclusions

Activation of carbon with synthetic white liquor is feasible. The specific surface area (SSA) of 650 m$^2$/g and an activation yield of 60% were achieved with synthetic white liquor at 600°C in 2 hours. However, the SSA values obtained with white liquor were about 60% lower than that of NaOH alone, suggesting a hindering effect on pore development during activation.
Thermodynamic simulations showed that sodium sulfide and sodium carbonate could hinder the porosity development. Under the activation conditions, sodium sulfide was inert and unable to participate in reactions with carbon based on thermodynamic simulations. Its presence in white liquor would make NaOH less available to the activation reaction with carbon. Sodium sulfide can form two inter-molecular compounds with NaOH, which have a melting or decomposition point of 675 and 875°C. Consequently, these compounds could make NaOH less reactive and less available for the activation reaction with carbon.

While being a key component of white liquor, Na$_2$CO$_3$ is also a main product of NaOH activation. Its presence in white liquor could affect equilibrium and hindered the development of pore during NaOH activation. Na$_2$CO$_3$ may become reactive with carbon when the temperature is over 1000°C.

XRD analyses confirmed the presence of both Na$_2$CO$_3$ and Na$_2$S in carbons activated at 1000°C with white liquor as the activating agent. At 600°C, the rate of the NaOH activation reaction would be too low to produce Na$_2$CO$_3$. 
Feasibility Study of Utilizing Pulp Mill Sludge-derived Activated Carbon to Remediate the Effect of Effluent on Fish Reproduction

Abstract

It is known that a group of unidentified organic compounds in some pulp mill effluents affect fish reproduction. Towards the development of a remediation strategy, this work was conducted to determine the effectiveness of pulp mill sludge-derived activated carbon in removing the effluents' effect on fathead minnow egg production and to compare the efficiency with a commercial activated carbon. Chemical activation with KOH was able to convert a set of pulp mill sludges into activated carbon that has physical characteristics similar to the commercial activated carbon. After treatment with activated carbon, effluent samples were analyzed using gas chromatography to estimate their total organic content. The NKS-activated carbon was particularly effective in removing dissolved organics by approximately 35% compared to the other produced activated carbon. A commercial activated carbon was used in trials to assess potential remediation strategies. Five-day reproduction tests on fathead minnows revealed that effluent treatment in a fixed bed reactor with a contact time of 0.54 minutes and a dosage not less than 5 g/L was sufficient to eliminate effects on fish reproduction tested by the short term assay. Therefore, the use of sludge-derived activated carbon is a technically feasible means to eliminate effluent effects on fish.

7.1 Introduction

It is well established that some unidentified chemicals in the pulp mill effluents affect fish reproduction (Kovacs et al. 2005; Fentress et al. 2006; Hewitt et al. 2008; Hall et al. 2009). The fish reproduction disruption has been reported in several pulp mills around the world (Hewitt et al. 2008; Chiang et al. 2010). In Canada, the regulatory Environmental Effects Monitoring (EEM) program showed that some pulp mill effluents have the potential to cause metabolic disruption in fish as evidenced by reducing gonad size, and increasing liver size (Lowell et al. 2003; Fox 2001; Kovacs et al. 2007). Several biological tests have
been applied by various research groups, which have led to questions about characteristics of these compounds and their sources (Dubé & Maclatchy 2001; Rickwood et al. 2006).

A remediation strategy to solve this problem has not been developed yet, mainly due to the lack of knowledge about the responsible compounds and their sources as well as the absence of a cost-effective way to remove the adverse effects of these compounds (Milestone et al. 2012). The investigation for causative agents has been focused on the pulp mill effluent composition and manufacturing processes through monitoring effluent quality at the mills in Canada (Hall et al. 2009; Kovacs et al. 2010).

Kovacs et al. (2011) showed that the gas chromatography (GC) index of an effluent is a representative of total organic content of effluent and it is correlated to the effect of effluent on fathead minnow egg production. The effluent monitoring studies showed that the total content of solvent-extractable organics in the pulp mill effluent is linked to the level of adverse effect on fish reproduction using a laboratory assay (Kovacs et al. 2011). The effluent’s effect on fish reproduction varies from one mill to another. It is caused by the effluent total amount of organics and is not related to the manufacturing and biotreatment process at the mills. The effect of the effluent on fish reproduction was positively correlated to total organic content as measured by biochemical oxygen demand (BOD) and the sum of GC peak areas of solvent-extracted effluents (Kovacs et al. 2011; Martel et al. 2011).

Kovacs et al. (2011) analyzed the effect of seven mills effluent exposure to fathead minnows. Their investigation indicated that four of the effluents did not significantly affect fish reproduction while others lowered or stopped fish reproduction. Total organic content and BOD level (< 20 mg/L) in the effluent were used as indicators of the effluent quality. Total organic content can be indicated with the GC index. Interestingly, fish reproduction disruption was reversible by improving the effluents quality (Kovacs et al. 2011).

Activated carbon is widely used to remove organics and bioactive compounds from water (Tanghe & Verstraete 2001; Asada et al. 2004; Choi et al. 2005; Fukuhara et al. 2006). Activated carbon from delayed petroleum coke removed higher than 90% of chlorinated
organic and color compounds from bleached pulp mill effluent. Pore size distribution, surface chemistry, and ash content are the most important factors related to the extent of adsorption of organic compounds (Shawwa et al. 2001). The adsorption capacity depends on the accessibility of the organic molecules to carbon surface and their size (Ren et al. 2007). Although the exact compositions of compounds that disrupt fish reproduction are not identified, adsorption by activated carbon seems to be an effective method of removing them from final effluents.

Pulp mills produce 40-50 kg of dry sludge per ton of pulp production (Monte et al. 2009). Managing the sludge disposal is costly and environmentally challenging. Conversion of pulp mill sludge into activated carbon for organic removal from pulp-mill effluents could be beneficial (Hojamberdiev et al. 2008). Currently the sludge is simply being burned or landfilled and such practices can cause environmental problems and greenhouse gas emissions (GHGs) (Monte et al. 2009). One potential alternative is using the pulp mill sludge for production of activated carbon, which could then be used as an adsorbent at the pulp mills. The feasibility of activated carbon production from pulp mill sludge has been studied in the past, along with the effect of operating conditions on the surface area of the produced activated carbon (Namazi et al. 2010).

