

**University of Alberta**

**Preparation of Activated Carbon from Oil Sands Coke by Chemical and  
Physical Activation Techniques**

by

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## **ABSTRACT**

Oil sands coke is a by-product resulting from the upgrading of heavy crude bitumen to light synthetic oil. This research investigates the preparation of activated carbon from oil sands cokes by using both chemical activation and physical activation techniques.

Chemical activation was completed using KOH as activation agent and heating with a muffle furnace. The highest iodine number obtained was 1942 mg/g and 1292 mg/g for delayed and fluid coke respectively. The highest BET surface area was obtained as 1654 m<sup>2</sup>/g and 1130 m<sup>2</sup>/g for delayed and fluid coke respectively at an activation temperature of 800°C using a KOH to coke ratio of 2. Physical activation was performed using steam and microwave heating. The highest iodine number obtained was 103 mg/g for delayed coke and 226 mg/g for fluid coke.

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# CHAPTER 1: INTRODUCTION

## 1.1 Introduction

### 1.1.1 Alberta Oil Sands and Oil Sands Coke

Oil sands are composed of sands containing extra-heavy non-conventional viscous petroleum called bitumen. The Alberta oil sands deposits are one of the largest accumulations of bitumen reserve in the world with a total reserve volume of crude bitumen estimated at  $259.2 \times 10^9 \text{ m}^3$  (ERCB 2008; Puttaswamy et al. 2010). The Alberta oil sands deposits are divided into three regions: Athabasca Wabiskaw-McMurray deposits, Cold Lake – Clear Water deposits, and Peace River Bluesky-Gething deposits (ERCB 2008).

Syncrude Canada Ltd. and Suncor Energy Inc. are the two major oil sands mining companies operating in the northeastern region of Alberta, most notably in Fort McMurray, which use surface mining techniques and excavate to a depth of approximately 50–100 m to access the oil soaked sands (Puttaswamy et al. 2010). Oil sands contain approximately 80 to 85 % sand, clay and other mineral matter, 5 to 10 weight percent water, and 1 to 18 weight percent of crude bitumen (Squires 2005). Crude bitumen is then separated by processing the mined oil sands with hot water and chemicals (Sodium Hydroxide) and is further processed through a coking or hydrocracking process to convert the heavy crude bitumen into synthetic crude oil (Gray 2002). Through this process coke is produced as a by-product. It was estimated that Syncrude Canada and Suncor Energy produced over

2 and 3 million tones of coke in the year 2003, respectively. The production of coke is projected to be nearly 1 billion m<sup>3</sup> over the lifetime of the oil sands operations (Fedorak and Coy 2006).

### **1.1.2 Activated Carbon and Activation Process**

Activated carbons are defined as a group of highly porous materials with high carbon content and surface area which are widely used in pollution control applications, including industrial gas separation, odor control, potable water and waste water treatment. The high removal efficiency of the pollutants, low energy cost, and reusability and possible product recovery makes activated carbon more applicable in adsorption science (Prakash et al. 1994; Mochida et al. 2000; Wu et al. 2005).

Activated carbons are available as granular activated carbon (GAC) and powdered activated carbon (PAC). The type of activated carbon also depends on the activation process. There are two basic methods of producing activated carbon from carbonaceous materials: physical activation, which is also called thermal activation, and chemical activation. It has been reported that, for the same precursor to produce activated carbon, chemical activation produces higher quality products compared to physical activation techniques. In physical activation, normally steam and carbon dioxide are used as the activating agents, and the activation temperature is carried out at 700 °C to 1100 °C. On the other hand, in chemical activation, some selected salts, bases and acids are used as the

activation agent; these agents are often called impregnating chemicals. Both physical and chemical activation involve two stages procedure: carbonization and activation (Paredes et al. 2006; Ajayi and Olawale 2009).

### **1.1.3 Adsorption and Adsorption Characteristics of Activated Carbon**

If a porous solid is exposed to a gas or vapors, the solid adsorbs the gas onto its surface, more specifically into its pores. The solid is considered to be an adsorbent, while the gas or vapor is considered to be the adsorbate. During adsorption, mainly two forces act between the solid and the gas molecules. The first is a physical force, Van-der-Waals, and the other is a chemical force. Based on these assumptions, adsorption is classified as both physical and chemical adsorption (Cal 1995).

During physical adsorption, the adsorption of gas molecules increases with decreasing temperature and increasing pressure. An adsorption isotherm measures the quantity of adsorbate that is adsorbed as a function of partial pressure  $P/P_0$ . There are a total of six types of isotherms which indicate the porosity of the adsorbent (Sattler 2010).

## **1.2 Research Objectives**

The objective of this research work was to prepare high quality activated carbon using Athabasca Oil Sands Coke as a precursor and to characterize it through different adsorption tests. This research work also investigated both

chemical and physical activation techniques in preparing the activated carbon. Both delayed coke and fluid coke were used. As a heat source, a traditional muffle furnace and microwave oven were used. In doing so, the following objectives were described:

1. Preparation of activated carbon using the chemical activation process and muffle furnace heating, and determination of the optimum activation parameters.
2. Comparison of the quality of the prepared activated carbon (chemical activation and muffle furnace heating) with activated carbon chemically activated using microwave heating.
3. Preparation of activated carbon using the physical activation process and microwave heating, and determination of the optimum activation parameters.
4. Comparison of the quality of the prepared activated carbon (physical activation and microwave heating) with the chemically activated carbon prepared using muffle furnace heating.

To achieve these goals, a muffle furnace with a traditional heating system and a customized kitchen microwave of 2.4 GHz were used to activate the raw oil sands coke. For chemical activation, potassium hydroxide (KOH) was used as the impregnation chemical, while for physical activation, dry nitrogen (N<sub>2</sub>) and carbon-di-oxide (CO<sub>2</sub>) in conjunction with steam were used. A standard iodine

adsorption test was performed as the major characterization test of the prepared activated carbon. To evaluate the adsorption capacity and to characterize the activated carbon, surface area, micropore volume and pore size distribution were determined through N<sub>2</sub> adsorption isotherm. Pore size distribution characterized the micro porous structure of the adsorbent. Scanning Electron Microscope (SEM) was used to evaluate the morphology, graphical orientation and size of the pores before and after activation of the oil sands coke. An x-ray photoelectron spectroscopy (XPS) analysis was also performed to evaluate the surface chemistry of the activated carbon.

The overall objective of this research is to utilize the oil sands petroleum coke, an upgrading waste by product, to prepare a demandable commercial product, activated carbon, in controlling air pollution.

### **1.3 Thesis Outline**

This thesis contains a total of five chapters. Each chapter focuses on and contributes to the overall goals for conducting this research investigation. Chapter 2 will briefly review oil sands coke and its suitability as a precursor, activated carbon and its different activation methods and adsorption principles isotherms. Chapter 3 will discuss the chemical activation of oil sands cokes through the use of a muffle furnace. This chapter will also include the optimum activation parameters for producing high quality activated carbon and characterize its quality. Chapter 4 will cover physical activation and the application of a

microwave as a heating source to prepare activated carbon from same precursor, oil sands coke. This chapter will also include details of the experimental set up and the characterization of the prepared activated carbon, results and discussion. Chapter 5 will denote the final summary and conclusion. It will also provide some recommendations for future research.



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## **CHAPTER 2: LITERATURE REVIEW**

This chapter presents an overview of activated carbon, oil sands coke and preparation of activated carbon from oil sands coke. It will also provide a review of microwave heating and its application for the preparation of activated carbon.

### **2.1 Activated Carbon**

Activated carbon is the collective name for a group of highly porous adsorbents mainly used in air and water treatment. Carbon-based materials are used as precursors for activated carbon, where the carbon-based materials are altered to have a highly porous, intra-particle surface area. This allows a variety of organic precursors with high carbon content to produce activated carbon, including petroleum coke, bituminous coal, wood char, coconut shells, bamboo, and peat (Bansal et al. 1988).

Activated carbons are most commonly available in granular (GAC) and in powdered (PAC) form. Powder-activated carbons are normally obtained by crushing the granular-activated carbon, whereas the granular-activated can be produced from granular raw material or from raw material which is bonded with a physical binder to form pellets. Granular-activated carbons are usually characterized by large surface areas and small pores, while powdered-activated carbons possess larger pores and less surface area (Di Panfilo 1995). Physical and chemical properties define the application of activated carbon in the fields of

purification, dechlorination, decolorization, detoxication, as a filter media, gas stream separation, organics adsorption and recovery. Physical and chemical properties include surface area, pore size distribution, surface chemistry, metal and ash content. The shape of pores in activated carbon also varies (e.g. slit shape, cylindrical, spherical, bottle shape.) and can determine the area of application (Bansal et al. 1988; Oshida et al. 1995). Iodine number and surface area are the two main physical characteristics that are generally used in the characterization of activated carbon. Iodine number (mg/g) shows the amount of iodine (mg) adsorbed by the activated carbon (g). Iodine number also indicates the adsorption capacity of activated carbon for low-molar-mass species. The surface areas are typically determined by the adsorption of pure N<sub>2</sub> gas on activated carbon which provides the total adsorption surface area (Li et al. 2008).

The most common types of activation procedures that produce activated carbon are physical, chemical, or a combination of the two (Ajayi and Olawale 2009). The application of different activation techniques and activating agents are the main factors affecting the quality of activated carbon (Jiang et al. 2008).

### **2.1.1 Activated Carbon Preparation**

Activated carbon preparation undergoes two subsequent stages: carbonization and activation. Carbonization involves the endothermic decomposition of non-carbon precursors by volatilization. More specifically, in the carbonization stage, precursors are heated in absence of oxygen to produce

charcoal-like material by driving off the non-carbonaceous substances. The carbonization stage is generally performed within an inert atmosphere by purging nitrogen gas and by using a stationary, rotary or fluidized bed oven (Bansal et al. 1988). The influencing factor in producing carbon char in this stage depends on the nature of the carbonaceous material, ultimate heating temperature, rate of heating, time of heating and the surrounding atmosphere. Among these factors, temperature plays a vital role. A low rate of heating leads to less volatilization and less shrinkage which affects the formation of micropores. The high rate of heating causes damage to the micropores and enlarges the mesopores and successive macropores (Bansal et al. 1988; Ji et al. 2007). Carbonization at a higher ultimate temperature may also cause the formation of graphite rather than carbon char, which is difficult to activate. Carbonization temperature normally ranges from 400 °C to 600 °C (Jankowska et al. 1991; Guo and Lua 2000; Bouchelta et al. 2008). Some literature uses carbonization temperatures as high as 1000 °C (Wang et al. 2009; Yang et al. 2010).

The activation stage involves the production of porous carbon (activated carbon) of desired physical and chemical properties by reacting carbon char with the activating agents at high temperature. This stage removes the decomposed substances produced during carbonization, which are trapped inside the developed pores. As a result, it produces further micropores. Physical activation and chemical activation are the main processes followed throughout the stage, and are involved in degradation, decomposition and removal of non-carbon products or

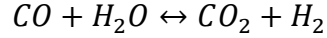
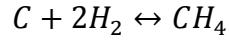
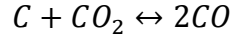
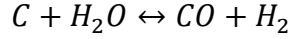
even disorganized carbons. The overall reaction rate is limited by the mass transport rate and the rate of chemical reaction between the activation agent and the carbonaceous material (Bansal et al. 1988).

#### **2.1.1.1 Physical Activation**

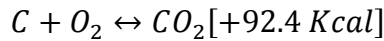
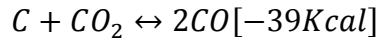
Physical activation occurs due to the reaction between the carbon char produced during carbonization and the activating agent at a high temperature of 800 °C to 1000 °C. Steam, CO<sub>2</sub>, N<sub>2</sub>, air and a combination of steam and CO<sub>2</sub>, or steam and N<sub>2</sub> are used as the activating agents.

Oxygen is the most active agent, but it is not typically applied because the reaction is very difficult to control. A process control with oxygen as the activating agent was performed by Williams et al. in 2008. The process was exothermic (Williams and Parkes 2008). At higher temperatures, carbon atoms at the precursor's surface as well as in the incipient micropores react with the activating agents and are removed mainly as carbon monoxide or carbon dioxide. This loss of carbon enlarges the existing micropores and develops new micropores, resulting in a highly porous material.

Among the different activating agents for physical activation, steam is the most widely used to produce activated carbons. The reactions during steam activation are as follows (Jankowska et al. 1991):



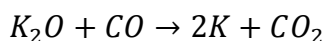
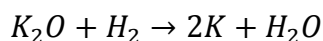
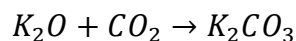
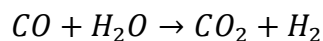
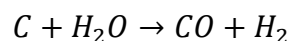
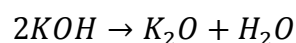
Listed below are the reactions for CO<sub>2</sub> and oxygen which are normally considered throughout the activation process (Bansal et al. 1988):



### 2.1.1.2 Chemical Activation

Impregnation with different chemicals is a common practice in chemical activation techniques. Researchers reported different types of bases, acids and salts, including KOH, NaOH, ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, as activating agents during their chemical activation. The impregnation of these chemicals is one of the main factors in obtaining the best quality of activated carbon. Chemicals are impregnated in either dry condition or aqueous mix. Normally 1 hr to 24 hrs of impregnation time is reported by different users (Lee and Choi 2000; Ramírez Zamora et al. 2000; Kawano et al. 2008; Zhang et al. 2008; Yuan et al. 2010). In some cases, agitation at 110 °C is performed to achieve more effective

impregnation. Among the different activating agents, KOH is found to be more effective in producing microporous activated carbon. Another benefit associated with using KOH is that it is environmental friendly. On the other hand, use of  $ZnCl_2$  is reported to produce mesoporous activated carbon, and Zn is an environmentally hazardous metal. The use of  $H_3PO_4$  was also reported repeatedly in the literature. The main advantages associated with using  $H_3PO_4$  include its role in the pyrolytic decomposition of non carbonaceous material and disordered carbon in the carbon char. It also helps in forming cross-linked structures in the carbon char to produce highly porous media (Liu et al. 2010). The activation temperature for chemical activation is reported to be 500 °C to 900 °C (Yang 2003) which is lower than temperature used in physical activation. Recovery of chemical after activation is another advantage in chemical activation technique which also determines the economic feasibility by reusing the chemical in the activation process. This also helps chemical activation become more economic and leads to industrial scale production. Main reactions associated with chemical activation with KOH as the activating agent are as follows (Otowa et al. 1993)





## 2.2 Activated Carbon Characterization

Activated carbon needs to be characterized to evaluate its performance in case specific use and to determine the efficiency of activation techniques during industrial production. This activation techniques and characterization also allows understanding of the process reaction among different materials. Activation yield, iodine number, BET surface area and pore size distribution are the main parameters used in evaluating the properties of activated carbon adsorbent.

### 2.2.1 Activation Yield

Activation yield describes the activation methods' effectiveness in obtaining the final product after losing some material. This parameter determines the effect of overall activation environment, including all the parameters. The yield of a material during activation can be defined as the ratio of the dry weight of the final product to the initial dry feedstock, as calculated by.

$$\% Yield = \frac{W_2}{W_1} * 100$$

Where  $W_1$  is the initial weight of carbon char (g) before activation and  $W_2$  the weight of the activated carbon after activation (g) (El Qada et al. 2008).

### 2.2.2 Iodine Number

Iodine number (mg/g) is the amount of iodine adsorbed by the activated carbonaceous materials per gram (ASTM 2006; Mianowski et al. 2007). It is a

fundamental parameter in characterizing the activated carbon's performance, and it also measures the porous media's activity. Typically, the activated carbon's iodine number ranges from 500 mg/g to 1500 mg/g depending on the activation procedure, precursor as well as the physical characteristics of raw material (Nunes and Guerreiro 2011).

Studies have indicated that iodine number and the surface area are correlated for the activated carbon which has a surface area is less than 1000 m<sup>2</sup>/g (Mianowski et al. 2007). It is also observed that iodine number generally relates to the surface area for pores ranging between 10 Å to 28 Å. As a result a material with a surface area larger than 1000 m<sup>2</sup>/g and with narrow micropores (<10 Å) provides a lower iodine number (Yang 2003; Budinova et al. 2006).

The iodine number can also be related to pore volume by calculating the iodine adsorption volume. Activated carbon with a high iodine number indicates a greater adsorption capacity, whereas low iodine numbers suggests less pore development during the carbonization and activation stage (Prakash Kumar et al. 2006).

Iodine adsorption is also affected by the amount of inner non carbonaceous materials, including volatiles, water and sulfur, which may cause a chemical reaction with iodine and provide false iodine uptake results. Thus, the use of the iodine number to measure the degree of exhaustion of a carbon bed is only recommended if the iodine is free of chemical interactions with adsorbates

and if an experimental relation between the iodine number and the degree of exhaustion is determined for the particular application (Madan 2009). Such aspects should be considered when determining the iodine number in order to accurately interpret the results.

### **2.2.3 BET Surface Area and Pore Size Distribution**

The multilayer adsorption was explained by the BET theory which was presented by Brunauer, Emmett and Teller to explain multilayer physical adsorption (Gregg and Sing 1991). BET theory was the modification of Langmuir monolayer adsorption theory. One of the basic assumptions of the Langmuir adsorption isotherm is that adsorption is monolayer in nature and the adsorption equation is applicable under low pressure conditions. Also according to Langmuir conditions, gaseous molecules would possess high thermal energy and high escape velocity which would result in fewer gaseous molecules being available near the surface of the adsorbent (Brunauer et al. 1938). However, in the BET multilayer adsorption theory, these limitations are overcome. According to the BET theory, at high pressure and low temperature, the thermal energy of gaseous molecules decreases and the availability per unit surface area increases (Webb et al. 1997).

Measuring the surface area of the activated carbon or adsorbent is one of the main applications of the BET equation. Nitrogen, at its boiling point of 77K, is used to perform surface area measurement. Krypton is also used to measure the

surface area (Masel 1996). Full scale adsorption of nitrogen from partial pressure ( $p/p_0$ )  $10^{-7}$  to 0.99 provides the pore size distribution of the activated carbon

### **2.3 Oil Sands and Oil Sands Coke**

Coke is a solid by-product resulting from the upgrading of heavy crude bitumen to light synthetic oil. The process used to upgrade heavy petroleum residues into light gasoline is called “coking” or “thermal cracking”. During thermal cracking, a noticeable percentage of product remains as refinery solid waste which is considered to be petroleum coke. The reaction during thermal cracking, involves either de-alkylation or dehydrogenation. In elevated temperatures, the asphaltenes and the resins convert to straight chain compounds through de-alkylation and produce compounds which are highly amorphous and impure. On the other hand, the dehydrogenation reaction involves subsequent polymerization and condensation of free radicals to produce compounds with large molecular weight and a high C-H ratio (Onder and Bagdoyan 1993).

Coke is primarily classified as being isotropic or anisotropic, based on the degree of large scale molecular ordering present in the deposit. Coke derived from the liquid and vapor phase is mainly considered to be anisotropic, because of their highly ordered and layered macroscopic structure. Isotropic cokes are typically formed from non-fluid precursors that inhibit molecular alignment and lack of large-scale order (Squires 2005).

Coking is mainly categorized into delayed and fluid coking. These two methods are used mostly for upgrading of heavy crude oils. Cokes produced in the delayed and fluid coking processes are termed as delayed coke and fluid coke, respectively. Rapid heating in a furnace under specific temperature and pressure take place in delayed coking. The cracking atmosphere also depends on the thermal cracking temperature of the corresponding materials. The delayed coking process normally results in the coke developing a sponge-like structure (Squires 2005). In the case of fluid coke, the residual oils are sprayed through steam injection over the hot coke particles. This spraying initiates more thermal reaction as well as the heat sources and results in the instantaneous conversion of coke by thermal cracking (Squires 2005).

Syncrude Canada Ltd. and Suncor Energy Inc. are the two largest companies producing fluid and delayed coke, respectively. Syncrude Canada Ltd. uses the conventional fluid coking system that involves a burner and reactor. Burning the coke in a fluidized bed produces heat which is transferred to the reactor through heating the solids. The temperature is maintained at 500 °C in the reactor on the coke surface. Preheated bitumen is then sprayed over the hot coke bed to crack the heavy molecules, producing lighter molecules. As a byproduct, the system produces more fluid cokes. Alternatively, Suncor Energy Inc. uses the delayed coking process with a batch-by-batch procedure. The system includes the heating unit and a pair of drums. Heavy bitumen is heated progressively in the drum at 490 °C. As a result, the molecules are cracked and produce vapors and

solid coke. The solid byproducts are then stored in the drums (Squires 2005; Small 2011).

It was reported that Syncrude Canada and Suncor Energy cumulatively produced over 6000 tonnes of petroleum coke per day in 2003. Total cumulative coke production was over 5 million tonnes in 2003. It is estimated that throughout the life time of oil sands' operation, a total of 1 billion m<sup>3</sup> of coke will be produced in Alberta (Furimsky 1998; Squires 2005; Fedorak and Coy 2006).

Petroleum coke from the Alberta Oil Sands contains high carbon content (80%) as well as 6% to 8% of sulfur which is relatively high compared to the other petroleum cokes (Guo and Lua 2000; Chen 2010). Without desulfurization, high sulfur content limits the use of coke in energy production. The costs associated with desulfurization limits the use of these cokes as energy source. As a result most of the produced cokes are stockpiled with minimal use. Scott and Fedorak (2004) reported that Suncor energy used some of its produced coke to generate heat for the boilers after removing sulfur by hydro-treatment. The use of delayed coke from Suncor Energy as the oil sands tailing pond cap was also reported (Caldwell et al. 2010).

Different studies were also performed regarding the environmental impact of storing these cokes outdoors and in open atmosphere. Furimsky (1998) reported that Syncrude coke is non-leachable with respect to regulated elements

and volatile organics from a earlier study. However, later experiments showed that coke leaches at a low pH, which is a concern to the environment (Furimsky 1998). Fedorak and Coy performed the anaerobic and aerobic culture of both delayed and fluid coke and found that these cokes were not inert in a biological system. The anaerobic study showed that selected heterotrophic bacteria with carbon and an energy source are capable of producing sulfate by reacting with sulfur from delayed coke (Fedorak and Coy 2006). Puttaswamy et al. (2010) analyzed the coke leachates for toxicity and the chemistry to the water and air shed in the upgrading area. They used both delayed and fluid coke and used two field lysimeters: a shallow and deep lysimeter. The study detected chronic trace metals, including Al, Mn, Ni and V. Vanadium concentration was much higher compared to the other metals. The study also revealed the acute toxicity of the coke leachate to *Ceriodaphniadubi* (Puttaswamy et al. 2010).

Proximate and ultimate analysis of both the delayed and fluid coke was performed by various researchers to find the constituents of the cokes. As the process of coking for delayed and fluid coke differs, the analysis of the components are also found to differ from one another. Table 2.3-1 shows the constituents of the oil sands coke both for delayed and fluid coke which is adapted from previous studies.

**Table 2.3-1 Constituents after proximate and ultimate analysis of fluid and delayed coke**

		<b>Fluid Coke</b>	<b>Delayed Coke</b>
<b>Proximate Analysis</b>	Volatiles	7.1 % <sup>1</sup>	11.9 % <sup>2</sup>
	Moisture	1.8 % <sup>1</sup>	1.8 % <sup>2</sup>
<b>Ultimate Analysis</b>	Carbon	78.5 % <sup>3</sup>	82.3 % <sup>3</sup>
	Nitrogen	1.8 % <sup>3</sup>	1.6 % <sup>3</sup>
	Hydrogen	1.9 % <sup>3</sup>	3.7 % <sup>3</sup>
	Sulfur	7.2 % <sup>3</sup>	6.8 % <sup>3</sup>

<sup>1</sup> (DiPanfilo and Egiebor 1996); <sup>2</sup> (Shawwa et al 2001); <sup>3</sup> (Chen 2010)

The presence of various contaminants and the existing studies of leaching, emission, bioaccumulation and toxicity of oil sands coke reveal that stockpiling the coke may cause serious environmental deterioration and affect the air and watershed in the long term.

It is vital to determine an alternate use of stockpiled coke. Though petroleum coke has a high calorific value of approximately 37 Mj/Kg, its high sulfur content limits its use in burning (Lee and Choi 2000). The high carbon content of oil sands coke, approximately 80%, makes it a suitable precursor in the production of activated carbon. Some studies were performed with traditional methods to produce activated carbon by using oil sands coke and found promising response towards the adsorption of both gaseous pollutants and water effluent.



## 2.4 Activated Carbon from Petroleum Coke

Zhang et al. (2007) used petroleum coke as the precursor for chemical activation with KOH as the activating agent. They activated petroleum coke to prepare the best quality adsorbent for natural gas. The raw petroleum coke had 4.8 % sulfur and was produced as a byproduct of the delayed coking system. Before activation, the raw coke was grinded from 124 to 150  $\mu\text{m}$  particle size and then mixed into the saturated KOH solution. The mix ratio varied from 2:1 to 5:1 of KOH to coke. A pre-activation stage followed at 400  $^{\circ}\text{C}$ . The activation was carried out at up to 900  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$  heating rate in a neutral atmosphere by using  $\text{N}_2$  gas at 100 mL/min. The yield and packing density of the final products were also investigated. It was found that at 850  $^{\circ}\text{C}$ , and 60 minute activation time with 4:1 KOH/coke ratio yields the best quality activated carbon adsorbent for natural gas adsorption. The observed BET surface area, micropore volume and the total pore volume for these optimum activation parameters were 2325  $\text{m}^2/\text{g}$ , 1.32  $\text{cm}^3/\text{g}$  and 1.4  $\text{cm}^3/\text{g}$ , respectively. Throughout the experiment, Zhang et al. found that with an increase in KOH/coke ratio, the yield and the packing density decreased, whereas the specific surface area, micropore volume and the total pore volume increased gradually. From the  $\text{N}_2$  adsorption isotherm, they concluded that activated carbon had dominating micropore, and adsorption isotherms followed the Type I pattern (Zhang et al. 2008).

