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Microwave heating for adsorbents regeneration and oil sands coke activation

by

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DEDICATION

I would like to dedicate this thesis to my wife, Fang Wu and my parents. I thank you for your love and encouragement through this process.

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I would like to express my sincere appreciation to my supervisor. Dr. Zaher Hashisho. His expertise and guidance during the thesis was invaluable. I also would like to thank Dr. Steven M. Kuznicki for providing molecular sieve samples and isotherm measurements. Additionally, I would thank National Science and Engineering Research Council of Canada for the financial support.

ABSTRACT

Microwave heating has unique advantages compared to convection-radiation heating methods including fast heating rate and selective heating of objects. This thesis studied two applications of microwave heating in the environmental field: adsorbent regeneration and oil sands coke activation.

The thermal behavior during microwave heating of select adsorbents when dry or saturated with selected adsorbates was studied to assess the potential for using microwave heating to regenerate adsorbents. Strong microwave-absorbing adsorbents depicted faster heating rate when dry. Weakly microwave-absorbing adsorbents depicted faster heating rate when saturated with polar adsorbates.

Fast activation of oil sands coke using microwave heating and KOH was successfully completed. The iodine number of the activated delayed coke obtained after 10 minutes of microwave activation was 1130 mg/g. The short activation time and simplicity of the process demonstrate that microwave-activation is a promising approach to convert oil sands coke into activated carbon adsorbent with high adsorption capacity.

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1 INTRODUCTION

1.1 Overview of Microwave Heating

Microwave heating has been used in many fields because of its unique advantages. The dielectric properties of materials mostly determine the efficiency of transferring microwave energy to heat. Therefore some material can be quickly heated with microwaves heating, whereas others may not be heated at all, giving microwave heating a kind of selectivity. An obvious example is that food can be easily cooked in a microwave oven while the plate is still cool. This kind of selective heating can greatly improve the energy efficiency when heating objects that strongly absorb microwaves. More information about microwave heating is provided in chapter 2.

This thesis investigates two applications of microwave heating in the environmental field which are adsorbent regeneration and oil sands coke activation.

1.2 Research Objectives and Significance

1.2.1 Microwave heating for adsorbent regeneration

The emission of organic vapors such as volatile organic compounds is a significant air pollution problem. Adsorption is an effective way to control these emissions. But the regeneration of adsorbents needs a more cost-effective method. Generally, the common method in industry for adsorbent regeneration is temperature swing adsorption, which will waste lots of energy in heating the ancillary parts. Microwave heating is selective due to the difference in the efficiency of microwave absorption among materials. The difference in microwave absorption between the adsorbent and the adsorbed compound (i.e. VOC) can allow for selective and energy efficient microwave regeneration. For instance, a microwave transparent adsorbent can be rapidly heated by microwaves when it is saturated with a polar VOC; however, as the VOC is desorbed from the adsorbent, less microwave energy is absorbed by that adsorbent. Therefore, the thermal behavior of adsorbents with or without adsorbate in microwave is important for adsorbent regeneration. Better selectivity of adsorbent and higher energy efficiency can be achieved if the thermal behaviors of different adsorbents and adsorbates during microwave heating can be determined.

The purpose of this study is to determine the thermal behavior of dry and solvent saturated adsorbents during microwave irradiation and test which adsorbent has potential to achieve most energy-efficiency for future application.

1.2.2 Microwave heating for oil sands coke activation

A carbonaceous material is a strong microwave absorber. This characteristic can be used to prepare activated carbon by microwave heating. Alberta is rich in oil sands and oil sands coke is a byproduct of upgrading oil sands bitumen, most of which is presently stockpiled. The coke has a high sulfur content which restricts its application as a fuel. But the high carbon content and low volatile matter make the coke an excellent precursor for activated carbon. The coke is abundant and at very low cost, whereas the demand for activated carbon keeps increasing.

Generally the preparation of activated carbon has two steps, carbonization and activation. The activation step occurs at high temperature, typically around 1000^{o}C for steam activation or around 700^{o}C for KOH activation (Bandosz, 2006). Since microwaves can greatly heat carbonaceous material, completing the activation using microwave heating can significantly save time and energy, and lower the production cost of activated carbon.

The purpose of this study is to 1) test the feasibility of preparing activated carbon from oil sands coke by microwave heating; 2) determine the appropriate microwave activation condition for oil sands coke, and 3) determine the impact of the activation conditions on the properties of the produced activated carbon. This study provides a promising approach to convert the millions of tonnes of oil sands coke currently stockpiled as waste, into useful adsorbent with high adsorption capacity.

1.3 Organization of Thesis

Chapter 2 briefly reviews microwave heating and adsorption principles, adsorbent regeneration and activated carbon preparation methods. Chapter 3 describes the methodology and results for the thermal behavior of adsorbents during microwave heating. Chapter 4 describes the experimental setup used for the preparation of activated carbon and determines the factors influencing the preparation of activated carbon from petroleum coke and the impact of the microwave activation conditions on the properties of the prepared activated carbon. Conclusions and recommendations are provided in chapter 5.

2 LITERATURE REVIEW

2.1 Microwave Heating Technology

2.1.1 History of microwaves

Microwaves lie between radio wave frequencies (RF) and infrared frequencies (IR) on the electromagnetic spectrum (Figure 2-1). Microwaves wavelengths range from 1 mm to 1m, or frequency is between 300 megahertz (MHz) and 300 gigahertz (GHz). However, two frequencies are typically used for microwave heating in industry: 915 MHz and 2450 MHz (Meredith, 1998; Metaxas and Meredith, 1983). Using microwaves to heat objects was recognized in 1946 and the first microwave oven was introduced to the marketplace by Raytheon in 1952 (Committee on Microwave Processing of Materials, 1994).

Presently, microwave generators include magnetron, power grid tube, traveling wave tube, klystron and gyrotron. Among those, magnetron is the most common and economic choice for low power applications because it has the highest efficiency among the microwave generators. The efficiency of converting electric energy to microwave energy for a magnetron can usually be 70 to 80 percent, and can reach 90 percent (Committee on Microwave Processing of Materials, 1994).

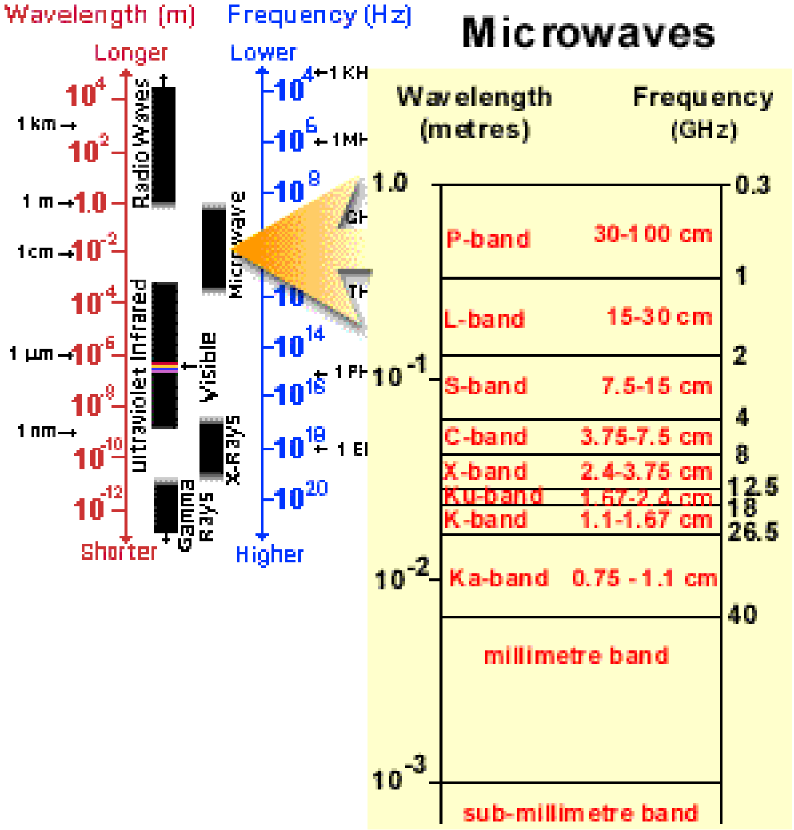


Figure 2-1 Diagram of electromagnetic wave spectrum (with copyright permission) (NRC, 2008)

2.1.2 Application of microwave

Nowadays microwave technology is widely used in the world and greatly changed the human life. Figure 2-2 illustrates the applications of microwave technologies as a function of wavelength or frequency. Generally, applications of microwaves can be divided into several groups: (1) communications and information transfer; (2) processing/manufacturing (microwave heating); (3) diagnostics/analyses; (4) medical treatment; and (5) weapons(Clark et al., 2005). Among those, the first two categories are widely used at present. Cell phones and the microwave ovens can be good examples of these applications.

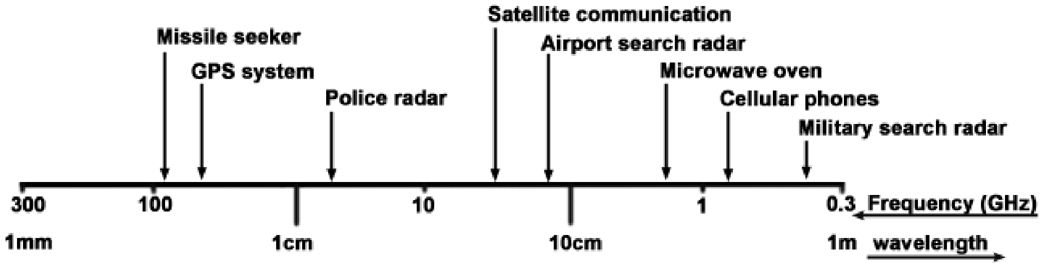


Figure 2-2 Microwave spectrum and application (with copyright permission) (Sebastian, 2008)

2.2 Overview of Microwave Heating Principle

When a material is put into an alternating electric field, this material will have potential energy. Part of this energy will be stored in material as electric energy, and other part will be dissipated as heat. It is assumed that the material has an electronic conduction σ_e, an ionic conduction σ_i, and a complex permittivity $\varepsilon' - i\varepsilon''$. If an electric filed $E = e^{i\omega t}$ is applied, a current will flow in the material. The current density is expressed as:

$$j = [\sigma_e + \sigma_i + i\omega\varepsilon_0(\varepsilon' - i\varepsilon'')]E = i\omega\varepsilon_0\varepsilon' E + \omega\varepsilon_o\varepsilon' \tan\delta E \text{ ....(1)}$$

The first term $i\omega\varepsilon_0\varepsilon' E$ in equation 1 is the displacement current that stores electric energy in a material. If this term is dominant, this kind of material can be used in capacitors. The second term $\omega\varepsilon_0\varepsilon' \tan\delta E$ is the component of the current which converts electric energy into heat. Dielectric loss is the dissipation of energy as heat in the material (Anderson, 1964;

Committee on Microwave Processing of Materials, 1994). If dielectric loss of a material is large, this kind of material can be rapidly heated in an electromagnetic field.

$$\tan\delta = \frac{\frac{\sigma_e + \sigma_i}{\omega\varepsilon_0} + \varepsilon''}{\varepsilon'} \quad \text{...(2)}$$

This term tanδ is called the dielectric loss tangent, ω is the angular frequency of the microwave, ε_0 is the free space permittivity or free space dielectric constant (8.854×10^{-12}F/m), ε' is the real relative permittivity (dielectric constant) of the material. From equation 2, it can be seen that conductive current has an important effect on the dielectric loss tangent.

The average power converted into heat per unit volume P_{ave} is expressed as:

$$P_{ave} = \frac{1}{2}\omega\varepsilon_0\varepsilon'\tan\delta E^2 \quad \text{...(3)}$$

Therefore, the material thermal behavior during microwave heating depends on the frequency, electric field intensity, permittivity and dielectric loss tangent. However, other factors can affect these parameters. For example, the polarization of the material has a strong relationship to the frequency, permittivity and loss tangent. The relationship between polarization and permittivity is shown in Equation 4. Generally, if a material can be polarized, it is expected to have high permittivity and good ability to be heated with microwaves. For example, water is rapidly heated by microwaves because it has permanent dipoles which results in large polarizability and large permittivity (Anderson, 1964).

$$\varepsilon = \varepsilon' - i\varepsilon'' = 1 + \frac{P}{E} = 1 + \frac{P' - iP''}{E} \quad \text{...(4)}$$

2.3 Adsorption

2.3.1 Factors influencing adsorption

Adsorption (strictly, physical adsorption) is defined as the enrichment (i.e. positive adsorption or simply adsorption) or depletion (i.e. negative adsorption) of one or more components in an interfacial layer (Gregg and Sing, 1982). Usually the adsorbent has porous structure so that it can have large surface area. For example, the surface area is reported about 900 to 1100 m^2/g for granular activated carbon and about 900 to 1400 m^2/g for zeolite (Yates, 1968). Adsorption can be grouped into physical adsorption and chemical adsorption. In physical adsorption, the adsorbate is attached to the surface of the adsorbent by weak physical forces, such as van de Waals force or hydrogen bonds. The adsorption energy usually doesn't exceed 80kJ/mole. Adsorption can also result in a surface complex, a union much stronger than a physical bond with heats of adsorption up to about 600kJ/mole for C-N bonds, and 800kJ/mole for chemical bonds. A chemical bond involves sharing of electrons between the adsorbate and the adsorbent and may be regarded as the formation of a surface compound. Due to the bond strength, chemical adsorption is difficult to reverse (Webb, 2003).

The adsorption capacity of a certain adsorbent is related to its physical structure, pore size and volume, specific surface area, and surface chemistry.

2.3.1.1 Physical structure

Physical structure refers to the arrangement of atoms or molecules in three dimensions in the material. For instance, zeolites are a family of crystalline aluminosilicate materials (Choi et al., 2006), which have a very regular pore structure of molecular dimensions made up of silicon/aluminum and oxygen atoms (Figure 2-3). Activated carbon structure mainly depends on the graphite microcrystal structures formed in the preparation, as illustrated in Figure 2-4.