The objective of this work is to determine the effectiveness of pulp mill sludge-derived activated carbon in removing pulp mill effluent compounds that affect fish reproduction. The activated carbon was produced from various pulp mill sludges under optimized conditions at University of Toronto. The sludge-derived carbon and a commercial activated carbon were evaluated for their ability to remove dissolved organics from pulp mill effluent at Forest Product Innovations (FPInnovations). Fathead minnow egg production tests were conducted with effluents treated with the commercial activated carbon to determine the feasibility of eliminating the disruptive effect of effluent on fish reproduction.
7.2 Materials and methods

7.2.1 Production and characterization of pulp mill sludge-derived activated carbon

Three sludge samples were collected from a kraft and a linerboard recycling mills in Ontario, Canada, and stored at -4 °C before analyses. The sludge samples were dried overnight at 110°C in the oven before analysis. The proximate analysis indicated the major components of a biomass. The dried sludge samples were characterized for their total ash, volatile matter, and fixed carbon, using standard methods (ASTM D3174-04 for ash analysis and ASTM D3175-89a for volatile matter). The ultimate analysis indicated the elemental composition of a biomass. Carbon, Oxygen, Sulfur and Nitrogen were determined by an elemental analyzer.

Pulp mill sludge samples were converted into activated carbon by a two-stage process developed earlier by Namazi et al. (2010). This process was developed and optimized at the University of Toronto and consisted of a carbonization stage at 400 °C for 4 h followed by a KOH chemical activation at 600 °C for 2 h. The effectiveness of the activation process was quantified using carbonization and activation yields, defined as follow:

\[
\text{Carbonization yield (\%)} = \frac{\text{Mass of char after carbonization}}{\text{Mass of dried raw material}} \times 100
\]

\text{Equation 7.1}

\[
\text{Activation yield (\%)} = \frac{\text{Mass of activated carbon produced}}{\text{Mass of dried raw material}} \times 100
\]

\text{Equation 7.2}
The produced activated carbon was characterized for specific surface area (SSA) and porosity using nitrogen adsorption isotherm data obtained with a surface analyzer (AUTOSORB 1). The samples were degassed at 200 °C for 2 h prior to the measurements. The Brauner, Emmett and Teller (BET) and Barrett, Joyner and Halenda (BJH) methods were used for surface area and pore size distribution measurements, respectively (Brunauer et al. 1938).

7.2.2 Adsorption of organic compounds from effluent by sludge-derived activated carbon

The potential of sludge-derived activated carbon in removal of the effluent compounds that affect fish was tested by batch adsorption experiments. The experiments were conducted by adding 0.1 g of the activated carbon to 100 mL effluent under well-mixed conditions in a shaker with 120 rpm for 17 h at 30 °C. The organic removal from pulp mill effluent was tested using three types of sludge-derived activated carbon along with a commercial activated carbon derived from coconut shell. The activated carbon particle size was less than 200 µm. Treated effluent samples were prepared for quantification of total dissolved organics using GC analysis.

7.2.2.1 Quantification of dissolved organics in effluents

Dissolved organics in the effluent samples were concentrated by liquid-liquid extraction to prepare them for GC analyses. 250 mL treated effluent was transferred to a separatory flask. One hundred mL methyl tert-butyl ether (MTBE-Fisher Scientific Canada) and an internal standard consisting of heneicosanoic acid (C21) and tricosanoic acid methyl ester (C23) as a methylation surrogate were added to the separatory flasks. After shaking for two minutes, the solvent was separated in a round bottom flask and the extraction was repeated. The solvent was removed by rotary evaporation at 30 °C under vacuum of 45 mmHg, and flasks containing the extractives were further dried in nitrogen stream to a final volume of 2 mL and transferred to a conical vial. Finally, the extract was evaporated under a nitrogen stream to a final volume of approximately 1.5 mL (Ankley et al. 2009).
7.2.2.2 Gas chromatography (GC) analyses of extracted organics

The organic extract from the samples including activated carbon treated samples, raw effluent, and control samples were analyzed by the GC. The GC used in this work was Hewlett Packard 6890+ GC with 5973 Mass Selective Detector. A sample of 1 µL was injected into the GC under the following conditions. The inlet temperature was 250 °C Inlet, splitless. The oven condition was 45 °C hold for 10 min, increased 5 °C/min to 290 °C hold for 20 min, 1.3 mL/min flow, and MS detector (HP 5973) in TIC mode 40-610 m/z. The peaks in each chromatogram were integrated and normalized based on the peak area of C21 standard for analyses.

The GC index does not provide information about individual compounds, but instead provides a useful measure of total compounds in the effluent that were detectable by GC. The total peak area of the chromatogram of each effluent was determined for the purpose of developing a relative estimate of total extractable organic content or the GC index. The total peak area of the raw effluent, which had the highest peak area, was assigned a GC index value of one, while other samples’ GC indices were calculated in relation to that.

\[
\text{Correction factor} = \frac{\text{C21 peak area of the sample}}{\text{C21 peak area of the reference effluent}}
\]

Equation 7.3

\[
\text{GC index} = \frac{\text{Correction factor} \times \text{GC area of the sample}}{\text{GC area of the reference}}
\]

Equation 7.4

7.2.3 Fish reproduction tests with activated carbon-treated effluents

Bio-treated effluent samples of 2000 L were collected from a thermo-mechanical pulp mill on two different dates and sent for testing the day after sampling. The effluent samples were screened using 210 µm mesh and stored at 4 °C. The effluent samples were labeled “effluent I” and “effluent II” and their characteristics are summarized in Table 7.1.
The two samples were similar particularly in their Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD). The NH₃ and suspended solids (SS) were different for the two effluent samples, but it was proved that they are not related to fish reproduction disruption effect (van den Heuvel 2010).