The use of petroleum coke to produce activated carbon by means of a chemical activation with KOH was also reported by Kawano et al. (2007). They

prepared the activated carbon to perform water adsorption to improve the heat pump. Granular petroleum coke of 95 % carbon content with particle size 0.85 to 1.00 mm was used as a precursor. 0.5 g of precursor was mixed with 85 % pure KOH at different KOH/coke mix ratios ranging from 2 to 5. The activation temperature was raised from 500 °C to 800 °C with a heating rate of 2 °C/min. Activation time was 1 hr. The activated sample was washed with de-ionized water to neutralize the pH. The BET surface area, micropore volume and total pore volume increased with an increase in activation temperature. The highest surface area was 990 m<sup>2</sup>/g at 800 °C. From the analysis of the BET surface area and pore volume, it was concluded that pore formation was insufficient at 500 °C. With the increase in temperature to over 600 °C, a higher BET surface area was observed, and the majority of the pores were less than 2 nm. The amount of the acidic surface groups for samples prepared at 600 °C was twice as high as that of 800 °C. The surface hydrophilicity of the activated carbon also greatly contributed to water adsorption at low relative pressure ranges. With an increase in KOH to coke ratio, the BET surface area, micropore and total pore volumes also increased (Kawano et al. 2008).

Yuan et al. (2010) also used oil sands petroleum coke as an activated carbon precursor. They used the chemical activation procedure with KOH as the activating agent. The activated product was used for the adsorption of five species of polyaromatic hydrocarbons (PAHs) from aqueous solution. A 1:1 mass mixing ratio for KOH and Coke was performed. The activation temperature was

maintained at 600 °C to 1000 °C and the activation time ranged from one to three hours. The highest specific surface area was obtained as 1904 m<sup>2</sup>/g (Yuan et al. 2010).

Lu et al. (2010) investigated the formation of K<sub>2</sub>CO<sub>3</sub> during chemical activation of petroleum coke with KOH. The dry weight mixing of petroleum coke and KOH was performed at a ratio of 3 in a grinder. The activation temperature was risen to 730 °C. To evaluate the effect of K<sub>2</sub>CO<sub>3</sub> during the activation reaction, another set of samples was prepared by mixing with K<sub>2</sub>CO<sub>3</sub> activated by the same procedure as that for KOH. The results were analyzed to evaluate the activation effect through XRD, FT-IR and GC-MS. It was found that for Coke-KOH mix, carbon oxidation started at 500 °C with the KOH as the predominant compound in the mix. When the temperature reached at 600 °C, KOH converted into K<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>O. With further increase in temperature to 730 °C, all the K<sub>2</sub>CO<sub>3</sub> converted into K<sub>2</sub>O. The activated coke's pore size distribution at different stages demonstrated that the K<sub>2</sub>CO<sub>3</sub> produced at intermediate steps of the chemical reaction acted as the main activating agent to form pores in petroleum coke, especially with KOH as the primary activating agent. However, the second set of activation experiments with direct K<sub>2</sub>CO<sub>3</sub> indicated very low surface areas compared to those in the KOH activation. The results also showed that well developed pores can only be formed with K<sub>2</sub>CO<sub>3</sub> if the precursor is lignocelluloses. However, for petroleum coke, K<sub>2</sub>CO<sub>3</sub> did not result in well developed pores (Lu et al. 2010).

Lee and Choi (2000) reported chemically activated petroleum coke using alkali metal compounds, including NaOH and KOH at a mixing ratio ranging from 1 to 4. The temperature was raised from 400 °C to 600 °C and was held for 1 to 2 hours for activation. The surface area was found to be 1350 m<sup>2</sup>/g for activated coke when using NaOH, and 1980 m<sup>2</sup>/g when using KOH. Lee and Choi also reported that sulfur content and desulfurization of both organic and inorganic sulfur play a vital role in developing the surface area. The breakage of the C-S bond and eruption of S helps in forming pores and increases the surface area. The main findings of their research showed that the physical and chemical structure of the activated coke surface was highly affected by the alkali metal hydroxide. They also concluded that the KOH was more effective in producing high surface area when compared to NaOH. The activated carbon produced by alkali activation becomes hydrophilic (Lee and Choi 2000).

Ramírez Zamora et al. (2000) used ZnCl<sub>2</sub>, NaOH and H<sub>3</sub>PO<sub>4</sub> as the impregnating compounds to activate petroleum coke. The coke-activation agent mix was boiled at 110 °C for two hours to diffuse the impregnated chemicals into the coke. The activation was carried out at 700 °C for 2 hours with nitrogen gas flow at 1 Lpm. The observed iodine numbers were 73 mg/g, 57 mg/g and 42 mg/g for ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> and NaOH, respectively. Methylene blue numbers were 146.3 mg/g, 160 mg/g and 203 mg/g for ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> and NaOH, respectively. ZnCl<sub>2</sub> provided the highest iodine number, whereas the NaOH provides the highest

methylene blue number. From the surface area analysis, it was observed that the NaOH treated coke provides the highest surface area at 35.4 m<sup>2</sup>/g. The activated carbon produced with these activating agents was more suitable for the adsorption of larger molecules. The H<sub>3</sub>PO<sub>4</sub> treated activated carbon results in better adsorption than the activated carbon treated by the other activating agents (Ramírez Zamora et al. 2000).

Wu et al. (2005) also prepared activated carbon from petroleum cokes. They used physical, chemical and co-activation method. KOH, H<sub>2</sub>O and KOH+H<sub>2</sub>O were used as activating agents. Surface area ranged from 2500 m<sup>2</sup>/g to 3000 m<sup>2</sup>/g. and the yield from 25 to 30 %. From the experiment, it was found that inorganic components, including transition metals in the raw coke, play an important role in the activation techniques. Co-activation with a mix of KOH and H<sub>2</sub>O provided the best quality of activated carbon. Chemical activation with KOH was therefore the better option for activation, and physical activation was less effective. In this experiment, the precursor was mixed with KOH in aqueous solution rather than traditional KOH powder, which was proved to be very effective. This method aided in increasing the contact of the starting materials with the agents, and also in shortening the diffusion time (Wu et al. 2005).

Chunlan et al. (2005) studied the effect of pre-carbonization during the activation of petroleum coke through chemical activation process with KOH. Pre-carbonization was carried out for three hours at 500 °C, 800 °C and 1200 °C. Both

the raw and pre-carbonized samples were mixed with KOH at a dry mix ratio of 3. The activation was performed with the flow of argon at 200 mL/min. From the TGA analysis showed the weight loss was up to 60 % for the raw coke, whereas the weight loss decreased from 40 % to 6 % with the increase of the pre-carbonization temperature from 500 °C to 1200 °C. The literature also indicated that pre-carbonized sample prepared at a higher temperature was more difficult to activate with KOH. From the pore size distribution, it was also found that activated carbon without pre-carbonization exhibited a microporous pore size distribution with a dominant pore diameter of 0.8 nm. Conversely, the activated carbon produced by the pre-carbonization showed a decreasing trend of micropore volume (Chunlan et al. 2005).

Jiang et al. (2007) investigated the effect of chemically pre-treating petroleum coke on the preparation of activated carbon before using chemical activation techniques with KOH. Chemical pretreatment was performed using HClO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. For KOH/coke ratio of 3, the highest BET surface area for the pretreated and untreated coke was observed as 2336 m<sup>2</sup>/g and 1032 m<sup>2</sup>/g respectively (Jiang et al. 2008).

Di Panfilo (1995) used oil sands coke to prepare activated carbon by physical with steam and chemical activation with KOH. The BET surface area was 318 m<sup>2</sup>/g for the steam-activated coke and 176 m<sup>2</sup>/g for the KOH-activated showed. The micropore volume was 0.244 cc/g and 0.164 cc/g for physically and

chemically activated carbon, respectively, which demonstrates the effectiveness of physical activation. The burn-off for chemical activation was higher than that of physical activation (DiPanfilo and Egiebor 1996).

Physical activation of the delayed oil sands coke was performed by Shawwa et al. (2001). The experiment was carried out to remove color and chlorinated organic from pulp mill effluent. Activation was carried out at 850 °C with a 10 °C/min heating rate for 1 to 6 hours with steam as the activation agent. The activated product was characterized by the adsorption of methylene blue. The literature indicates that the maximum methylene blue adsorption was achieved at 100.5 mg/g for 4 hours of activation time (Shawwa et al. 2001).

Bratu (2008) used fluid coke as the precursor to produce activated carbon to capture mercury from gases. Steam, carbon dioxide, and mixture of the two gases were used as the activating agents. Activation was completed at 200 °C to 800 °C. From the experimental analysis, it was found that the CO<sub>2</sub>+H<sub>2</sub>O mix provides a higher surface area compared to the pure CO<sub>2</sub>. Activation with a CO<sub>2</sub> and H<sub>2</sub>O mix provided microporous activated carbon. The highest surface area obtained was 500 m<sup>2</sup>/g (Bratu 2008).

## **2.5 Microwave Application and Activated Carbon**

Microwaves had potential for the rapid, energy-efficient heating of materials. The current applications of microwave heating include food processing,

wood drying, plastic and rubber treating as well as the curing and preheating of ceramics. Microwaves cover a wide band in the electromagnetic wave spectrum and lie in between radio wave and infrared frequencies. The wave lengths and frequency of microwaves range from 1 mm to 1 m, 300 MHz to 300 GHz respectively, where two frequencies, 915 MHz and 2450 MHz, are typically used for industrial microwave heating (Osepchuk 2009).

### **2.5.1 Microwave Heating**

Microwave heat is generated by the interaction of dielectric materials also being termed as dielectric heating, which occurs due to a net polarization of the substance. Several mechanisms, including electronic, ionic, molecular (dipole), and interfacial (space-charge) polarization, are involved in dielectric heating. Throughout the heating process, the presence of dipole molecules in oscillating fields try to orient themselves or become in phase with the field. During this orientation, a resisting force restricts their motion which results in the generation of heat (Osepchuk 2009).

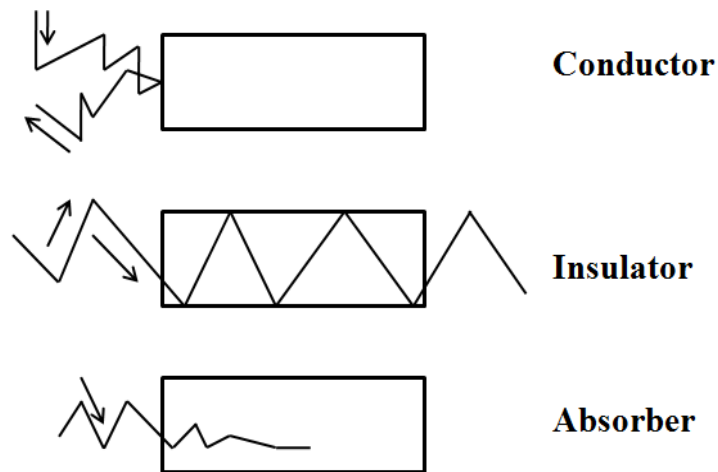
Based on their interaction with microwaves, materials can be classified generally into three categories (Figure 2.5-1),

1. Conductors. These types of materials reflect microwaves and are typified by bulk metals and alloys, e.g. copper.

2. Insulators. These types of materials are transparent to microwaves and are typified by fused quartz, several glasses, ceramics, and Teflon.



3. Absorbers. These types of materials absorb microwaves. For microwave heating, these types of materials are the most important class. Aqueous solution, sand and polar solvents can be classified in this group (Jones et al. 2002).



**Figure 2.5-1. Different materials for microwaves (adapted from (Yuen and Hameed 2009))**

Materials that absorb microwave radiation are called dielectrics, which have two important properties: 1. Dielectric materials have very few free charge carriers. As a result, after the application of an external electrical field, there is very little charge carried through the material matrix. 2. The molecules or atoms comprising the dielectric exhibit a dipole movement.

A dipole is two equal and opposite charges separated by a finite distance. Water molecules are an excellent example in this respect because of the

stereochemistry of covalent bonds. As a result, the water molecule exhibits a dipole movement. Water is the typical case of a non-symmetric molecule. When a material is held in an alternating electric field, it gains potential energy. Some of this energy is stored inside the material as electric energy and the rest is dissipated as heat. Materials' behavior in a microwave field is predicted by the dissipation factor, often called the loss tangent ( $\tan \delta$ ) which is a ratio of the dielectric loss or the loss factor to the dielectric constant (Guo and Lua 2000; Yuen and Hameed 2009).

### **2.5.2 Microwave Activation**

Since carbonaceous materials are found to be good microwave absorbers because of their dielectric properties, microwave assisted heating is a promising technique in producing activated carbon. As a result, in recent years, the research that considers both the use of carbons and microwave heating has increased significantly. The main motivation for using microwave heating over the traditional heating of carbon precursors involves selective, rapid and volumetric heating, non contact heating, energy transfer instead of heat transfer, low energy (electricity) consumption throughout the heating process, the smaller space required for set up and the ease of control (Yuen and Hameed 2009; Menéndez et al. 2010). Despite being a relatively new technology in activated carbon production, microwaves have numerous advantages over traditional heating.

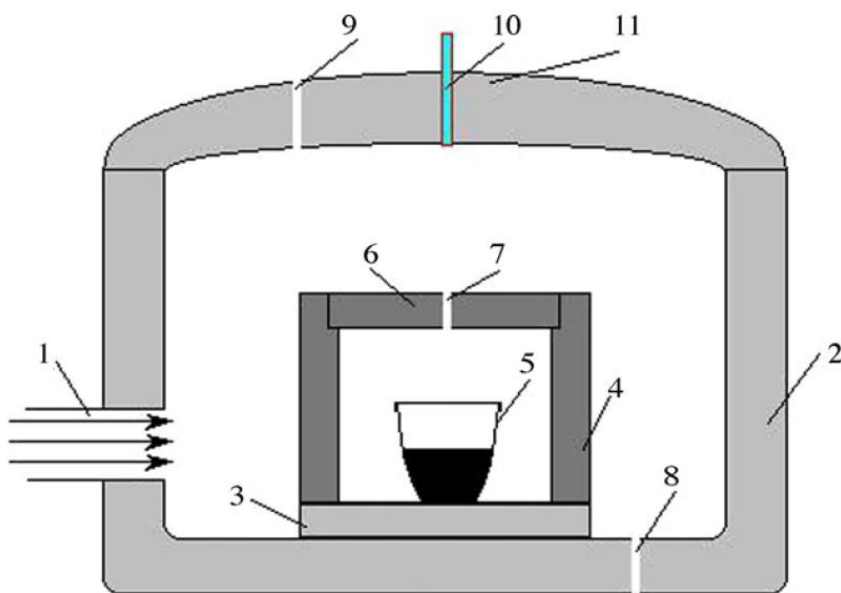
Liu et al. (2010) carried out microwave induced chemical activation with  $\text{H}_3\text{PO}_4$  for bamboo waste from handicrafts. Before the experiment was performed, the bamboo precursor was washed and milled to a particle size range of 1 to 2 mm. To perform the activation, five grams of precursor was mixed with  $\text{H}_3\text{PO}_4$  at different impregnation ratios and was placed in a modified microwave with a 2.45 GHz frequency and continuous output power. Throughout the activation process,  $\text{N}_2$  gas was introduced at a rate of 40 mL/min to ensure an inert reaction environment. After activation, the sample was washed with distilled water until the product's pH reached 6. Before characterization, the washed sample was dried at 105 °C for 12 hours. It was observed that a 350 W microwave power, 20 minutes of microwave heating, and impregnation ratio of 1 provided the highest surface area of 1432  $\text{m}^2/\text{g}$ . The surface chemistry analysis also demonstrated the existence of acidic groups, which play an important role in determining the carbons' surface properties and have significant implications on their behavior as ion exchangers, adsorbents, catalysts, and catalyst supports (Liu et al. 2010).

Wang et al. (2009) reported the production of activated carbon by using a microwave induced chemical activation technique with  $\text{ZnCl}_2$  and a wood precursor. During the experiment,  $\text{ZnCl}_2$  was used as the activation agent and heat carrier, because a wood precursor without  $\text{ZnCl}_2$  is an ineffective receptor for microwave energy. Before the activation, 10 g of wood particles of about 0.3 mm to 3.3 mm particle size were mixed with  $\text{ZnCl}_2$  at an impregnation ratio of 0:1 to 3:1. It was concluded that the  $\text{ZnCl}_2$  impregnation ratio could control the

mesopore formation of the porous carbon. The highest surface area was 1459 m<sup>2</sup>/g with a 2.5:1 impregnation ratio for a 10 minute activation time and 700 Watt microwave heating (Wang et al. 2009).

Ji et al. (2007) used coal-tar pitch derived meso carbon micro beds (MCMB) as the precursor in preparing activated carbon with microwave heating and KOH as an activating agent. The microwave set up for the experiment is shown in Figure 2.5-2. Before activation, the hydrophobic MCMB of 20  $\mu$ m particle size was mixed with alcohol and impregnated with KOH solution at different mix ratios. To perform the experiment, a microwave of 3 kW power and a frequency of 2.45 GHz was used. From the experiment, it was found that BET surface area, and micropore and mesopore volume increased with an increase in KOH/MCMB ratio up to 8. However, the surface area and pore volumes began to decrease at KOH/MCMB ratio of 9 due to the collapse of micropores and enlargement of mesopores at higher KOH/MCMB ratios. The highest surface area was found to be 4106 m<sup>2</sup>/g at an impregnation ratio of 8. The microwave activated MCMB had larger surface area than MCMB activated with traditional electric furnace (EF) heating. This result happened as microwave heating starts from the center to the surface of the material and creating a gradual temperature gradient from the inside to the outside which removes light components from the materials and results in more pores formation. The most effective activation time was 20 minutes, as longer times provide a greater number of mesopores than micropores, when the latter are destroyed. Surface functional groups were also

analyzed by FTIR. Microwave activation provides less oxygen containing surface functional groups, as these groups are readily released during microwave heating (Ji et al. 2007).



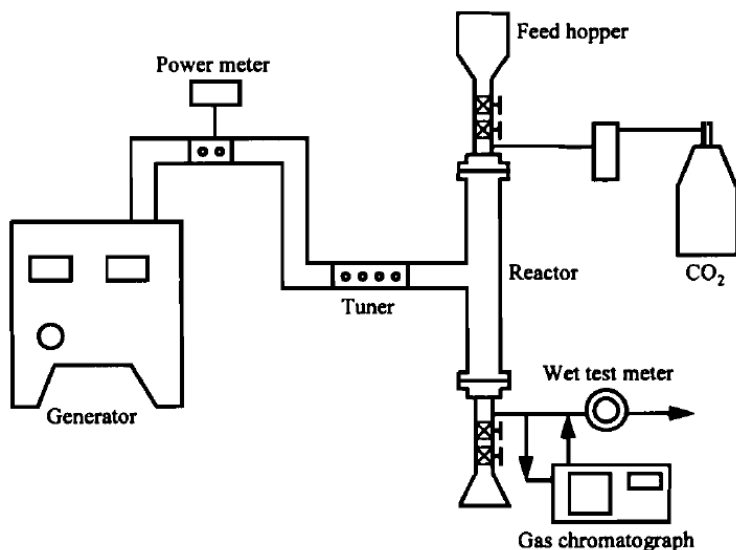
**Figure 2.5-2: Microwave set up adapted from (Ji et al. 2007) where 1. MW input, 2. Steel Shell, 3. Rotary Plate, 4. Insulated Materials, 5. Corundum Crucible, 6. Lid, 7. Hole for Temperature Measurement, 8. Nitrogen Inlet, 9. Nitrogen outlet, 10. Infrared Pyrometer, 11. Cover**

A recent study on activated preparation was conducted by He et al. (2010), where petroleum coke was used as the activated carbon precursor. Activation was carried out by a chemical activation with the widely used KOH activating agent and microwave assisted heating. Petroleum coke with less than 75  $\mu\text{m}$  particle size was mixed with KOH solution in a dry weight ratio of 1:5. The highest BET surface area (2312  $\text{m}^2/\text{g}$ ), micropore volume (1.05  $\text{cc}/\text{g}$ ) and total pore volume (1.13  $\text{cc}/\text{g}$ ) was found at 35 minutes activation time. When increasing the

activation time up to 35 minutes, all the above properties increased; however, a further increase to 37 minutes activation time resulted in a decrease in BET surface area, and micropore and total pore volume. From the N<sub>2</sub> adsorption isotherm, it was also observed that the prepared activated carbons represented Type I isotherm, which indicates the domination of micropores. Though temperature during microwave activation measurement was difficult, a thermocouple determined the material temperature immediately after activation. After 30 minutes of activation, the activation temperature was 800 °C and a rapid rise in temperature occurred immediately after running the microwave.

Norman and Cha (1996) also performed microwave induced activation to produce activated carbon with coal char by using physical activation techniques and CO<sub>2</sub> gas as the activating agent. The activation temperature was measured in a passive manner from the microwave induced power. The microwave set up for experiment is illustrated in Figure 2.5-3. The production of activated carbon required two procedural steps: de-volatilization followed by activation. De-volatilization was carried out at a skin temperature of 93.3 °C, and char was produced at an operating temperature of 760 °C. The microwave was generated by an industrial microwave generator of power ranging from 0 to 6000 Watts. The main set process parameters in evaluating the set-up's performance are CO<sub>2</sub> inlet flow rate, input microwave energy and char residence time. The internal maximum surface area was measured to be less than 400 m<sup>2</sup>/g for 700 watts of microwave energy input, 0.755 Lpm flow rate of CO<sub>2</sub> and two hours of residence

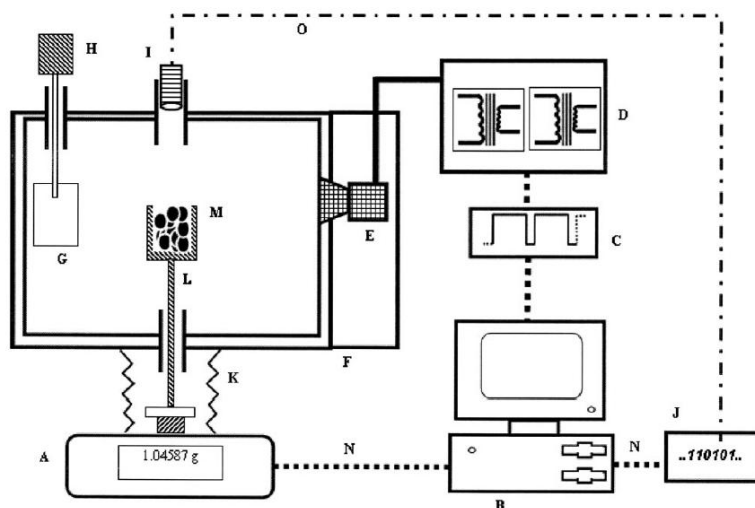
time. From the experiment, it was concluded that the rate of activation was controlled by the electric field strength which was directly related to microwave power and controlled the formation of internal surface area. The experiment also revealed that devolatilization contributes to an increase in internal surface area (Norman and Cha 1996).



**Figure 2.5-3 Microwave activation system with reactor adapted from (Norman and Cha 1996)**

Williams and Parkes (2008) used microwave thermogravimetry to produce activated carbon from phenolic resin derived carbon. An exothermic approach was followed by using CO<sub>2</sub> and air as the activating agents. As a microwave heating source, the domestic microwave oven was custom modified (Figure 2.5-4) to provide 800 W power and 2.45 GHz frequency. The precursor for activation was produced by the carbonization of a mix containing 10 wt% hexamethylene tetramine and the cross-linking agent, 99% hexamine. The carbonization

temperature was maintained at 500 °C and 900 °C. The dielectric properties of the precursors were 0.0064 for 500 °C carbonization, and 2.465 for 900 °C carbonization. In a silica supported crucible, 0.5 to 15 g of carbonized precursors was used. The precursors, carbonized at 500 °C were hardly heated by the microwaves, whereas the precursors carbonized at 900 °C were immediately heated by the microwaves.. The activated carbon prepared from the precursor carbonized at 900 °C had a higher Langmuir surface area of 1240 m<sup>2</sup>/g for around three hours of activation (Williams and Parkes 2008).



**Figure 2.5-4: Development of a microwave thermo gravimetric analyzer based on a multimode oven After (Parkes and Williams 2005)**

Guo and Lua (2000) also reported the use of physical activation in preparing activated carbon with microwave heating. They used oil-palm-stone agriculture waste with N<sub>2</sub> and CO<sub>2</sub> gas, used separately as activating agents. From the experiment, it was observed that activation with N<sub>2</sub> resulted in no reaction and



provided a 100% product yield, whereas the activation with CO<sub>2</sub> provided moderate yield. The presence of oxygen groups induced the microwave heating to react with carbon. The highest BET surface area of the activated carbon was 320.6 m<sup>2</sup>/g and 195.2 m<sup>2</sup>/g for CO<sub>2</sub> and N<sub>2</sub> activating agents, respectively, for 750 W power and 20 minutes of activation. The raw carbon precursor had a BET surface area of 194.3 m<sup>2</sup>/g, so the change in surface area was not significant. To increase the surface area, CuO was used as the microwave receptor and the surface area was observed to be 527.6 m<sup>2</sup>/g for 10 minutes of activation at 750 W.