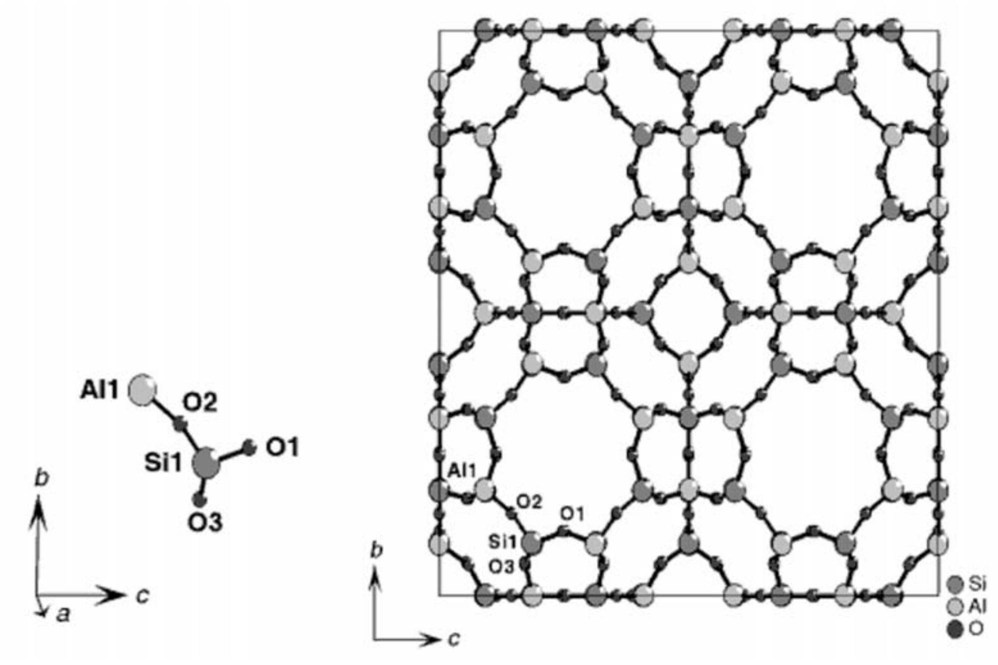


Figure 2-3 Schematic diagram of the zeolite A framework (with copyright permission) (Čejka et al., 2007)

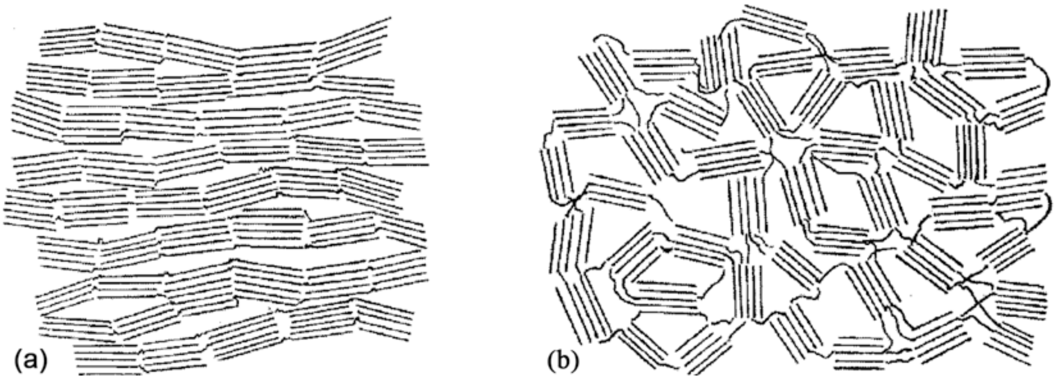


Figure 2-4 Schematic illustration of the structure of activated carbon: (a) easily undergoing graphitization, (b) undergoing graphitization to a small degree (with copyright permission) (Franklin, 1951)

2.3.1.2 Pore size

Based on the pore size, the pore can be broadly divided into three groups: micropore, mesopore and macropore. Pore less than 2 nm in diameter are classified as micropores, pores larger than 50 nm are classified macropores, while pores between 2nm and 50 nm are classified as mesopores (Webb and Orr, 1997).

Different adsorbents have different pore size distributions. For example, activated carbon has a wide pore size distribution, which means all three kinds of pores can be found in it. Molecular sieves have narrow pore size distributions and a regular pore size close to some molecular dimension. It can adsorb gas/liquid molecules that are less or close to the pore size, but hardly adsorb molecules larger than the pore size. Zeolite is a well-known molecular sieve which has been widely used in gas separation (Bekkum et al., 2001).

The pore size distribution can be obtained from Nitrogen adsorption isotherms. Several models have been developed to extract information about the pore size of porous materials from physical adsorption isotherms. The t-method can give the micropore volume of the material by plotting the V-t curve (Lippens, Linsen et al. 1964; Lippens and de Boer 1965; de Boer, Lippens et al. 1966). The first linear region of the plot is extrapolated to the y-axis to determine the micropore volume (Webb and Orr, 1997). The MP method also can get the micropore volume by analyzing the nonlinear part of the V-t curve (Mikhail et al., 1968). Dubinin and Radushkevich developed a model applicable for carbon with micropores whose width is only a little more than one gas molecule. Later Dubinin-Astakhov method modified the DR model (Webb and Orr, 1997). There are other models which are used for adsorbents with specific pore types. For instance, the Horvath-Kawazoe (HK) model is commonly used for silt-shaped pores, the Saito-Foley model is commonly used for cylindrical pores and the Cheng-Yang model is commonly used for spherical pores (Webb and Orr, 1997). However, those models are not used over the complete pressure range of the isotherm and are restricted to a confined range of relative pressures or pore sizes. Density functional theory (DFT) is a molecular-based statistical thermodynamic theory that relates the adsorption isotherm to the microscopic properties of the system. The parameters of this model are the fluid-fluid and fluid-solid interaction energy parameters, the pore size, the pore geometry, and the temperature.

Therefore, it has a significant advantage that it applies over the complete range of the isotherm and is not restricted to a confined range of relative pressures or pore sizes.

2.3.1.3 Specific surface area

Specific surface area is a property of solids that indicates the total surface area per unit of mass (or bulk volume). The total surface area includes the area of the micropores, mesopores, and macropores. In general, the larger the surface area, the more adsorbate can be adsorbed, and the higher the adsorption capacity.

2.3.1.4 Surface chemistry

The surface chemistry has a significant effect on the adsorption capacity. Zeolite has fixed pore structure after manufacture, but its surface chemistry can be changed by ions exchange. As for activated carbon, the heteroatoms, especially oxygen followed by hydrogen, are responsible for the surface chemistry. These heteroatoms usually combined with each other to form different functional groups, such as phenols (-OH) and carboxyls (-COOH), which can greatly influence the chemical properties of activated carbon. These functional groups can be broadly divided into two groups, acidic and basic groups, which may be beneficial to adsorb basic or acidic adsorbate (Bandosz, 2006). These functional groups can be modified after the preparation of the activated carbon. For instance, the quantity of oxygen on activated carbon can be increased by oxidization by exposing the carbon to an oxidizing environment at a high temperature or immersing it in nitric or sulfuric acid.

2.3.2 Adsorption isotherms

The physical adsorption of gases onto solids increases with decreasing temperature and with increasing pressure. Adsorption isotherms give a measure of the amount of adsorbate (typically the standard volume V_a or molar quantity n) as a function of the partial pressure P/P0 of the adsorbate at a given temperature. Isotherms are classified by one of six forms as shown in Figure 2-5.

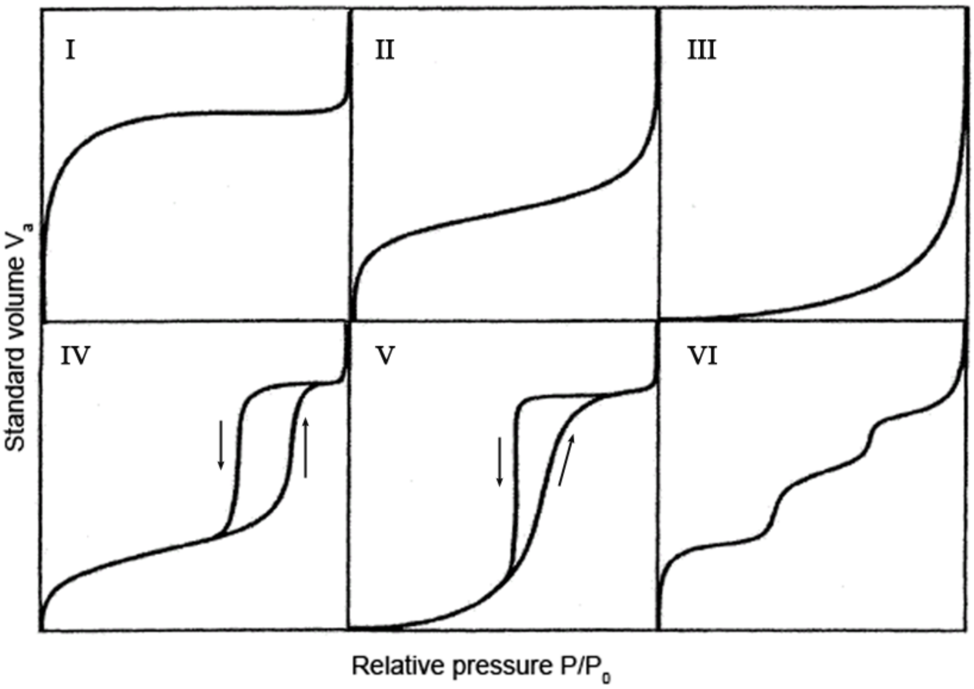


Figure 2-5 Six basic adsorption isotherm types (The up arrow means adsorption, the down arrow means desorption) (with copyright permission) (Webb and Orr, 1997)

Type I is commonly observed in microporous materials. Type II and IV indicates that material is either nonporous or having large pores. Type III and V shows that there are only weak gas-adsorbent interactions. Type VI, stepwise adsorption demonstrates the multiple layers of gas molecules on the extremely smooth surface of nonporous material (Webb and Orr, 1997).

2.3.2.1 Langmuir theory

Langmuir developed an adsorption theory to explain how gas molecules are adsorbed. In his model, a monolayer of gas molecules are adsorbed onto the surface of solid based on assumptions of independent adsorption and equal adsorption sites (Langmuir, 1918). His model is expressed as:

$$V_a = \frac{V_m bP}{1+bP} \quad \text{(5)}$$

Here, V_a is the quantity of gas adsorbed at pressure P, V_m is the quantity of gas adsorbed when the entire surface is covered with a monomolecular layer, and b is an empirical constant (Webb and Orr, 1997). The main limitation of this theory is that it does not take into account multilayer adsorption.

2.3.2.2 Brunauer, Emmett and Teller (BET) theory

This model, developed by Brunauer, Emmett and Teller, assumes that multilayer gas molecules can be adsorbed on the solid (Brunauer et al., 1938). The forces active in the condensation of gases also are responsible for the binding energy in multimolecular adsorption. The specific surface area can be obtained by determining the amount of gas adsorbed at certain pressures (Webb and Orr, 1997). Generally, BET surface area is measured at 77K, liquid nitrogen boiling point. It is assumed that one nitrogen molecule cover 0.162 nm^2. The BET equation can be stated as:

$$\frac{P}{V_a(P_0-P)}=\frac{1}{V_mC}+\frac{C-1}{V_mC}\left(\frac{P}{P_0}\right) \quad \text{...(6)}$$

Here, C is the BET constant, P_0 is the saturation pressure of the gas, and the other parameters are the same as the one in Langmuir equation.

2.4 Activated Carbon

2.4.1 General properties of activated carbon

In general, the most common adsorbent for air and water treatment is activated carbon, a high carbon, high porosity, and high surface area material with high adsorption capacity. Activated carbon is widely used because of its large porous surface area, controllable pore structure, thermal stability, low acid/base reactivity and low cost. As for environmental applications, activated carbon has been commonly used in pollution control applications, such as potable water and waste water treatment, decolorization, gas separation, and odor control. In addition, it is also used in the recovery of precious metals from leach liquors in the metallurgical industry. In the chemical industry, it is used as a support for catalyst for various chemical processes (Jüntgen, 1986; Maruyama and Abe, 2003).

The type of application of activated carbon depends on its physical and chemical properties including pore structure, surface area, ash content and surface chemistry. Pores in the activated carbon have a complicated shapes (slit, cylinder, sphere and bottle-shape) with different sizes which are different than the regular pore shape and size of molecular sieves (Oshida.K et al., 1995).

Ash content refers to the mineral content in the activated carbon, which originates from the mineral content of the precursor material. Ash is mainly oxides, and some sulfates, carbonates and other compounds. The cations generally contain iron, aluminum, calcium, sodium, potassium, magnesium, transition metals and some other ions. Mineral matter can have either positive effect or negative effect during the activation as it can reduce the rate of activation by blocking areas of the carbon from the activating gases or accelerate the activation rate by catalyzing carbon conversion reactions (Jankowska et al., 1991).

The nature of the precursor, the type of activation (chemical or physical) and the processing conditions are the main three factors to influence the adsorptive properties of activated carbon.

In industry, the adsorption capacity can be indicated by iodine number or methylene blue number, which indicates how much iodine or methylene blue in milligrams, can be adsorbed by unit gram of adsorbent. Iodine number generally indicates the adsorption performance of activated carbon for low-molar-mass species, like solvent and gaseous pollutants. On the other hand, the amount of methylene blue adsorbed is often regarded as a measure of its performance for high-molar-mass species, such as dye and aqueous-phase pollutants, since the size of methylene blue is larger than iodine (Li, Zhang et al. 2008). In addition, the BET surface area and the pore size distribution are important parameters for activated carbon characterization.

2.4.2 Preparation of activated carbon

Activated carbon is produced from any carbonaceous material, and can be manufactured as granular activated carbon (GAC) or powder activated carbon (PAC). GAC is produced from crushed material, granular raw material, or pellets formed from fine raw material and a binder, whereas PAC is obtained from crushed or ground carbon particles. The particle size of PAC is typically less than 100 μm; while the particle size of GAC is typically around 1 to 5mm. Typically PAC is widely used for water treatment, while GAC is used for adsorption from gas phase. These distinctions have become blurred in recent years. Thereby, either PAC or GAC can be used for both gas and liquid phase applications (Bandosz, 2006).

The activated carbon manufacturing process generally involves two steps: carbonization and activation. Carbonization process proceeds at 500-800^{o}C (usually at 600°C). It can help the raw material acquire mechanical strength, increase the carbon content and develop the initial porous structure by evolution of volatile matter (Jankowska et al., 1991). This step is critical if raw materials have a high content of volatile matter. The activation step develops the physical and chemical properties of the final products via the reaction of carbon and activation agent. The activation methods are typically classified as physical activation or chemical activation. The goal of the activation step is to enhance the pore volume by enlarging the existed pore diameter and creating new pores. 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. At high temperature, the transport rate of the activation agent into the particle may be the limiting factor for the activation because the reaction of carbon with the activation agent is rapid. Therefore, the temperature and the properties of activation agent are the most important factors influencing the properties of the final product (Bandosz, 2006).

Irrespective of the activation type, the yield is a very important parameter to assess the preparation of activated carbon. The yield is defined as the ratio of the mass of the activated carbon to the initial mass of the precursor carbonaceous material before carbonization. The more carbon burns off, the higher porosity and lower yield will be.

2.4.2.1 Physical activation

The activation agent in physical activation can be steam, carbon dioxide, air or any mixture of these gases. Oxygen is the most reactive agent, but it is not typically applied because the reaction is very difficult to control. At temperatures between 800°C and 1000°C, carbon atoms at the surface of the precursor and in the incipient microspores react with gases and are removed as carbon monoxide or carbon dioxide. At the same time, the solid enlarges the existing microspores and develops new microspores resulting in a microporous material (Bandosz, 2006)

Steam activation is the most widely used method to produce activated carbons. Steam reaction is conducted at 750-950°C. It can be catalyzed by alkali metals, iron, copper, oxides and carbonates. Carbon dioxide, which is a by-product of steam activation, is another agent for physical activation. However, the reaction rate of carbon with carbon dioxide is 30% lower than that with water vapor, at a given temperature (Jankowska et al., 1991). The main reactions during steam activation are as follows.

$$C + H_2O \leftrightarrow CO + H_2 \quad (7)$$

$$C + 2H_2O \leftrightarrow CO_2 + 2H_2 \quad (8)$$

$$C + CO_2 \leftrightarrow 2CO \quad (9)$$

$$C + 2H_2 \leftrightarrow CH_4 \quad (10)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (11)$$

2.4.2.2 Chemical activation

There are various chemical activation agents which can react with the carbonaceous precursor to produce different porosity in the final carbon product. The chemical activation agents usually used in industry are $ZnCl_2$, H_3PO_4 and KOH. The precursor is impregnated with the chemical activation agent in the form of concentrated solution. Then the mixture is heated to appropriate temperature, typically 400-800^{o}C, for chemical activation. The product is cooled and washed to remove the remaining agent, which can be recycled and reused. The recycle of chemical agent is so important that it determines the economic feasibility of chemical activation (Bandosz, 2006). The main reactions during KOH activation are as follows (Otowa et al., 1993).

$$2KOH \rightarrow K_2O + H_2O \quad (12)$$

$$C + H_2O \rightarrow CO + H_2 \quad (13)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (14)$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \quad (15)$$

$$K_2O + H_2 \rightarrow 2K + H_2O \quad (16)$$

$$K_2O + CO \rightarrow 2K + CO_2 \quad (17)$$

2.5 Microwave Application in Adsorbent Regeneration and Preparation of Activated Carbon

2.5.1 Adsorbent regeneration

Adsorbent regeneration is used to restore the adsorptive capacity of the used adsorbent. Generally, the regeneration methods are based on either desorption or decomposition of the adsorbate. The former can be achieved by increasing the temperature, reducing the pressure, or displacing the adsorbate, while the latter can be achieved by thermal, chemical or microbiological processes. The widely used regeneration method is thermal regeneration by steam or in an inert atmosphere (Ania et al., 2005; Bonjour et al., 2002; Martin and Swanton, 1997).