Table 7.1. Characteristics of two bio-treated thermo-mechanical pulp mill effluents

<table>
<thead>
<tr>
<th>Effluent</th>
<th>pH</th>
<th>Hardness (mg/L)</th>
<th>NH₃ (mg/L)</th>
<th>COD (mg/L)</th>
<th>DO (mg/L)</th>
<th>BOD (mg/L)</th>
<th>SS (mg/L)</th>
<th>Colour (CU)</th>
<th>Conductivity (μS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effluent I</td>
<td>6.8</td>
<td>94</td>
<td>6.1</td>
<td>425</td>
<td>3.5</td>
<td>16</td>
<td>24</td>
<td>809</td>
<td>911</td>
</tr>
<tr>
<td>Effluent II</td>
<td>6.7</td>
<td>90</td>
<td>3.4</td>
<td>445</td>
<td>4.2</td>
<td>13</td>
<td>7</td>
<td>800</td>
<td>865</td>
</tr>
</tbody>
</table>

7.2.3.1 Treatment of effluent with activated carbon

Six activated carbon columns were used in this set of experiments to find out the optimum amount of activated carbon and contact time needed to remove the effluent effect. A commercial activated carbon derived from coconut shell (FPI) was used to treat the effluent for the fish reproduction tests. The activated carbon was rinsed to remove carbon dust and soaked in distilled water for 24 h to impregnate the pores of the carbon with water. The activated carbon was then packed in a column reactor while the effluent was introduced from the top. The flow rate of effluent through the column was kept constant at 500 mL/min. The amount of carbon in the column was determined based on the carbon dosage which varied from 1 to 100 g/L. The columns characteristics are summarized in Table 7.2.
Table 7.2. Characteristics of activated carbon columns

<table>
<thead>
<tr>
<th>Test code</th>
<th>Carbon mass (kg)</th>
<th>Bed volume (L)</th>
<th>Bed diameter (cm)</th>
<th>Bed height (cm)</th>
<th>Treated effluent volume (L)</th>
<th>Treated effluent label</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.25</td>
<td>0.55</td>
<td>5</td>
<td>28</td>
<td>250</td>
<td>I</td>
</tr>
<tr>
<td>B</td>
<td>2.5</td>
<td>5.82</td>
<td>15</td>
<td>33</td>
<td>500</td>
<td>I</td>
</tr>
<tr>
<td>C</td>
<td>2.5</td>
<td>5.82</td>
<td>15</td>
<td>33</td>
<td>250</td>
<td>I</td>
</tr>
<tr>
<td>D</td>
<td>2.5</td>
<td>5.82</td>
<td>15</td>
<td>33</td>
<td>250</td>
<td>II</td>
</tr>
<tr>
<td>E</td>
<td>12.5</td>
<td>33.91</td>
<td>40</td>
<td>27</td>
<td>250</td>
<td>II</td>
</tr>
<tr>
<td>F</td>
<td>25</td>
<td>63.58</td>
<td>45</td>
<td>40</td>
<td>250</td>
<td>II</td>
</tr>
</tbody>
</table>

7.2.3.2 Fish exposure to the treated effluent

Fathead minnow exposure tests were carried out for five days in water, untreated effluent, and activated carbon treated effluents. The test is a potential indicator of adverse reproductive effect caused by the effluent (van den Heuvel et al. 2010). Fish reproduction tests were adapted from a procedure described by Kovacs et al. (2007). The tests were initiated by forming groups of four adult females and two adult males. These groups were kept in water for eight days as the pre-exposure phases, during which time egg production was monitored. The egg production ranged from one to 80 eggs per female per day and 2–8 spawns. At the end of the pre-exposure phase, groups that demonstrated consistent egg production capacity of 27–80 eggs per female per day and 6–8 spawns were randomly assigned to control water, untreated effluent, and the effluent treated with the commercial activated carbon. In each experiment there was one replicate of control and effluent-exposed fish, each replicate being represented by a 12.5 L aquarium four females and two males. During the five day exposure tests, the water and the effluents in the aquaria were aerated at a rate of 6.5 mL/min/L to ensure higher than 70% oxygen saturation. The pH of the control water was 8.3 and the effluent pH ranged from 6.7 to 7.9 and pH does not exert an effect on fish reproduction disruption. The fish were fed freshly hatched brine shrimp (Artemia salina) three times daily. During the test, egg production was monitored daily. At the end of the test, the numbers of the eggs and spawns per female per day were determined.
7.3 Results and discussions

7.3.1 Production and characterization of activated carbon from pulp mill sludge

The results of proximate and ultimate analyses of dried raw materials are shown in Table 7.3. Among the three pulp mill sludge samples, primary sludge had the highest fixed carbon and the lowest elemental carbon whereas secondary sludge was the opposite. The ash content of all sludge samples was over 18%, which is high for the purpose of activated carbon production. Both the fixed carbon % and volatile matter contain carbon. The fixed carbon is basically the char formed by proximate analysis, while elemental carbon is determined in ultimate analysis. It is important to retain more carbon during the process of pyrolysis and activation. The yield of activated carbon should be within these two values. The other compounds composing the 100% in ultimate analysis included hydrogen, heavy metals, etc.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Proximate analysis (%)</th>
<th>Ultimate analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed carbon (%)</td>
<td>Ash (%)</td>
</tr>
<tr>
<td>Linerboard recycled sludge</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>News and kraft primary sludge</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>News and kraft secondary sludge</td>
<td>5</td>
<td>25</td>
</tr>
</tbody>
</table>

For both of the news and kraft sludge samples, the carbonization yield was close to the sum of carbon and ash contents. As shown in Table 7.4, secondary sludge had the highest carbonization yield of 59% among all the sludge samples, which could be explained by its high elemental carbon content of 40%. Assuming the 25% ash remains after carbonization, 34% of the solid after carbonization were attributed to carbon, which is very close to its elemental carbon content of ~40% and much greater than its fixed carbon content of 5%. The
observation suggests that the carbonization process was very effective in retaining carbon from volatile matters, via carbon condensation during carbonization.