Yang et al. (2010) performed a comparative study of steam, CO<sub>2</sub> and a combination of steam and CO<sub>2</sub> by using physical activation techniques with microwave heating. Coconut shell was used as the precursor. To perform the research, the coconut shell first undergoes the carbonization stage at 1000 °C with N<sub>2</sub> gas flow at 200cc/m in, then activation with steam at 1.35 g/min, CO<sub>2</sub> at 600 cc/min and a combination of these two activating agents at 900 °C. Temperature in the activation chamber was measured by a K-Type thermocouple (chromel-alumel). From the study, it was found that CO<sub>2</sub>-activated carbon provided a higher surface area (2280 m<sup>2</sup>/g) compared to steam (2079 m<sup>2</sup>/g) and CO<sub>2</sub>+steam (2194 m<sup>2</sup>/g). However, the activation time for CO<sub>2</sub> activated carbon was longer (210 min) than that of steam (75 min) and CO<sub>2</sub>+steam (75 min). It was found that CO<sub>2</sub> activated carbon provided the lowest rate of decreasing yield with an increase in time, then steam activated carbon and lastly steam+CO<sub>2</sub> activation. CO<sub>2</sub> required

2.5 times longer activation time than the other two activating agents, it provided the highest surface area (Yang et al. 2010).

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## **CHAPTER 3:      CHEMICAL ACTIVATION OF DELAYED AND FLUID COKE.**

### **3.1 Introduction**

Oil sands are naturally occurring mixtures of sand or clay, water and a thick heavy substance called bitumen. The total oil sands reserve contains over 174 billion barrels of bitumen in Alberta (AEUB. 2005). Fluid coking and the delayed coking process are used to upgrade bitumen (Fedorak and Coy 2006). These coking processes produce a huge amount of coke as a waste by-product. Alberta is experiencing a massive production and accumulation of oil sands coke, which is now more than 6000 tons per day. In 2003, Syncrude Canada and Suncor Energy produced 2 and 3 million metric tons of coke, respectively. In 2007, about 5 million metric tons of cokes were produced in Alberta and 23 million tons were stockpiled as long term storage. In 2011, total production was increased to 12 million metric tons which was more than double compared to the production in 2007. Coke production is expected to increase at 25 million metric tons per year by 2010 (Isaacs 2007). It is estimated that, over the lifetime of the oil sands extraction operations, the total volume of coke will be 1 billion m<sup>3</sup> (Fedorak and Coy 2006).

Activated carbon is widely used as an adsorbent for gas separation, air purification, mercury capture, organic vapor adsorption, de-colorization, potable

water purification and sewage water treatment (Mochida et al. 2000; Wu et al. 2005). Different precursors are used to produce activated carbon, including petroleum coke, bituminous coal, coconut shells, macadamia nutshell, date stones, cherry stones and cork waste (Verheyen et al. 1995; Ahmadpour et al. 1998; Hsu and Teng 2000; Carvalho et al. 2003; Chunlan et al. 2005; Arjmand et al. 2006). The Alberta oil sands coke is considered a suitable precursor for the production of activated adsorbent as it has a high carbon content (more than 80 %) and a non-graphitic structure (Gao et al. 2010).

Activated carbon preparation methods can be grouped into physical activation and chemical activation. The physical activation methods involve the presence of active agents such as steam, carbon dioxide, nitrogen, or a mixture of these gases (Marsh and Rodríguez-Reinoso 2006). In chemical activation methods, the starting feedstock is first impregnated with an active agent prior to heat treatment. The active agents used in chemical activation process are usually KOH, ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub> (Verheyen et al. 1995; Ahmadpour et al. 1998; Teng et al. 1998; Carvalho et al. 2003; Chunlan et al. 2005).

Activated carbon produced by the physical activation of delayed and fluid coke was used to remove the naphthenic acids from the process affected tailings water of oil sands tailing ponds. The highest surface area was found to be 578 m<sup>2</sup>/g for delayed coke and 494 m<sup>2</sup>/g for fluid coke at the activation temperature of 900°C and activation time of 6 hours (Small 2011). In another study, activated

delayed coke was used to reduce the color and chlorinated organic from pulp mill wastewater. The activated carbon derived from the delayed coke had a maximum methylene blue adsorption of 100 mg/g (Shawwa et al. 2001). Also, activated fluid coke was used to remove mercury from a gas stream. In this case, the activated coke was prepared by physical activation with an activation temperature of 800°C and the maximum surface area was found to be 500 m<sup>2</sup>/g (Bratu 2008).

In this study, delayed and fluid oil sands cokes are used as precursors to produce activated carbon with high surface area. Chemical activation with KOH as the impregnation chemical is performed. The effect of activation parameters, including activation time, KOH/coke ratio (impregnation ratio), and activation temperature has been investigated. The iodine number, specific surface area and pore size distribution are also obtained to determine the impact of activation conditions on the properties of the activated carbon produced.

## **3.2 Experiments**

### **3.2.1 Sample Preparation**

Both the delayed and fluid coke samples were used. The particle size for delayed cokes varies from micrometers to decimeters, and the fluid cokes were generally around hundreds of micrometers in scale. Coke particle size of 420 µm to 300 µm was selected to perform the entire activation, as it was found to be the most effective size for oil sands coke activation (Chen 2010). ASTM Sieve of #40

and #50 produced the desired particle size of fluid coke and ground delayed coke samples.

Potassium Hydroxide (KOH) (American Chemical Standard grade) was used as the impregnation chemical. KOH was dissolved in water to produce an aqueous solution and then mixed with coke at different dry weight ratios. Before mixing, the ground raw coke samples were dried in an electric oven for 24 hours at  $110 \pm 5^\circ\text{C}$ . The dried coke sample was mixed with KOH in a ceramic crucible and was kept for two hours. The crucible and mixed sample were placed in the electric oven at  $150^\circ\text{C}$  for 4 hours to remove the moisture. The dried mixed sample was then transferred to a fixed-bed muffle furnace for activation.

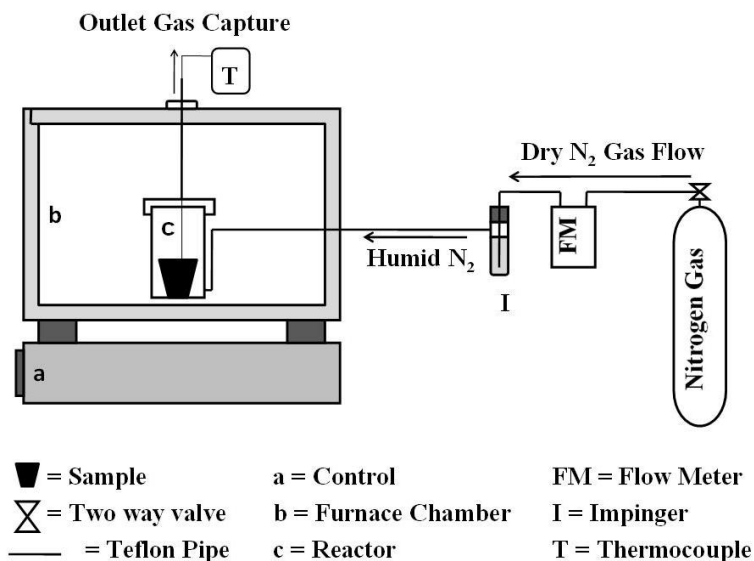
After activation, the activated coke samples were washed with 5% HCl and ultra-pure de-ionized water until the pH of the solution reached 7. The washed samples were then dried at  $110^\circ\text{C}$  in the electrical oven. The weight of the raw coke, as well as that of the activated coke after washing and drying, was measured to calculate the burn-off and yield.

### **3.2.2 Experimental Setup and Activation**

Activation of the coke samples was performed with a fixed bed muffle furnace where heat was produced through heating the coil with electricity. A ceramic crucible of 50 mm top diameter held the sample during activation. The sample held by the ceramic crucible was placed in a quartz reactor to seal the

surrounding environment. The quartz reactor consisted of two parts, the gas inlet and outlet, to neutralize the activation atmosphere and collect the waste burned gas respectively. The whole reactor was cylindrical, and the gas was purged from the bottom to ensure sufficient circulation. Quartz material was used to withstand higher temperature. The University of Alberta Glass Shop manufactured the reactor.

Before activation, the raw coke was dried in an electric furnace. During the activation process, the influence of different parameters is monitored, including activation time, activation temperature, and impregnation ratio. Throughout the chemical activation, humid nitrogen gas was used as the activation gas. Humid nitrogen was reported as the most effective activating atmosphere for producing activated carbon from petroleum coke (Chen 2010). Pure dry nitrogen was fed into an impinger containing ultra-pure de-ionized water to make it humid. The flow rate was maintained at 0.5 Lpm. Teflon gas tubing of ¼ inch sizes carried the gas into the quartz reactor. The burned out gas was allowed to exit into the fume hood. To measure the temperature of the sample, and monitor the performance of the furnace, a K-Type thermocouple was placed through the top outlet of the reactor towards the precursor. The schematic diagram of the whole experimental set up is presented in the following Figure 3.2-1.



**Figure 3.2-1: Schematic diagram of chemical activation reactor set up for the preparation of activated carbon from delayed and fluid coke.**

### 3.2.3 Sample Characterization

Sample characterization of the activated coke was performed to evaluate the performance of different activation parameters in determining the quality of produced activated carbon.

#### 3.2.3.1 Iodine Number

Iodine number is considered to be one of the main measures of the quality of activated carbon. The iodine number of activated carbon refers to the iodine adsorption capacity. The American Society of Testing and Materials (ASTM) standard ASTM 4607-94 (ASTM 2006) was the method used to conduct the iodine test for this research work. Iodine number was measured by the volumetric

titration of the filtrate obtained after the adsorption of standard iodine solution by three different amounts of activated carbon. The volumes of different chemicals were changed from the standard amount. To conduct the iodine test, 25 ml of HCl, 50 mL of KI/I<sub>2</sub> and 40 mL of filtrate were used. The iodine number provides the amount of iodine (mg) adsorbed per weight of carbon (g). It also provides a good estimate of the specific surface area and the micropore volume of the activated carbon, as the diameter of the iodine molecule is 4.94 Å (Juhola 1975).

### **3.2.3.2 Nitrogen Adsorption Isotherm and BET Surface area**

N<sub>2</sub> adsorption on activated carbon was performed at 77 K with the instrumentation of Quantacrome, Autosorb 1-MP. N<sub>2</sub> adsorption isotherms determined the BET surface area and pore size distribution of the activated carbon. To obtain the N<sub>2</sub> adsorption isotherm, approximately 10 mg to 100 mg of activated carbon was used. The sample was first degassed at 250 °C for 3 to 4 hours. After degassing, the vacuum sample cell was filled with helium gas to avoid any moisture contacting the activated carbon.

The 11 point Brunauer, Emmett and Teller (BET) model was used to determine the surface area from the N<sub>2</sub> adsorption isotherm. The relative pressure ( $p/p_0$ ) ranged from 0.02 to 0.055 as the relative pressure within these range provide linear region on BET equation (Marsh and Rodríguez-Reinoso 2006; ASTM 2010). The DFT model determined the pore size distribution as well as the

total pore volume of the samples where the relative pressure ranged from  $10^{-6}$  to 1 to have full scale adsorption isotherm. Micropore volume was calculated by the t-method analysis when the relative pressure ranged from 0.2 to 0.5 (Lowell 2004; Quantachrome 2010).

### **3.2.3.3 Scanning Electron Micrographs (SEMs)**

Scanning Electron Micrographs of both the raw and activated coke samples were taken by Hitachi S-2500's scanning electron microscopy. Before scanning, the coke samples were coated with gold to improve conductivity. The acceleration voltage was maintained at 8 kV to allow a better surface view and the magnification scale was set at 200 to 6000.

## **3.3 Result and Discussion**

### **3.3.1 Activation Parameters and Sample Preparation**

The carbonization stage takes place at a relatively low temperature when compared to the activation temperature. Temperature is one of the main parameters affecting activation. It influences the structural behavior of the activated carbon by changing the pore formation as well as by decomposing organic materials. A Thermo Gravimetric Analysis (TGA) identifies the thermal behavior of a precursor which can then be used to design the activation process. To perform this experiment, TGA of the raw delayed and fluid coke was adapted from previous study of Small (2011). The analysis was performed in a  $N_2$  gas



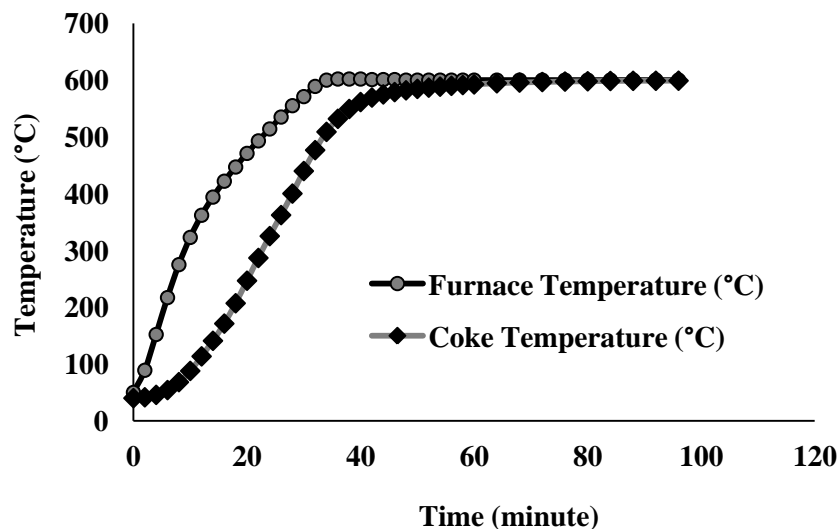
atmosphere up to 800 °C, and then with CO<sub>2</sub> up to 950 °C. From the analysis, it was observed that, up to 450 °C, both the delayed and fluid coke follow the same weight loss pattern, while at temperatures up to 800 °C, delayed coke undergoes gradual weight loss and fluid coke shows almost constant weight loss. The author attributed this situation to the content difference of the raw cokes. The content of the raw coke differs due to their coking process. Delayed coke experiences a lower coking temperature compared to the fluid coke, which causes more organic materials to become trapped inside. After 800 °C, the delayed coke experienced a weight loss of 21 %, whereas the fluid coke experienced a 10 % weight loss up to 950 °C. These results occurred due to the initial structural differences of the raw delayed and fluid coke, as well as the presence of foreign materials. This type of significant weight loss is only observed until potential pathways and channels of a range of pores are created. From this TGA result, it is expected that, to produce high quality activated carbon, the raw precursor should be heated to over 800 °C. Chemical activation requires a lower activation temperature than the physical activation. As a result, temperatures below 800 °C are ideal to conduct this chemical activation experiment. In this experiment, the activation temperature ranged from 500 °C to 800 °C. The carbonization stage was ignored, as the coking process experienced a temperature of 400 °C to 500 °C.

The precursor's particle size for both the delayed and fluid coke was selected to be 420 µm to 300 µm, as these sizes are most effective for activation (Chen 2010).

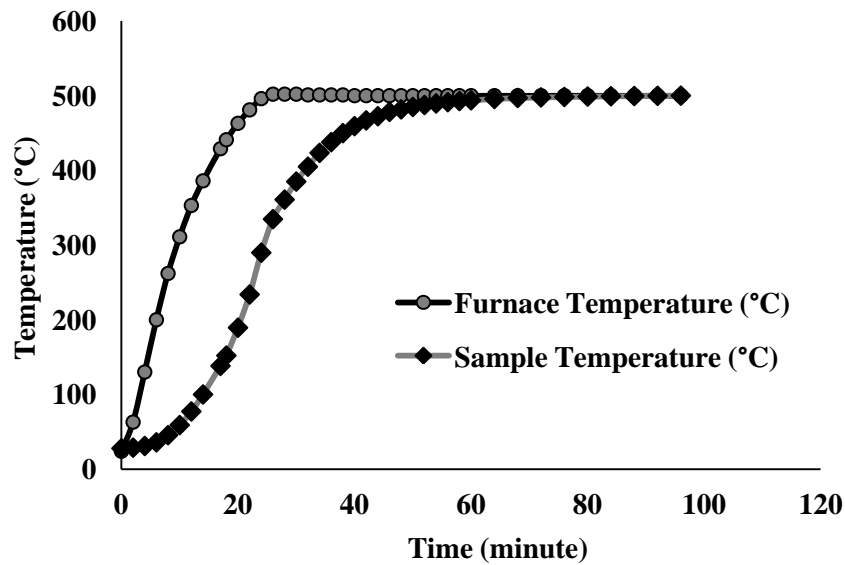
### 3.3.2 Temperature Profile and Activation Time

A muffle furnace was used as the heating source for activation. It used electricity to produce heat through a coil. As there was a gap between the activation reactor and the heating coil of the furnace, the temperature reading from the furnace, was different from the sample temperature inside the reactor. To determine this difference in heating time, as well as measure the sample temperature, a K-Type thermocouple was inserted through the reactor and inside the sample.

Figure 3.3-1 and Figure 3.3-2 present the temperature profile of the furnace and sample for an activation temperature of 500 °C and 600 °C.



**Figure 3.3-1: Furnace and raw delayed coke temperature profile for the activation temperature of 500 °C.**



**Figure 3.3-2: Furnace and raw delayed coke temperature profile for the activation temperature of 600 °C.**

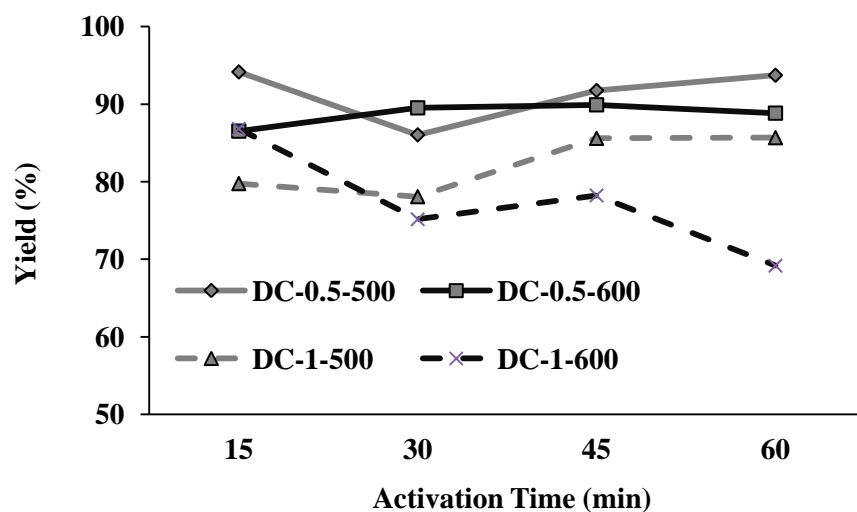
The temperature profile in an activation experiment follows three stages: the temperature at ramping up stage, steady state activation stage and cooling down stage. From the above temperature profile, a time lag for the ramping up stage for both the furnace and sample were observed. It also found that, to reach a particular activation temperature, it took 60 minutes for both the sample and furnace. Depending on this time lag, the ramping up time was set to 60 minutes for 500 °C to 800 °C activation temperature. The steady state activation time was set as the experimental parameter. There was no time limit for cooling down. When the temperature of the sample cooled down to room temperature, the sample was taken out and processed for further characterization.

### **3.3.3 Sample Characterization**

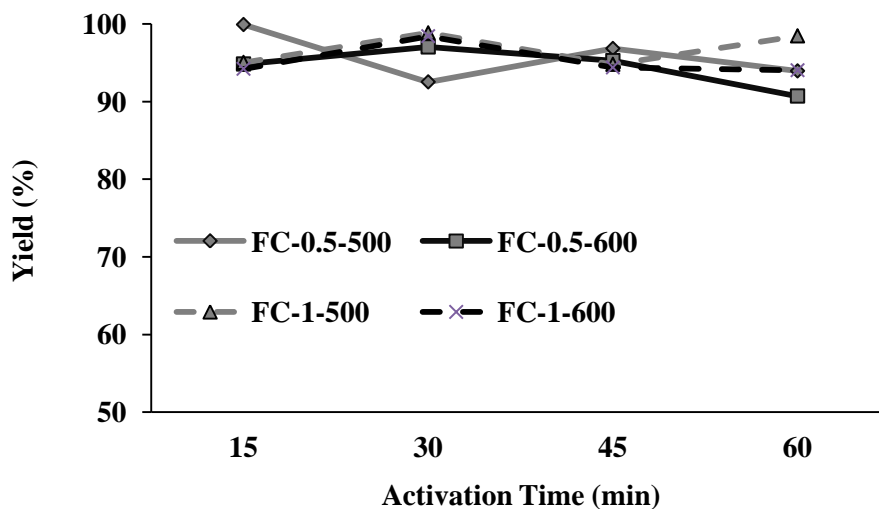
#### **3.3.3.1 Activation Yield**

Yield is the parameter that determines the overall activation as well as the material loss. Throughout the experiment, the yield of the raw coke was determined by considering the dry weight of the activated coke and the dry weight of the raw coke. As both the delayed and fluid cokes are activated at 500 °C to 800 °C with an activation time of 15 minutes to 4 hours, the production yield in each case has been investigated. The activation time started after 60 minutes of ramping up time which was required for the precursor to reach the activation temperature in the muffle furnace.

Figure 3.3-3 represents the yield of delayed coke at 500 °C and 600 °C with respect to an activation time of 15 minutes to 1 hour. Figure 3.3-4 represents the change in yield for fluid coke over the activation time at activation temperatures of 500 °C and 600 °C.

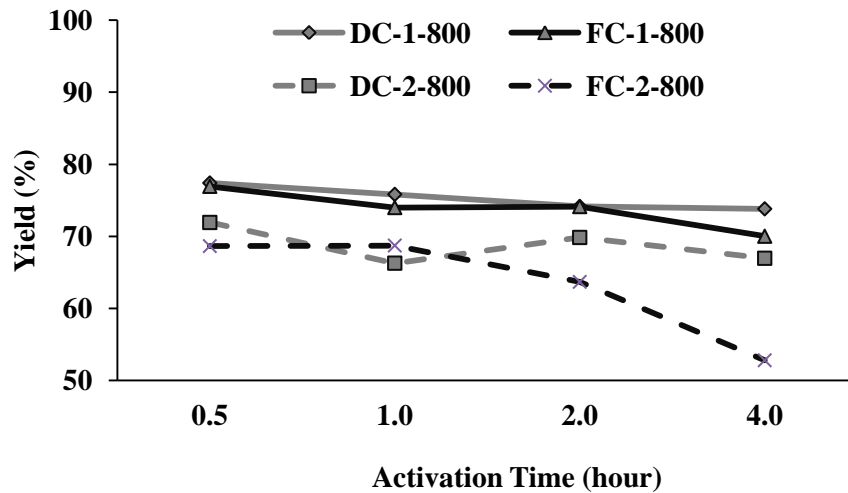


**Figure 3.3-3: Yield (%) of delayed coke activated carbon prepared at 500 °C and 600 °C with KOH/coke ratio of 0.5 and 1. Activation was started after 60 minutes ramping up temperature. [DC = Delayed Coke, 0.5, 1 = KOH/coke ratio, 500, 600 = Activation temperature °C]**



**Figure 3.3-4: Yield (%) of fluid coke activated carbon prepared at 500 °C and 600 °C with KOH/coke ratio of 0.5 and 1. Activation was started after 60 minutes ramping up temperature. [FC = Fluid Coke, 0.5, 1 = KOH/coke ratio, 500, 600 = Activation temperature °C]**

From these two plots, it was concluded that temperatures of 500 °C and 600° C had very little significance on the yield and activation in general. As yield presents the material loss, and successively, better activation, Jankowska et al. (1991) indicated that at least 50 % yield or burn-off is required for higher quality activated carbon. From the analysis of the yield, it can be conclude that a higher temperature of 800 °C is more suitable for activation, as shown in Figure 3.3-5.



**Figure 3.3-5: Change of activated carbon yield (%) both for delayed and fluid coke versus activation time from 30 minutes to 4 hours with impregnation ratio of 1 and 2 at temperature 800 °C. Activation was started after 60 minutes ramping up temperature. [DC = Delayed Coke, FC = Fluid Coke, 1, 2 = KOH/coke ratio, 800 = Activation temperature in °C]**

From Figure 3.3-5, it is observed that both the delayed and fluid coke provide a moderate yield at 30 minute activation time, and with an increase in activation time, the yield decreases. Figure 3.3-5 denotes that, with an increase in the chemical impregnation ratio, the product yield also decreases. A change in yield with an increase in activation time is higher for delayed coke compared to

fluid coke. This result supports the effect of higher activation temperature, as higher temperature leads to higher gasification, as well as higher carbon removal.

### **3.3.3.2 Iodine Adsorption**

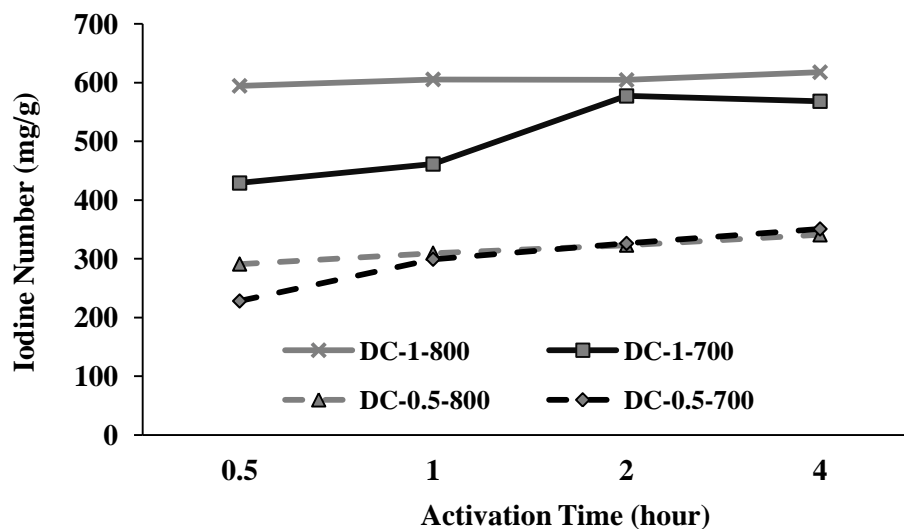
Initially, both the delayed and fluid coke were activated at low temperatures of 500 °C and 600 °C with an activation time of 15 minutes to 60 minutes. The iodine number of the activated coke was very low. The iodine adsorption results are shown in Table 3.3-1. For both the delayed and fluid coke, low iodine numbers were resulted which were less than 100 mg/g. The activation temperature was then increased to 700 °C and 800 °C, which resulted the increase in iodine number.