2.5.2 Adsorbent regeneration by microwaves

Microwave heating is a new regeneration technique compared to the conventional techniques used in the industry to regenerate adsorbents. Since microwave energy is volumetric and internal to the heated object, energy consumption can be greatly reduced during microwave heating. Microwave heating is also selective due to the difference in microwave absorption among materials, depending on their dielectric properties (Meredith, 1998; Metaxas and Meredith, 1983). In general, non-polar materials have low dielectric loss factor and weakly absorb microwaves while polar materials have high dielectric loss factor and strongly absorb microwaves. The difference in microwave absorption between the adsorbent and the adsorbed compound (i.e. the organic vapor) can allow for selective and energy efficient microwave regeneration of the adsorbent. In the case of polar adsorbate and microwave-transparent adsorbent, the microwave energy will be mainly absorbed by the adsorbate while minimal energy will be transferred to the adsorbent. Microwave regeneration has become a promising technology for its ability to achieve both higher energy efficiency and lower regeneration cost.

Recently, many researchers have studied microwave regeneration of individual adsorbents such as granular activated carbon(Cha and Carlisle, 2001; Coss and Cha, 2000), activated carbon fibre cloth (Hashisho et al., 2007; Hashisho et al., 2005), zeolite (Polaert et al., 2008) and silica gel (Reuss et al., 2002). However, there are no studies that have compared the thermal behaviour of these adsorbents.

2.5.3 Preparation of activated carbon using microwave heating

Recently, limited studies have tested the use of microwave heating for the preparation of activated carbon. Li et al (2008) investigated the preparation of activated carbons from carbonized tobacco stems using microwave heating and K_2CO_3 as activation agent. The iodine number was 1834 mg/g for activated carbon prepared with 30 minutes of microwave heating at a power of 700W and K_2CO_3/C ratio of 1.5:1. The BET surface area of the prepared activated carbon was 2557m^2/g. However, the yield was only 16.65%, which is very low (Li et al., 2008).

Activated carbons were also prepared via KOH activation process by microwave heating and by conventional heating (Ji et al., 2007). The precursor was mesocoarbon microbead (MCMB) which is a residual after heat treatment of commercial coal-tar pitch. The surface area and pore volume increased to a maximum with increasing KOH/MCMB ratio and then decreased for both methods. For the same KOH/MCMB ratio, higher surface area and larger total pore volume can be achieved by microwave heating than by conventional heating. In addition, the microwave activation method considerably shortened the activation time from 3 hours to less than half an hour (Ji et al., 2007).

Microwave-induced CO_2 reaction was used for the preparation of activated carbons from oil-palm-stone chars (Guo and Lua, 2000). The results showed that the important process parameters are CO_2 gas flow rate, input microwave power and microwave heating time. CuO receptors were added to increase the surface temperature and reduce the processing time. However, these receptors also caused heterogeneous pore structures (Guo and Lua, 2000). Microwave heating was also used to modify the activated carbon surface and resulted in a significant increase in the pH of carbon in a short time (Menendez et al., 1999; Nabais et al., 2004). These studies illustrated that the microwave heating is an efficient way to prepare or modify activated carbon.

2.6 Activated Carbon from Petroleum Coke

2.6.1 Oil sands coke in Alberta

Alberta contains the second largest proven reserve of oil in the world, the vast majority of which is found in oil sands deposits. Alberta's oil sands have 173 billion barrels of proven recoverable reserves. Oil sands are naturally occurring mixtures of sand or clay, water and a thick, heavy substance called bitumen (Oilsands, 2009). The extraction of oil sands is to separate bitumen from oil sands. Because bitumen is so viscous it has to be treated before it can be used by refineries to produce usable fuels in a process called upgrading. Upgrading of bitumen can be categorized into primary and secondary upgrading. Primary upgrading involves removing carbon from bitumen or adding hydrogen to bitumen or a combination of both. Secondary upgrading involves hydroprocessing the products from primary upgrading to make a high quality, fungible and saleable product (Ashar, 2008).

During primary upgrading of bitumen, huge amounts of a byproduct, oil sands coke or petroleum coke, are produced. Suncor Energy burns part of its coke to generate power; however, the majority of the coke is presently of limited use and is stockpiled on site. In Alberta, 54 million tonnes were stockpiled in 2007 and the number is increasing rapidly. Figure 2-6 shows the prediction of petroleum coke stockpile in Alberta for the next decade. It is expected that the stockpile of petroleum coke will be doubled in 2015 in comparison to 2007, which means a method to effectively dispose or utilize petroleum coke is needed urgently (Isaacs, 2007).

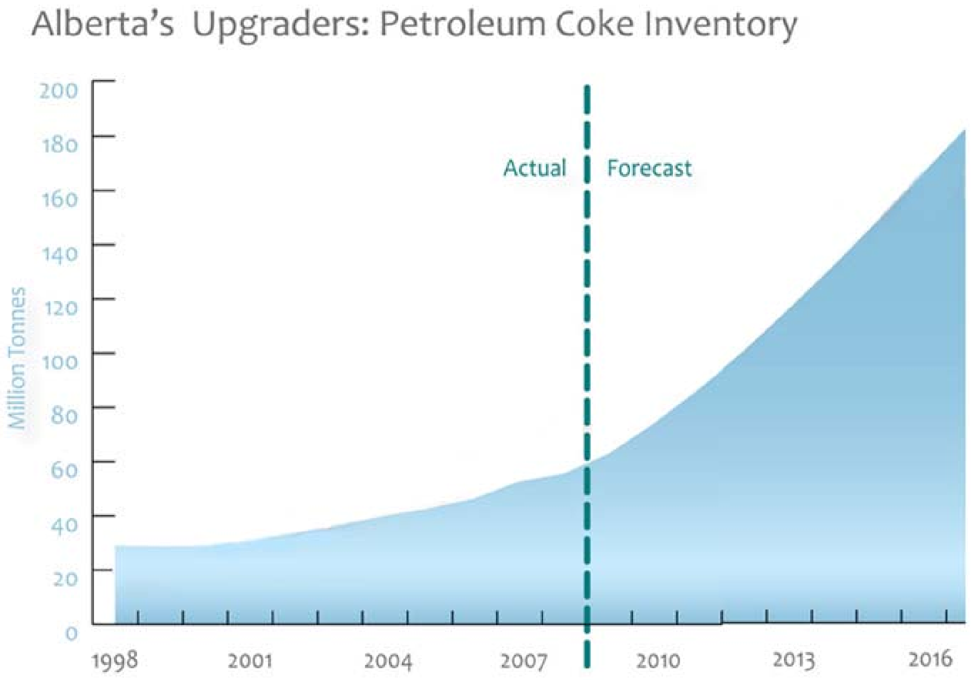


Figure 2-6 Petroleum coke inventory in Alberta (with copyright permission) (GreatPoint-Energy, 2008)

2.6.2 Types of petroleum coke

There are three types of petroleum coke which are produced by different processes and have different physical and chemical properties: delayed coke, fluid coke and flexicoke. Delayed coking and fluid coking will be described in the following sections. Flexicoking process is rarely applied. It is similar to fluid coking, but it also includes a gasification loop, which can greatly improve the yield of liquid phase product (Fernando, 2001).

Delayed coking is the most widely used process for heavy oil upgrading. For example, Suncor Energy and Petro-Canada use this technology. Bitumen is upgraded in a coking drum under suitable conditions of pressure and temperature. After distillation of the volatile materials and sufficient cooling, the delayed coke is cut by high-pressure hydraulic drill into small chunks and emptied out through the bottom of the drum. It still needs to be broken up or grounded for proper utilization. Delayed coke is relatively soft compared to fluid coke (Ashar, 2008; Scott and Fedorak, 2004).

Fluid coking occurs in a fluidized bed reactor operating at a slightly higher temperature than delayed coking. A thin film of bitumen is sprayed onto a fluidized bed with hot coke particles. The coke particles are coated with a layer of coke when the volatile part is driven off to be upgraded into synthetic crude oil. This process burns some of the petroleum coke produced for heat, but it has slightly better liquid yields. Fluid cokes are solid, spherical particles. The size of particles ranges from micrometer to centimeter and is mostly around 100 micrometers. The fluid coke particles are very abrasive and can have a Hardgrove Grindability Index (HGI) as low as 17 (Fernando, 2001).

The processing temperature is about 415-450^{o}C for delayed coke and about 480-565^{o}C for fluid coking. Because coke has experienced thermal treatment, the volatile proportion is lower in comparison with typical coal, which is about 25% to 30% (Fernando, 2001). The higher operating temperatures for fluid coke yields a lower volatiles content in comparison with delayed coke. The fluid cokes generally contain 4-6% volatiles, while delayed cokes typically have 7-13% volatiles (Anthony, 1995; Fedorak and Coy, 2006).

2.6.3 Applications of petroleum coke

How to utilize the petroleum coke is an urgent issue to be solved in Alberta. The physical and chemical properties of petroleum coke determine its use. In general, petroleum coke is mainly used as an energy source for power generation, cement production and the iron and steel industry. Electrode manufacturing can use coke with low electrical resistivity and coefficient of thermal expansion. However, petroleum coke from bitumen upgrading seems not suitable for these applications. The low volatiles content makes the petroleum coke have poor ignition and burnout characteristics. The high level of sulfur and heavy metals raise considerable concerns regarding environmental emissions from the combustion process (Fernando, 2001). Although Suncor Energy burns a fraction of produced coke for power generation there are still millions of tonnes of petroleum coke stockpiled in Alberta at present. Gasification is a possible way to utilize petroleum coke and some studies focused on it. However, because of its high carbon content and its low cost, petroleum coke is a promising precursor for activated carbon. The market price of petroleum coke fluctuates with the crude oil, but it is still very low compared to other precursor materials such as coal. In addition, the sulfur in the coke can be beneficial for certain applications, such as adsorption of mercury from flue gas (Krishnan et al., 1994).

2.6.4 Petroleum coke-based activated carbon

The raw material of activated carbon can be any carbon containing material. Generally, wood, coal and coconut shell are the most common raw materials. Since petroleum coke has higher carbon content than coal, some studies have been done to prepare activated carbon by traditional heating methods using petroleum coke as precursor. Chemical activation of coke can result in larger surface area. Otowa et al. (1993) used KOH as activating agent to obtain an activated petroleum coke with an area of 3100 m^2/g. In their study, two steps were applied in the activation: the first step was to heat the mixed material up to 400-500°C for dehydrating purpose. Then the product was activated at 800 to 900°C in a furnace in a nitrogen atmosphere. Finally the excess KOH and salts were removed via washing. The KOH/coke ratio varied from 1 to 10 and the maximum BET surface area was obtained when the ratio is above 4. The pore size also increased with the KOH/coke ratio, and the largest total pore volume was obtained when the ratio was 10 (Otowa et al., 1993).

Lee at al. (2000) used petroleum coke with 7 wt% sulfur content as starting material to study the effects of NaOH and KOH on the development of surface area. The activation temperature was 400 to 600°C and the activating agent/coke ratio varied from 2 to 4. The results showed that KOH was more effective for the development of surface area (up to 1980 m^2/g) than NaOH (1350 m^2/g). The authors claimed that desulfurisation plays a role in the development of surface area since the breakage of C-S bonds followed by the evolution of sulfur from carbon matrix leads to the formation of pores and sites where activation can occur (Lee and Choi, 2000).

Surface areas between 1000-1750 m^2/g were obtained during activation of two petroleum cokes with KOH as the activating agent (Wu et al., 2005). KOH/carbon ratio was 2, and the activation temperature was 800°C. Activated carbon with a surface area less than 1000 m^2/g was obtained by physical activation, while a surface area as high as 3000 m^2/g was obtained with the co-activation (KOH/water vapor) method. The co-activation method provided higher surface area but a much lower yield (29%) compared to physical activation (31%) and chemical activation (63%). The authors compared two different petroleum cokes and claimed that the presence of transitional metals in the coke matrix may play a role in the development of surface area, since the transitional metals act as catalysts for the reaction between carbon and activation agents (Wu et al., 2005).

Activated carbon with very low surface areas was obtained when NaOH, H_3PO_4 and $ZnCl_2$ were used as activating agents (Zamora et al., 2000). The starting material was petroleum coke with 6 wt% sulfur. The activating agent/carbon ratio was 1 and the activation temperature was 700°C. The surface areas and the iodine number of the obtained activated carbon were 16.3 to 35.4 m^2/g and 42 to 73 mg/g, respectively. However the experiments showed high methylene blue number (146 to 203 mg/g) and high yield (above 80%), which made it valuable for wastewater treatment (Zamora et al., 2000).

Palfino et al. (1995) had studied the production of activated carbon from oil sands coke by a two-step pyrolysis and activation process. The activation agent was steam and the activation temperature was 850°C by traditional heating at atmospheric pressure. The adsorption capacity of the activated coke was significantly higher than that of the raw coke. BET surface area of 318 m^2/g was obtained for untreated coke activated for 6 hours. The addition of potassium hydroxide catalyst during activation increased activation rates but did not result in a higher surface area for the potassium-treated activated coke. Surface area generally increased with activation time, but the yield of activated coke significantly decreased with the activation time (DiPanfilo, 1995).

Activation of delayed coke has been studied by Shawwa et al. (2001) in order to remove organic pollutants from pulp mill wastewater (Shawwa et al., 2001). Both carbonization and activation processes were completed at 850^{o}C in a tube furnace. Steam was used as activation agent and activation time was varied from 1 to 6 hours. The results showed that a maximum methylene blue value of 100.5 mg/g was obtained with 4 hours activation. Activated coke adsorbed methylene blue 10 times more than raw petroleum coke. Increasing heating time to 6 hours reduced the surface area and methylene blue number (Shawwa et al., 2001).

Bratu et al. (2008) had studied the activation of fluid coke to remove mercury from gas streams. A mixture of steam and CO_2 was used as activation agents at temperatures lower than 800^{o}C and pressure between 100 to 620 kPa. Maximum surface areas of activated coke were more than 500m^2/g. The average pore diameter for the activated coke was about 2 nm. The existence of sulfur increased the adsorption capacity for mercury (Bratu, 2008).

Table 2-1 presents a summary of petroleum coke activation studies. The properties of activated coke from petroleum coke can vary depending on the precursor material, the activation process, But these activations still need long activation time (hours). Therefore, a faster activation process is needed in order to activate coke in a faster and more cost effective way.