It was expected that carbonization yield will be greater than activation yield for all three sludge samples due to carbon loss during activation which is basically a carbon oxidation process. The ash content of the activated carbon from Linerboard recycled sludge was 10% ± 2 which indicated that acid washing during the production of activated carbon has removed part of the initial ash content.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Carbonization yield (%)</th>
<th>Activation yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linerboard recycled sludge</td>
<td>42±4</td>
<td>25</td>
</tr>
<tr>
<td>News and kraft primary sludge</td>
<td>50±3</td>
<td>40</td>
</tr>
<tr>
<td>News and kraft secondary sludge</td>
<td>59±6</td>
<td>26</td>
</tr>
</tbody>
</table>

The yield results were comparable to those using similar waste biomass. Table 7.5 shows the yield of production of activated carbon from several biomasses. The activated carbon yield is in the range of 4-26% depending on the raw material properties and activation method.

<table>
<thead>
<tr>
<th>Reference</th>
<th>(Salman &amp; Hameed 2010)</th>
<th>(Khezami et al. 2007)</th>
<th>(Okada et al. 2003)</th>
<th>(Tay et al. 2009)</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>Oil frond</td>
<td>palm</td>
<td>Virgin wood</td>
<td>fir</td>
<td>Waste newspaper</td>
</tr>
<tr>
<td>KOH:C mass ratio</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Activation yield</td>
<td>18%</td>
<td>23%</td>
<td>10%</td>
<td>4%</td>
<td>25-40%</td>
</tr>
</tbody>
</table>

Table 7.6 shows the specific surface area (SSA) and porosity of the activated carbon used for the adsorption experiments. The activated carbon was produced by this work, except for the FPI carbon which is a commercial activated carbon. The porosity of the various
activated carbons were categorized into three groups based on the system proposed by IUPAC: micropores with pore diameter less than 2 nm, mesopores with pores between 2 and 50 nm, and macropores with pores greater than 50 nm. Among the sludge-derived activated carbons, secondary sludge activated carbon had the highest pore volume and specific surface area. With KOH chemical activation, NKS reached a porous surface close to that of the commercial activated carbon.

Table 7.6. Specific surface area (SSA) and porosity of activated carbon applied for the removal of compounds affecting fish reproduction

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Raw materials</th>
<th>SSA (m²/g)</th>
<th>Micropore volume (cc/g)</th>
<th>Mesopore volume (cc/g)</th>
<th>Macropore volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIN</td>
<td>Linerboard recycled sludge</td>
<td>570</td>
<td>0.39</td>
<td>3.61</td>
<td>0.40</td>
</tr>
<tr>
<td>NKP</td>
<td>News and kraft primary sludge</td>
<td>250</td>
<td>0.09</td>
<td>1.60</td>
<td>0.35</td>
</tr>
<tr>
<td>NKS</td>
<td>News and kraft secondary sludge</td>
<td>770</td>
<td>0.45</td>
<td>4.46</td>
<td>0.70</td>
</tr>
<tr>
<td>FPI</td>
<td>Commercial coconut shell</td>
<td>1000</td>
<td>0.62</td>
<td>4.1</td>
<td>0.73</td>
</tr>
</tbody>
</table>

7.3.2 Adsorption of dissolved organics from the pulp mill effluent by activated carbon

The GC index was used to quantify the fraction of remaining organic compounds that may affect fish reproduction. Figure 7.1 illustrates GC profiles and GC indices of effluent samples before and after treatment with activated carbon.

In order to provide a relative scale, the GC index was normalized to that of the raw effluent, so the GC index of the raw effluent is one. Samples of activated carbon treated effluent had lower GC index than one, demonstrating that part of the organics were removed from the effluents. The GC index of the FPI-treated effluent (0.41) showed that its performance in the removal of effluent organics is lower than LIN and NKS activated carbon with GC indices of 0.35 and 0.26, respectively.
Figure 7.1. GC profiles and GC indices of effluent and activated carbon treated effluents

Table 7.7. GC indices of activated carbon treated effluents and P-value

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>GC Index</th>
<th>P value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NKP</td>
<td>0.6±0.09</td>
<td>0.052</td>
</tr>
<tr>
<td>NKS</td>
<td>0.29±0.04</td>
<td>0.001</td>
</tr>
<tr>
<td>LIN</td>
<td>0.37±0.03</td>
<td>0.001</td>
</tr>
<tr>
<td>FPI</td>
<td>0.44±0.04</td>
<td>0.003</td>
</tr>
<tr>
<td>Effluent</td>
<td>1</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*P<0.05 indicates statistically significant difference

The adsorption experiments were repeated three times and the GC indices were calculated and summarized in Table 7.7. Statistical t-tests showed that NKS, LIN and FPI-activated carbon had a statistically significant effect on removal of the organics from the
effluent. However NKP \( (p = 0.052) \) did not have significant effect probably due to its low surface area of \( 250 \text{ m}^2/\text{g} \). Most of the sludge-derived activated carbon samples were effective in removing the effluent compounds that were detectable by GC. Surface area played a key role in determining the effectiveness of organic removal. The NKS was more capable in removing the effluent compounds than the commercial one, although it had a smaller specific surface area of \( 770 \text{ m}^2/\text{g} \). Since the organic molecules have larger diameters, the high mesopore and macropore volumes of the secondary sludge activated carbon were expected to be beneficial in removal of the effluent compounds.

### 7.3.3 Effect of activated carbon treated effluent on fish reproduction

The fish reproduction tests required large amount of activated carbon which was not possible to produce in lab scale. Therefore the commercial carbon with similar properties to the NKS was used for fish reproduction tests. Six fish reproduction tests were conducted with effluent treated with the commercial activated carbon in a fixed bed reactor. Carbon dosage, contact time, effluent type, and number of passes through the activated carbon column were changed for each test.