**Table 3.3-1: Iodine number for activated delayed and fluid coke at activation temperature of 500 °C and 600 °C with KOH/coke ratio of 0.5 and 1. Activation took place after 60 minutes of ramping up temperature time**

Coke	Temperature (°C)	Activation Time (min)	Iodine Number (mg/g)	
			at KOH/coke ratio 0.5	at KOH/coke ratio 1
Delayed Coke	500	15	14	63
		30	44	69
		45	62	64
		60	54	66
	600	15	41	45
		30	33	58
		45	40	61
		60	90	91
Fluid Coke	500	15	14	26
		30	24	36
		45	23	32
		60	21	37
	600	15	21	17
		30	23	28
		45	22	35
		60	28	41

Figure 3.3-6 represents the observed iodine number for delayed coke activated at 700 °C and 800 °C with a KOH/coke ratio of 0.5 and 1. Delayed coke at 800 °C with KOH/coke ratio 1 provided the highest iodine number of around 600 mg/g. The iodine number trend also supported the yield. The change in iodine number over the activation time was less significant, except for the activated coke prepared at 700 °C with a KOH/coke ratio of 1. The effect of this KOH/coke ratio was the most important activation parameters in obtaining a higher iodine number.

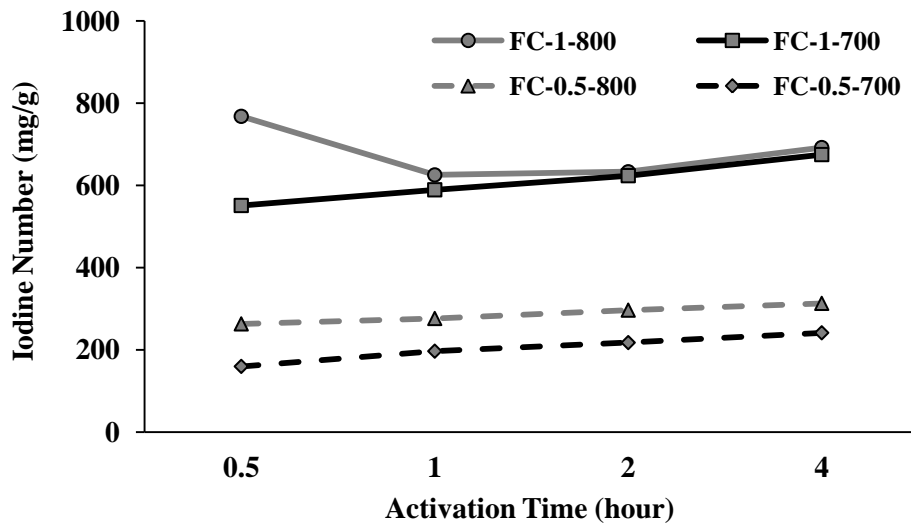




**Figure 3.3-6: Iodine number of activated delayed coke prepared at 700 °C and 800 °C with KOH/coke ratio of 0.5 and 1. Activation was started after 60 minutes ramping up temperature. [DC = Delayed Coke, 0.5, 1 = KOH/coke ratio, 700, 800 = Activation temperature in °C]**

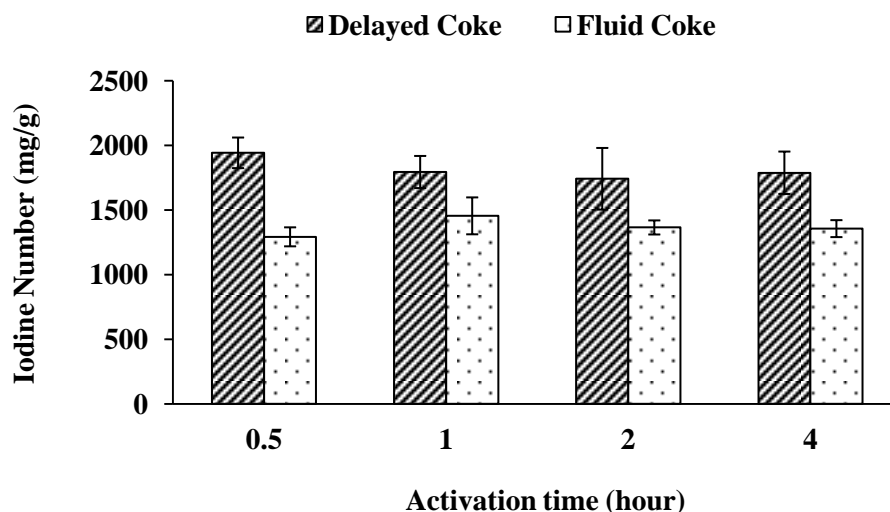
Figure 3.3-7 shows the iodine number for activated fluid coke prepared at 700 °C to 800 °C with a KOH/coke ratio of 0.5 and 1. The activated coke prepared at 800 °C with 30 minutes activation time and a KOH/coke ratio of 1, provides the highest iodine number. It can be described by the effects of longer activation time with high activation temperature. With the increase in activation time of more than 30 minutes, and at activation temperature of 800 °C, the micropores' walls, formed at low temperature are damaged and the nearby micropores are merged and formed mesopores which results low iodine adsorption and low iodine number. From the yield analysis, it is also found that, at 4 hours of activation time, yield is 10% lower than that of at 30 minutes activation time, which also support these abrupt change in iodine number with the increase in activation time. For the other activation conditions including KOH/coke ratio

0.5 and 800 °C , KOH/coke ratio 1 and 0.5 with 700 °C, an increase in the chemical impregnation ratio and activation temperature, results in an increased iodine number for the activated coke, which follows the yield trend.



**Figure 3.3-7: Iodine number for the activated fluid coke prepared at 700 °C and 800 °C with KOH/coke ratio of 0.5 and 1. [FC = Fluid Coke; 0.5, 1 = KOH/coke ratio; 700, 800 = Activation temperature in °C]. Activation took place after 60 minutes of ramping up temperature time.**

From Figure 3.3-6 and Figure 3.3-7, the observed iodine number for the activated delayed and fluid coke were low compared to the commercially available activated carbon of which the iodine number is around 1050 mg/g. As a result, a change in the activation parameter was made. Both the delayed and fluid coke was then activated at 800 °C with a chemical impregnation ratio of 2 (Figure 3.3-8).



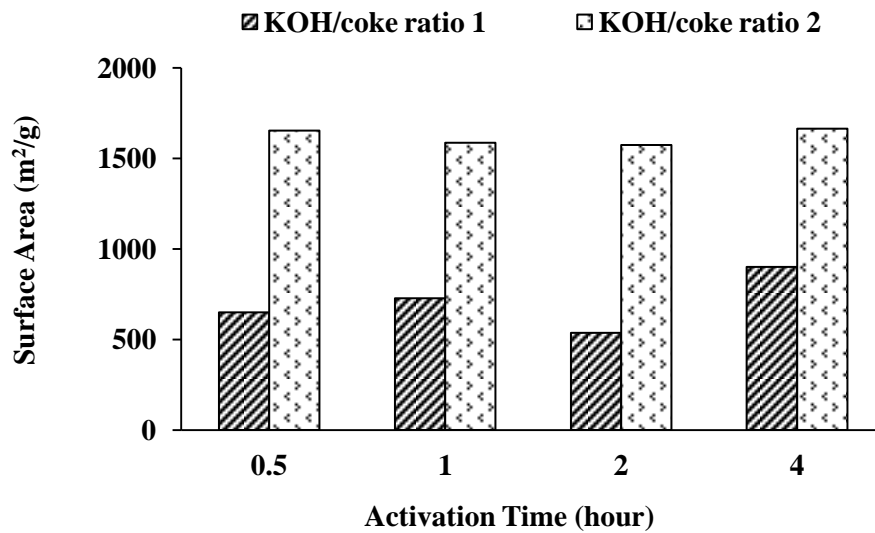
**Figure 3.3-8: Change of iodine number for the activated coke over activation time prepared both from delayed and fluid coke at 800 °C and KOH/coke ratio of 2. Activation took place after 60 minutes of ramping up time.**

From Figure 3.3-8, it was observed that the iodine number was very high for both the delayed and fluid activated coke. By noting the variation of iodine number over the activation time, 30 minutes represented the best activation time at 800 °C with a KOH/coke ratio of 2 for the delayed and fluid coke. The observed iodine numbers were also higher than those for the commercially available activated carbon (Calgon GAC F 100, Iodine number 1050 mg/g). From the above test, it was found that activated delayed coke has a higher iodine number compared to activated fluid coke. This difference is due to their different structural formation. Delayed coke was reported to have a sponge-like structure, whereas the fluid coke was reported to have a layered structure (Fedorak and Coy 2006). These structural differences create a barrier for the KOH diffusion and the

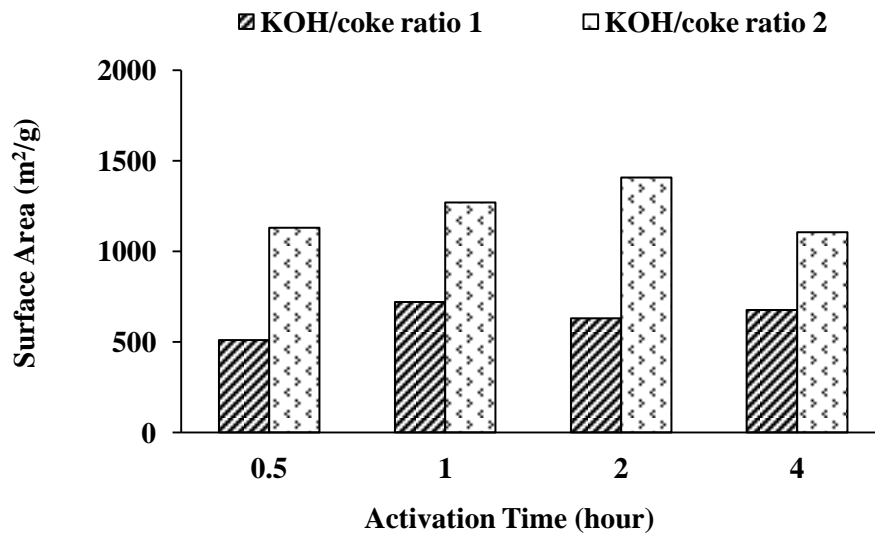
removal of carbon as CO<sub>2</sub> or CO, and resulted in differences in pore structure and iodine adsorption.

### **3.3.3.3 BET Surface Area and Pore Size Distribution**

The BET surface area and pore size distribution were characterized for the selected activated carbon, including both the delayed and fluid coke with higher iodine number. Figure 3.3-9 and Figure 3.3-10 show the BET surface area for activated delayed and fluid cokes. The BET surface area for the activated delayed coke prepared at 800 °C and with a KOH/coke ratio of 1, ranges from 536 m<sup>2</sup>/g to 900 m<sup>2</sup>/g. The activated delayed coke at 800 °C with KOH/coke ratio 2 gives 1574 m<sup>2</sup>/g to 1664 m<sup>2</sup>/g, which is much higher than the coke produced with KOH/coke ratio of 1. The change in the surface area over the activation time is less significant: ± 2.43 % for KOH/coke ratio 1 and ± 15.7 % for KOH/coke ratio of 2.

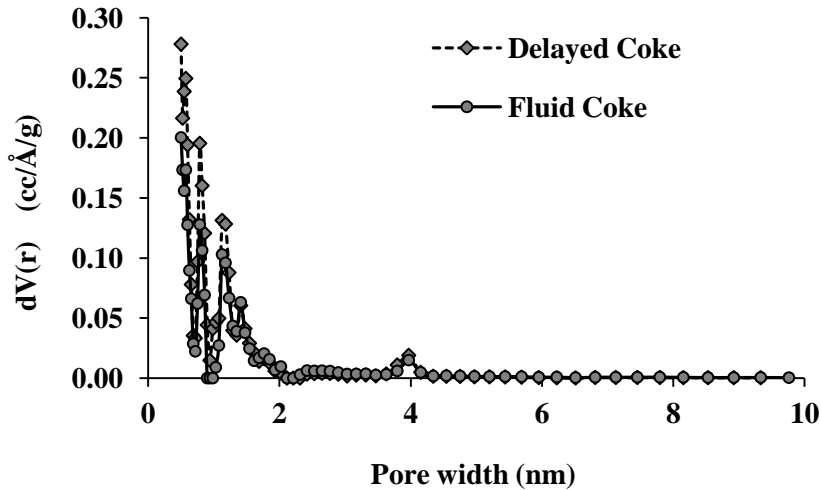


**Figure 3.3-9: Change in surface area of activated delayed coke prepared at 800 °C with KOH/coke ratio of 1 and 2 versus the activation time. Activation took place after 60 minutes of ramping up temperature time.**



**Figure 3.3-10: Change in surface of activated fluid coke versus the activation time, prepared at 800 °C and with KOH/coke ratio of 1 and 2. Activation took place after 60 minutes of ramping up temperature time.**

From Figure 3.3-10, the surface area for activated fluid coke for activation time of 30 minutes to 4 hours, varies from 510 m<sup>2</sup>/g to 720 m<sup>2</sup>/g for a KOH/coke ratio of 1 and 1105 m<sup>2</sup>/g to 1408 m<sup>2</sup>/g for KOH/coke ratio of 2. The overall change in surface area for the KOH/coke ratio 1 is ± 10.2%, and for KOH/coke ratio 2 is ± 9%. The pore size distribution for the activated delayed and fluid cokes, prepared at 800 °C with KOH/coke ratio 2 at 30-minute activation time, is illustrated in Figure 3.3-11. Both delayed and fluid coke have dominating micropores. Total pore volume and micropore volume has been determined by the DFT model and t-method. From the DFT model, the total pore volume was 0.72 cc/g and 0.57 cc/g for activated delayed and fluid cokes, respectively. Micropore volume was 0.62 cc/g and 0.42 cc/g for delayed and fluid coke, respectively.

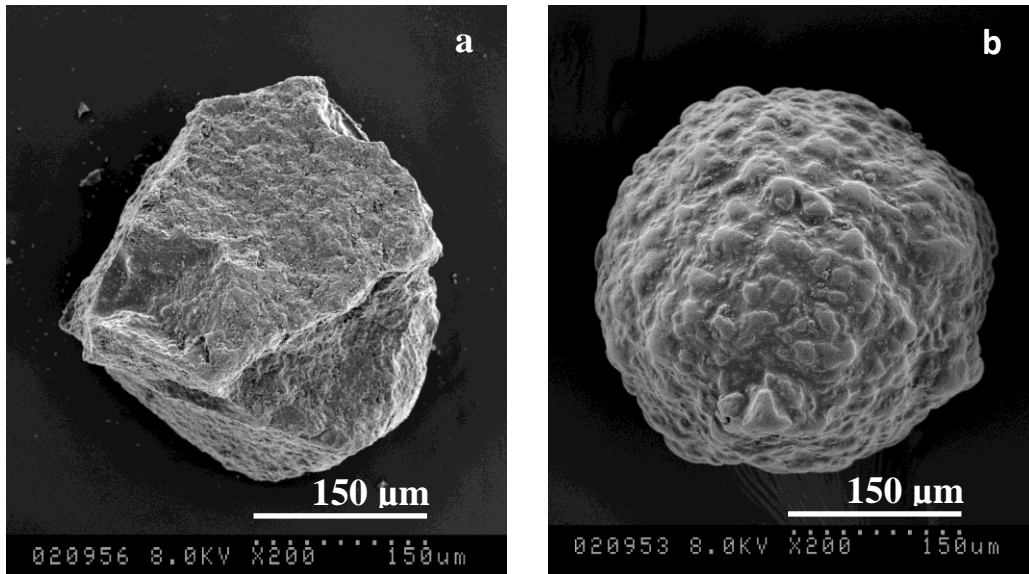


**Figure 3.3-11: Pore size distribution of activated delayed and fluid coke prepared at 800 °C of activation temperature, 30 minutes activation time and with KOH/coke ratio of 2.**

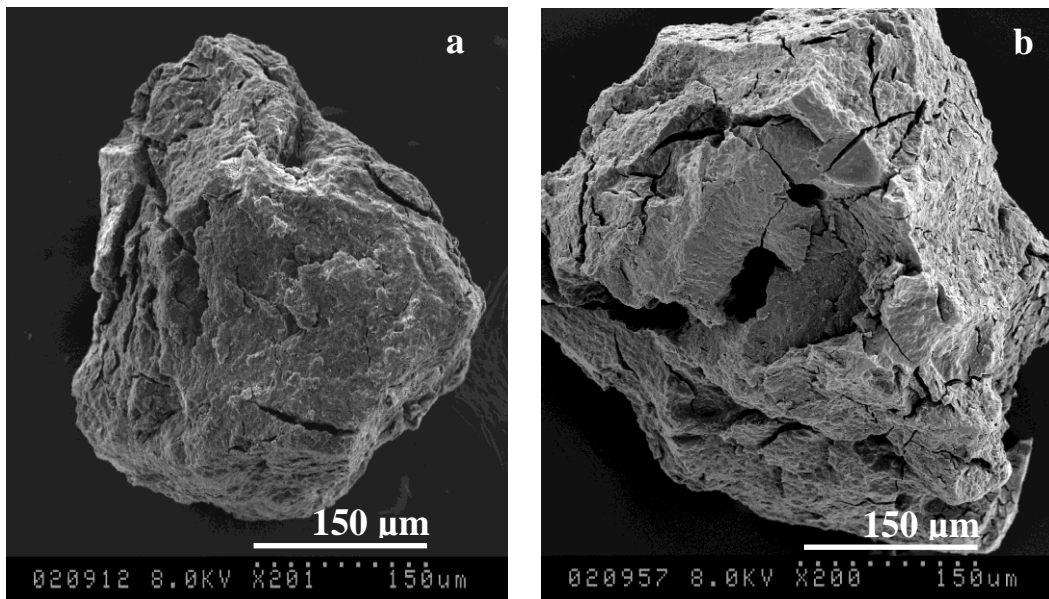
#### **3.3.3.4 Scanning Electron Micrographs**

Morphology of raw and activated cokes was investigated by the Scanning Electron Microscopy (SEM). SEMs provided an approximate idea of the physical change after activation compared to the initial raw product structure. Figure 3.3-12 presents the SEMs of raw delayed coke (part a) and fluid coke (part b). The SEMs of raw coke present clean, flake-free and smooth surfaces.

Figure 3.3-13 represents the activated delayed coke prepared at 800 °C with two KOH/coke ratios of 1 (part a) and 2 (part b). These SEMs show the effect of KOH/coke and the changing of KOH/coke ratio on the activation. At a higher KOH/coke ratio of 2, the activated delayed coke has more cracks and pores compared to the activated delayed coke produced at KOH/coke ratio 1. The Figure also shows the formation of larger pores which act as the main channel in producing further micropores inside the coke.



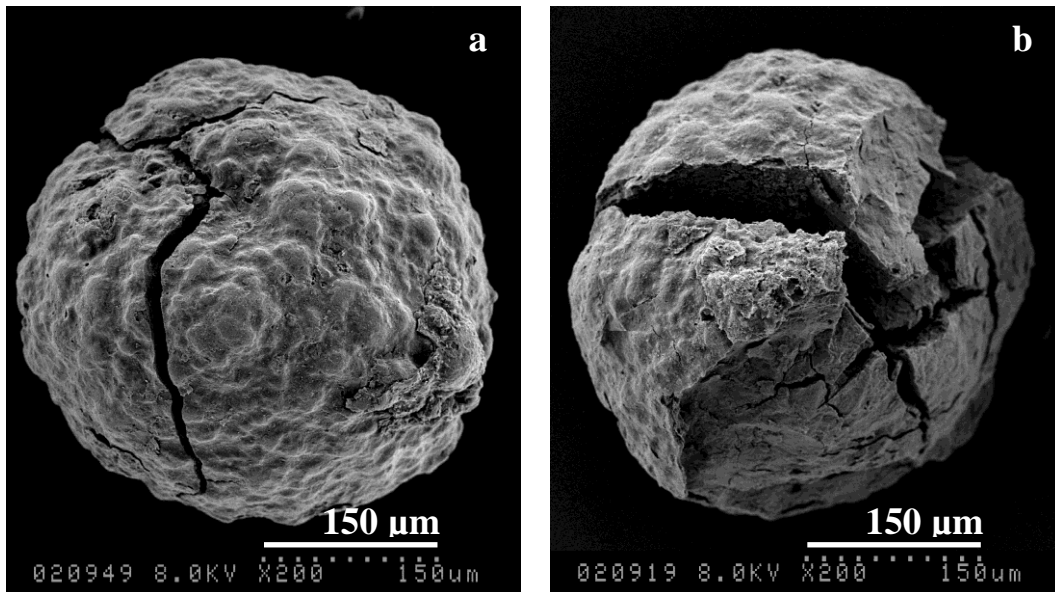
**Figure 3.3-12: Scanning Electron Micrograph at magnification scale of 200 of raw delayed (a) and fluid (b) coke.**



**Figure 3.3-13: Scanning Electron Micrograph of activated delayed coke prepared at 800 °C and 4 hours activation time with impregnation ratio of 1 (a) and 2 (b).**



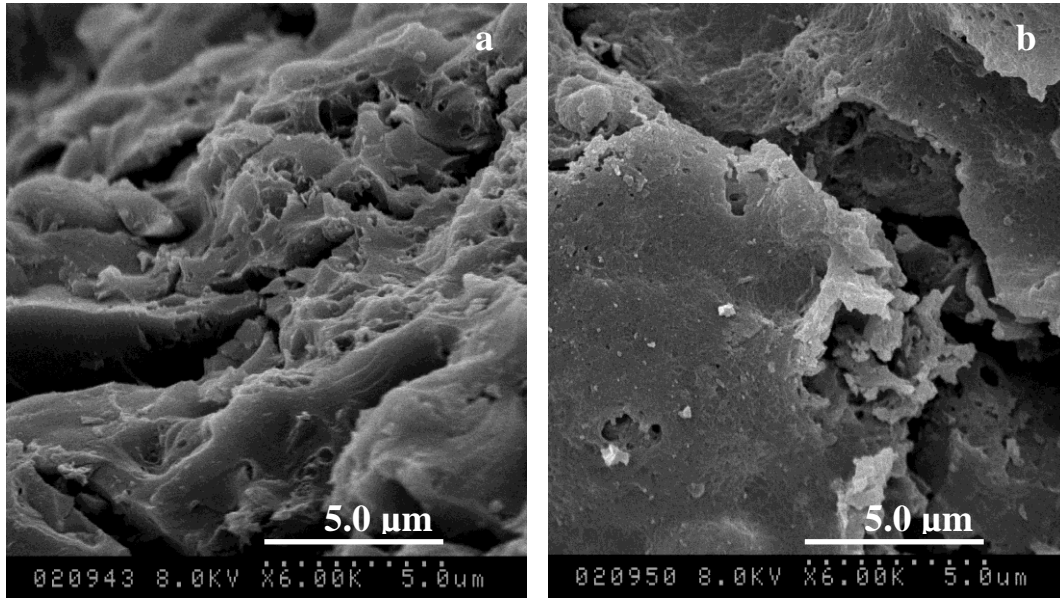
Figure 3.3-14 shows the SEMs for the activated fluid coke for KOH/coke ratio 1 (part a) and 2 (part b). Similar to the delayed coke, the higher KOH/coke ratio produces higher amount of cracks. With higher heating temperature and a high KOH/coke ratio, mesopores and larger cracks are formed with the merger of nearby micropores (Ji et al. 2007). Therefore it can be assumed that formation of larger cracks create the pathway for additional pore formation, resulting in a highly microporous structure.



**Figure 3.3-14: Scanning Electron Micrograph of activated fluid coke prepared at 800 °C and 30 minutes activation time with impregnation ratio of 1 (a) and 2 (b)**

Figure 3.3-15 shows the surface of the activated delayed (a) and fluid (b) coke prepared at 800 °C and 30 minutes of activation time. KOH/coke ratio was maintained as 2. Figure 3.3-15 provides the effect of activation parameters on the activation of coke by comparing to the raw coke (Figure 3.3-12). A loss of carbon

at higher activation temperature and higher KOH/coke ratio is expected to produce the rough and porous surface.



**Figure 3.3-15: Scanning electron micrograph of the surface of activated delayed Coke (a) and fluid coke (b) prepared at 800 °C with KOH/coke ratio of 2 and in 30 minutes activation time.**

### 3.3.4 Comparison of Results

The properties of activated cokes were compared to those in a previous study (DiPanfilo and Egiebor 1996; Chen 2010) on chemical activation through both traditional and microwave heating. Table 3.3-2 compares the iodine number, surface area, micropore volume and total pore volume of the activated delayed and fluid coke. KOH was used for each of the chemical activations.