Table 2-1 Summary of activations of petroleum coke in literatures

Activation agent	Temperature and time of activation	Surface area	Reference
KOH, ratio is from 1 to 10	800-900°C, <2h	$3100m^2/g$	(Otowa et al., 1993)
KOH or NaOH, ratio is from 2 to 4	400-600°C, ≤1h	$1980m^2/g$ for KOH, $1350m^2/g$ for NaOH	(Lee and Choi, 2000)
KOH, ratio = 2	800°C, ≤1h	$1750m^2/g$	(Wu et al., 2005)
KOH and steam		$3000m^2/g$	
Steam		$<1000m^2/g$	
NaOH, H_3PO_4 or $ZnCl_2$, ratio = 1	700°C, 2h	16.3 to 35.4 m^2/g	(Zamora et al., 2000)
Steam	850°C, 6h	$318m^2/g$	(DiPanfilo, 1995)
Steam	850°C, 4h	NA*	(Shawwa et al., 2001)
Steam and CO_2	≤800°C, 8h	$>500m^2/g$	(Bratu, 2008)

* surface area measurement was not reported; however, A Methylene blue number of 100.5mg/g is reported

3 MICROWAVE HEATING OF DRY AND SOLVENT SATURATED ADSORBENTS

3.1 Introduction

More than 1.9 million tonnes of volatile organic compounds (VOCs) were emitted to the atmosphere in Canada in 2007 from anthropogenic sources, with Alberta contributing 21% (0.4 million tonnes) to the total anthropogenic VOC emissions (Environment-Canada, 2009). Major sources of these emissions include the oil sand, oil and gas sectors as well as processes that use organic solvents, such as surface coatings. The oil sand, oil and gas sectors contributed 65% of total VOC emissions and 93% of industrial VOC emissions in Alberta in 2007 (Environment-Canada, 2009). VOCs are precursors to ground-level ozone and many VOCs are carcinogenic and/or neurotoxic. Therefore, technologies need to be developed to efficiently control these emissions at a suitable cost. Technologies should also foster sustainable development by promoting recycling and reusing whenever feasible.

Methods for removing VOCs from gas streams include absorption, adsorption, condensation, incineration, and biofiltration. Adsorption with regeneration is an efficient and cost-effective method for treating moderate to low VOC concentration streams, for it allows reuse of the adsorbent and recovery of the desorbed VOC for recycle and reuse. Adsorbents are typically regenerated with vacuum, steam, or hot inert gas. A drawback of conventional technologies for the regeneration of adsorbents is the large energy consumption (Bonjour et al., 2002; Martin and Swanton, 1997; Sullivan et al., 2004). The key to reducing the cost and energy consumption for the adsorption-based control of VOCs is to improve the energy efficiency of the regeneration cycle.

Unlike convective heating with steam, microwave heating is volumetric and internal to the heated object. Microwave heating is also selective due to the difference of microwave absorption ability among materials (Meredith, 1998; Metaxas and Meredith, 1983). The difference in microwave absorption between the adsorbent and the adsorbed compound (i.e. VOC) can allow for selective and energy efficient microwave regeneration. For instance, a microwave transparent adsorbent can be rapidly heated by microwaves when it is saturated with a polar VOC; however, as the VOC is desorbed from the adsorbent, less microwave energy is absorbed by that adsorbent. After the VOC is completely desorbed, the adsorbent will be minimally heated by microwaves.

This chapter investigates the thermal behaviour of select adsorbents with different adsorbates during microwave heating. These adsorbents and adsorbates were selected to cover a wide range of microwave absorption and polarity.

3.2 Experiments

3.2.1 Sample Preparation

Four types of virgin (unmodified) adsorbents and two modified adsorbents were examined in this study. The virgin adsorbents consisted of granular activated carbon (GAC), zeolite 4A (“zeolite” for short in the following text), Engelhard titanosilicate structure 10 (ETS-10), and silica gel. The modified adsorbents consisted of silver-exchanged ETS10 and oxidized granular activated carbon.

ETS10 is a mixed coordination titanosilicate molecular sieve, synthesized as reported by Kuznicki (Kuznicki, 1991). The cation of ETS10, sodium, can be exchanged with silver (Ag) by refluxing in excess aqueous $AgNO_3$ to form Ag-ETS10 (Kuznicki et al., 2007). Ag-ETS10 was thoroughly washed with deionized water and dried at 80^oC before further treatment. Elemental analysis indicated that the material was completely exchanged with silver, and contained slightly in excess of 30% by weight silver (Kuznicki et al., 2007). Both ETS10 and Ag-ETS10 were mixed with colloidal silica (Ludox Hs-40) and made into pellets of the same size with zeolite and silica gel by pressing, grounding and sieving between 10 and 20 mesh sieves (2.00 mm and 0.85 mm).

The oxidized GAC (OGAC) sample was obtained by treating a virgin GAC (VGAC) sample (25 g) with 50 ml of 1:1(V:V) concentrated HNO_3 and H_2SO_4 solution for 8 hours (Dimotakis et al., 1995). Next the OGAC was washed with distilled water until water became neutral and then was dried in an oven at 150°C for two days.

3.2.2 Schematic of experimental setup

3.2.2.1 Microwave heating of dry adsorbents

All adsorbent samples were put into an electric oven at 180°C for one full day in order to completely degas any adsorbed impurities. A temperature higher than 180°C was avoided since it may cause structure breakdown of some adsorbents, such as silica gel and ETS10. An adsorbent sample of 20 g was placed in a 50 ml glass beaker and placed in a microwave oven (Quarter microwave oven, 850W) and heated for a specified period to reach a temperature of 180°C, as shown in Figure 3-1.

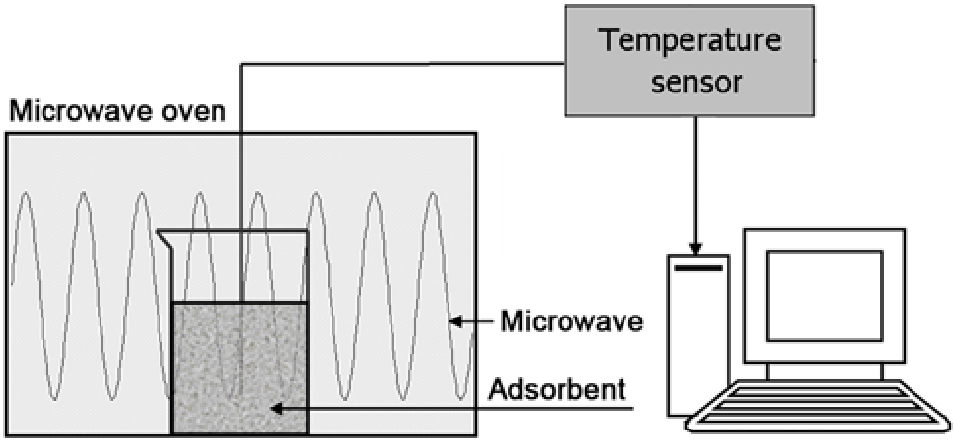


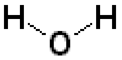
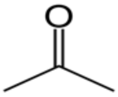
Figure 3-1 Schematic diagram of experimental setup

Since the power output of a commercial microwave oven is determined by controlling the duty cycle of the magnetron, the microwave oven was run at “high power” level to ensure that the magnetron working time was the same as the heating time. A fiberoptic temperature sensor (Neoptix Reflex) was used since it can measure temperature without being affected by microwaves. The temperature of the adsorbent was automatically recorded at a 0.2 second acquisition rate.

3.2.2.2 Microwave heating of saturated adsorbents

Water, acetone, and n-heptane were tested as the solvents in this study. These solvents cover a wide range of dielectric properties as well as other physical and chemical properties, as depicted in Table 3-1.

Table 3-1 Properties of the selected solvents

Property	water	acetone	n-heptane
Chemical structure			
Molecular weight	18.0	58.1	100.2
Liquid density (g/cm^3)	1.00 at 4°C	0.784 at 25°C	0.679 at 25°C
Boiling point (°C)	100	56	98
Vapor pressure (kPa)	2.33 at 20°C	30.8 at 25°C	6.093 at 25°C
Specific heat capacity (kJ/kg·K at 20°C)	4.18	2.15	2.24
Latent heat of vaporization (kJ/kg)	2257	518	318
Thermal conductivity (W/m·K at 25°C)	0.606	0.123	0.161
Effective dielectric loss	12.04 (at 25°C, 3×10^9Hz) [a]	0.96 (at 20°C, static value) [b]	1.97×10^{-4} (at 25°C, 3×10^9Hz)[a]
Dipole moment (D)	1.84 [b]	2.9 [c]	0.0 [c]

Note: [a] Value is from (Hippel, 1954); [b] Value is from (Gabriel et al., 1998); [c] Value is from (Reid et al., 1977)

All dry samples were put in a sealed enclosure which contained one of these three solvents, where they remained for five days to obtain the saturated samples. After adsorption, the temperature profiles of saturated samples were also measured with the same microwave heating time as the dry adsorbent. Since the maximum temperature of the fiber optic probe is 250°C, the microwave oven was shut down when the temperature was close to 250°C even if the heating time was shorter.

3.3 Results and Discussion

3.3.1 Temperature profiles of dry adsorbents.

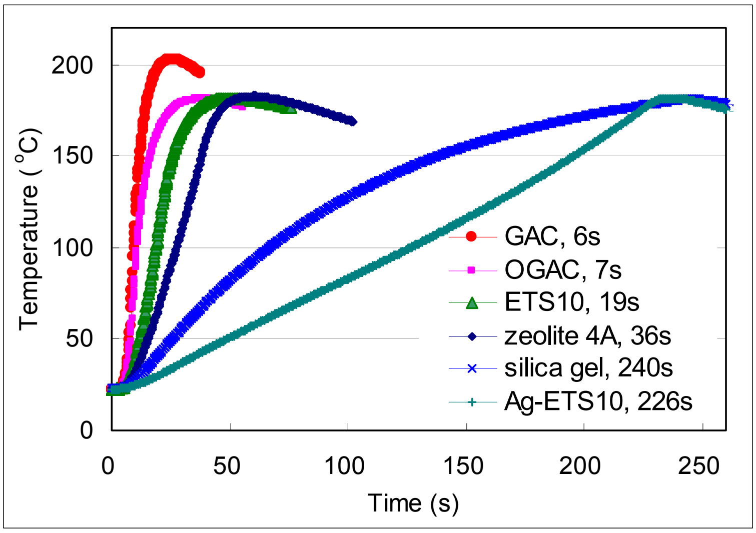


Figure 3-2 Temperature profiles of dry samples during microwave heating (Time in the legend indicates the microwave heating time)

Figure 3-2 shows the temperature profiles of dry samples during microwave heating. Microwave heating time of each sample to reach 180°C is indicated in the legend. Since the direction of heat flux during microwave heating is from inside to outside of the heated object, the temperatures at the surface and inside of the adsorbent particle are different. Therefore some time is needed, depending on the thermal conductivity of the adsorbent, before the heat is conducted to the surface of the adsorbent particle where temperature is measured. In addition, the slow response time of the temperature sensor would further delay measuring the change in temperature. Therefore a delay of few seconds appears in the measured temperature at the start and end of microwave heating.

Activated carbon is a strong microwave-absorbing material. This is a characteristic of carbonaceous material due to the semiconducting properties of carbon. Both VGAC and OGAC needed a shorter microwave heating time to reach 180°C and depicted a high heating rate. The peak heating rate of GAC was 28°C/sec (Figure 3-3). Acid treatment reduced the peak microwave heating rate to 19°C/sec. The reduction in microwave heating after acid treatment of activated carbon has been attributed to the impact of the oxygen functional groups that limit the mobility of the charge carriers, hence reducing the contribution of conduction losses to microwave heating (Hashisho et al., 2009).

The other four samples rank from highness to lowness by the capacity to absorb microwaves: ETS10, zeolite, silica gel and Ag-ETS10. The peak heating rate of virgin ETS10 is 10°C/sec, which is more than 10 times higher that Ag-ETS10. The fact that Ag-ETS10 has a lower heating rate in comparison with virgin ETS10 demonstrates that the silver can significantly affect the dielectric properties of materials. A possible reason for this is that the silver cations become metallic silver at high temperatures and change the dielectric properties of the sample. The heating rate of silica gel decreased with the increase of temperature. Such behavior indicates a reduction in the dielectric loss with the rising temperature. This is why silica gel needed more time than Ag-ETS10 to reach 180°C.

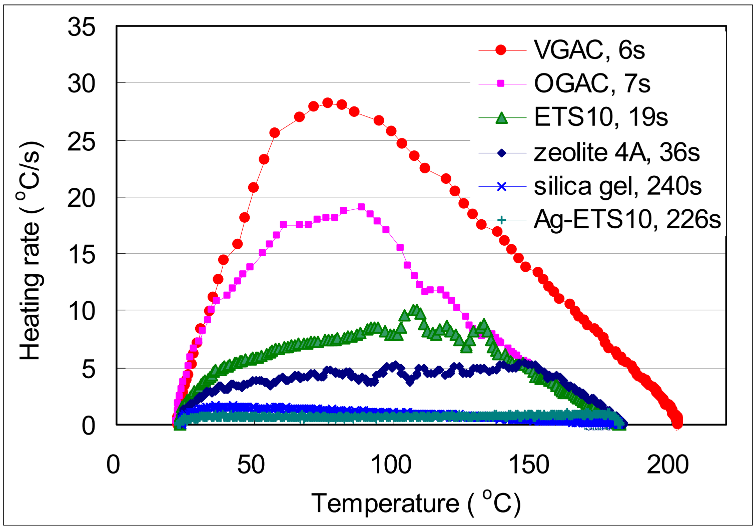


Figure 3-3 Heating rate of dry adsorbents during microwave heating

3.3.2 *Temperature profile of solvent-saturated adsorbents*

The temperature profiles of each adsorbent sample were measured when the adsorbent was saturated with different adsorbates. To allow better comparison of the thermal behavior of dry and saturated adsorbents, the microwave heating time for each saturated adsorbent sample was the same as the heating time for the dry one.

For VGAC and OGAC, the heating rates of the dry samples are much higher than those of the saturated samples (Figure 3-4 and Figure 3-5). This reflects the fact that the carbon has very high dielectric loss factor, therefore it can be heated very fast when saturated with either strong or weak microwave-absorbing adsorbates. Because activated carbon has lower specific heat capacity (typically less than 1 kJ/kg·K) than the tested adsorbates (Wang et al., 2003), the same energy that is sufficient to raise the temperature of the dry activated carbon to 180°C can only raise the temperature of saturated activated carbon to approximately 80°C or less.