Table 7.8 shows the conditions of the effluent treatment with various carbon dosages from 1g/L to 100g/L. The contact time varied from 0.05 to 6 minutes, depending on carbon dosage and flow rate in the fixed bed reactor. The number of passes through the column represents the ratio of the treated effluent to the carbon bed volume and shows carbon usage for treatment of the raw effluent. Test D was a repeat of Test C, but with Effluent II. As shown in the experimental section, effluents I and II were collected from the same mill on different dates and had similar properties.
Table 7.8. Conditions of activated carbon treatments (1-100g/L)

<table>
<thead>
<tr>
<th>Test code</th>
<th>Carbon dosage (g/L)</th>
<th>Contact time (min)</th>
<th>Number of passes through the column</th>
<th>Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>0.05</td>
<td>428</td>
<td>I</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>0.54</td>
<td>85</td>
<td>I</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>0.54</td>
<td>42</td>
<td>I</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>0.54</td>
<td>42</td>
<td>II</td>
</tr>
<tr>
<td>E</td>
<td>50</td>
<td>3.18</td>
<td>8</td>
<td>II</td>
</tr>
<tr>
<td>F</td>
<td>100</td>
<td>5.97</td>
<td>4</td>
<td>II</td>
</tr>
</tbody>
</table>

Figure 7.2. Fish reproduction test results- control I and II showed the reproduction in water. For each test the carbon dosage and contact time are : A 1g/L and 0.05 min, B 5g/L and 0.054min, C 10g/L and 0.054min, D 10 g/L and 0.054min, E 50g/L and 3.41min, F 100g/L and 6.27 min

Figure 7.2 shows the results of six fish reproduction tests conducted with the treated effluents along with two tests with untreated effluents and two control tests in well water. The adverse effect of the raw effluent on fish reproduction was clearly evident from the data. Egg production could be considered as normal when the mean egg production per female was in the range of 19-74 per day with the standard error of 15 based on Kovacs et al.’s (2011)
analyses on egg production. Activated carbon treatment of effluent showed a significant improvement in egg production compared to the untreated effluent. The only exception was test A where the carbon dosage was 1g/L and the contact time was 0.05 min. When 5 g/L or more activated carbon was used, no significant difference from the control test was observed. The results of Tests C and D were very similar, confirming the repeatability of the test.

At 1 g/L with a contact time of 0.05 min, the activated carbon was not capable of removing the effect on fish reproduction. However, a contact time of 0.54 minutes was sufficient to remove the effect if the carbon dosage was not less than 5 g/L. Overall, the five-day fish reproduction tests revealed that the treatment of the effluent with the activated carbon was able to eliminate the adverse effects and allowed normal egg production, if the amount of activated carbon is more than 5g/L. The sludge-derived carbon has been proven to be more or equally effective in removing the effluent compounds compared to the commercial activated carbon, therefore pulp mill sludge can be used to generate activated carbon that removes adverse effect on fathead minnow egg production. Further research would be required to investigate the minimum or optimal carbon dosage and/or contact time as the main controlling factors in the adsorption of these compounds.

A large amount of activated carbon is needed to remove this effluent’s effect on fish reproduction. Assuming that 20,000 L of effluent is generated from the production of one ton of pulp, and 5g/L activated carbon is required for the removal of the effect of pulp mill effluent on fish, 100 kg of activated carbon is needed to remove the effect of the effluent per ton of pulp. For example, if a pulp mill produces 700 tonnes of pulp per day, 70 tonnes of activated carbon would be needed per day to remove the effect of pulp mill effluent on fish reproduction in one mill, which is clearly an impractical method for treatment. However, the opportunity for applying this research to practice lies in the application of the pulp mill derived carbon to specific mill streams.

Future work can be focused on treating the key effluent streams that can be treated and determining the optimal activated carbon load required. One of the possible key streams could be the condensates. Dube et al. (2001) exposed mummichog to dilutions of reverse
osmosis feed and permeate of bleach kraft pulp mill and showed that some condensates depress plasma testosterone concentrations. The compounds were mainly low molecular weight phenolics, including phenols and guaiacol. Another valuable subject for research would be the regeneration of spent activated carbon.

7.4 Conclusions

With KOH chemical activation, pulp mill sludge-derived activated carbons were able to reach the porosity similar to that of a coconut shell-derived commercial activated carbon.

The sludge-derived activated carbon was effective in removing organics that may affect fish reproduction. The secondary sludge-derived activated carbon showed the highest removal of the organics for the batch experiments of 250mL effluent treatment overnight. Surface area played a key role in determining the effectiveness of the organic removal that affects fish reproduction.

The secondary sludge-derived activated carbon was comparable to the commercial one in the removal of the organic compounds, although the commercial carbon had a higher specific surface area (~1000 m²/g) than the NKS-activated carbon (~770 m²/g).

The five days fathead minnow reproduction tests revealed that the treatment of effluent with the activated carbon column was able to eliminate the adverse effect and allow normal egg production, if a sufficient amount of activated carbon (5g/L) was added.
8 Overall Conclusions

This work explored the technical feasibility of producing activated carbon from pulp mill sludge with microwaves as the energy source and white liquor as the activating agent. The main conclusions are as follows:

Production of activated carbon from various pulp mill sludge samples is feasible with using the common activating agent, KOH. Activated carbon properties i.e. Specific Surface Area (SSA) and yield, strongly depend on the type of pulp mill sludges. The highest surface area was 770 m$^2$/g obtained from news and kraft secondary sludge and cow manure, which was in the range of the commercial activated carbon. The overall yield varied from about 20 to 40 wt%, depending on the activation conditions.

Microwave pyrolysis of pulp mill sludge is not possible without the addition of a microwave absorber like KOH. Pulp mill sludge and wood polymers are weak absorbers of microwave radiation with small loss tangent of less than 0.1. Adding a well dispersed alkali metal hydroxide enabled pyrolysis and improved the heating uniformity of the sludge. The properties of the char produced by microwave pyrolysis are controlled by the amount of microwave absorber, heating time, microwave power, and raw material properties such as ash content, density, composition and microwave absorbability. Combining pyrolysis with activation is recommended, considering the need to add a microwave absorbing agent during pyrolysis.

Activated carbon can be produced from pulp mill sludge using microwaves with KOH or NaOH activation. The activation yields for NaOH or KOH activation were in the range of 40-70 wt% or 60-80 wt%, respectively. The highest SSA achieved from NaOH-activation was 2300 m$^2$/g. In this work, NaOH was found to be more effective in pore development compared to KOH; although KOH has been reported to be a better activating agent for many precursors.

Activated carbons produced with both microwave oven and conventional furnace had similar properties in terms of SSA and yield. The surface area of NaOH-activated carbon was
60% and 15% higher than the KOH-activated carbon produced in microwave oven and conventional furnace, respectively. The total processing time with the microwave oven, however, was from 3 to 5 minutes, compared to 1 to 2 hours with conventional furnace, suggesting a potentially significant non-thermal effect of microwaves on activation reaction.