**Table 3.3-2: Comparison of iodine number, surface area, total pore volume and micropore volume of chemically activated delayed and fluid coke using different activation set up from previous research work.**

<b>Activated Coke Type</b>	<b>Heat Source</b>	<b>Activation time</b>	<b>Iodine number (mg/g)</b>	<b>Surface Area (m<sup>2</sup>/g)</b>	<b>Total Pore Volume (cm<sup>3</sup>/g)</b>	<b>Micropore Volume (cm<sup>3</sup>/g)</b>
Delayed (This study)	Muffle Furnace	30 minutes*	1942	1654	0.72	0.62
Fluid (This study)	Muffle Furnace	30 minutes*	1292	1130	0.56	0.42
Delayed (Chen 2010)	Microwave	40 minutes	1240	1163	0.48	0.45
Fluid (Chen 2010)	Microwave	40 minutes	686	658	0.29	0.25
Fluid Coke (Di Panfilo 1995)	Furnace	6 hours	235-300	176	NA	0.16

\* Activation took place after 60 minutes of ramping up temperature time

Table 3.3-2 represents the highest iodine number, surface area and pore volume for different activation times and heating types. According to the test results, chemical activation with a muffle furnace and 30-minute activation time results in the highest iodine number, surface area and pore volume in this research work. The results also reflect the potential use of oil sands coke as activated carbon by means of chemical activation with muffle furnace heating.

### 3.4 Summary and Conclusions

The activation of delayed and fluid oil sands cokes was performed by chemical activation techniques with KOH as the activation agent. The particle size in this study varied from 420  $\mu\text{m}$  to 300  $\mu\text{m}$  and humid nitrogen gas flow was used as the neutralizing gas. Different operating conditions, including activation temperature, ratio of chemical agents (KOH/coke) and activation time, were all factors in controlling activation. Their corresponding effects have been illustrated. Characterization of the activated carbon was performed by the iodine number test,  $\text{N}_2$  adsorption test for BET surface area, and pore size distribution. The obtained results support the following conclusions:

- Throughout the activation process, activation temperature and the chemical impregnation ratio (KOH/coke) play the most important roles in producing high quality and high surface area in activated carbon from both delayed and fluid cokes.
- The effect of activation time is less significant in obtaining higher quality activated carbon from both delayed and fluid cokes. To produce a commercial grade activated carbon from the oil sands coke, it was found that 30 minutes of activation time is sufficient, along with 800 °C activation temperature and a KOH/coke ratio 2.
- Activated carbon prepared from delayed coke had a higher iodine number and surface area compared to activated carbon prepared from fluid coke at the same activation temperature, KOH/coke ratio and activation time. The reason behind this variation can be attributed to the differing structure of

delayed and fluid cokes. The structure of delayed coke is sponge-like, whereas fluid coke has a layered structure. These differing structural forms particularly affect chemical diffusion and pore formation.

- Surface areas of both the delayed and fluid cokes prepared in this study method are found higher compared to the other chemical activation studies with this same precursor. The obtained surface areas are also in the same range as of commercial grade activated carbon.
- According to the pore size distribution of the best produced activated carbon with higher iodine number, micropore volume is 85 % of the total pore volume, where the total pore volume is 0.72 cc/g for delayed coke. For fluid coke, the micropore volume is 75% of the total pore volume, which is 0.57 cc/g.

The experiment is successful as it fulfilled its goal to produce high quality of activated carbon. The short activation time and simplicity of the activation process demonstrate a promising potential to produce high surface area activated carbon from the oil sands cokes. It also provides a solution in reducing the stock piling of oil sands coke.

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## **CHAPTER 4: PHYSICAL ACTIVATION WITH MICROWAVE HEATING.**

### **4.1 Introduction**

The major development of microwave energy as a heat source took place after World War II. The main applications of microwave heating today include food processing, wood drying, plastic and rubber treating and the curing and preheating of ceramics. Microwaves cover a wide band in the electromagnetic wave spectrum, ranging from 1 mm to 1 m wave length and 300 MHz to 300 GHz frequency. In industries, two microwave frequencies, 915 MHz and 2450 MHz, are typically used for heating (Gupta 1983; Osepchuk 2009). In microwave technology, heat is generated by the interaction of dielectric materials, which is also termed as dielectric heating. It occurs due to a net polarization of the substance. Throughout the heating process, dipole molecules in an oscillating electric field try to orient themselves or become in phase with the field, and at that time, a resisting force restricts their motion and generates heat (Osepchuk 2009).

Based on the interaction with microwaves, materials can be classified generally into three categories. 1. Conductors. These types of materials reflect microwaves. Typically, bulk metals and alloys, e.g. copper, are considered to be conductors. 2. Insulators. These types of materials are transparent to microwaves and typified by fused quartz, several glasses, ceramics, and Teflon; and 3.

Absorbers, which absorb microwaves. For microwave heating, these types of materials are the most important class. Aqueous solutions and polar solvents can be classified in this group (Jones et al. 2002; Osepchuk 2009). Dielectric materials possess two important properties: 1. They have very few free charge carriers. As a result, after the application of an external electrical field, there is very little charge carried through the material matrix. 2. The molecules or atoms comprising the dielectric exhibit a dipole movement.

Since carbonaceous materials are good microwave absorbers due to their dielectric properties, microwave assisted heating is a promising technique in producing activated carbon. As a result, in recent years, the research on using microwave heating for the preparation of activated carbon has increased. The main motivation for microwave heating over the traditional heating involves selective, rapid and volumetric heating, non contact heating, low energy (electricity) consumption throughout the heating process, smaller space required for set up and ease of control (Yuen and Hameed 2009; Menéndez et al. 2010). Despite being a relatively new technology in carbon activation, the microwave has numerous advantages over traditional heating.

Several researchers have reported the use of microwaves in preparing activated carbon through both the chemical and physical activation methods. Microwave induced chemical activation was carried out with  $H_3PO_4$  for bamboo waste precursor from handicrafts (Liu et al. 2010). The chemical activation of

wood was also reported in preparing activated carbon by using  $\text{ZnCl}_2$  (Wang et al. 2009). Coal-tar pitch derived meso carbon microbeds (MCMB) were used as the precursors for activated carbon preparation by using microwave heating and chemical activation with KOH (Ji et al. 2007). The chemical activation of petroleum coke with KOH was reported (He et al. 2010). In this study, the highest BET surface area, micropore volume and total pore volume was found to be 2312  $\text{m}^2/\text{g}$ , 1.05  $\text{cc}/\text{g}$  and 1.13  $\text{cc}/\text{g}$ , respectively, for an activation time of 35 minutes. Physical activation through microwave heating was reported with  $\text{CO}_2$  gas as the activating agent. In this study, the maximum internal surface area was measured as less than 400  $\text{m}^2/\text{g}$  for 700 watts of microwave energy input, 0.755 Lpm  $\text{CO}_2$  flow rate and two hours of residence time (Norman and Cha 1996). Several researchers have used  $\text{CO}_2$  gas as an activating agent with microwave heating to produce activated carbon from phenolic resin and oil-palm-stone agriculture waste (Guo and Lua 2000; Williams and Parkes 2008). Yang et al. (2010) performed a comparative study of steam,  $\text{CO}_2$  and a combination of steam and  $\text{CO}_2$  with microwave heating. Coconut shell was used as the precursor. From the study, it was found that  $\text{CO}_2$  provides a higher surface area activated carbon, 2280  $\text{m}^2/\text{g}$ , compared to the other two activating agents, steam (2079  $\text{m}^2/\text{g}$ ), and  $\text{CO}_2$ +steam (2194  $\text{m}^2/\text{g}$ ). The activation time for  $\text{CO}_2$  activated carbon time was 210 min, which was higher than steam (75 min), and  $\text{CO}_2$ +steam (75 min).

In this study, fluid and delayed oil sands cokes are used as precursors to produce activated carbon. Physical activation with microwave heating is

performed. As the activating agent, carbon dioxide gas, nitrogen gas and steam, as well as their mixtures, are used. The effects of activation parameters, including activating agent, steam rate, and particle sizes are investigated. The iodine number, specific surface area and pore size distribution are used to characterize the activated carbon derived from the petroleum cokes and evaluate the impact of activation conditions on the properties of the activated carbon obtained.

## **4.2 Experiments**

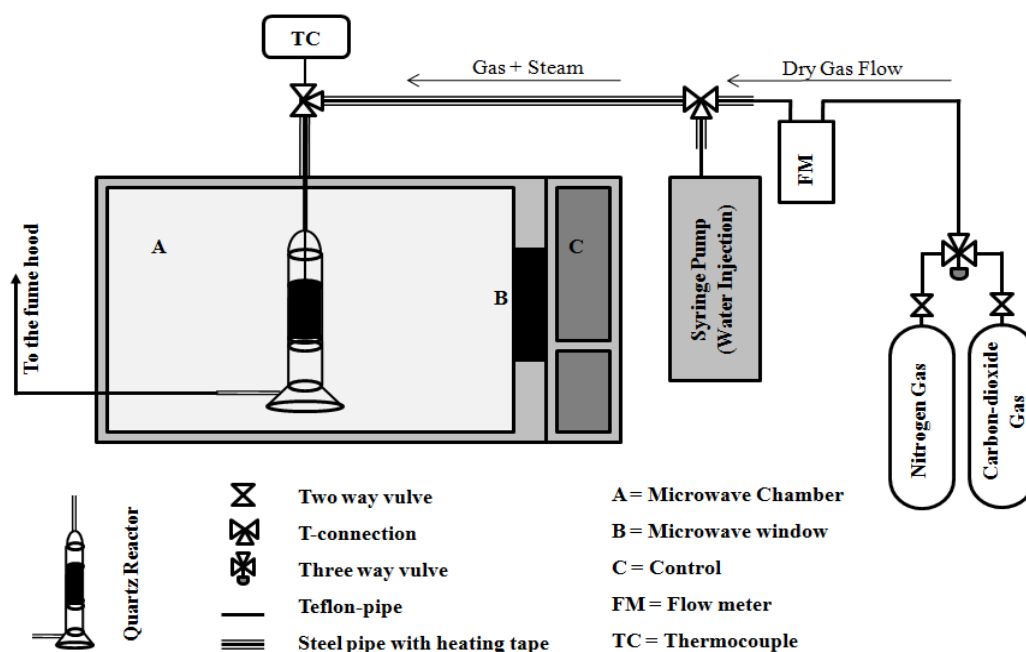
### **4.2.1 Sample Preparation**

To perform the experiment, both the raw delayed and fluid cokes were used, as supplied by Suncor Energy and Syncrude Canada Ltd. Two different particle sizes ranging from 75  $\mu\text{m}$  to 150  $\mu\text{m}$  and 300  $\mu\text{m}$  to 420  $\mu\text{m}$  of raw coke were used to perform activation. Delayed coke samples were supplied in a wide range of particle sizes ranging from micrometers to decimeters. To obtain the desired size to perform activation, the raw delayed cokes were ground. Fluid coke is sieved to obtain the desired sizes for the activation experiment. Before activation, all samples are dried at  $110 \pm 5$  °C for 24 hours. Each activation experiment used 20 g of raw coke. The weight of the raw coke, and that of the coke after activation, was measured to calculate the activation yield.

### **4.2.2 Experimental Setup and Activation**

Activation of the raw coke samples was performed in a customized kitchen microwave with a frequency of 2.45 GHz and nominal power output of

800 watts. The output power of the microwave was controlled by varying the operation time of the magnetron. The microwave used for this experiment had three separate and their combination power levels as output power including high, medium and low. The power is maintained by the magnetron during two consecutive cycles, turning on and turning off, and the whole combination runs for 22 seconds. For the high power level, the turning on cycle runs for 22 seconds and there is no turn off cycle. For the medium power level, the magnetron remains turned on for 17 seconds and then turns off for 5 seconds. For low power, the turning on and turning off lasts for 8 seconds and 14 seconds respectively. A quartz reactor with an outer diameter of 40 mm held the raw coke samples. The reactor was separated into three parts, including the top cap with gas inlet; the middle part for the sample holder, which is equipped with porous support to hold the raw coke sample and allow the neutralizing and activating gas to pass through the raw materials. The bottom part includes the exhaust gas outlet. The whole experimental set up is shown in Figure 4.2-1.



**Figure 4.2-1: Schematic diagram for the setup of physical activation with microwave heating for both fluid and delayed coke.**

The inlet and outlet of the quartz reactor were connected to a ¼” steel and teflon tube, respectively. Physical activation was carried out at the high power level of the customized microwave. Nitrogen gas, carbon dioxide gas, steam and their different combinations were used as the activating agent. The flow rate of the dry nitrogen and carbon dioxide was maintained at 100 mL/min measured with a flow meter. Steam was generated by injecting water through the syringe pump (model NE-300, New Era Pump System) and using a 100 mL glass syringe (Hamilton). Two different injection rates of ultra pure de-ionized water were maintained to study the effect of steam flow rate on activation. Steam was produced by heating the steel pipe using a heating tape connected to a variac. The

temperature of the steel pipe was maintained at  $210 \pm 10$  °C to ensure all the liquid water was converted into steam. It was assumed that 100 % of the water was turned into steam and injection rate of water was considered as the steam rate. Dry gas mixed with steam was purged through the top of the reactor to avoid building steam pressure which could throw the coke sample out of the reactor. The outlet pipe from the reactor was vented to the fume hood.

### **4.2.3 Sample Characterization**

To evaluate the effects of the activation parameters and of microwave heating, both the delayed and fluid activated coke samples were characterized by activation yield, iodine number standard test, N<sub>2</sub> adsorption isotherm and BET surface area, and XPS analysis.

#### **4.2.3.1 Iodine Number**

Iodine number is one of the main methods of measuring the quality of activated carbon. The iodine number of activated carbon refers to its iodine adsorption capacity. The American Society of Testing and Materials (ASTM) standard ASTM 4607-94 (ASTM 2006) method was used to conduct the research work. The iodine number was measured by volumetric titration of the filtrate, obtained after the adsorption of the standard iodine solution, with three different amounts of activated carbon. The volumes of the different chemicals were changed in increments from the standard amount. To conduct the iodine test, 25

ml of HCl, 50 mL of KI/I<sub>2</sub>, and 40 mL of filtrate were used. The iodine number provided the amount of iodine (mg) adsorbed per weight of carbon (g). It also gave an estimate of BET surface area. The iodine adsorption isotherm also provided information on the microporosity of the activated carbon, as an iodine molecule's diameter is 4.94 Å (Juhola 1975)

#### **4.2.3.2 N<sub>2</sub> Adsorption Isotherm and BET Surface Area**

N<sub>2</sub> adsorption on activated carbon was performed at 77 K with a Quantacrome, Autosorb iQ2. The N<sub>2</sub> adsorption isotherms determined the BET surface area and pore size distribution of the activated carbon. To obtain the N<sub>2</sub> adsorption isotherm, approximately 10 mg to 100 mg of activated carbon was used. Prior testing, the sample was degassed at 300 °C for 3 hours. After degassing, the vacuum sample cell was filled with helium gas to avoid any moisture contacting the activated carbon. Surface area of the activated carbon was determined by using BET model. The DFT model and t-method analysis were used to determine the pore size distribution and the micropore volume respectively.

#### **4.2.3.3 X-ray Photoelectron Spectroscopic (XPS) Analysis**

The X-ray Photoelectron Spectroscopy (XPS) technique performed the surface elemental analysis of the coke. In XPS analysis, X-ray photons of 1 to 2 KeV irradiated the coke samples. As a result, the surface of the sample's atom



absorbed energy from incoming X-ray photoelectrons and reached an excited state. As it returned to its steady state, the target atom emitted photoelectrons. Photoelectrons' energy characterizes target materials. Analysis of this energy spectrum provides information about materials, including their chemical composition up to 20 atomic layers. Sometimes, the depth of the surface analysis extends up to 5 nm to 10 nm. From the energy spectra, the peak position and the peak area were used to evaluate the surface composition. Peak shape of energy spectra provided the information regarding the chemical shifts or chemical bonds of the elements. In this study, a Kratos AXIS 165 instrument with Mono AL  $K\alpha$  radiation at 210 watts and 14 KV was used. It was operated at an ultra-high vacuum of  $10^{-9}$  Torr pressure, and all the spectra were calibrated by a C1s peak at 284.5 eV.

### **4.3 Result and Discussion**

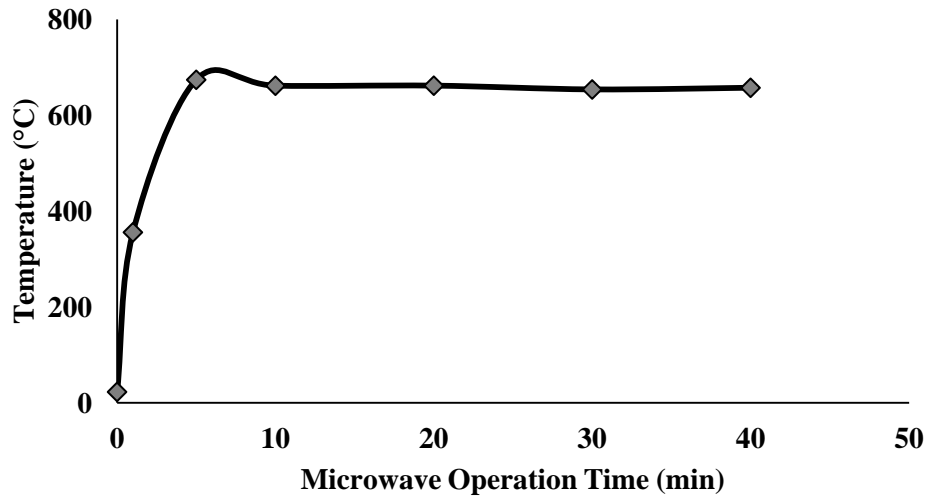
#### **4.3.1 Microwave Activity Test by Water Heating**

To evaluate the performance of the microwave and the magnetron, ultra pure de-ionized (DI) water was heated at medium and high power levels and compared to the data previously obtained with the same microwave system (Chen 2010). To perform the test, 2 L ultra pure DI water was used and heating was performed for 5 minutes. The temperature of the water sample was measured by a K-type thermocouple. The thermocouple was inserted into the water immediately after shutting down the microwave. The reason that the thermocouple was not used during microwave heating was the disturbance caused by the metal wire

thermocouple to the electromagnetic field. This disturbance in the electromagnetic field would damage the thermocouple and also microwave (Knoerzer et al. 2009). The response time for thermocouple was considered while measuring the temperature of the water as it takes a few seconds to respond to the actual temperature of water. To evaluate the time lag, a second order regression equation and method of extrapolation was used to obtain the actual temperature immediately upon shutting down the magnetron. Test results match with previous study (Chen 2010) and are shown in Appendix D.

#### **4.3.2 Microwave Temperature Profile**

As in physical activation techniques, the main activation mechanism involves the oxidation of carbon as carbon dioxide or carbon monoxide; temperature and activating gas play important roles in this respect. Prior activation, temperature profiles of the precursors was evaluated. Figure 4.3-1 presents the fluid coke's temperature profile with the microwave's operation time, at high microwave power level and for particle sizes ranging from 75  $\mu\text{m}$  to 150  $\mu\text{m}$ . While measuring the temperature profile, dry nitrogen gas flow was maintained at 0.1 Lpm. From Figure 4.3-1, it was observed that the raw coke sample's temperature rose drastically to 674  $^{\circ}\text{C}$  within 5 minutes of microwave operation time from a room temperature of 22.5  $^{\circ}\text{C}$ .

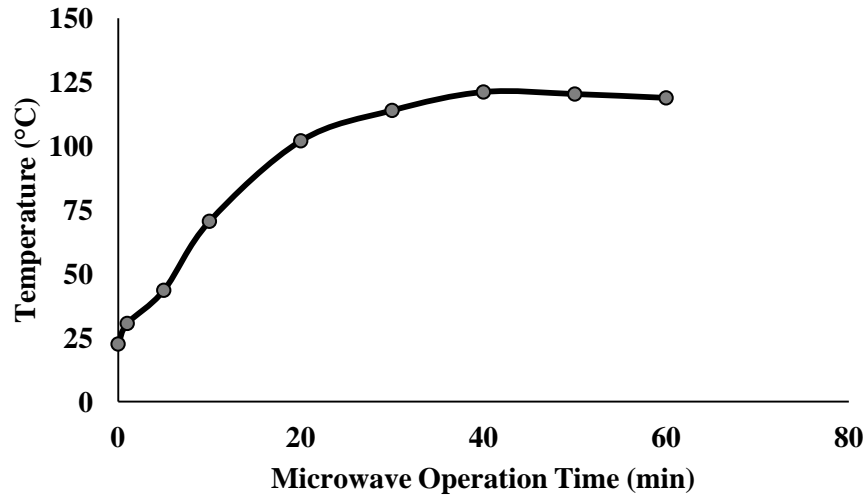


**Figure 4.3-1: Temperature profile for fluid coke through microwave heating at high power level and for particle size ranging from 75  $\mu\text{m}$  to 150  $\mu\text{m}$ .**

With an increase in microwave operation time, the temperature became steady and less fluctuation was observed. A change in temperature after 10 minutes to 40 minutes of microwave operation time was observed as  $\pm 3\text{ }^\circ\text{C}$  and afterwards, it was assumed that temperature remained at steady state with increasing microwave operation time.

The temperature profile of raw delayed coke with 0.1 Lpm dry nitrogen gas flow rate and of particle sizes ranging from 75  $\mu\text{m}$  to 150  $\mu\text{m}$  is illustrated in Figure 4.3-2. From the temperature profile of delayed coke, it was observed that 40 minutes of heating at a high microwave power level were required to reach the steady temperature of 120  $^\circ\text{C}$ , a longer time relative to the fluid coke. After reaching the steady state temperature, with an increase in microwave power levels, the variation of temperature was very low:  $\pm 1\text{ }^\circ\text{C}$ . The highest temperature

observed for delayed coke was 121 °C, which is around five times lower than the fluid coke temperature for the same heating parameters and atmosphere.



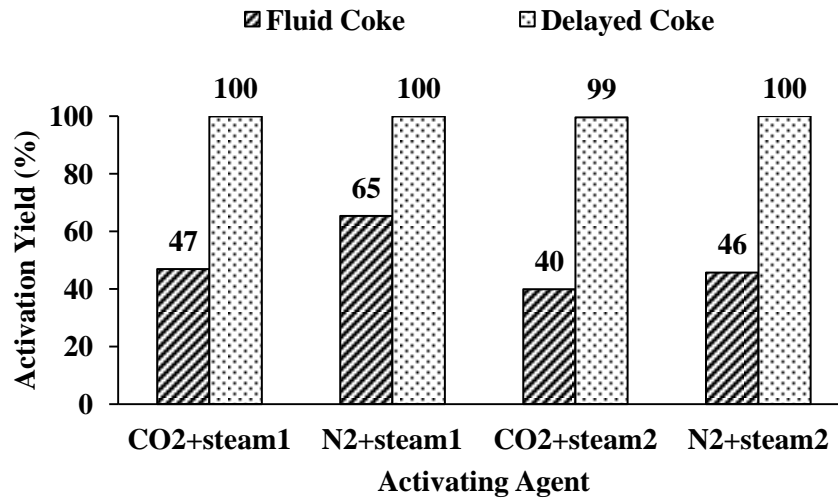
**Figure 4.3-2: Temperature profile for delayed coke through microwave heating at high power level and for particle size ranging from 75  $\mu\text{m}$  to 150  $\mu\text{m}$ .**

As physical activation techniques involved an activation temperature range of 700 °C to 900 °C, delayed coke was difficult to activate even with the highest power level and with higher activation time. The quality of activated carbon prepared by this microwave are illustrated in the following sections.

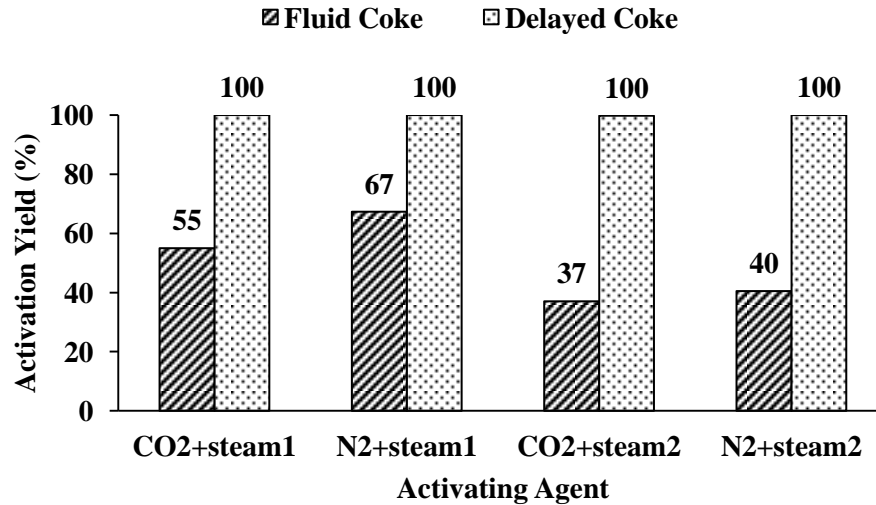
### 4.3.3 Activation Yield

The overall efficiency and the percentage of material loss throughout the activation process are evaluated by analyzing the yield. Figure 4.3-3 and Figure 4.3-4 represent the yield (%) of both fluid and delayed coke for two particle sizes,

ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$  and 75  $\mu\text{m}$  to 150  $\mu\text{m}$ , respectively. Throughout the activation, four different compositions of activating gases were used. These figures also illustrate the effect of activating agent. For particle size 300  $\mu\text{m}$  to 420  $\mu\text{m}$ , fluid coke showed a moderate yield compared to delayed coke. Yield for fluid coke varied from 40 % to 65 % for different activating gas compositions, whereas delayed coke showed 100% yield for all the conditions.