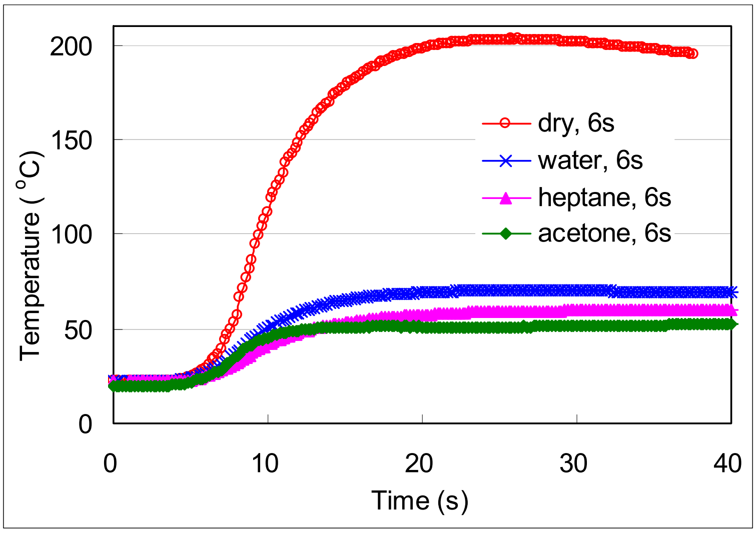


Figure 3-4 Temperature profiles of dry and saturated VGAC during microwave heating

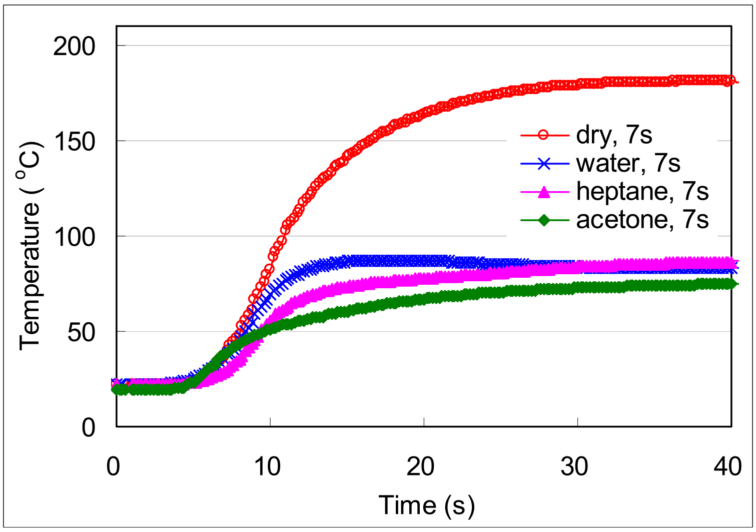


Figure 3-5 Temperature profiles of dry and saturated OGAC during microwave heating

Figure 3-6 depicts the temperature profiles of zeolite when dry and when saturated with water, heptane and acetone. Below 100°C, the water-saturated zeolite depicts the highest heating rate (8.3°C/sec). This is because water has the highest polarity and highest dielectric loss factor among the tested adsorbates. Then the heating rate drops at around 100°C and the temperature reaches a plateau as depicted in Figure 3-6. During this stage, the microwave energy is mainly used to overcome the heat of adsorption of water while it was desorbing from zeolite as vapor. The heat of adsorption is subject to the influence of a number of factors, such as polarizability, heat of vaporization, ionization potential, surface tension and average micropore width (Giraudet et al., 2006). Popescu et al. studied adsorption and desorption of several organic solvents on activated carbon and found that, in general, desorption enthalpies were close to or slightly larger than the evaporation enthalpies (Popescu et al., 2003). In this study, the heat of vaporization was used as an indicator for the heat of adsorption, since it was easy to be found and it was close to the heat of adsorption when the adsorbate was saturated.

The leveling of temperature during heating was only observed when heating the water-saturated zeolite, but not the acetone or n-heptane saturated zeolite. This is because the latent heat of vaporization of water is 4 to 7 times that of n-heptane and acetone. Above 100°C, the temperature profile increased again, but at a lower rate (3.9°C/sec) since most of the water was desorbed. Hence, it can be concluded that the dry zeolite is not as effective as the water-saturated zeolite in absorbing microwaves.

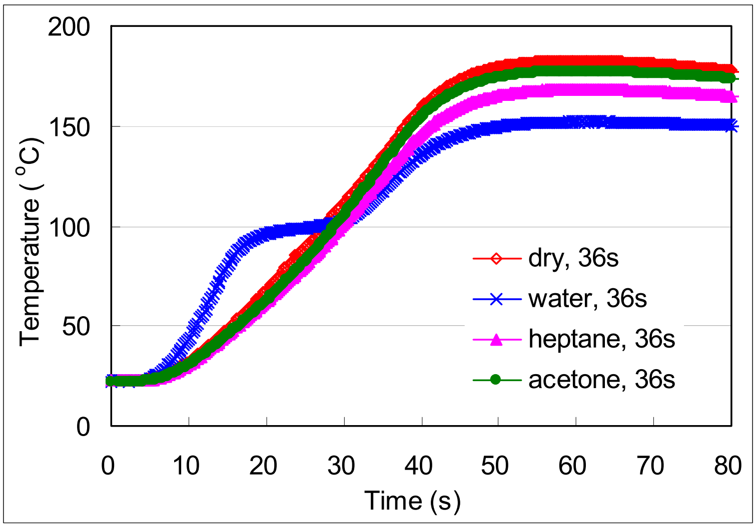


Figure 3-6 Temperature profiles of dry and saturated zeolite during microwave heating

The temperature profile of heptane-saturated zeolite is very similar to acetone-saturated zeolite (Figure 3-6) although the dielectric loss of n-heptane is five orders of magnitudes smaller than that of water and three orders smaller than that of acetone. This is possibly due to the presence of trace water in the zeolite. It could enhance the conductivity of zeolite which enhances microwave absorption by zeolite. In addition, the water itself can absorb microwaves and transfer heat to zeolite. To confirm this assumption, the zeolite sample was further dried in a convection oven at a higher temperature (300^{o}C) until the weight of the sample was stable. The mass loss of the zeolite sample after heating at 300^{o}C was about 4. A water molecule has a strong affinity to the pores in zeolite and more energy and time is needed to release it after adsorption. Figure 3-7 shows the results for microwave heating of zeolite that was saturated with heptane after drying at 180^{o}C and 300^{o}C. The peak heating rate of zeolite dried at 300^{o}C is 3.8^{o}C/sec, which is lower than that dried at 180^{o}C, 4.8^{o}C/sec. This phenomenon demonstrates that a strong polar adsorbate, even in a trace amount, can greatly enhance microwave heating of adsorbents saturated with non-polar adsorbates. This may also explain why the temperature profiles of dry, acetone-saturated and heptane-saturated zeolite display very similar behaviors in Figure 3-6. Adsorbates with low dielectric loss factor has weak effect on the temperature of an adsorbent containing adsorbate with a high dielectric loss factor (Turner et al., 2000).

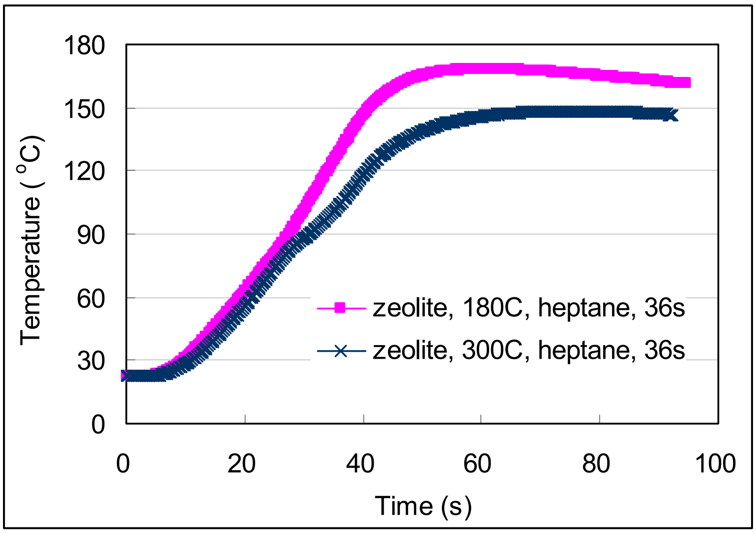


Figure 3-7 Temperature profiles of zeolite saturated with n-heptane after drying at 180°C and 300°C

ETS10 saturated with water vapor is heated at a faster rate than ETS10 saturated with n-heptane or acetone (Figure 3-8). Before the boiling point of acetone (58°C), the heating rate of acetone-saturated ETS10 was higher than that of heptane-saturated ETS10 because acetone is more polar than n-heptane. Such trend is reversed after acetone boiling point since less acetone would remain adsorbed on ETS10 compared to heptane which has higher boiling point (98 °C).

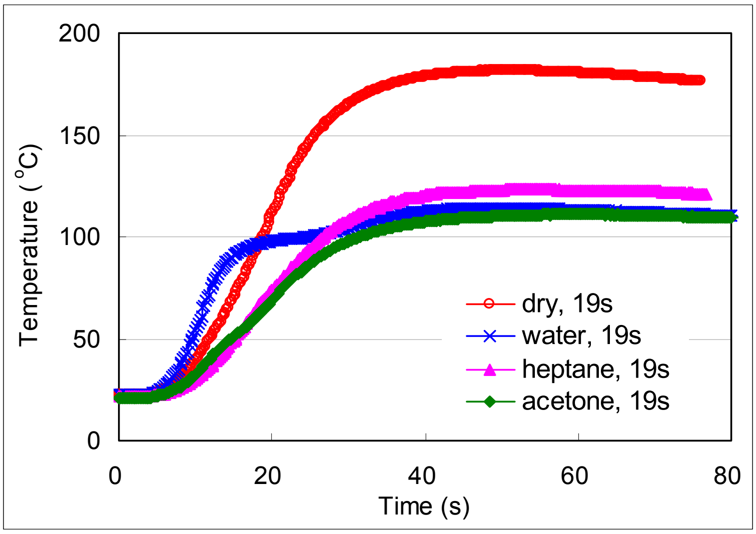


Figure 3-8 Temperature profiles of dry and saturated ETS10 during microwave heating

Dry Ag-ETS10 has the lowest heating rate compared to saturated Ag-ETS10 from Figure 3-9, which indicates that Ag-ETS10 is a weak microwave-absorbing adsorbent with a low dielectric loss factor. Therefore the dielectric property of the adsorbate has an important effect on the heating rate of the saturated Ag-ETS10. Polar adsorbates can absorb microwave energy and transfer heat to the adsorbent. The plateaus in the temperature profiles of water and acetone saturated Ag-ETS10 near the boiling point of the adsorbate are attributed to the latent heat of vaporization. Water has the largest heat of vaporization; the heating rate of the water-saturated sample before the boiling point is almost zero, whereas the heating rate of acetone-saturated sample only drops a little before the boiling point. The small difference in the heating rate of heptane and acetone saturates Ag-ETS10 could be attributed to the presence of trace water in the adsorbent as previously discussed.

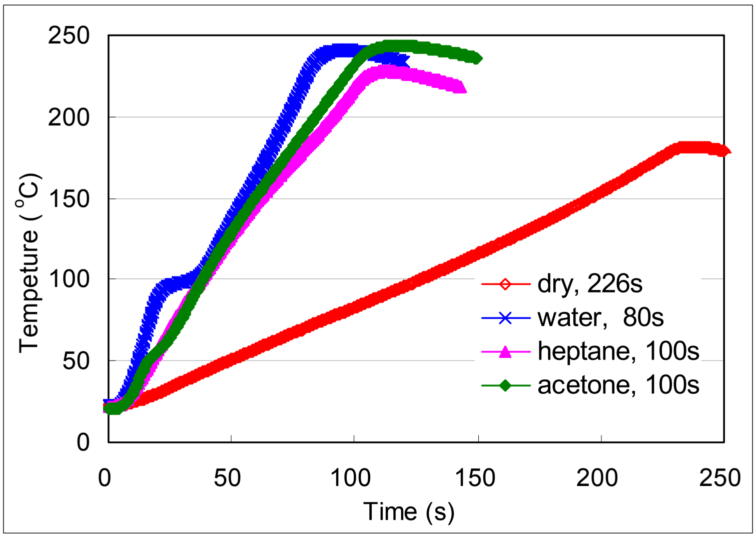


Figure 3-9 Temperature profiles of dry and saturated Ag-ETS10 during microwave heating

The thermal behavior of solvent saturated silica gel is similar to that of Ag-ETS10 (Figure 3-10). Solvent-saturated silica gel is heated at faster rate than dry silica gel (3.9 to 6.2°C/sec vs. 1.5°C/sec). The results obtained suggest that Ag-ETS10 and silica gel are the most microwave-transparent adsorbents. These adsorbents depicted clear selectivity during microwave heating of polar and non-polar adsorbates. This selectivity is demonstrated through the clear difference in the temperature profiles of the saturated and dry adsorbents. The lower heating rates of the dry silica gel and Ag-ETS10 compared to the saturated ones are encouraging as they indicate a potential for lower energy consumption and more energy efficient regeneration of these adsorbents.

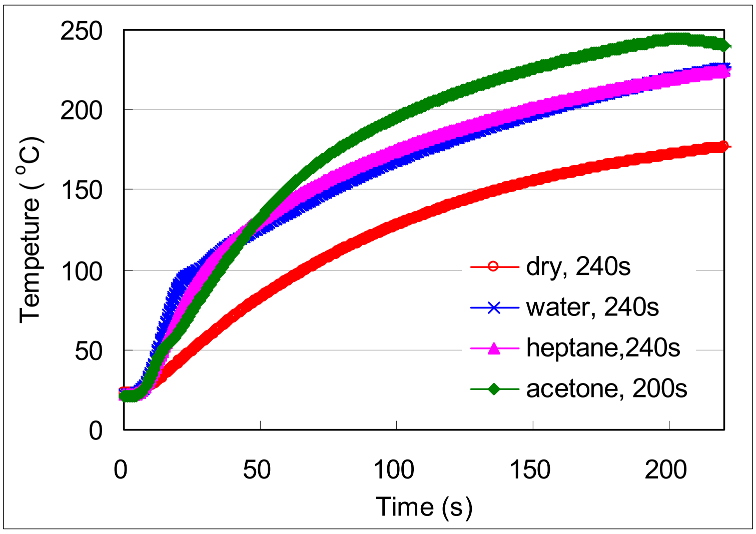


Figure 3-10 Temperature profiles of dry and saturated silica gel during microwave heating

4 PREPARATION OF ACTIVATED CARBON FROM OIL SANDS COKE USING MICROWAVE HEATING

4.1 Introduction

In Alberta Suncor Energy and Syncrude Canada are the largest oil sands companies and generate millions of tonnes of petroleum coke from bitumen upgrading. The price of coke fluctuates with the crude oil, but it is still low. The large amount and low cost of petroleum coke as well as its high carbon content make it a potential precursor for activated carbon.

The price of activated carbon makes converting oil sands coke to activated carbon very attractive. Suncor Energy's coke was sold at about $100 per tonne in 2008 (Brethor, 2008). The global price of activated carbon can vary between $500-5000/tonne depending on the location of manufacture, currency exchange and activity level (Freedonia, 2008). The retail price of activated carbon could be even higher. Besides, the global demand of activated carbon is expected to keep increasing at a rate of 5% till 2012 (Freedonia, 2007). All these factors leave large profit margin for preparing activated carbon from petroleum coke.

The energy consumption of traditional methods to prepare activated carbon is high because of the long heating time and the nature of convection-radiative heating. Hence there is a need for a more energy efficient method to prepare activated carbon. In this study, microwave heating was used as an energy source to prepare activated carbon from petroleum coke. Petroleum coke has low volatile content since it is produced at high temperature, during bitumen upgrading. Therefore, the carbonization step typically used in activated carbon preparation is not necessary in this process (Fedorak and Coy, 2006). The coke was chemically activated using KOH as activation agent. The preparation conditions, such as particle size, the KOH/Coke ratio, the microwave heating time were investigated. The properties of the produced activated carbon were characterized using Iodine number as well as BET surface area and pore size distribution.

4.2 Experiments

4.2.1 Sample preparation

The raw petroleum coke samples tested in this study were delayed coke from Suncor Energy and fluid coke from Syncrude Canada. The size of delayed coke particles covers a wide range (from micrometers to decimeters), but most of fluid coke particles is very fine (around one hundred micrometers). Therefore delayed coke was ground first and then sieved into select sizes; while fluid coke was directly sieved without grinding. Three different particle sizes were selected for activation; size I (4.76-2mm), size II (0.85-0.6mm), and size III (0.42-0.3mm).

Before activation, all samples were put in an electric oven at 110^{o}C for one day to remove humidity. KOH was dissolved in water and mixed with coke at select ratios. Then the mixture was dried in the oven at 110 °C until the weight was constant.