A new pressure-based temperature probe was designed, fabricated and used for measuring the temperature of lignocellulosic materials heated in microwave oven. A 3-D model was developed to simulate the temperature distribution in samples heated in microwave oven using COMSOL multiphysics 4.4. The simulated temperature versus time agreed with the one that was measured with the probe. Simulation results demonstrated that microwave radiation would result in a non-uniform temperature distribution even after reaching the plateau, which is different from heating in a conventional furnace. The degree of non-uniformity would change with thermal properties of samples, such as heat conductivity and capacity, as well as the location of sample in the microwave oven.

The activated carbon produced with white liquor at the optimum conditions had the SSA of 650 m$^2$/g and an activation yield of 61%, while activating the same sample with NaOH yielded an activated carbon with an SSA of 2100 m$^2$/g and activation yield of 48% under similar conditions. With the aim of reusing available pulp mill chemicals, the simulated recycled white liquor with NaOH (53 wt%), Na$_2$S (21 wt%), and Na$_2$CO$_3$ (15 wt%) was used for activation of pulp mill sludge. The experimental and thermodynamic analyses showed that the lower surface area of white liquor-activated carbon was attributed to the hindering effect of both Na$_2$S and Na$_2$CO$_3$ on the availability and reactivity of NaOH in white liquor.

The sludge-derived activated carbon was effective in removing these compounds, with the secondary sludge-derived activated carbon being the most effective case with up to 70% removal based on the GC index measurements. The applicability of sludge-derived activated carbon in effluent treatment was tested with the actual pulp mill effluent that was known to contain compounds that affect fish reproduction. The five-day fathead minnow reproduction tests revealed that treating the final effluent with 5 g/L activated carbon in a packed bed reactor eliminated the adverse effect and normal egg production was resumed.
9 Implications and Recommendations

Pulp mills produce large amount of waste every day that causes environmental and economic issues. This work investigated the production process of activated carbon from the pulp mill sludge. Utilizing pulp mill sludge for production of activated carbon not only reduces the amount of waste that is generated, but also addresses the removal of effluent contaminants.

This work analyzed the effect of pulp mill sludge source and composition on the produced activated carbon. In this work, it was shown that the activated carbon produced from the same pulp mill treatment plant had similar properties (surface area and yield). The operating conditions for activated carbon production with conventional furnace were investigated. The activating agent ratio to carbon was identified as the most important factor in surface area development. KOH-chemical activation of pulp mill sludges generates activated carbon with similar properties to the commercial products. However, drying of the sludge, thermal treatment duration, and activating agent cost might negatively affect the economics of the process and further works should investigate the cost effectiveness of the process.

In order to potentially improve the process of activated carbon production, microwave radiation was used for pyrolysis and activation of the sludge. The challenge of using microwave radiation is the uniformity of the temperature distribution inside samples. In the pyrolysis process, the produced chars had a low uniformity. The uniformity was enhanced by modifying the properties of sludge such as increasing microwave absorbability and grinding of the sludge. In contrast to the conventional method, the produced chars by microwave radiation had lower retained carbon of 10%; however the pyrolysis process was 12 times faster in a microwave. Using microwave fluidized bed reactor for pyrolysis and activation is recommended to improve the uniformity of the product.

The chemical activation process by microwave radiation was investigated and compared with the conventional furnace activation. The produced activated carbon by both
methods had similar properties (surface area and yield), when using the same activating agent ratio to carbon. Interestingly, the activated carbon production in a microwave oven was 12 times faster than conventional furnace. The homogeneity of produced activated carbon was comparable for the two methods, because the addition of alkali hydroxides as the activating agent caused uniform heating in a microwave oven. The thermal runaway was the challenge that needs to be controlled during microwave activation. Another benefit of the microwave processing is that the pyrolysis and activation could be combined. However, in the conventional furnace and microwave activation, the combination of the two steps has lowered the surface area of the activated carbon. Economic analysis of microwave assisted and conventional activation showed that the ROI of the processes are 17.3 and 18 %, respectively (calculations are presented in Appendix D).

Utilizing white liquor as the activating agent was proposed by this work to provide the activating agent inside kraft mills and improve the economics of activated carbon production process. The benefits of using white liquor are that its recycling process has been established at the pulp mills for many years and it contains 50% sodium hydroxide. This work has found that white liquor is not an effective activating agent even though it contains 50% sodium hydroxide, which is shown to be a suitable activating agent for sludge activation. The thermodynamic analysis by FactSage and HSC demonstrated that some of the white liquor compounds (Na₂S and Na₂CO₃) inhibit the activation reaction. Therefore, considering other types of activating agents at the pulp mills for the production of activated carbon is recommended.

The performance of the produced activated carbon was analyzed by the removal of the effluent compounds that affect fish reproduction. In some of the pulp mill effluents, a group of compounds has been shown to affect fish reproduction. The elimination of these compounds at the sources has not yet been established. Currently, the best practice could be the removal of these compounds from the final effluent. Since the individual compounds are unknown, the GC index was used as the indicator of the total amount of these compounds that affect fish reproduction. An adsorption study in this work showed that several produced activated carbons can reduce the GC index to the level of pure water. Additionally, 5 days
fish exposure experiments indicated that activated carbon is able to remove the effect of these compounds on fish. The amount of activated carbon needed for the removal process can be optimized by targeting specific suspicious streams at the pulp mills. The removal of compounds that affect fish reproduction with produced activated carbon is a good example of their applicability at the pulp mills.

The following works are recommended for future research:

1. Study the behavior of biologically treated-biomass, such as municipal secondary sludge, during microwave-assisted pyrolysis and activation. Such a study will help elucidate the contributions of various wood polymer and proteins to the production of activated carbon.

2. Analyze the possibility of using a lower amount of chemical activating agent by combining physical and chemical activation process and soaking the char into the activating agent prior to activation.

3. Combine a fluidized bed reactor with microwave for pyrolysis and activation. Study the effect of fluidization on product uniformity. Investigate the potential benefit of intermittent microwave radiation in improving product uniformity.