**Figure 4.3-3: Activation yield (%) of fluid and delayed coke of particle size ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$  for 6 hour activation time and with four types of activating agent gas composition including CO2+steam 1 = carbon dioxide gas at 100 mL/min and steam at 0.3 mL/min, N2+steam 1 = nitrogen gas at 100 mL/min and steam at 0.3 mL/min, CO2+steam 2 = carbon dioxide gas at 100 mL/min and steam at 0.5 mL/min, N2+steam 2 = nitrogen gas at 100 mL/min and steam at 0.5 mL/min flow rate**



**Figure 4.3-4: Activation yield (%) of fluid and delayed coke of particle sizes ranging from 75  $\mu\text{m}$  to 150  $\mu\text{m}$  for 6 hour activation time and with four types of activating agent gas composition including CO<sub>2</sub>+steam 1 = carbon dioxide gas at 100 mL/min and steam at 0.3 mL/min, N<sub>2</sub>+steam 1 = nitrogen gas at 100 mL/min and steam at 0.3 mL/min, CO<sub>2</sub>+steam 2 = carbon dioxide gas at 100 mL/min and steam at 0.5 mL/min, N<sub>2</sub>+steam 2 = nitrogen gas at 100 mL/min and steam at 0.5 mL/min flow rate**

As delayed coke was difficult to heat even at the microwave's highest power level, it can be concluded that no activation occurred for delayed coke at these activation parameters. Increasing the steam rate from 0.3 mL/min to 0.5 mL/min in the gas combinations, resulted in a lower yield. The flow rate for both the carbon dioxide and nitrogen gas was maintained as 100 mL/min.

For particle sizes 75  $\mu\text{m}$  to 150  $\mu\text{m}$ , the fluid coke responded to the activation parameters and provided a yield varying from 37 % to 67 % for different activating gas compositions. The yield of fluid coke was almost the same for both particle sizes. In the case of delayed coke, the yield was 100 % for

different activating agents. From the overall analysis of the activation yield of fluid and delayed coke for different activating gas compositions, high microwave power levels, and six hour activation time, it was found that particle size had little effect on the activation yield.

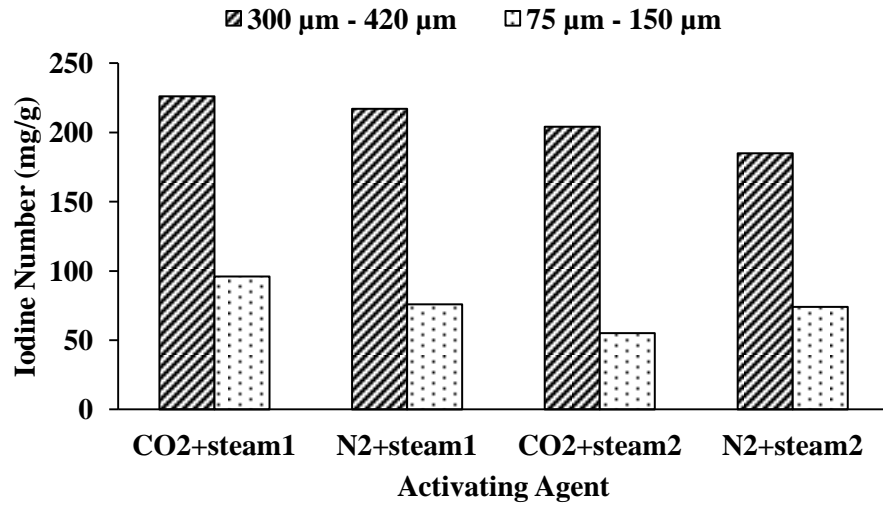
#### **4.3.4 Iodine Adsorption and Iodine number**

The iodine adsorption test and the iodine number were considered the main characterization tests to determine the effect of activation parameters on the prepared activated carbon. The effects of different activation parameters, including coke particle sizes, activating agents and their combinations, and steam rates was investigated and illustrated in the following subsections.

##### **4.3.4.1 Effect of Particle size**

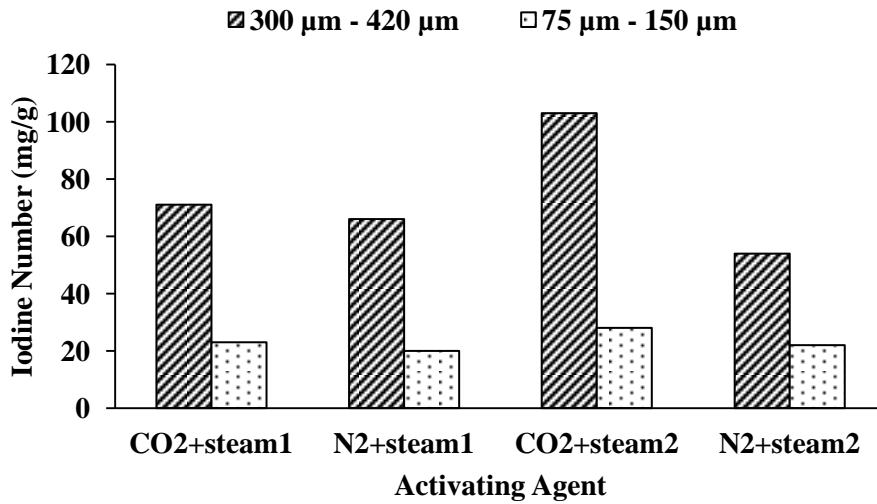
The effect of particle sizes on physical activation and microwave heating for both fluid and delayed coke is illustrated in Figure 4.3-5 and Figure 4.3-6, respectively. For the fluid coke, particle sizes ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$  provided an iodine number around 200 mg/g. For all the gas compositions, the iodine number varied from 226 mg/g to 185 mg/g. For particle sizes ranging from 75  $\mu\text{m}$  to 150  $\mu\text{m}$ , the iodine number was less than 100 mg/g for all the gas compositions. The highest iodine number is 96 mg/g for a mixture of carbon-dioxide (100 mL flow rate) and steam activating gas where the steam flow rate was 0.3 mL/min and the lowest iodine number is 55 mg/g for the carbon dioxide

(100 mL/min flow rate) and steam activating gas mixture where the steam rate was 0.5 mL/min. From Figure 4.3-5, it is clear that particle sizes ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$  had an iodine number that was nearly two times higher than that of 75  $\mu\text{m}$  to 150  $\mu\text{m}$  particles.



**Figure 4.3-5: Effect of particle sizes on the physical activation of fluid coke through microwave heating, 6 hour activation time, and with four types of activating agent gas compositions including CO<sub>2</sub>+steam 1 = carbon dioxide gas at 100 mL/min and steam at 0.3 mL/min, N<sub>2</sub>+steam 1 = nitrogen gas at 100 mL/min and steam at 0.3 mL/min, CO<sub>2</sub>+steam 2 = carbon dioxide gas at 100 mL/min and steam at 0.5 mL/min, N<sub>2</sub>+steam 2 = nitrogen gas at 100 mL/min and steam at 0.5 mL/min flow rate**





**Figure 4.3-6: Effect of particle sizes on the physical activation of delayed coke through microwave heating 6 hour activation time and with four types of activating agent gas composition including CO<sub>2</sub>+steam 1 = carbon dioxide gas at 100 mL/min and steam at 0.3 mL/min, N<sub>2</sub>+steam 1 = nitrogen gas at 100 mL/min and steam at 0.3 mL/min, CO<sub>2</sub>+steam 2 = carbon dioxide gas at 100 mL/min and steam at 0.5 mL/min, N<sub>2</sub>+steam 2 = nitrogen gas at 100 mL/min and steam at 0.5 mL/min flow rate**

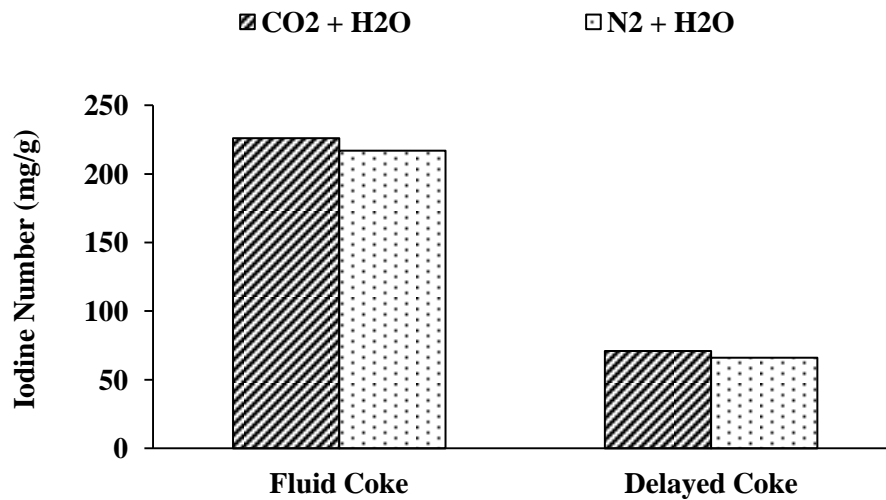
For delayed coke, the iodine number was less than 100 mg/g for almost all activating agents, except for the carbon dioxide and steam mixture where the steam rate is 0.5 ml/min. Similar to the fluid coke, the particle sizes from 300 μm to 420 μm of delayed coke had a higher iodine number than particle sizes ranging from 75 μm to 150 μm (Figure 4.3-6).

From the analysis of particle size, it was found that precursors' particle size had great effect on the quality of activated carbon. In this experiment, particle size ranging from 300 μm to 420 μm provided higher iodine number for both the delayed and fluid coke. As a larger particle has more inter-particle space, more

particle surface comes into contact with the activating gas agent. As a result, larger particles showed higher iodine number than smaller particles. For delayed coke, the iodine number was relatively low for larger particles; however, for smaller particles, the iodine numbers were nearly the same as that of raw delayed coke at (21.8 mg/g). The low iodine number of the delayed coke can also be described by analyzing the temperature profile and the activation yield. For delayed coke, the highest temperature reached was 120 °C with high microwave power level, which was much lower than the normal temperature range, 700 °C to 900 °C, for the physical activation of petroleum coke. On the other hand, activated delayed coke showed an activation yield of 100 %, which means no activation occurred.

#### **4.3.4.2 Effect of activating agent**

The effect of activating agent gas composition on both fluid and delayed coke are illustrated in Figure 4.3-7. Two gases, carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>), along with steam were used. Steam has a great influence on activation, especially for pore formation. Steam was mixed with different ratio with CO<sub>2</sub> and N<sub>2</sub>. Mole percentage of the gas composition was also evaluated. From the analysis, it was found that, for steam ratio of 0.3 and 0.5 mL/min, % mole are CO<sub>2</sub>:H<sub>2</sub>O = 16.1:83.9 and CO<sub>2</sub>:H<sub>2</sub>O = 12.9:87.1 respectively. For N<sub>2</sub> and steam composition, % mole ratio are N<sub>2</sub>:H<sub>2</sub>O = 32.7:67.3 and N<sub>2</sub>:H<sub>2</sub>O = 27.2:72.8 for steam rate 0.3 and 0.5 mL/min respectively.



**Figure 4.3-7: Effect of activating agent gas composition on physical activation through microwave heating for both the delayed and fluid coke, of particle size ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$ , 6 hour activation time. Gas flow rate was maintained at 100 mL/min for CO<sub>2</sub> and N<sub>2</sub> and steam flow rate was maintained at 0.3 mL/min.**

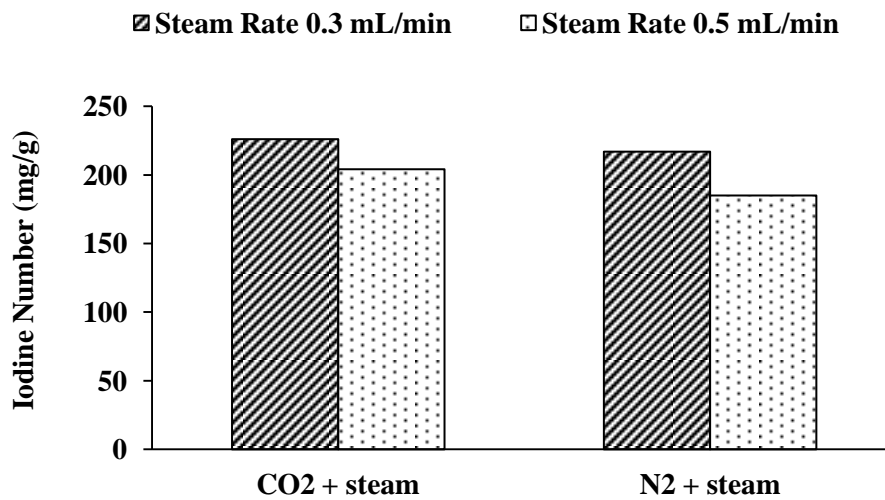
Effect of the activating gas composition on iodine adsorption showed that, CO<sub>2</sub> gas mixed with steam had a significant influence on preparing high quality activated carbon compared to N<sub>2</sub> mixed with steam. For carbon dioxide gas (100 mL/min flow rate) mixed with steam (0.3 mL/min flow rate), the iodine number for fluid coke was 226 mg/g, whereas nitrogen gas (100 mL/min flow rate) mixed with steam (0.3 mL/min flow rate), had an iodine number of 217 mg/g. In the case of delayed coke, the iodine number was 71 mg/g for carbon dioxide (100 mL/min flow rate) and steam (0.3 mL/min flow rate) and 66 mg/g for nitrogen gas (100 mL/min flow rate) and steam (0.3 mL/min flow rate) mix. In all cases, the effect of nitrogen with steam was less than that of carbon dioxide with steam. This

difference may be due to the effect of the oxygen group in the gas composition. For activation of oil-palm-stone with microwave, it was found that microwave activation with oxidizing gas provide higher quality activated carbon compared to that of non-oxidizing gas (Guo and Lua 2000). During activation with CO<sub>2</sub> and steam, the main gasification reactions involve C-H<sub>2</sub>O and C-CO<sub>2</sub>. This results in the removal of carbon atoms and causing most of the weight loss in the precursor (Chang et al. 2000). It can be concluded that, the use of CO<sub>2</sub> along with steam provides more oxygen groups compared to N<sub>2</sub> and steam which enhance the overall activation reactions and subsequent pore formation. As a result higher iodine adsorption was observed for CO<sub>2</sub> and steam composition of activating agent.

#### **4.3.4.3 Effect of Steam Rate**

Two different flow rates of steam, including 0.3 mL/min and 0.5 mL/min, were used throughout the experiment. Figure 4.3-8 presents the effect of steam flow rate on the activation of fluid coke with 300 µm to 420 µm particle size, and of the activating gas carbon dioxide and nitrogen. Analysis of the effect of steam rate on the physical activation with microwave heating showed that, a steam rate of 0.3 mL/min used with CO<sub>2</sub> increased the iodine number by 11 % compared to a steam rate of 0.5 mL/min used with CO<sub>2</sub>. Similarly, a steam rate of 0.3 ml/min used with N<sub>2</sub> increased the iodine number by 17 % compared to a steam rate of 0.5 mL/min used with N<sub>2</sub>. The effect of flow rate was the same with both

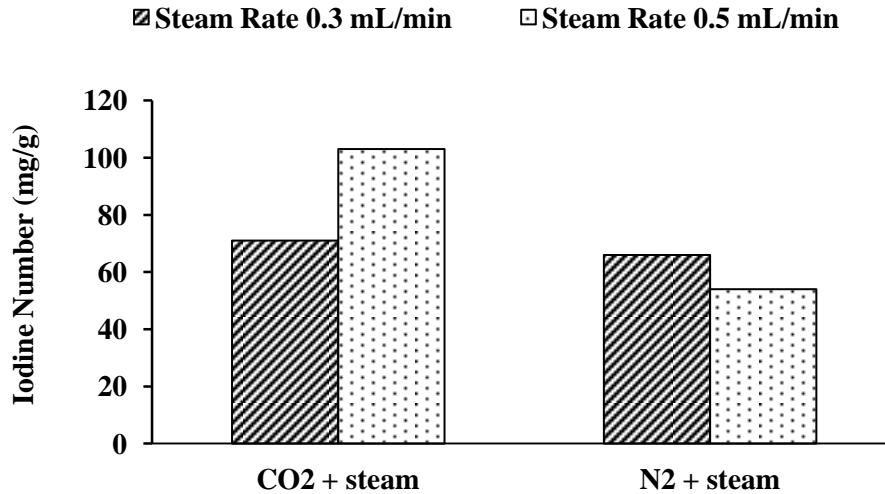
activating agents, carbon dioxide and nitrogen. For carbon dioxide and steam mix, the iodine number obtained for 0.3 mL/min and 0.5 mL/min steam flow rate were 226 mg/g and 204 mg/g, respectively. For nitrogen and steam composition, the iodine number was 217 mg/g for 0.3 mL/min and 185 mg/g for 0.5 mL/min steam flow rate.



**Figure 4.3-8: Effect of steam rate on fluid coke activation through physical activation techniques and microwave heating with particle size ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$ , 6 hour activation time.**

Figure 4.3-9 presents the effect of steam rate on delayed coke activation. For the carbon dioxide gas and steam, the activated delayed coke's iodine number increased with an increase in the steam rate from 0.3 ml/min to 0.5 mL/min; however, for nitrogen and steam with the same increase in steam rate, the iodine number decreased from 66 mg/g to 54 mg/g. As delayed coke's iodine number

was quite low, below 100 mg/g, it was difficult to find a clear trend for the change in iodine number.



**Figure 4.3-9: Effect of steam rate on delayed coke activation through physical activation techniques and microwave heating with particle sizes ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$ , 6 hour activation time.**

#### 4.3.5 BET Surface Area and Pore Size Distribution

The characterization of activated fluid and delayed coke was also performed by determining the BET surface area and pore size distribution. Two samples were characterized; each was prepared at 6 hour of activation time under high microwave power, and with the activating gas composition of carbon dioxide (100 mL/min flow rate) and steam (0.5 mL/min flow rate) The particle size for these two activated carbon samples varied from 300  $\mu\text{m}$  to 420  $\mu\text{m}$ . Table 4.3-1 represents the BET surface area, micro pore volume and total pore volume both for the fluid and delayed cokes. From Table 4.3-1, it is found that fluid coke

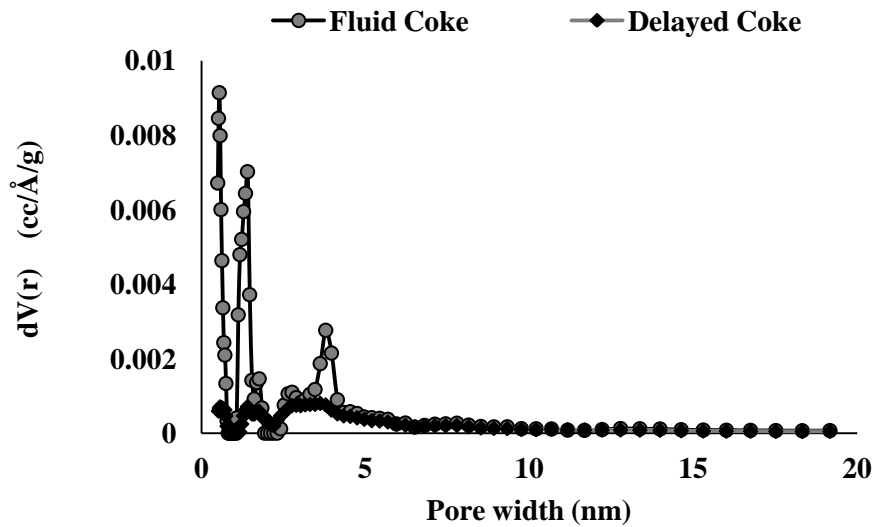
provides a higher BET surface area and micropore volume than the delayed coke, which is consistent with the iodine number results.

**Table 4.3-1: BET surface area, micropore volume and total pore volume for activated fluid and delayed coke prepared with carbon dioxide and steam mix activating gas agent where steam flow rate is 0.5 mL/min, particle size ranging from 350  $\mu\text{m}$  to 420  $\mu\text{m}$  and high microwave power level for six hours of activation time.**

<b>Activated Coke</b>	<b>BET Surface Area (<math>\text{m}^2/\text{g}</math>)</b>	<b>Micropore Volume (<math>\text{cm}^3/\text{g}</math>)</b>	<b>Total Pore Volume (<math>\text{cm}^3/\text{g}</math>)</b>
<b>Fluid</b>	112	0.01	0.05
<b>Delayed</b>	64	NA*	0.02

NA\* = not applicable

Figure 4.3-10 illustrates the pore size distribution for both the fluid and delayed coke. From the figure, it is found that fluid coke's maximum pore volume lies within 0 to 2 nm, which represents the domination of micropore in the total pore distribution. For delayed coke, the total pore volume is found to be 0.02  $\text{cm}^3/\text{g}$ , which is almost half of the total pore volume of fluid coke. From the pore size distribution, it can be concluded that most of the delayed coke's pores are over 2 nm. As a result, the micropore volume is found to be insignificant.



**Figure 4.3-10: Pore size distribution of fluid and delayed coke prepared at carbon dioxide and steam mix activating gas agent where steam flow rate is 0.5 mL/min, particle size ranging from 350  $\mu\text{m}$  to 420  $\mu\text{m}$  and high microwave power level for six hours of activation time.**

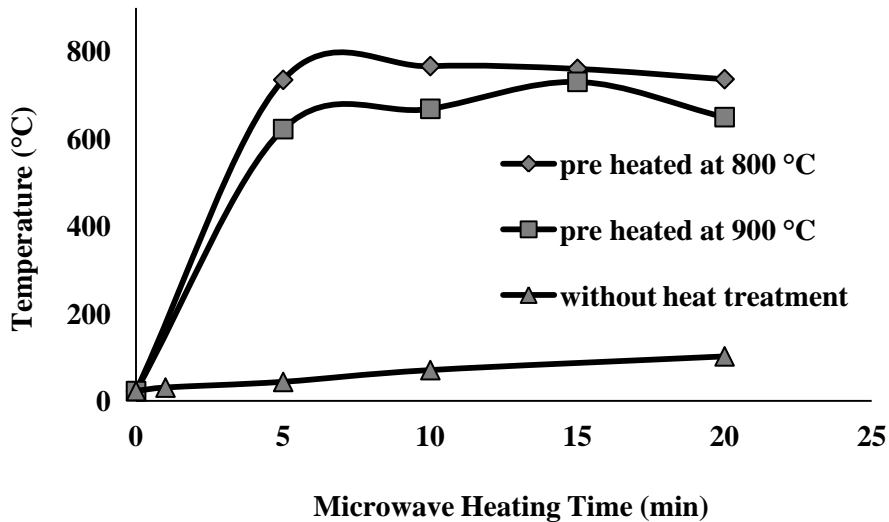
#### 4.3.6 Pre-Heating Effect on Activation of Delayed Coke

Due to the low temperature profile during microwave heating and low iodine number after activation compared to the fluid coke, delayed coke was given a heat treatment. In the heat treatment, the delayed coke was heated at 800  $^{\circ}\text{C}$  and 900  $^{\circ}\text{C}$  with a muffle furnace for 1 hour. The heating chamber's atmosphere was neutralized by purging dry nitrogen gas. This pre-heat treatment was performed for the delayed coke with particles ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$ .

After the heat treatment, the delayed coke samples underwent microwave heating to determine the temperature profile. Figure 4.3-11 presents the



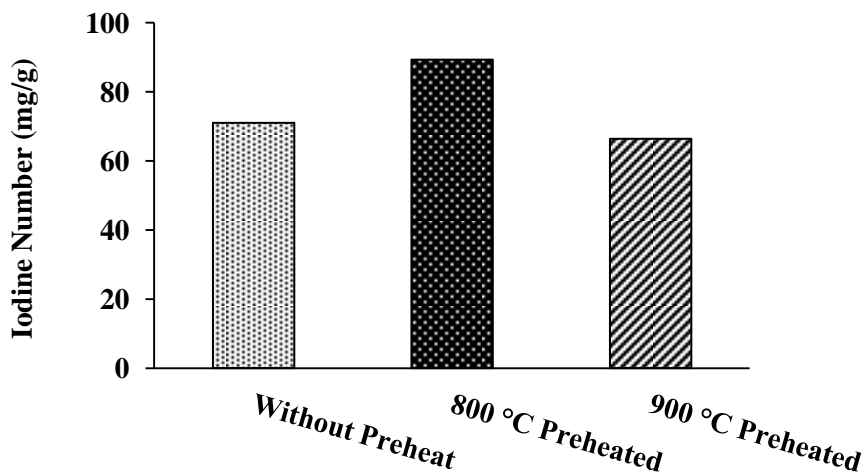
temperature profile for the raw delayed coke after heat treatment at 800 °C and 900 °C and also the comparison of these temperature profiles with the untreated raw delayed coke.



**Figure 4.3-11: Microwave temperature profile of pre heated and untreated raw delayed coke.**

From the Figure 4.3-11, it is found that the microwave heating response for the pre-heated delayed coke was high compared to the untreated delayed coke. Pre-heated delayed coke at 800 °C showed a high temperature profile of around 750 °C after 5 minutes ramping up time. For the pre-heated delayed coke at 900 °C, after 5 minutes ramping up time, the temperature was 620 °C. The temperature profile for delayed coke without heat treatment shows the highest temperature of 102 °C after 20 minutes of microwave heating and 44 °C after 5 minutes ramping up time.

The pre-heated delayed coke was then activated by microwave heating with a mix of carbon dioxide gas (100 mL/min flow rate) and steam (0.3 mL/min flow rate). Activation was carried out for six hours. The iodine number of the untreated and heat treated delayed cokes were determined. From Figure 4.3-12, it is found that delayed coke heated at 800 °C provides a marginally higher iodine number, 90 mg/g, compared to that of the untreated delayed coke, 71 mg/g. The delayed coke pre-heated at 900 °C provided an iodine number of 66 mg/g.