After activation, the activated coke was washed by dilute hydrochloric acid and de-ionized water till neutralization. Then it was dried in the oven at 110 °C until the weight was stable. The ratio of the weight of activated coke obtained after washing and drying to the weight of the dry raw coke is defined as the activation yield.

4.2.2 Microwave activation setup

The setup for the microwave activation of coke is illustrated in Figure 4-1. 25g of a dry mixture of coke and KOH is put in a glass holder and heated in the microwave activation setup. Nitrogen flowed through the glass holder at 500 cm^3/min to provide an inert atmosphere.

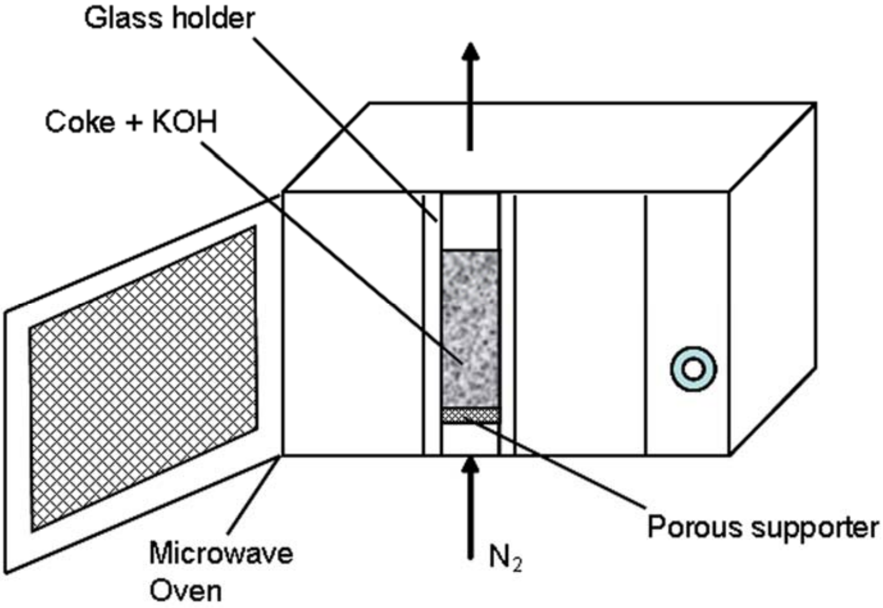


Figure 4-1 Experimental setup for microwave activation

Microwave heating was carried out in a 2.45GHz customized kitchen microwave oven with 800W nominal power output. The power output of the microwave oven was controlled by varying the duty cycle of the magnetron. The magnetron in a kitchen microwave oven has a certain operating time period. For instance, each cycle for the microwave oven used in this experiment was 22 seconds. The low power level of this oven is achieved by turning on the magnetron for 8 seconds and turning it off for 14 seconds. The relationship between power level and the magnetron operation time is illustrated in Table 4-1. In these experiments, the low level and medium level was selected for activation of petroleum coke.

Table 4-1 Power level as a function of operation time

	Magnetron operating time in each cycle (second)	
Power	Turn-on	Turn-off
High	22	0
Medium	17	5
Low	8	14

While fiberoptic temperature sensors can measure the temperature without being affected by the microwave field, their temperature measurement range (-80 to 250^{o}C) is lower than the temperature used for coke activation (400 to 800^{o}C). Therefore, preliminary experiments were conducted to estimate the temperature during microwave heating and to select the appropriate power level.

4.2.3 Sample characterization

4.2.3.1 Iodine number

The iodine number of the activated coke was determined according to American Standard Test Method D4607 (ASTM, 2006). Three different weights of activated coke were treated with a certain amount of standard iodine solution. After shaking and filtering, the filtrate was titrated by standard sodium thiosulfate in order to calculate the amount of iodine adsorbed by carbon and the residual iodine concentration. An adsorption isotherm was plotted based on the results. The amount of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine concentration of 0.02N was reported as the iodine number which was obtained from the plot. In this study, the iodine number test was completed for each sample at least twice.

4.2.3.2 Surface area and pore size distribution

Nitrogen adsorption isotherms, which are used to characterize the surface area and pore size distribution, were measured using Autosorb-1 (Quantachrome Instruments) at 77K with nitrogen as the testing gas. The adsorption isotherm covered pressure starting from very low partial pressure (10^{-5} to 10^{-4} atm) to near saturation. The adsorption step was followed by desorption during which the partial pressure was then reduced to very low values (10^{-5} to 10^{-4} atm).

The surface area of carbon was determined from the isotherm based on the multipoint BET method (Brunauer et al., 1938), which was been introduced in section 2.3.2.2. The pore size distribution was also obtained from nitrogen adsorption isotherms using the density functional theory (DFT) model, which was introduced in section 2.3.1.2. (Webb and Orr, 1997). The slit pore is selected in the DFT model. Activated carbon consists of elementary graphitic crystallites, slit pores are formed between neighboring graphite layers by intercalation (Bandosz, 2006; Dunne and Manos, 2010).

4.2.3.3 Elemental analysis

The composition of the raw as well as the activated coke was analyzed for carbon, hydrogen, nitrogen, and sulfur using CHNOS Elemental Analyzer (model vario MICRO, Elementar Analysensysteme GmbH). The elements of Carbon, Hydrogen, Nitrogen, and Sulfur in the sample are oxidized into CO_2, H_2O, N_2, NO_x, SO_2,and SO_3 in a combustion tube. Then NO_x and SO_3 are reduced to N_2 and SO_2 in a reduction tube for analysis. Then these gases are separated and analyzed in the order of N_2, CO_2, H_2O and SO_2 (Elementar-Analysensysteme, 2007).

4.2.3.4 X-ray photoelectron spectroscopy (XPS)

The elemental analysis at the surface of the raw coke and activated coke was performed using XPS technique. In XPS, a surface atom of a solid absorbs the energy carried by the incoming X-ray photoelectron and is raised into an excited state from which it relaxes by emission of a photoelectron. The electron energy spectrum is characteristic of the emitting atom type. XPS utilizes this energy distribution to study the elemental and chemical composition of the surface and near the surface up to a maximum depth of about 5nm to 10 nm (Rao, 2003; Yen, 2008). The analysis was conducted using Kratos AXIS 165 instrument with Mono Al Kα radiation at 210 W and 14 kV under ultrahigh vacuum (10^{-9} Torr). All the spectra were calibrated by C1s peak at 284.5eV.

4.2.3.5 Scanning electron microscopy (SEM)

The morphology of the coke and activated coke was characterized by SEM (HITACHI S-2500 scanning electron microscope). Since coke is the carbonaceous residual of cracking of high molecular weight hydrocarbon mixtures, the samples were coated with gold to ensure that the particles have suitable conductivity. For better image quality, the secondary electron image was selected. The acceleration voltage was set at 8kV and the magnification ranged from 60 to 25000 times.

4.3 Results and Discussion

4.3.1 Temperature profile of raw coke during microwave heating

Since coke is a strong microwave absorber, low power level was selected first in preliminary experiments with petroleum coke (raw fluid coke, size III) without addition of the activating agent to measure the temperature of the coke sample as a function of heating time. A thermocouple was inserted into the coke when the microwave system was shut down immediately after certain microwave heating time to obtain the temperature. However, because of the thermocouple response time, the peak temperature was obtained few seconds later, which means that it was lower than the exact temperature when the microwave oven was shut down. Therefore a second order regression equation was used to extrapolate the temperature immediately after the magnetron was shut down from the plot of measured temperature and the time elapsed after shutdown, which is shown in Appendix A. The temperature profile of fluid coke as a function of the microwave heating time is illustrated in Figure 4-2.

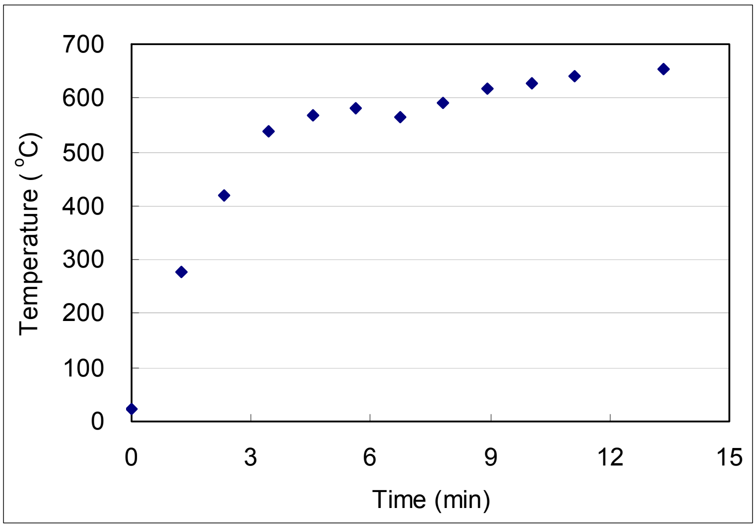


Figure 4-2 Temperature of petroleum coke immediately after magnetron shutdown as a function of microwave heating time at the low power level (raw fluid coke, size III)

The temperature of the coke increased with the microwave heating time (Figure 4-2). The temperature reached about 510^{o}C after 3.5 minutes of microwave heating and around 650^{o}C after about 13 minutes of microwave heating. The heating rate was much higher at the beginning, while the temperature increased very slowly above 500^{o}C. Since the temperature of the coke reached 650^{o}C after 13 minutes of low power level microwave heating, the low level power was chosen for the initial activation experiments.

4.3.2 Properties of Raw coke

4.3.2.1 Iodine number

The iodine number of the raw delayed coke and fluid coke were measured. In addition, the iodine number of a commercial granular activated carbon (GAC, Calgon F100) was also tested for comparison. The results are illustrated in Figure 4-3 and the numerical values are provided in Appendix B. The iodine number of raw delayed and fluid coke was 21.8 mg/g and 28.2 mg/g, respectively, while that of GAC used in the experiment was 1162 mg/g. The low iodine numbers of both raw cokes are expected because the raw cokes do not have large surface area and have limited adsorption capacity.

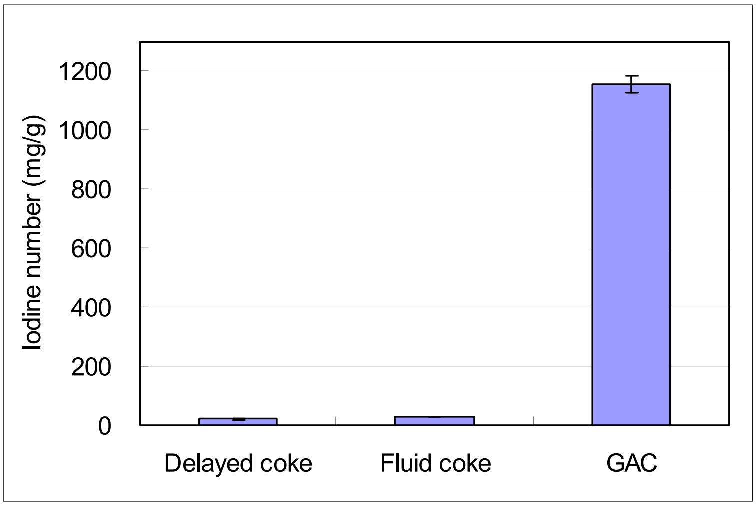


Figure 4-3 Iodine number of raw delayed coke, fluid coke and commercial GAC

4.3.2.2 Surface area and pore size distribution

The BET surface area from nitrogen adsorption isotherm (Appendix C) was 2.7 m^2/g for raw delayed coke and 27.3 m^2/g for raw fluid coke. The total pore volume was 0.0049 cm^3/g for raw delayed coke and 0.0164 cm^3/g for raw fluid coke. These results indicate that the raw coke has limited adsorption capacity.

Table 4-2 presents structural properties of the raw and delayed activated coke. The micropore volume was calculated based on the t-method. The total pore volume and the pore size distribution were obtained using the DFT model for slit pore since the pore shape in carbon is mostly slit-like. From Figure 4-4, the pores of raw delayed coke consolidate in the range from 2.5nm to 10nm, which corresponds to the mesopore range. No micropore is found in raw delayed coke, while some micropores can be found in raw fluid coke. The results agree with what is reported in the literature (Fedorak and Coy, 2006).

The micropore volume of raw fluid coke occupy is less than a half of total pore volume and most pores are in the mesopore range (Table 4-2).

Table 4-2 Structural properties of raw delayed and fluid coke

Parameter	Raw delayed coke		Raw fluid coke	
	This study	Literature[a]	This study	Literature[a]
Iodine number (mg/g)	21.8	-	28.4	-
BET area (m^2/g)	2.7	2.9	27.3	11
Total pore volume (cm^3/g)	0.0049	-	0.0164	-
Micropore volume (cm^3/g)	0.000	<0.001	0.0069	0.004
Micropore volume (%)	0%	-	42%	-

[a]: (Fedorak and Coy, 2006);

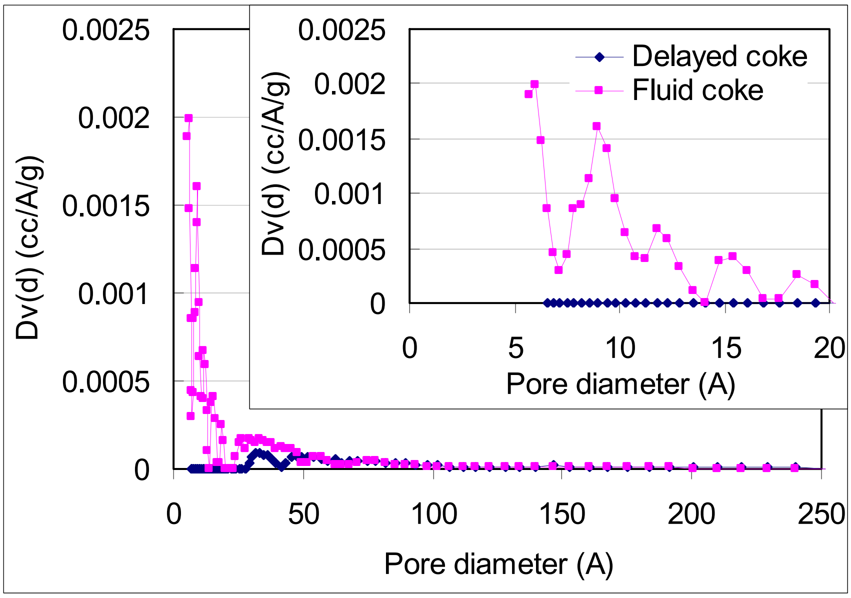


Figure 4-4 Pore size distribution of raw delayed coke and fluid coke (Micropore size distribution is presented in the inner figure)

4.3.2.3 Elemental analysis

Table 4-3 presents the elemental composition of raw delayed and fluid coke and compares them to values reported in the literature. The carbon content is the highest component in the raw coke, which is up to 80%wt. The second is, sulfur, which is almost 7%wt for either coke. Compared to fluid coke, the delayed coke has more hydrogen content. This is because the delayed coke has more volatile component than fluid coke, which is because fluid coking occurs at a higher temperature than delayed coking (Fedorak and Coy, 2006). The coking temperature is around 415^{o}C to 450^{o}C for delayed coke, while it is around 480^{o}C to 565^{o}C for fluid coke (Fernando, 2001).