4. Analyze the possibility of producing bio-oil using microwave pyrolysis which is a faster process. A fast pyrolysis might favor the production of bio-oil. The operating conditions of microwave pyrolysis need to be analyzed to find out the optimum conditions for bio-oil production.

5. Investigate the other chemicals readily available at pulp mills as activating agents. The surface area of activated carbon produced with white liquor was lower than the NaOH-activated carbon. The surface area may be improved by using other possible activating agents available at pulp mills.

6. Identify the wastewater streams within pulp mills that are the sources of compounds that affect fish reproduction. This would reduce the amount of water that needs treatments and therefore the amount of activated carbon required.
References


Arrougé, T., Moresoli, C., Soucy, G., 1999. Primary and secondary sludge composting: A feasibility study Suggestions are offered on how to reduce the disposal problem, Pulp and Paper Canada 100(4), 33-36.


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Appendices

Appendix A - Power distribution inside microwave oven

The power was measured by heating 200mL of water in a cylindrical beaker for 1 min. The temperature rise was recorded and the power was calculated shows the power variation inside microwave oven. The power inside microwave oven was estimated by an energy balance, when heating a constant mass of distilled water inside microwave.

\[ P_{\text{abs}} = \rho \ C_p \ \frac{dT}{dt} \]

\[ \text{Figure A.1. Power variation inside microwave oven calculated based on the heating of 200mL water} \]

The electric field inside microwave oven can be calculated from the energy balance in knowing that for water \( \varepsilon' = 78, \varepsilon'' = 12 \) at frequency of 2.45GHz.

\[ 2\pi f \varepsilon'' \varepsilon_0 E^2 = \rho \ C_p \ \frac{\Delta T}{\Delta t} \]

Equation A.1
where $\rho$ and $C_p$ are density and heat capacity of water, respectively. $t$ is the heating time, $P_{abs}$ shows the power absorbed by the material, and $2\pi f E^2$ is related to microwave oven properties. For our Panasonic microwave at the power of 1200W, a general absorbed power into the surface of the material can be derived as:

$$P = 0.28 \varepsilon$$
Appendix B- Mesh for the simulation studies

The selected mesh for this work was free tetrahedral. The domain characteristics of the mesh in the modeling are summarized in Table B.1.

![Meshing used in the simulation studies](image)

**Figure B.0.1.** Meshing used in the simulation studies

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum element size</td>
<td>0.0277</td>
</tr>
<tr>
<td>Minimum element size</td>
<td>0.00346</td>
</tr>
<tr>
<td>Curvature factor</td>
<td>0.5</td>
</tr>
<tr>
<td>Maximum element growth rate</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Table B.1. Domain characteristics defined for the mesh in the model

Appendix C-HSC simulations of four reactions

Figure C.1. shows the HSC simulation for four reactions of NaOH-C, NaOH-Na₂CO₃-C, NaOH-Na₂S-C, and NaOH-Na₂S-Na₂CO₃-C at the temperature range of 200-1200 °C. The comparison of NaOH-C and NaOH-Na₂S-Na₂CO₃-C indicate that the extent of the reaction was higher for NaOH-C system.
(A) NaOH-C

(B) NaOH-Na₂CO₃-C
Figure C.1. HSC simulation of temperature dependence of equilibrium composition of (A) NaOH-C (B) NaOH-Na₂CO₃-C (C) NaOH-Na₂S-C and (D) White liquor-C system.
Appendix D - Economic analyses of activated carbon production with microwaves and conventional furnace

The conditions of activated carbon production in this work are very similar to the conditions used in the economic analysis by Choy et al. (2005). In their work, activated carbon was produced by a conventional furnace at 850°C with 70%wt KOH (Choy et al. 2005). Therefore, the manufacturing costs, working capital and general expenses were applied from their work.

In industrial microwave processing, magnetrons are the only consumable units and they last longer than 5000h. If magnetron works with 65% power efficiency and an electrical unit costs 0.11$/Kw.h, it costs 1188$ when works for 6000 h. An example of industrial microwave dryer unit needs 75 kW power. If the microwave power efficiency is 70%, the source requires 97.5kW and the electrical input for microwave consume 108kW considering the electrical losses. The annual cost of the microwave unit is 110500$, if the unit works 6000h per working year and the price of the 0.11$/Kw.h (Hasna 2011).

In the designing of microwave assist activation unit, the working capital, indirect costs, fixed operating cost, raw materials cost and general expenses were assumed to be the same as the conventional activation unit. The utilities cost for conventional and microwave activation unit is summarized in the Table D.1. Table D.1 and D.2 showed the price of the raw materials and the major equipment’s. The sludge pyrolysis yield is considered to be 40% and it will be mixed with KOH mass ratio of 2:1. The KOH is assumed to be recycled in this process with 10% loss every day. Tables of D.3, D.4, and D.5 showed the total capital investment cost, total revenue and return of investment, respectively.
Figure D.1. Economic analysis flowchart for production of activated carbon
### Table D.1. Cost of the raw material

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Quantity (tonnes per year)</th>
<th>Price US$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge pyrolysis</td>
<td>9,900,000</td>
<td>0</td>
</tr>
<tr>
<td>40%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH (2KOH:C ratio)</td>
<td>792,000 1.1$/kg</td>
<td>871200</td>
</tr>
</tbody>
</table>

### Table D.2. Cost of Utilities

<table>
<thead>
<tr>
<th>Utility</th>
<th>Quantity</th>
<th>Unit price</th>
<th>Price (US$) for conventional method</th>
<th>Price (US$) for microwave</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>134000 tonnes</td>
<td>0.54$/ton</td>
<td>73,000</td>
<td>73,000</td>
</tr>
<tr>
<td>Electricity</td>
<td></td>
<td></td>
<td>38,000</td>
<td>110,500</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>79200 kg</td>
<td>2.31 $</td>
<td>182,952</td>
<td>182,952</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>293,952</td>
<td>366,452</td>
</tr>
</tbody>
</table>