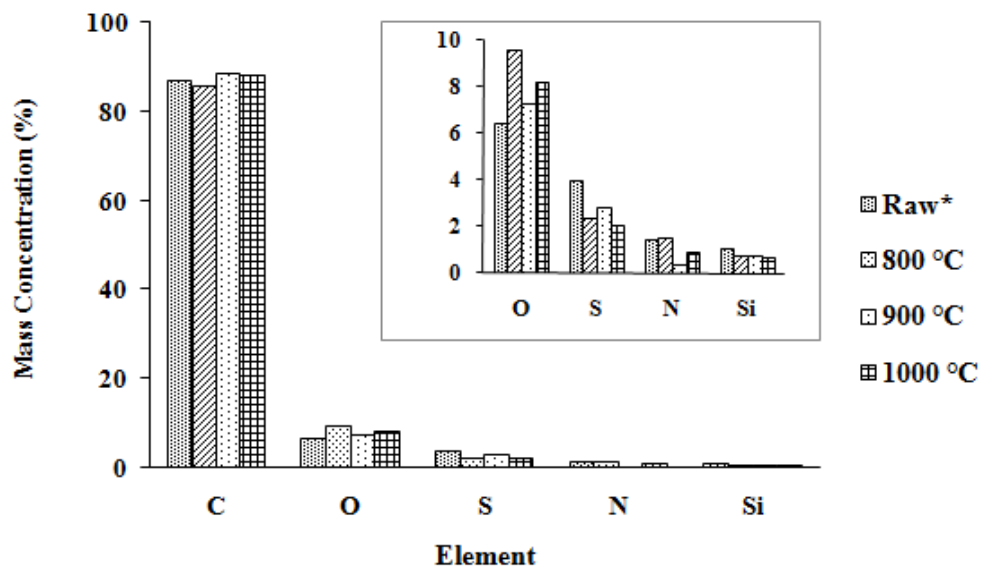


**Figure 4.3-12: Iodine number of the activated preheated delayed coke at different temperature and comparing with non heated activated delayed coke. Activation condition was maintained as, 6 hours activation time, activating gas composition as carbon dioxide gas (100 mL/min) and steam (0.3 ml/min) and of particle sizes ranging from 300  $\mu\text{m}$  to 420  $\mu\text{m}$ .**

Though pre-heating the delayed coke increased the activation temperature from 120 °C to 750 °C, its iodine number was comparable to that of the untreated

activated fluid coke for the same activation conditions. The change in temperature profile can be attributed to the microwave's effect on the oxygen groups, present on the coke. With an increase in oxygen groups, both the microwave activity and the matter's temperature profile increased.

To evaluate the change in temperature profile, the pre-heated delayed cokes were analyzed with X-ray Photoelectron Spectroscopy (XPS) technique (Figure 4.3-13). It was found that after heat treatment, the mass concentration of oxygen was 10 %, 7 % and 8 % for heat treatments at 800 °C, 900 °C and 1000 °C, respectively, whereas the mass concentration of oxygen for raw delayed coke was 6 %. Except oxygen, the mass concentration for all other elements including sulfur, nitrogen and silicon decreased after the heat treatment compared to the raw coke.



**Figure 4.3-13: XPS analysis of the preheated delayed coke prepared at temperature 800 °C, 900 °C and 1000 °C and compared to raw delayed coke. The data for raw delayed coke was adapted from \*(Chen 2010)**

#### 4.3.7 Comparison of Results

The properties of the activated carbon prepared from delayed and fluid coke through physical activation and microwave heating, are compared to previous research on the physical activation of delayed and fluid coke. Table 4.3-2 compares the iodine number, surface area and micropore volume of the activated delayed and fluid coke.

**Table 4.3-2: Comparison of iodine number, surface area, and micropore volume of physically activated fluid and delayed coke from previous research works and this study.**

<b>Activated Coke Type</b>	<b>Heat Source</b>	<b>Activation time (hour)</b>	<b>Iodine number (mg/g)</b>	<b>Surface Area (m<sup>2</sup>/g)</b>	<b>Micropore Volume (cm<sup>3</sup>/g)</b>
Fluid Coke	Microwave	6	226	112	0.01
Delayed Coke	Microwave	6	103	64	NA*
Fluid Coke (Small 2011)	Muffle Furnace	6	620	494	0.13
Delayed Coke (Small 2011)	Muffle Furnace	6	670	578	0.17
Fluid Coke (DiPanfilo and Egiebor 1996)	Horizontal Tube Furnace	6	200	318	0.24
Fluid Coke (Bratu 2008)	Vertical Tube Furnace	4	NA	533	0.19

NA\* = Not Applicable

From Table 4.3-2, it can be concluded that the activation parameters that were used in this experiment are not the most efficient means of acquiring high quality activated carbon through microwave heating and physical activation techniques. However, compared to the physical activation with a horizontal tube furnace performed by DiPanfilo and Egiebor (1996), microwave activation yielded better iodine number.

#### **4.4 Summary and Conclusion**

Physical activation with microwave heating was performed on oil sands coke. Two types of particle size ranges were used for both the fluid and delayed

coke. A series of activation parameters, including different activating gas compositions and steam were studied for their effects on activation. The following conclusions are drawn.

- For activation with the high microwave power level, the highest temperature was 673 °C for fluid coke and 121 °C for delayed coke. These temperatures were lower than the typical temperature range for physical activation of coke.
- Throughout the experiment, carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) were used as activating agents. Flow rate of both gases was maintained at 100 mL/min. From the analysis and characterization of the properties of the activated coke, it was found that CO<sub>2</sub> gas resulted in higher quality activated carbon than the activated carbon prepared with N<sub>2</sub> as an activating agent.
- Two different steam rates, 0.3 mL/min and 0.5 mL/min, were used to c along with CO<sub>2</sub> and N<sub>2</sub> as activating agents. It was found that, for fluid coke, a steam rate of 0.3 mL/min provided higher quality activated carbon compared to 0.5 mL/min, with both CO<sub>2</sub> and N<sub>2</sub> as activating gas agents. The flow rate for both CO<sub>2</sub> and N<sub>2</sub> was maintained at 100 mL/min. However, for delayed coke with CO<sub>2</sub> (100 mL/min) as an activating gas agent, the 0.3 mL/min steam rate resulted in lower quality activated carbon than the 0.5 mL/min steam rate. For N<sub>2</sub> (100 mL/min) activating

gas, the 0.3 mL/min steam rate resulted in higher quality activated carbon than the 0.5 mL/min steam rate for delayed coke.

- Microwave activation temperature of the raw delayed coke was increased from 120 °C to 766 °C by pre-heating the coke at 800 °C with a muffle furnace for 1 hour before heating with microwave. After pre-heating, the highest temperature of the pre-heated coke was obtained within five minutes of ramping up time by the microwave heating at high power level. The effect of pre heating was evaluated by performing an XPS analysis of the raw and pre-heated delayed coke. From the XPS analysis, the mass concentration for oxygen was found to be higher in the pre-heated delayed coke compared to the raw delayed coke. After the XPS analysis, it was concluded that oxygen plays an important role in microwave heating delayed coke.
- The BET surface area for the activated fluid coke was 112 m<sup>2</sup>/g, whereas that of delayed coke was 64 m<sup>2</sup>/g. From the pore size distribution, it was found that the micropore dominated the total pore volume of the activated fluid coke, but in the case of delayed coke, the micropore volume was insignificant.
- From the overall study of physical activation with microwave heating of fluid and delayed coke, it was found that fluid coke resulted in higher quality activated carbon than the delayed coke. However, it is important to note that the fluid coke's BET surface area and total pore volume were relatively low compared to commercially available activated carbon.

## 4.5 References

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## **CHAPTER 5: SUMMARY, CONCLUSION AND RECOMMENDATIONS**

### **5.1 Introduction**

A suitable and economical solution is necessary to manage the stockpiled oil sands cokes in Alberta. In this research work, the preparation of activated carbon from oil sands coke is studied. Chemical activation with KOH and physical activation with microwave heating were investigated. The Outcomes from this study are illustrated in the following sections.

### **5.2 Chemical Activation of Delayed and Fluid Coke**

Delayed and fluid cokes were used to prepare activated carbon using chemical activation techniques with KOH. The particle size during the study was limited to within 420  $\mu\text{m}$  and 300  $\mu\text{m}$ . During activation, humid nitrogen gas was used as the activation atmosphere. Different operating conditions and their effects were studied. The activated carbon was characterized based on the iodine number, BET surface area and pore size distribution. The obtained results support the following conclusions:

- Throughout the activation process, activation temperature and chemical impregnation ratio (KOH/coke) played the most important role in producing high quality and high surface area activated carbon.

- The effect of activation time was less significant in obtaining higher quality activated carbon. From the experiment, it was found that 30 minutes activation time and 60 minutes of temperature ramping up time, with 800 °C activation temperature and a KOH/coke ratio of 2, was sufficient to produce commercial grade activated carbon from the oil sands coke.
- Activated carbon prepared from delayed coke, provided higher iodine number and surface area compared to the fluid coke for the same activation temperature, KOH/coke ratio and activation time. The reason behind this difference can be as attributed to structural differences between delayed and fluid cokes. Delayed coke has a sponge-like structure, whereas fluid coke has a layered structure. Such differences can affect diffusion of the activation agent and formation of pores.
- The surface areas of the activated carbon prepared from delayed and fluid cokes prepared in this study are comparable to values typically reported in commercial grade activated carbon.
- The pore size distribution of the activated delayed coke showed that the micropore volume represents 85 % of the total pore volume which was 0.72cc/g. For fluid coke, the total pore volume was 0.565 cc/g, and the micropore volume was 75 % of the total pore volume.

The preparation of high surface area activated carbon from the oil sands cokes demonstrates a promising potential to convert this refinery byproduct into a useful adsorbent.

### **5.3 Physical Activation and Microwave Heating of Delayed and Fluid Coke**

Physical activation of delayed and fluid cokes was performed using microwave heating. Two different types of particle size 420  $\mu\text{m}$  to 300  $\mu\text{m}$  and 150  $\mu\text{m}$  to 75  $\mu\text{m}$  were used during the activation. The experiment investigated the effect of different activation parameters, including activation gas composition ( $\text{CO}_2$ ,  $\text{N}_2$  and steam), steam rate, microwave power, and particle sizes on the properties of the prepared activated carbon. The obtained results support the following conclusions:

- During the physical activation, the effect of different gas composition was evaluated.  $\text{CO}_2$  with steam provided higher quality activated carbon than  $\text{N}_2$  with steam.
- Two different steam rates, 0.3 mL/min and 0.5 mL/min, were used to conduct the experiment along with  $\text{CO}_2$  and  $\text{N}_2$  activating agent. The flow rate of  $\text{CO}_2$  and  $\text{N}_2$  was maintained at 100 mL/min. For fluid coke, a steam rate of 0.3 mL/min with  $\text{CO}_2$  or  $\text{N}_2$  provided higher quality activated carbon compared to a steam rate of 0.5 mL/min with  $\text{CO}_2$  or  $\text{N}_2$ . For delayed coke, a steam rate of 0.3 mL/min with  $\text{CO}_2$  gave lower quality activated carbon compared to a steam rate of 0.5 mL/min with  $\text{CO}_2$ .

However, for delayed coke, a steam rate of 0.3 mL/min with N<sub>2</sub> gave higher quality activated carbon than a steam rate of 0.5 mL/min with N<sub>2</sub>.

- To increase the temperature profile for delayed coke through microwave heating, pre-heating was performed at temperature of 800 °C with muffle furnace. The highest activation temperature of the pre-heated delayed coke was 766 °C after microwave application at high power level. The effect of pre-heating was also evaluated by XPS analysis. XPS analysis showed higher mass concentration of oxygen in the pre-heated delayed coke compared to the raw delayed coke. Increase in oxygen content is important as it plays the vital role during in physical activation reaction to remove carbon from precursor's surface as well as from the incipient micropores as carbon monoxide and carbon dioxide.
- BET surface area for the activated fluid coke was 112 m<sup>2</sup>/g where as for activated delayed coke it was 64 m<sup>2</sup>/g. Based on the pore size distribution, the micropore constituted 20 % of the total pore volume of the activated fluid coke, but for activated delayed coke, no micropore volume was observed.
- From the overall study of physical activation through microwave heating of fluid and delayed cokes, it was found that fluid coke gave higher quality activated carbon than the delayed coke though the BET surface area and total pore volume of the fluid coke was very low compared to the surface area and pore volume of commercially available activated carbon.

#### 5.4 Recommendation

Although chemical activation with KOH in this study produced commercial grade activated carbon, further studies are required for industrial scale production. A pilot scale study can be performed to optimize the activation parameters including the use of chemical KOH, lower the activation temperature to obtain higher yields, and make the process more economical. Recovery of impregnation chemical KOH after chemical activation and use for further activation is another scope for future study. This will help to reduce the chemical cost for large scale production of activated carbon from delayed and fluid coke. Future recommendation also includes the use of environmentally-friendly impregnation chemicals, such as  $\text{H}_3\text{PO}_4$ , and to assess the quality of activated carbon. Changing the impregnation chemical also affects the surface chemistry or surface functional groups.

For physical activation, fluid coke provided better quality activated carbon than the delayed coke although its iodine number and surface area were low compared to commercial grade activated carbon. The use of a customized microwave oven as a heating source was effective in heating the fluid coke, but not for the delayed coke. Improvement of the setup is required to increase the activation temperature and microwave power. Delayed coke should be the focus of future studies to evaluate its weak response to microwave heating. Metal oxide ( $\text{Fe}_2\text{O}_3$  or  $\text{CuO}$ ) during physical activation can be used to enhance microwave

heating of delayed coke as metal oxides are good receptor for microwaves which can also lead to increase the activation temperature and reduce the activation time.



## APENDICES

### Appendix A. Pore Size Distribution Data for the Activated Delayed and Fluid Coke Prepared with Chemical Activation Techniques

**Table A-1: DFT Model data for the pore size distribution of activated delayed coke prepared at 800 °C of activation temperature, 30 minutes activation time and with KOH/coke ratio of 2.**

Half pore width	Cumulative Pore Volume	Cumulative Surface Area	dV(r)	dS(r)
Å	cc/g	m <sup>2</sup> /g	cc/Å/g	m <sup>2</sup> /Å/g
2.50	1.60E-01	7.11E+02	2.78E-01	1.11E+03
2.62	1.85E-01	8.06E+02	2.16E-01	8.26E+02
2.74	2.14E-01	9.11E+02	2.39E-01	8.70E+02
2.87	2.45E-01	1.02E+03	2.49E-01	8.70E+02
3.00	2.71E-01	1.11E+03	1.94E-01	6.47E+02
3.14	2.89E-01	1.16E+03	1.32E-01	4.21E+02
3.28	3.00E-01	1.20E+03	7.79E-02	2.37E+02
3.43	3.05E-01	1.21E+03	3.53E-02	1.03E+02
3.59	3.11E-01	1.23E+03	3.32E-02	9.25E+01
3.75	3.27E-01	1.27E+03	9.68E-02	2.58E+02
3.93	3.60E-01	1.36E+03	1.95E-01	4.97E+02
4.11	3.89E-01	1.43E+03	1.60E-01	3.90E+02
4.30	4.12E-01	1.48E+03	1.21E-01	2.81E+02
4.49	4.21E-01	1.50E+03	4.42E-02	9.83E+01
4.70	4.24E-01	1.51E+03	1.47E-02	3.13E+01
4.92	4.33E-01	1.53E+03	4.11E-02	8.36E+01
5.14	4.43E-01	1.55E+03	4.65E-02	9.03E+01
5.38	4.55E-01	1.57E+03	4.97E-02	9.24E+01
5.63	4.88E-01	1.63E+03	1.31E-01	2.33E+02
5.89	5.21E-01	1.68E+03	1.28E-01	2.18E+02
6.16	5.45E-01	1.72E+03	8.78E-02	1.43E+02
6.44	5.56E-01	1.74E+03	3.97E-02	6.16E+01
6.74	5.66E-01	1.75E+03	3.57E-02	5.30E+01
7.05	5.85E-01	1.78E+03	6.04E-02	8.56E+01

7.37	5.99E-01	1.80E+03	4.11E-02	5.58E+01
7.71	6.08E-01	1.81E+03	2.90E-02	3.76E+01
8.07	6.16E-01	1.82E+03	2.12E-02	2.63E+01
8.44	6.21E-01	1.83E+03	1.39E-02	1.65E+01
8.83	6.27E-01	1.83E+03	1.62E-02	1.83E+01
9.23	6.33E-01	1.84E+03	1.27E-02	1.37E+01
9.66	6.35E-01	1.84E+03	5.94E-03	6.15E+00
10.10	6.37E-01	1.84E+03	4.27E-03	4.22E+00
10.57	6.37E-01	1.84E+03	0.00E+00	0.00E+00
11.06	6.37E-01	1.84E+03	0.00E+00	0.00E+00
11.56	6.37E-01	1.84E+03	0.00E+00	0.00E+00
12.10	6.39E-01	1.84E+03	3.27E-03	2.70E+00
12.65	6.41E-01	1.85E+03	3.74E-03	2.95E+00
13.24	6.43E-01	1.85E+03	4.01E-03	3.03E+00
13.85	6.45E-01	1.85E+03	3.89E-03	2.81E+00
14.48	6.48E-01	1.85E+03	3.23E-03	2.23E+00
15.15	6.49E-01	1.85E+03	1.74E-03	1.15E+00
15.85	6.50E-01	1.85E+03	2.45E-03	1.55E+00
16.58	6.52E-01	1.85E+03	2.52E-03	1.52E+00
17.34	6.54E-01	1.86E+03	1.85E-03	1.07E+00
18.14	6.56E-01	1.86E+03	3.45E-03	1.90E+00
18.97	6.66E-01	1.86E+03	1.09E-02	5.77E+00
19.84	6.82E-01	1.87E+03	1.90E-02	9.55E+00
20.76	6.87E-01	1.87E+03	4.82E-03	2.32E+00
21.71	6.88E-01	1.87E+03	1.54E-03	7.09E-01
22.71	6.89E-01	1.87E+03	1.49E-03	6.55E-01
23.76	6.91E-01	1.87E+03	1.40E-03	5.91E-01
24.85	6.92E-01	1.87E+03	1.07E-03	4.29E-01
26.00	6.93E-01	1.87E+03	1.04E-03	4.01E-01
27.19	6.94E-01	1.88E+03	9.31E-04	3.42E-01
28.44	6.95E-01	1.88E+03	7.53E-04	2.65E-01
29.75	6.96E-01	1.88E+03	4.44E-04	1.49E-01
31.12	6.96E-01	1.88E+03	2.11E-04	6.77E-02
32.56	6.96E-01	1.88E+03	8.56E-05	2.63E-02
34.05	6.97E-01	1.88E+03	5.20E-04	1.53E-01
35.62	6.98E-01	1.88E+03	5.21E-04	1.46E-01
37.26	6.99E-01	1.88E+03	5.27E-04	1.42E-01
38.98	7.00E-01	1.88E+03	4.86E-04	1.25E-01
40.77	7.00E-01	1.88E+03	3.92E-04	9.63E-02
42.65	7.01E-01	1.88E+03	3.43E-04	8.05E-02

44.61	7.02E-01	1.88E+03	3.36E-04	7.53E-02
46.66	7.02E-01	1.88E+03	3.27E-04	7.00E-02
48.81	7.03E-01	1.88E+03	2.36E-04	4.83E-02
51.06	7.03E-01	1.88E+03	2.33E-04	4.57E-02
53.41	7.04E-01	1.88E+03	2.30E-04	4.31E-02
55.87	7.04E-01	1.88E+03	1.74E-04	3.11E-02
58.44	7.05E-01	1.88E+03	1.55E-04	2.66E-02
61.13	7.05E-01	1.88E+03	1.95E-04	3.20E-02
63.94	7.06E-01	1.88E+03	2.03E-04	3.18E-02
66.88	7.06E-01	1.88E+03	1.94E-04	2.91E-02
69.96	7.07E-01	1.88E+03	1.91E-04	2.73E-02
73.18	7.07E-01	1.88E+03	1.57E-04	2.15E-02
76.55	7.08E-01	1.88E+03	1.40E-04	1.83E-02
80.07	7.08E-01	1.88E+03	1.32E-04	1.65E-02
83.76	7.09E-01	1.88E+03	1.26E-04	1.50E-02
87.61	7.09E-01	1.88E+03	1.18E-04	1.34E-02
91.65	7.10E-01	1.88E+03	1.09E-04	1.19E-02
95.87	7.10E-01	1.88E+03	1.18E-04	1.23E-02
100.28	7.11E-01	1.88E+03	1.28E-04	1.28E-02
104.89	7.11E-01	1.88E+03	1.02E-04	9.73E-03
109.72	7.12E-01	1.88E+03	9.66E-05	8.80E-03
114.77	7.12E-01	1.88E+03	9.24E-05	8.05E-03
120.05	7.13E-01	1.88E+03	8.77E-05	7.30E-03
125.58	7.13E-01	1.88E+03	6.22E-05	4.95E-03
131.36	7.13E-01	1.88E+03	3.96E-05	3.02E-03
137.41	7.14E-01	1.88E+03	6.02E-05	4.38E-03
143.73	7.15E-01	1.88E+03	1.62E-04	1.13E-02
150.35	7.16E-01	1.88E+03	1.33E-04	8.88E-03
157.27	7.16E-01	1.88E+03	8.50E-05	5.40E-03
164.51	7.17E-01	1.88E+03	8.13E-05	4.94E-03
172.08	7.17E-01	1.88E+03	7.72E-05	4.50E-03
180.00	7.18E-01	1.88E+03	1.43E-04	7.95E-03

**Table A-2: DFT Model data for the pore size distribution of activated fluid coke prepared at 800 °C of activation temperature, 30 minutes activation time and with KOH/coke ratio of 2.**

<b>Half pore width</b>	<b>Cumulative Pore Volume</b>	<b>Cumulative Surface Area</b>	<b>dV(r)</b>	<b>dS(r)</b>
<b>Å</b>	<b>cc/g</b>	<b>m<sup>2</sup>/g</b>	<b>cc/Å/g</b>	<b>m<sup>2</sup>/Å/g</b>
2.5041	1.11E-01	4.95E+02	2.00E-01	8.00E+02
2.6194	1.31E-01	5.71E+02	1.73E-01	6.62E+02
2.74	1.50E-01	6.40E+02	1.56E-01	5.69E+02
2.8661	1.72E-01	7.16E+02	1.73E-01	6.05E+02
2.998	1.89E-01	7.72E+02	1.28E-01	4.26E+02
3.136	2.01E-01	8.12E+02	8.96E-02	2.86E+02
3.2803	2.11E-01	8.41E+02	6.60E-02	2.01E+02
3.4313	2.15E-01	8.53E+02	2.86E-02	8.34E+01
3.5893	2.19E-01	8.63E+02	2.23E-02	6.21E+01
3.7545	2.29E-01	8.90E+02	6.21E-02	1.65E+02
3.9273	2.51E-01	9.47E+02	1.28E-01	3.25E+02
4.108	2.70E-01	9.93E+02	1.06E-01	2.59E+02
4.2971	2.83E-01	1.02E+03	6.92E-02	1.61E+02
4.4949	2.83E-01	1.02E+03	0.00E+00	0.00E+00
4.7018	2.83E-01	1.02E+03	0.00E+00	0.00E+00
4.9182	2.83E-01	1.02E+03	0.00E+00	0.00E+00
5.1446	2.85E-01	1.03E+03	8.98E-03	1.75E+01
5.3814	2.92E-01	1.04E+03	2.72E-02	5.05E+01
5.6291	3.17E-01	1.09E+03	1.03E-01	1.83E+02
5.8882	3.42E-01	1.13E+03	9.59E-02	1.63E+02
6.1592	3.60E-01	1.16E+03	6.66E-02	1.08E+02
6.4427	3.72E-01	1.18E+03	4.34E-02	6.74E+01
6.7392	3.84E-01	1.19E+03	3.89E-02	5.77E+01
7.0494	4.04E-01	1.22E+03	6.31E-02	8.95E+01
7.3739	4.16E-01	1.24E+03	3.78E-02	5.12E+01
7.7133	4.24E-01	1.25E+03	2.46E-02	3.19E+01
8.0683	4.29E-01	1.25E+03	1.44E-02	1.79E+01
8.4397	4.36E-01	1.26E+03	1.69E-02	2.00E+01
8.8282	4.43E-01	1.27E+03	2.04E-02	2.31E+01