Table 4-3 Elemental analysis of raw coke

Parameter	Delayed coke		Fluid coke	
	This study	Literature[a]	This study	Literature[a]
N (%)	1.6	1.4-1.6	1.8	1.7-2.0
C (%)	82. 3	81.5-84.3	78.5	80.7-83.7
H (%)	3.7	3.3-3.7	1.9	1.6-1.8
S (%)	6.8	5.9-6.2	7.2	6.2-6.8
Volatile content (%)[b]	-	8.3-11.0	-	4.9-6.2

[a]:(Scott and Fedorak, 2004);

[b]: volatile content is weight lost upon heating at 925^{o}C for 7 min in oxygen-free atmosphere.

4.3.2.4 XPS

Figure 4-5 illustrates the wide scan XPS spectra of raw delayed coke and fluid coke. The elements of C, N, O, S and Si can be found from the spectra. Small amount of K can be found on the surface of fluid coke. The High resolution XPS spectra of each peak and the deconvolution will be given in the section 4.3.11 with the activated coke. The weight percentages of these elements on the raw coke surface are illustrated in Figure 4-6 and the numerical value is provided in Appendix D.

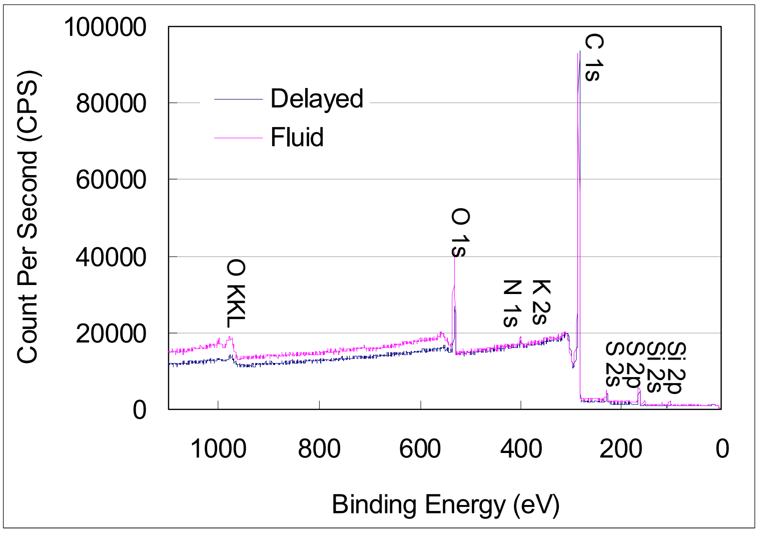


Figure 4-5 The wide scan XPS spectra of raw delayed coke and fluid coke

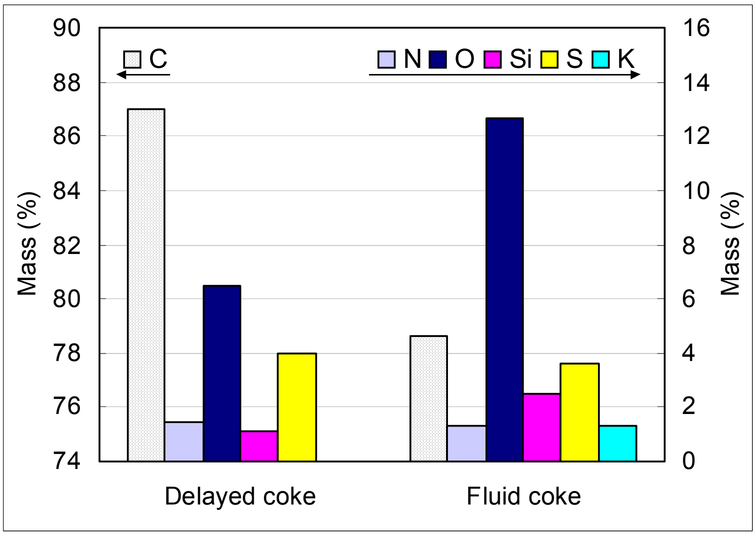


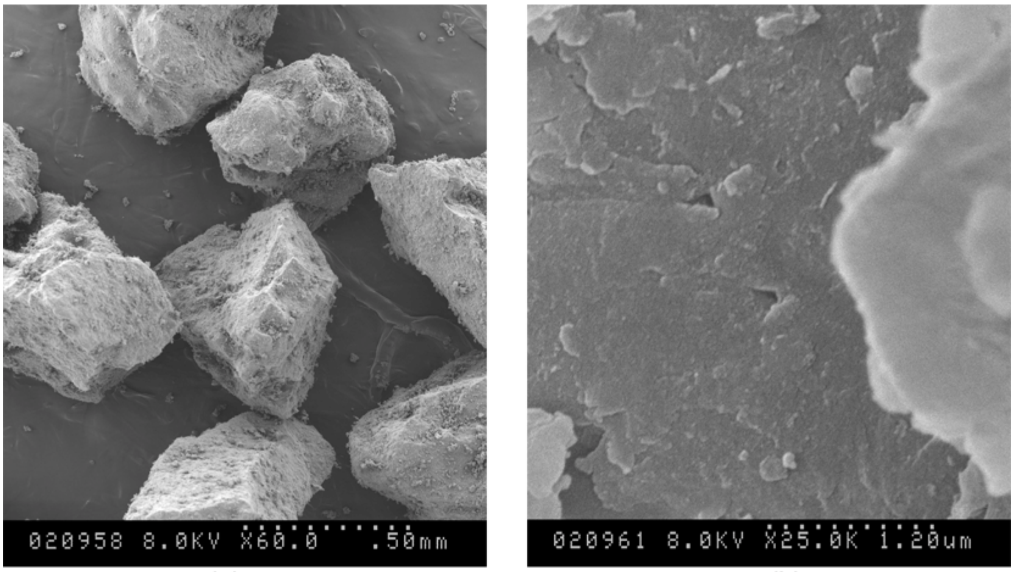
Figure 4-6 Mass percentage of elements on the raw coke surface

The carbon content on the surface of fluid coke is much lower than that of the delayed coke, while the content in the bulk is an inverse trend as discussed in section 4.2.3.3. The oxygen content on the surface of raw fluid coke is higher than that of delayed coke, which is consistent with the fact that bulk oxygen content of raw fluid coke is higher than that of raw delayed coke

(Scott and Fedorak, 2004). Besides, more silicon and potassium can be found on the surface of the fluid coke. The particle of fluid coke is exposed to the ambient environment during generation, while the particle of delayed coke is cut from a large bulk since the coking is proceeded in a coking drum. Therefore, more other elements will be found on the surface of the particles of fluid coke, which reduces the carbon content on the surface.

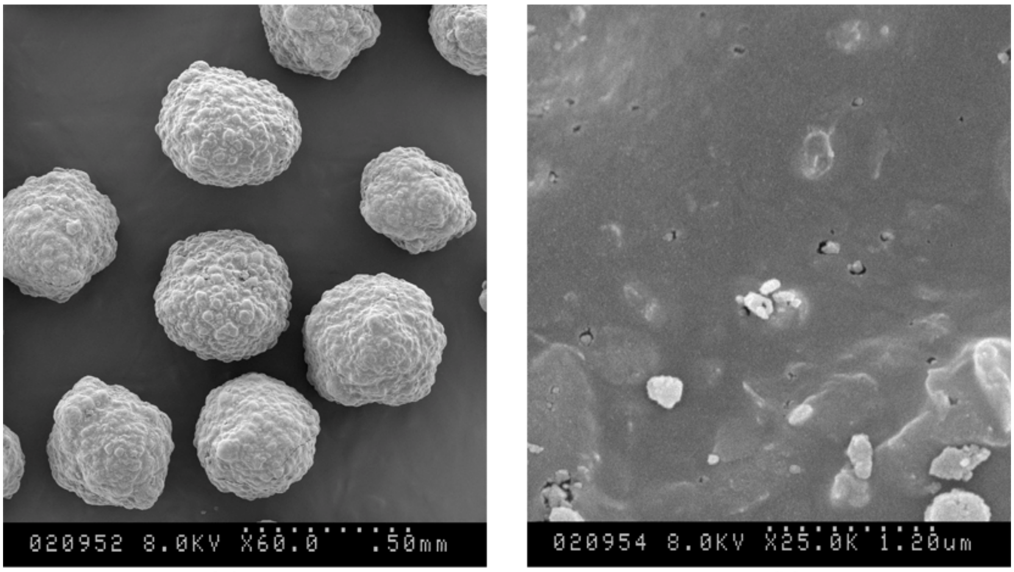
4.3.2.5 SEM micrographs

The SEM images of raw delayed and fluid cokes are illustrated in Figure 4-7 and Figure 4-8, respectively. The delayed coke particle is obtained after grounding so that it has random shape, whereas each particle of fluid coke has regular spherical shape. Large magnification (25,000 times) provides more details about the pores. Since the micropores are less than 2nm, they are invisible by SEM. However, the visible pores can give some information about the pore structure of raw coke. Figure 4-7b depicts limited number of pores on the surface of delayed coke particle, while Figure 4-8b shows that pores are more common on the surface of fluid coke. Previous work reported that Syncrude fluid coke is nonporous while the Suncor delayed coke is sponge-like and highly porous (Fedorak and Coy, 2006). However, the results from the SEM as well as iodine number, BET surface area and pore size distribution (Sections 4.3.2.1 and 4.3.2.2), demonstrate that the raw fluid coke has more porous structure than raw delayed coke.



(a) (b)

Figure 4-7 SEM of raw delayed coke (a: the view of whole particle; b: the pores observed on the surface of coke)



(a) (b)

Figure 4-8 SEM of raw fluid coke (a: the view of whole particle; b: the pores observed on the surface of coke)

4.3.3 Particle size effect

The iodine number of activated coke for different coke particle sizes is illustrated in Figure 4-9. The coke particles are classified into size I (4.76-2mm), size II (0.85-0.6mm), and size III (0.42-0.3mm) as mentioned before. The iodine numbers of activated delayed and fluid cokes in particle size I were much lower than those in particle sizes II and III. For the delayed coke, iodine numbers of particle size II and III were very close to each other. The activation for delayed coke of size II was done twice to confirm that the particle size has minimal effect on the degree of coke activation if the particle size is smaller than 0.85mm. However, for fluid coke, the iodine number increased with decreasing particle size. The larger the coke particle is, the more difficult for KOH to reach inside the coke particle and react with the carbon atoms. Therefore, smaller coke particles can have better activation and higher iodine number in general.

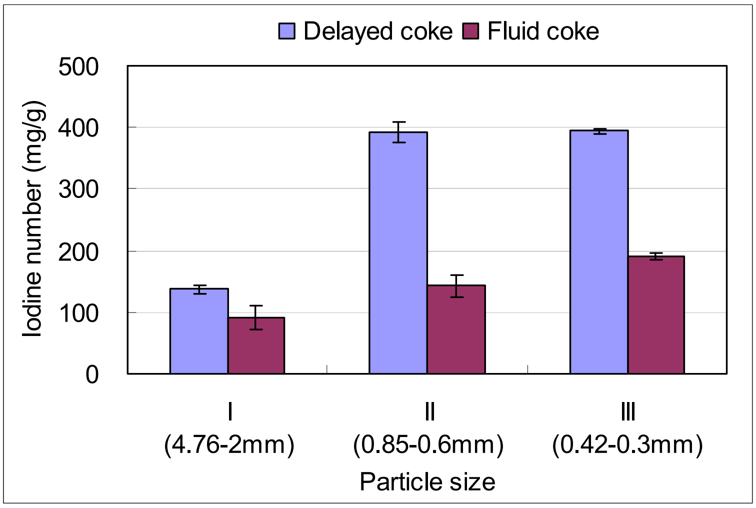


Figure 4-9 Iodine number of activated coke for different particle sizes (Low power level, microwave heating time is 30 minutes, KOH/Coke ratio is 0.5)

In comparison with the delayed coke, the iodine number of fluid coke is lower, which can be explained based on the difference in the structure of the two coke types. Delayed coke is made at relatively lower temperature and longer coking time than fluid coke, which results in a higher volatile content in delayed coke (8.3-11.0% volatile content in delayed coke vs. 4.9-6.2% volatile content in fluid coke). It is possible that the pores in the delayed coke are interconnected because the volatile components need to be released during the coking process. Thus KOH can spread to inside of the particle through the interconnected pores, which can help in building a well-developed micropore structure inside the particle. In addition, the volatile components are released during microwave heating which can cause development of more pores for delayed coke. On the other hand, in fluid coking a thin film of feed is sprayed onto a fluidized bed consisting of hot small coke particles. The volatile component is released and the solid part is deposited on the surface of the coke particles. Therefore each particle of fluid coke has an “onion” like structure and consists of about 30 to 100 layers of deposited coke (DiPanfilo, 1995; Jack et al., 1979). This kind of structure makes it possible that the pores in the particle are isolated from each other. The pores at the surface of the coke particle are hard to connect to other pores inside the particle. During activation, KOH is mixed and reacts mainly with the outer layers of the fluid coke. Therefore, the adsorption capacity is lower than that of delayed coke.

Figure 4-10 shows the activation yield as a function of particle size and the numerical value is provided in the Appendix E. The main weight loss of coke could have occurred during the activation and the washing. The pores were formed by losing the carbon as gaseous carbon compound during activation. For smaller particle, higher activation level could be achieved resulting in more weight loss. In addition, compared to larger particles, smaller particles depicted more loss during washing. Therefore, the activation of smaller particles resulted in lower yield.

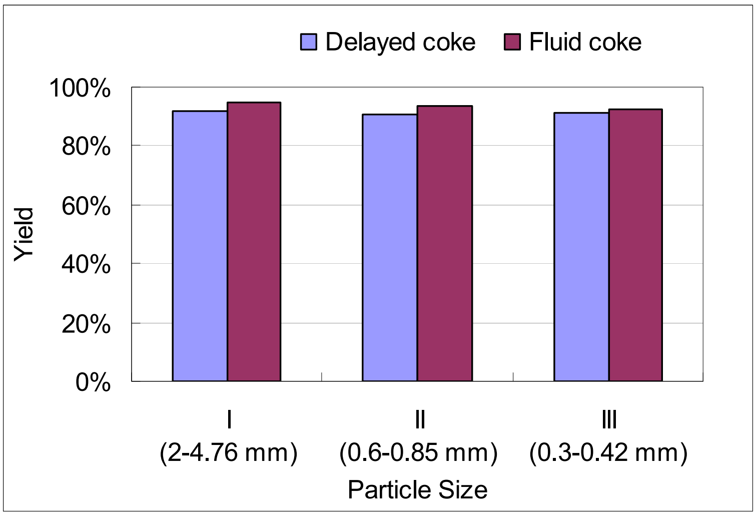


Figure 4-10 Activation yield as a function of particle size (Low power level, microwave heating time is 30 minutes, KOH/Coke ratio is 0.5)

4.3.4 Humidity effect

The effect of humidity of the carrier gas during microwave activation was also studied. Steam is a typical activation agent in the physical activation of activated carbon. Previous research reported that the maximum adsorptive capacity during chemical activation of petroleum coke was obtained when a fixed quantity of steam vapor mixed with nitrogen was continuously fed into the reactor (Wu et al., 2005). Therefore, the dry nitrogen was fed into a bubbler containing water to humidify the nitrogen stream in this study

The presence of water vapor during microwave activation improved the adsorptive properties of the microwave activated coke as demonstrated in Figure 4-11. Possible reasons would be as follows.