### Table D.3. Cost of the major equipment in the activated carbon production

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Conventional furnace (Choy et al. 2005)</th>
<th>Microwave unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonization furnace</td>
<td>130115</td>
<td>1188</td>
</tr>
<tr>
<td>Dryer</td>
<td>51266</td>
<td></td>
</tr>
<tr>
<td>Activated carbon dryer</td>
<td>39862</td>
<td></td>
</tr>
<tr>
<td>Crusher</td>
<td>44940</td>
<td></td>
</tr>
<tr>
<td>Nitrogen tank</td>
<td>19260</td>
<td></td>
</tr>
<tr>
<td>Mixing tank</td>
<td>14124</td>
<td></td>
</tr>
<tr>
<td>Scrubber</td>
<td>6948</td>
<td></td>
</tr>
<tr>
<td>Activated carbon tank</td>
<td>64200</td>
<td></td>
</tr>
<tr>
<td>Waste water treatment</td>
<td>94380</td>
<td></td>
</tr>
</tbody>
</table>

### Table D.4. Total capital investment calculation

<table>
<thead>
<tr>
<th>US ($)</th>
<th>Conventional furnace method</th>
<th>Microwave method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major equipment</td>
<td>334980</td>
<td>206053</td>
</tr>
<tr>
<td>Direct costs</td>
<td>3269196</td>
<td></td>
</tr>
<tr>
<td>Indirect costs</td>
<td>1756254</td>
<td></td>
</tr>
<tr>
<td>Working capital</td>
<td>1063133</td>
<td></td>
</tr>
<tr>
<td>Total capital investment</td>
<td>6,423,563</td>
<td>6,294,636</td>
</tr>
</tbody>
</table>
Table D.5. Total revenue for furnace and microwave assisted activation

<table>
<thead>
<tr>
<th>Total revenue of activated carbon production US($)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dry sludge per day (tonnes)</td>
<td>30,000</td>
</tr>
<tr>
<td>Activated carbon production yield (%)</td>
<td>25</td>
</tr>
<tr>
<td>Activated carbon production per day (tonnes)</td>
<td>7500</td>
</tr>
<tr>
<td>Price of activated carbon ($/kg)</td>
<td>1.6</td>
</tr>
<tr>
<td>Total revenue per year US$</td>
<td>3,960,000</td>
</tr>
</tbody>
</table>

Table D.6. Return of investment (ROI) calculation

<table>
<thead>
<tr>
<th>US ($)</th>
<th>Furnace activated carbon</th>
<th>Microwave activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable operating cost</td>
<td>1,165,000</td>
<td>1,237,000</td>
</tr>
<tr>
<td>Fixed operating cost</td>
<td>1,116,000</td>
<td>1,116,000</td>
</tr>
<tr>
<td>General expenses</td>
<td>511,000</td>
<td>511,000</td>
</tr>
<tr>
<td>Total production cost</td>
<td>2,793,000</td>
<td>2,865,000</td>
</tr>
<tr>
<td>Total capital investment</td>
<td>6,423,000</td>
<td>6,294,000</td>
</tr>
<tr>
<td>ROI</td>
<td>18</td>
<td>17.3</td>
</tr>
</tbody>
</table>
Appendix E- Statistical tests for microwave activation

Table E.1. Statistical test for microwave-assisted activation with KOH

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
<th>P-value* for SSA</th>
<th>P-value for activation yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH:C ratio</td>
<td>1 versus 2</td>
<td>0.0003</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>2 versus 3</td>
<td>0.43</td>
<td>1</td>
</tr>
<tr>
<td>Power level</td>
<td>Medium versus high</td>
<td>0.011</td>
<td>0.0049</td>
</tr>
<tr>
<td>Activation time</td>
<td>3 min versus 4 min</td>
<td>0.0003</td>
<td>0.0075</td>
</tr>
<tr>
<td></td>
<td>4 min versus 5 min</td>
<td>0.0004</td>
<td>0.1955</td>
</tr>
</tbody>
</table>

Table E.2. Statistical tests for NaOH microwave-assisted activation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
<th>P-value for SSA</th>
<th>P-value for activation yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH:C ratio</td>
<td>1 versus 2</td>
<td>1.2 x10^{-5}</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>2 versus 3</td>
<td>4 x10^{-5}</td>
<td>0.024</td>
</tr>
<tr>
<td>Power level</td>
<td>Medium versus high (NaOH:C=1)</td>
<td>0.0001</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>Medium versus high (NaOH:C =2)</td>
<td>0.1774</td>
<td>0.0003</td>
</tr>
<tr>
<td>Activation time</td>
<td>3 min versus 4 min</td>
<td>0.0780</td>
<td>0.3086</td>
</tr>
<tr>
<td></td>
<td>4 min versus 5 min</td>
<td>0.0044</td>
<td>0.3873</td>
</tr>
</tbody>
</table>

* If P-value is smaller than 0.05, the difference is statistically significant
Appendix F- Pore size distribution and pore volume of KOH and NaOH activation

Pore size distributions were calculated based on Density Functional Theory (DFT) method. DFT uses atomic level parameters to describe adsorption while traditional model use bulk parameters.

Non-local Density Functional Theory (NLDFT) was used for pore size distributions. NLDFT treats the pore walls as homogeneous graphite-like plane surfaces and assumes a constant density of the solid atoms surrounding absorbed gases.

![Graph showing pore volume and SSA vs. temperature]
KOH: C mass ratio

Figure F.1. Effect of (A) activation temperature, (B) KOH ratio and (C) time on pore volume, pore size distribution, and SSA of KOH-activated carbon in furnace

KOH-activated carbon was more microporous compared to NaOH-activated carbon. By increasing the temperature from 800 to 1000°C, pore widening occurred. However, the total pore volume was reduced. Also increasing the activation time from 1 to 2 and increasing activating agent from 2 to 3 caused higher mesoporous volumes.
Figure F.2. Effect of (A) activation temperature, (B) time on pore volume, pore size distribution, and SSA of NaOH-activated carbon in furnace.
The NaOH-activated carbon contains both mesoporous and microporous. The activation conditions affect the pore size distribution, especially the activation temperature. By increasing the temperature from 600 to 800°C, micropore widening occurred and mesopore volume was increased. Further increase to 1000°C destroyed both micro and mesopores. Porosity was also affected by activation time by a lesser extent.