9.2345	4.50E-01	1.28E+03	1.57E-02	1.70E+01
9.6595	4.53E-01	1.28E+03	6.79E-03	7.03E+00
10.1041	4.57E-01	1.28E+03	9.60E-03	9.50E+00
10.5692	4.57E-01	1.28E+03	0.00E+00	0.00E+00
11.0557	4.57E-01	1.28E+03	0.00E+00	0.00E+00
11.5646	4.58E-01	1.29E+03	2.90E-03	2.51E+00
12.0969	4.62E-01	1.29E+03	6.28E-03	5.19E+00
12.6537	4.65E-01	1.29E+03	6.01E-03	4.75E+00
13.2361	4.69E-01	1.29E+03	6.16E-03	4.65E+00
13.8453	4.72E-01	1.30E+03	5.86E-03	4.23E+00
14.4826	4.75E-01	1.30E+03	4.67E-03	3.22E+00
15.1492	4.78E-01	1.30E+03	3.40E-03	2.25E+00
15.8465	4.80E-01	1.30E+03	3.49E-03	2.20E+00
16.5758	4.83E-01	1.30E+03	3.57E-03	2.16E+00
17.3388	4.85E-01	1.30E+03	2.58E-03	1.49E+00
18.1369	4.87E-01	1.31E+03	3.13E-03	1.73E+00
18.9717	4.92E-01	1.31E+03	5.97E-03	3.15E+00
19.8449	5.05E-01	1.32E+03	1.50E-02	7.56E+00
20.7583	5.10E-01	1.32E+03	4.77E-03	2.30E+00
21.7138	5.11E-01	1.32E+03	1.75E-03	8.06E-01
22.7132	5.13E-01	1.32E+03	1.95E-03	8.60E-01
23.7586	5.15E-01	1.32E+03	1.77E-03	7.43E-01
24.8522	5.17E-01	1.32E+03	1.42E-03	5.70E-01
25.9961	5.18E-01	1.32E+03	1.33E-03	5.11E-01
27.1926	5.20E-01	1.32E+03	1.27E-03	4.68E-01
28.4443	5.21E-01	1.32E+03	1.20E-03	4.22E-01
29.7535	5.22E-01	1.32E+03	7.53E-04	2.53E-01
31.123	5.23E-01	1.32E+03	8.52E-04	2.74E-01
32.5555	5.24E-01	1.32E+03	4.26E-04	1.31E-01
34.054	5.25E-01	1.32E+03	7.43E-04	2.18E-01
35.6214	5.26E-01	1.32E+03	7.55E-04	2.12E-01
37.261	5.27E-01	1.32E+03	7.66E-04	2.05E-01
38.976	5.29E-01	1.32E+03	8.15E-04	2.09E-01
40.77	5.30E-01	1.32E+03	6.48E-04	1.59E-01
42.6465	5.31E-01	1.32E+03	5.00E-04	1.17E-01
44.6095	5.32E-01	1.33E+03	4.81E-04	1.08E-01
46.6628	5.33E-01	1.33E+03	5.33E-04	1.14E-01
48.8105	5.34E-01	1.33E+03	3.79E-04	7.77E-02
51.0572	5.35E-01	1.33E+03	3.86E-04	7.55E-02
53.4072	5.36E-01	1.33E+03	4.56E-04	8.53E-02

55.8655	5.37E-01	1.33E+03	3.65E-04	6.54E-02
58.4368	5.37E-01	1.33E+03	3.25E-04	5.55E-02
61.1265	5.38E-01	1.33E+03	3.58E-04	5.86E-02
63.9401	5.39E-01	1.33E+03	3.69E-04	5.77E-02
66.8831	5.40E-01	1.33E+03	3.52E-04	5.26E-02
69.9616	5.42E-01	1.33E+03	3.52E-04	5.03E-02
73.1818	5.43E-01	1.33E+03	3.15E-04	4.31E-02
76.5502	5.43E-01	1.33E+03	2.82E-04	3.68E-02
80.0736	5.44E-01	1.33E+03	2.65E-04	3.31E-02
83.7592	5.45E-01	1.33E+03	2.51E-04	3.00E-02
87.6145	5.46E-01	1.33E+03	2.36E-04	2.69E-02
91.6472	5.47E-01	1.33E+03	2.18E-04	2.38E-02
95.8655	5.48E-01	1.33E+03	2.44E-04	2.54E-02
100.278	5.49E-01	1.33E+03	2.60E-04	2.59E-02
104.8936	5.50E-01	1.33E+03	2.07E-04	1.97E-02
109.7216	5.51E-01	1.33E+03	1.96E-04	1.79E-02
114.7718	5.52E-01	1.33E+03	1.88E-04	1.64E-02
120.0545	5.53E-01	1.33E+03	1.78E-04	1.48E-02
125.5804	5.54E-01	1.33E+03	1.26E-04	1.01E-02
131.3606	5.54E-01	1.33E+03	8.04E-05	6.12E-03
137.4068	5.56E-01	1.33E+03	2.29E-04	1.67E-02
143.7314	5.58E-01	1.33E+03	3.60E-04	2.51E-02
150.347	5.60E-01	1.33E+03	2.56E-04	1.70E-02
157.2672	5.61E-01	1.33E+03	1.63E-04	1.04E-02
164.5059	5.62E-01	1.33E+03	1.56E-04	9.44E-03
172.0777	5.63E-01	1.33E+03	1.48E-04	8.58E-03
179.9981	5.65E-01	1.33E+03	2.73E-04	1.52E-02

**Appendix B.** Calculation of the Mole Percentage of Gas Composition in the Gas Mix

<b>Gas Component</b>	<b>Molecular Weight (g/mole)</b>	<b>Density at 25 °C (g/mL)</b>
CO <sub>2</sub>	44	0.001799
H <sub>2</sub> O	18	0.997
N <sub>2</sub>	14	0.00145

<b>Gas Component</b>	<b>Flow rate (mL/minute)</b>
CO <sub>2</sub>	100
N <sub>2</sub>	100
H <sub>2</sub> O	0.5
	0.3

<b>Gas Component</b>	<b>Amount of gas per minute (g) = (Flow rate of the gas) * (Density of the gas)</b>	<b>Number of mole per minute = (Amount of gas per minute)/(Molecular weight of the gas)</b>
CO <sub>2</sub>	0.1799	0.004089
N <sub>2</sub>	0.145	0.010357
H <sub>2</sub> O (0.5 mL/min)	0.4985	0.027694
H <sub>2</sub> O (0.3 mL/min)	0.2991	0.021364

<b>Gas Composition</b>	<b>H<sub>2</sub>O Flow rate mL/min</b>	<b>Mole Percentage of H<sub>2</sub>O (%)</b>	<b>Mole percentage of 2<sup>nd</sup> gas (%)</b>
CO <sub>2</sub> + H <sub>2</sub> O	0.3	83.9	16.1
	0.5	87.1	12.9
N <sub>2</sub> + H <sub>2</sub> O	0.3	67.3	32.7
	0.5	72.8	27.2

**Appendix C. Pore Size Distribution Data for the Activated Delayed and Fluid Coke Prepared with Physical Activation Techniques**

**Table C-1: DFT Model data for the pore size distribution of fluid coke prepared at carbon dioxide and steam mix activating gas agent where steam flow rate is 0.5 mL/min, particle size ranging from 350  $\mu\text{m}$  to 420  $\mu\text{m}$  and high microwave power level for six hours of activation time.**

Half pore width	Cumulative Pore Volume	Cumulative Surface Area	dV(r)	dS(r)
$\text{\AA}$	cc/g	$\text{m}^2/\text{g}$	cc/ $\text{\AA}/\text{g}$	$\text{m}^2/\text{\AA}/\text{g}$
2.5041	3.61E-03	1.60E+01	6.71E-03	2.68E+01
2.6194	4.59E-03	1.97E+01	8.45E-03	3.23E+01
2.74	5.69E-03	2.38E+01	9.14E-03	3.34E+01
2.8661	6.69E-03	2.73E+01	7.99E-03	2.79E+01
2.998	7.49E-03	2.99E+01	6.00E-03	2.00E+01
3.136	8.12E-03	3.20E+01	4.63E-03	1.48E+01
3.2803	8.61E-03	3.34E+01	3.37E-03	1.03E+01
3.4313	8.98E-03	3.45E+01	2.43E-03	7.08E+00
3.5893	9.31E-03	3.54E+01	2.10E-03	5.84E+00
3.7545	9.53E-03	3.60E+01	1.33E-03	3.55E+00
3.9273	9.59E-03	3.62E+01	3.35E-04	8.53E-01
4.108	9.59E-03	3.62E+01	0.00E+00	0.00E+00
4.2971	9.59E-03	3.62E+01	0.00E+00	0.00E+00
4.4949	9.59E-03	3.62E+01	0.00E+00	0.00E+00
4.7018	9.59E-03	3.62E+01	0.00E+00	0.00E+00
4.9182	9.59E-03	3.62E+01	0.00E+00	0.00E+00
5.1446	9.59E-03	3.62E+01	0.00E+00	0.00E+00
5.3814	9.68E-03	3.63E+01	4.07E-04	7.56E-01
5.6291	1.05E-02	3.77E+01	3.18E-03	5.64E+00
5.8882	1.17E-02	3.98E+01	4.79E-03	8.14E+00
6.1592	1.31E-02	4.21E+01	5.20E-03	8.45E+00
6.4427	1.48E-02	4.48E+01	5.95E-03	9.23E+00
6.7392	1.67E-02	4.76E+01	6.44E-03	9.55E+00
7.0494	1.89E-02	5.07E+01	7.02E-03	9.96E+00
7.3739	2.01E-02	5.23E+01	3.72E-03	5.04E+00
7.7133	2.06E-02	5.29E+01	1.42E-03	1.84E+00
8.0683	2.09E-02	5.33E+01	9.15E-04	1.13E+00
8.4397	2.14E-02	5.39E+01	1.36E-03	1.61E+00



8.8282	2.20E-02	5.46E+01	1.46E-03	1.65E+00
9.2345	2.22E-02	5.49E+01	6.76E-04	7.32E-01
9.6595	2.22E-02	5.49E+01	0.00E+00	0.00E+00
10.1041	2.22E-02	5.49E+01	0.00E+00	0.00E+00
10.5692	2.22E-02	5.49E+01	0.00E+00	0.00E+00
11.0557	2.22E-02	5.49E+01	0.00E+00	0.00E+00
11.5646	2.22E-02	5.49E+01	0.00E+00	0.00E+00
12.0969	2.23E-02	5.49E+01	1.15E-04	9.48E-02
12.6537	2.27E-02	5.53E+01	7.54E-04	5.96E-01
13.2361	2.33E-02	5.57E+01	1.05E-03	7.97E-01
13.8453	2.40E-02	5.62E+01	1.10E-03	7.92E-01
14.4826	2.46E-02	5.66E+01	9.52E-04	6.57E-01
15.1492	2.52E-02	5.70E+01	8.20E-04	5.41E-01
15.8465	2.58E-02	5.74E+01	9.01E-04	5.69E-01
16.5758	2.66E-02	5.78E+01	1.04E-03	6.28E-01
17.3388	2.74E-02	5.84E+01	1.17E-03	6.75E-01
18.1369	2.89E-02	5.92E+01	1.87E-03	1.03E+00
18.9717	3.12E-02	6.04E+01	2.76E-03	1.46E+00
19.8449	3.31E-02	6.13E+01	2.15E-03	1.08E+00
20.7583	3.39E-02	6.17E+01	8.96E-04	4.32E-01
21.7138	3.45E-02	6.20E+01	5.55E-04	2.55E-01
22.7132	3.50E-02	6.22E+01	5.74E-04	2.53E-01
23.7586	3.56E-02	6.25E+01	5.27E-04	2.22E-01
24.8522	3.61E-02	6.26E+01	4.34E-04	1.75E-01
25.9961	3.65E-02	6.28E+01	4.15E-04	1.60E-01
27.1926	3.70E-02	6.30E+01	3.97E-04	1.46E-01
28.4443	3.75E-02	6.32E+01	3.72E-04	1.31E-01
29.7535	3.78E-02	6.33E+01	2.48E-04	8.32E-02
31.123	3.82E-02	6.34E+01	2.71E-04	8.70E-02
32.5555	3.84E-02	6.35E+01	1.63E-04	4.99E-02
34.054	3.87E-02	6.36E+01	2.07E-04	6.09E-02
35.6214	3.91E-02	6.37E+01	2.40E-04	6.73E-02
37.261	3.95E-02	6.38E+01	2.49E-04	6.69E-02
38.976	4.00E-02	6.39E+01	2.66E-04	6.82E-02
40.77	4.03E-02	6.40E+01	2.15E-04	5.28E-02
42.6465	4.07E-02	6.41E+01	1.78E-04	4.16E-02
44.6095	4.10E-02	6.41E+01	1.68E-04	3.76E-02
46.6628	4.14E-02	6.42E+01	1.68E-04	3.61E-02
48.8105	4.16E-02	6.43E+01	1.20E-04	2.45E-02
51.0572	4.19E-02	6.43E+01	1.16E-04	2.27E-02

53.4072	4.21E-02	6.44E+01	1.11E-04	2.09E-02
55.8655	4.23E-02	6.44E+01	8.07E-05	1.45E-02
58.4368	4.25E-02	6.44E+01	7.46E-05	1.28E-02
61.1265	4.28E-02	6.45E+01	9.59E-05	1.57E-02
63.9401	4.31E-02	6.45E+01	1.23E-04	1.92E-02
66.8831	4.35E-02	6.46E+01	1.17E-04	1.75E-02
69.9616	4.38E-02	6.46E+01	1.11E-04	1.59E-02
73.1818	4.41E-02	6.47E+01	9.12E-05	1.25E-02
76.5502	4.44E-02	6.47E+01	8.29E-05	1.08E-02
80.0736	4.47E-02	6.47E+01	7.78E-05	9.72E-03
83.7592	4.49E-02	6.48E+01	7.36E-05	8.79E-03
87.6145	4.52E-02	6.48E+01	6.93E-05	7.91E-03
91.6472	4.55E-02	6.48E+01	6.42E-05	7.00E-03
95.8655	4.57E-02	6.49E+01	6.79E-05	7.08E-03
100.278	4.61E-02	6.49E+01	8.72E-05	8.69E-03
104.8936	4.64E-02	6.49E+01	6.91E-05	6.59E-03
109.7216	4.68E-02	6.50E+01	6.56E-05	5.98E-03
114.7718	4.71E-02	6.50E+01	6.28E-05	5.47E-03
120.0545	4.74E-02	6.50E+01	5.95E-05	4.96E-03
125.5804	4.76E-02	6.50E+01	4.23E-05	3.37E-03
131.3606	4.78E-02	6.50E+01	2.70E-05	2.05E-03
137.4068	4.80E-02	6.51E+01	3.86E-05	2.81E-03
143.7314	4.85E-02	6.51E+01	8.14E-05	5.66E-03
150.347	4.90E-02	6.51E+01	7.60E-05	5.05E-03
157.2672	4.94E-02	6.52E+01	4.84E-05	3.08E-03
164.5059	4.97E-02	6.52E+01	4.62E-05	2.81E-03
172.0777	5.00E-02	6.52E+01	4.38E-05	2.55E-03
179.9981	5.07E-02	6.52E+01	8.17E-05	4.54E-03

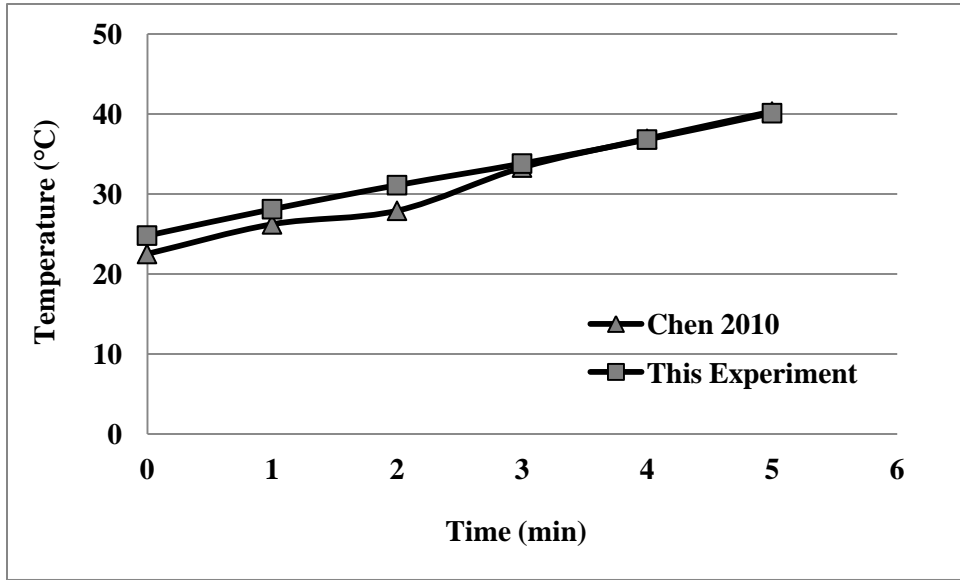
**Table C-2: DFT Model data for the pore size distribution of delayed coke prepared at carbon dioxide and steam mix activating gas agent where steam flow rate is 0.5 mL/min, particle size ranging from 350  $\mu\text{m}$  to 420  $\mu\text{m}$  and high microwave power level for six hours of activation time.**

<b>Half pore width</b>	<b>Cumulative Pore Volume</b>	<b>Cumulative Surface Area</b>	<b>dV(r)</b>	<b>dS(r)</b>
<b>Å</b>	<b>cc/g</b>	<b>m<sup>2</sup>/g</b>	<b>cc/Å/g</b>	<b>m<sup>2</sup>/Å/g</b>
2.6194	3.91E-04	1.70E+00	5.91E-04	2.26E+00
2.74	4.71E-04	1.99E+00	6.64E-04	2.42E+00
2.8661	5.60E-04	2.30E+00	7.04E-04	2.46E+00
2.998	6.51E-04	2.60E+00	6.89E-04	2.30E+00
3.136	7.45E-04	2.90E+00	6.79E-04	2.17E+00
3.2803	8.40E-04	3.19E+00	6.59E-04	2.01E+00
3.4313	9.37E-04	3.48E+00	6.44E-04	1.88E+00
3.5893	1.04E-03	3.75E+00	6.21E-04	1.73E+00
3.7545	1.11E-03	3.95E+00	4.59E-04	1.22E+00
3.9273	1.14E-03	4.03E+00	1.84E-04	4.69E-01
4.108	1.14E-03	4.03E+00	0.00E+00	0.00E+00
4.2971	1.14E-03	4.03E+00	0.00E+00	0.00E+00
4.4949	1.14E-03	4.03E+00	0.00E+00	0.00E+00
4.7018	1.14E-03	4.03E+00	0.00E+00	0.00E+00
4.9182	1.14E-03	4.03E+00	0.00E+00	0.00E+00
5.1446	1.14E-03	4.03E+00	0.00E+00	0.00E+00
5.3814	1.14E-03	4.03E+00	0.00E+00	0.00E+00
5.6291	1.14E-03	4.03E+00	0.00E+00	0.00E+00
5.8882	1.15E-03	4.04E+00	2.62E-05	4.44E-02
6.1592	1.22E-03	4.15E+00	2.43E-04	3.95E-01
6.4427	1.35E-03	4.35E+00	4.62E-04	7.17E-01
6.7392	1.53E-03	4.63E+00	6.19E-04	9.19E-01
7.0494	1.75E-03	4.94E+00	7.11E-04	1.01E+00
7.3739	1.95E-03	5.21E+00	6.20E-04	8.40E-01
7.7133	2.13E-03	5.44E+00	5.13E-04	6.65E-01
8.0683	2.31E-03	5.66E+00	5.09E-04	6.31E-01
8.4397	2.52E-03	5.91E+00	5.73E-04	6.79E-01
8.8282	2.75E-03	6.17E+00	5.84E-04	6.61E-01
9.2345	2.94E-03	6.38E+00	4.69E-04	5.08E-01
9.6595	3.09E-03	6.54E+00	3.63E-04	3.76E-01

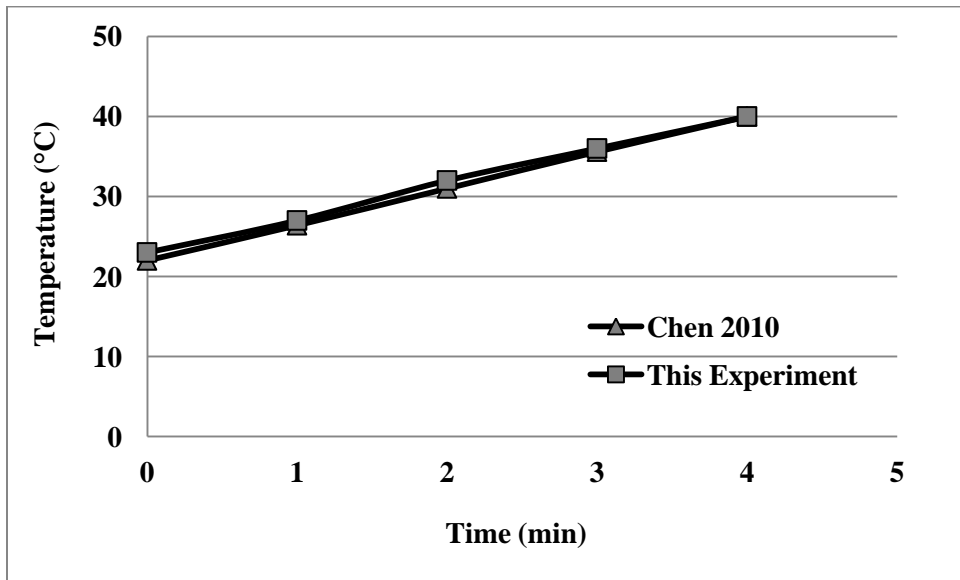
10.1041	3.25E-03	6.69E+00	3.55E-04	3.52E-01
10.5692	3.35E-03	6.79E+00	2.25E-04	2.13E-01
11.0557	3.45E-03	6.88E+00	1.99E-04	1.80E-01
11.5646	3.62E-03	7.03E+00	3.40E-04	2.94E-01
12.0969	3.87E-03	7.23E+00	4.64E-04	3.84E-01
12.6537	4.18E-03	7.48E+00	5.56E-04	4.40E-01
13.2361	4.57E-03	7.77E+00	6.63E-04	5.01E-01
13.8453	5.02E-03	8.10E+00	7.39E-04	5.34E-01
14.4826	5.49E-03	8.42E+00	7.48E-04	5.16E-01
15.1492	5.98E-03	8.75E+00	7.37E-04	4.86E-01
15.8465	6.51E-03	9.08E+00	7.60E-04	4.80E-01
16.5758	7.08E-03	9.42E+00	7.70E-04	4.65E-01
17.3388	7.67E-03	9.76E+00	7.73E-04	4.46E-01
18.1369	8.30E-03	1.01E+01	7.98E-04	4.40E-01
18.9717	8.93E-03	1.04E+01	7.56E-04	3.99E-01
19.8449	9.47E-03	1.07E+01	6.17E-04	3.11E-01
20.7583	9.94E-03	1.09E+01	5.16E-04	2.49E-01
21.7138	1.04E-02	1.11E+01	4.63E-04	2.13E-01
22.7132	1.08E-02	1.13E+01	4.49E-04	1.98E-01
23.7586	1.13E-02	1.15E+01	4.10E-04	1.73E-01
24.8522	1.17E-02	1.17E+01	3.72E-04	1.50E-01
25.9961	1.21E-02	1.18E+01	3.34E-04	1.28E-01
27.1926	1.24E-02	1.20E+01	3.26E-04	1.20E-01
28.4443	1.28E-02	1.21E+01	3.01E-04	1.06E-01
29.7535	1.31E-02	1.22E+01	2.37E-04	7.95E-02
31.123	1.34E-02	1.23E+01	2.11E-04	6.79E-02
32.5555	1.37E-02	1.24E+01	1.69E-04	5.18E-02
34.054	1.39E-02	1.25E+01	1.87E-04	5.49E-02
35.6214	1.42E-02	1.26E+01	1.97E-04	5.53E-02
37.261	1.46E-02	1.26E+01	2.00E-04	5.37E-02
38.976	1.49E-02	1.27E+01	2.06E-04	5.29E-02
40.77	1.52E-02	1.28E+01	1.71E-04	4.19E-02
42.6465	1.55E-02	1.29E+01	1.39E-04	3.25E-02
44.6095	1.57E-02	1.29E+01	1.26E-04	2.83E-02
46.6628	1.60E-02	1.30E+01	1.22E-04	2.62E-02
48.8105	1.62E-02	1.30E+01	9.82E-05	2.01E-02
51.0572	1.64E-02	1.31E+01	9.29E-05	1.82E-02
53.4072	1.67E-02	1.31E+01	1.06E-04	1.99E-02
55.8655	1.69E-02	1.31E+01	9.27E-05	1.66E-02
58.4368	1.71E-02	1.32E+01	8.23E-05	1.41E-02

61.1265	1.73E-02	1.32E+01	8.41E-05	1.38E-02
63.9401	1.76E-02	1.33E+01	8.42E-05	1.32E-02
66.8831	1.78E-02	1.33E+01	8.06E-05	1.21E-02
69.9616	1.80E-02	1.33E+01	7.59E-05	1.09E-02
73.1818	1.82E-02	1.34E+01	6.31E-05	8.62E-03
76.5502	1.84E-02	1.34E+01	5.63E-05	7.36E-03
80.0736	1.86E-02	1.34E+01	5.27E-05	6.58E-03
83.7592	1.88E-02	1.34E+01	4.98E-05	5.94E-03
87.6145	1.90E-02	1.34E+01	4.69E-05	5.35E-03
91.6472	1.92E-02	1.35E+01	4.38E-05	4.78E-03
95.8655	1.94E-02	1.35E+01	4.69E-05	4.89E-03
100.278	1.96E-02	1.35E+01	5.50E-05	5.49E-03
104.8936	1.98E-02	1.35E+01	4.47E-05	4.26E-03
109.7216	2.00E-02	1.35E+01	4.22E-05	3.85E-03
114.7718	2.02E-02	1.36E+01	4.04E-05	3.52E-03
120.0545	2.04E-02	1.36E+01	3.80E-05	3.16E-03
125.5804	2.06E-02	1.36E+01	2.73E-05	2.17E-03
131.3606	2.07E-02	1.36E+01	1.81E-05	1.38E-03
137.4068	2.08E-02	1.36E+01	2.46E-05	1.79E-03
143.7314	2.11E-02	1.36E+01	4.31E-05	3.00E-03
150.347	2.15E-02	1.37E+01	5.58E-05	3.71E-03
157.2672	2.17E-02	1.37E+01	3.68E-05	2.34E-03
164.5059	2.20E-02	1.37E+01	3.45E-05	2.10E-03
172.0777	2.22E-02	1.37E+01	3.35E-05	1.95E-03
179.9981	2.27E-02	1.37E+01	6.16E-05	3.42E-03

**Appendix D. Microwave Activity Test Data for Water Heating**



**Figure D-1: Temperature versus time for de-ionized water after heating by microwave at medium power level and comparison with Chen (2010)**



**Figure D-2: Temperature versus time for de-ionized water after heating by microwave at high power level and comparison with Chen (2010)**