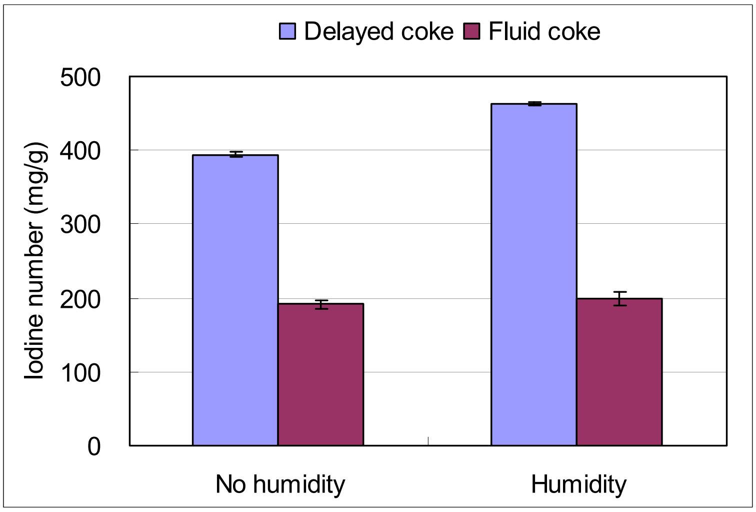


Figure 4-11 Humidity effect during microwave activation of petroleum coke (Low power level, microwave heating time is 30 minutes, KOH/Coke ratio is 0.5, particle size is III)

First of all, physical activation could occur since the atmosphere contained steam. Second, the physical activation is a heterogeneous, solid-gas reaction that can be limited by diffusion of steam. The impregnation of KOH made the coke touch the active agent sufficiently, thus the reaction of KOH and carbon could be proceeding immediately. The resulting coke skeleton had more pores accessible to the steam, which alleviated diffusion limitation and left more chance for physical activation. In addition, potassium acting as the catalyst can increase the rate of activation of steam and carbon atom (Jankowska et al., 1991; Patrick, 1995; Wu et al., 2005). As a result, compared to using dry nitrogen as purge gas, the use of humidified nitrogen stream increased the iodine number for delayed coke by more than 15%, while it didn’t have significant impact on the iodine number for fluid coke. This also originated from the layered structure of fluid coke. Humidity has insignificant influence during fluid coke activation because it is hard for KOH to reach the core of a fluid coke particle and generate inter-connected pore system for water vapor to diffuse. Since the rate of the steam activation is greatly affected by the diffusion of steam, the activation of fluid coke would be dominated by the effect of KOH and the effect of steam activation could be.

Compared to the case of dry nitrogen stream, the activation yield was reduced by 7% for delayed coke while it was increased by 1% for fluid coke when using humidified nitrogen stream (Figure 4-12). As discussed in section 4.3.3, the unique layered structure of fluid coke restricted the reaction of the activation agent with coke. Thus the yield of fluid coke in humid atmosphere was very close to that without humidity. However, it had clear effect on the delayed coke as discussed before. Therefore, humidified nitrogen was used in the following experiments to obtain better activation effect.

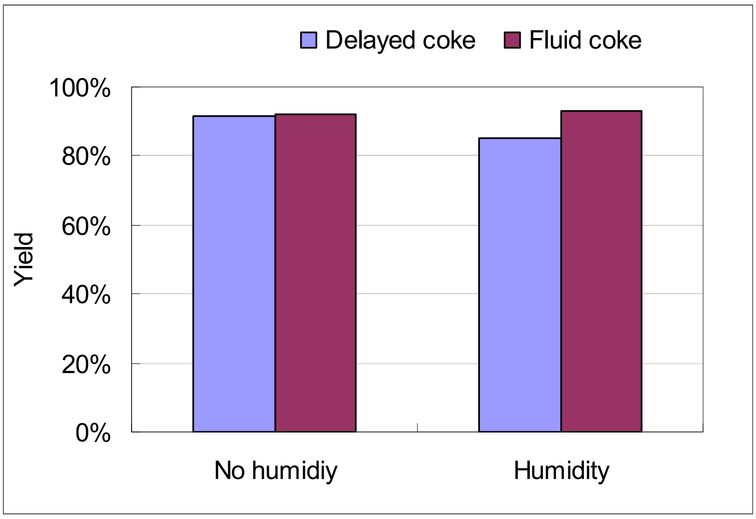


Figure 4-12 Activation yield as a function of purge gas humidity (Low power level, microwave heating time is 30 minutes, KOH/Coke ratio is 0.5, particle size is III)

4.3.5 Power level effect

The activated carbon has a strong relationship with the applied power level of the microwave oven. Figure 4-2 illustrates the temperature of pure raw fluid coke during microwave heating at low power level. However, the coke was mixed with potassium hydroxide during coke activation. The temperature of the coke-KOH mixture decreased with the increase of proportion of KOH, because KOH weakly absorbs microwaves as demonstrated in Figure 4-13. The temperature of pure KOH increased by about 20°C after 15 minutes of microwave heating at low power level, whereas the temperature of petroleum coke increased by more than 500°C after 3 minutes of microwave heating at the same power level.

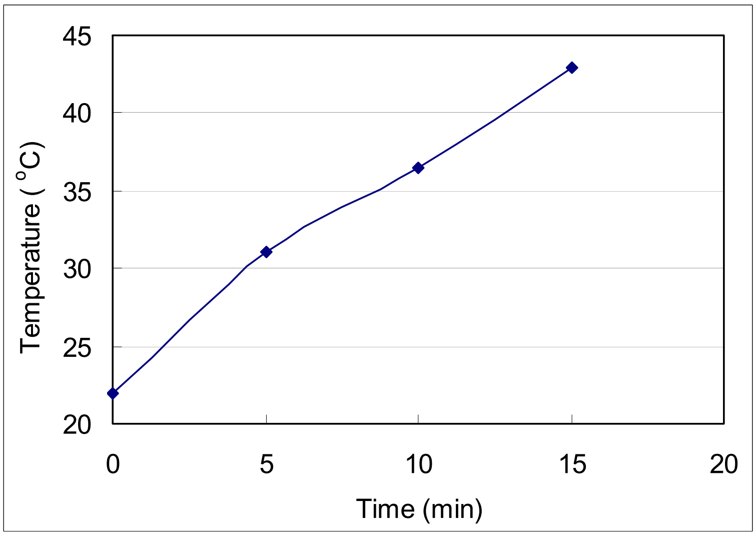


Figure 4-13 Temperature profile of KOH during microwave heating at low power level

When the ratio of KOH/coke equaled one, the low power level was not enough to activate the reaction. In fact, the temperature measured immediately after 30 min low level microwave heating was less than 100°C;

while the appearance and iodine number was not changed at all. Therefore, medium power level was chosen for the higher KOH/Coke ratio. Other KOH/Coke ratios were also tested at medium power for better comparison.

Figure 4-14 illustrates that iodine number of delayed coke or fluid coke increased by 74 and 135 % respectively, when the microwave power was increased to the medium level while other conditions were kept unchanged. This is because the total reactions of activation are endothermic. More energy input will result in more reactions between activation agents and coke, and more pores in the coke. Therefore, the low yield can be expected with medium power level, which is demonstrated in Figure 4-15. When the power was increased to medium level, the yield decreased by 10% for delayed coke and 9% for fluid coke.

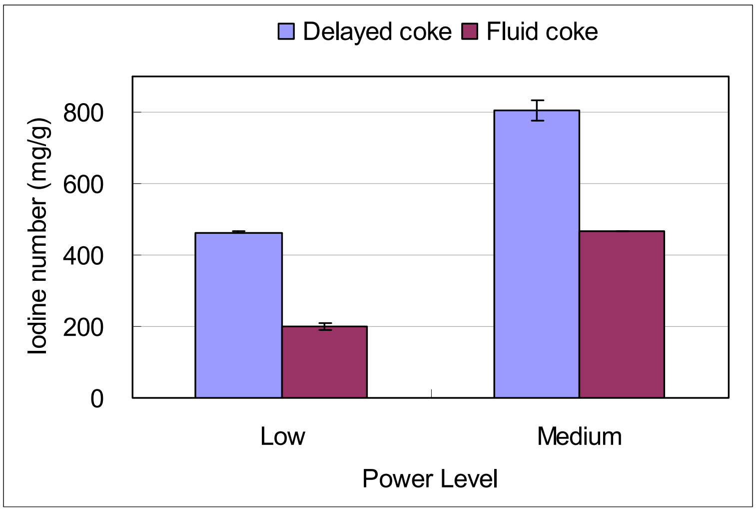


Figure 4-14 Effect of microwave power level on activation of petroleum coke (Particle size is III, KOH/Coke ratio is 0.5, microwave heating time is 30 minutes, humidified nitrogen)

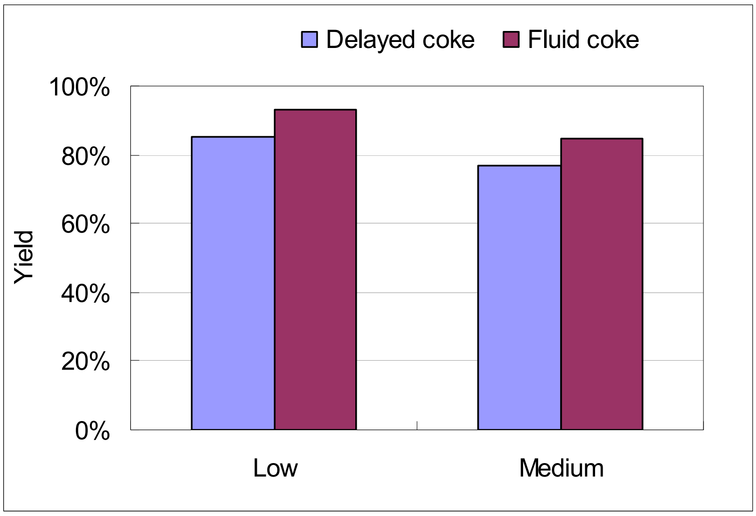


Figure 4-15 Effect of microwave power level on petroleum coke activation yield (Particle size is III, KOH/Coke ratio is 0.5, microwave heating time is 30 minutes, humidified nitrogen)

4.3.6 KOH/Coke ratio effect

Figure 4-16 and Figure 4-17 illustrate the iodine number and yield as a function of the KOH/Coke ratio. When the KOH/Coke ratio was 0.25, the iodine numbers were 125 mg/g for activated delayed coke and 89 mg/g for activated fluid coke. When the ratio increased to 0.5, the iodine number reached up to 804mg/g for the activated delayed coke, and 467mg/g for the activated fluid coke. When the KOH/coke ratio reached 1, the iodine number increased to 901 mg/g for activated delayed coke and to 509 mg/g for activated fluid coke. Obviously, there was not enough KOH for coke activation when the ratio was as low as 0.25. Although the iodine number increased with higher KOH/coke ratio, the improvement was not directly proportional. The improvement from 0.5 to 1 (12% for delayed coke and 9% for fluid coke) was much less than that from 0.25 to 0.5 (544% for delayed coke and 425% for fluid coke). When the ratio was 0.5, KOH could activate the coke very well. The activation could be better with more activating agent. Otowa et al. investigated the effect of KOH/Coke ratio on the activation from 1 to 10 in traditional heating. It was reported that the largest BET surface area was obtained when the KOH/Coke ratio was 4, (Otowa et al., 1993). Since the results demonstrated that the increase in the iodine number is not directly proportional to KOH/Coke ratio, it is not necessary to achieve small improvement in iodine number by using a higher KOH/Coke ratio to save on the cost of KOH. Therefore, in this thesis, KOH/Coke ratio at 1 was selected for further study.

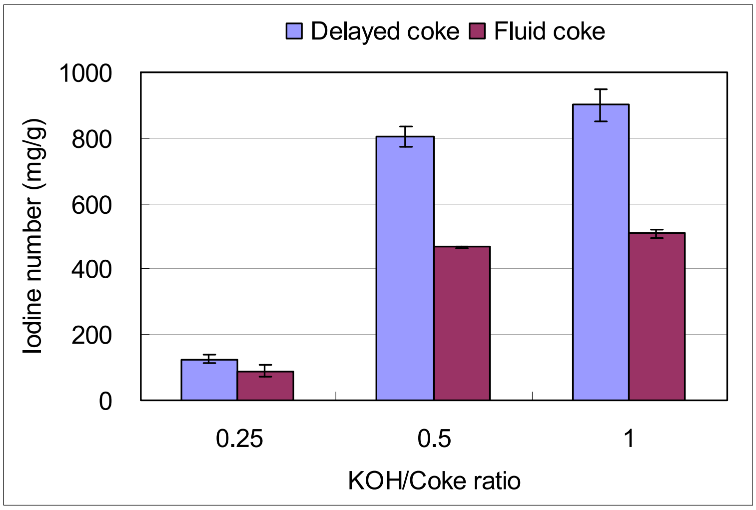


Figure 4-16 Iodine number of activated coke at different KOH/Coke ratios (Particle size is III, microwave heating time is 30 minutes, nitrogen with humidity, power level is medium)

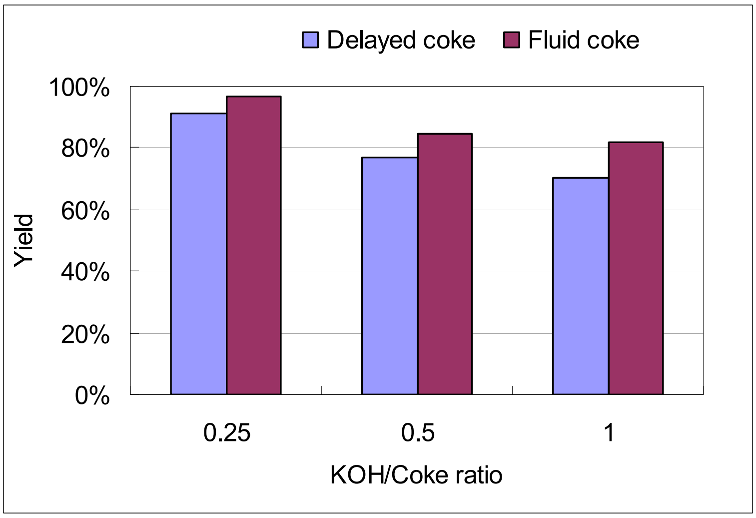


Figure 4-17 Activation yield as a function of KOH/Coke ratio (Particle size is III, microwave heating time is 30 minutes, nitrogen with humidity, power level is medium)

The activation yield for delayed coke dropped from 91.4% to 76.8% and further to 70.2% when the ratio was 0.25, 0.5 and 1, respectively. As for the fluid coke, the value was 96.6%, 84.9%, and 82.0% respectively. The yield drop when the ratio was from 0.5 to 1 was not as large as it when the ratio was from 0.25 to 0.5. Therefore the trend of yield agreed with the change in the iodine number. Higher KOH/Coke ratio results in better activation of coke and lower activation yield.

4.3.7 Microwave heating time effect

The microwave heating time is related to the heat applied. The longer the microwave heating time, the more energy is applied to the coke. Figure 4-18 illustrates the iodine number of activated carbon at different microwave heating times. Even for a time as short as 10 minutes of microwave heating the iodine number of activated delayed coke increased to more than 1100 mg/g. The iodine number didn't vary monotonically with the microwave heating time. 20 minutes of microwave heating resulted in a small increase in iodine number; however, the iodine number dropped to 901 mg/g with 30 minutes of microwave heating and increased to 1240 mg/g with 40 minutes of microwave heating. The activation of delayed coke with 10, 20, 30, and 40 minutes of microwave heating was done twice to confirm the obtained trend. Such a change in the iodine number is related to pore volume and pore size distribution as explained in section 4.3.8. Yang reported that a typical iodine number for activated carbon is 900mg/g with values >1000 mg/g for better grades of activated carbon (Yang, 2003). Hence the obtained activated coke can be regarded as better grade and have comparable or better adsorption properties than typical activated carbon. The iodine number for activated fluid coke showed a similar trend with microwave heating time. The only difference was that the iodine number was around half of the delayed coke value.

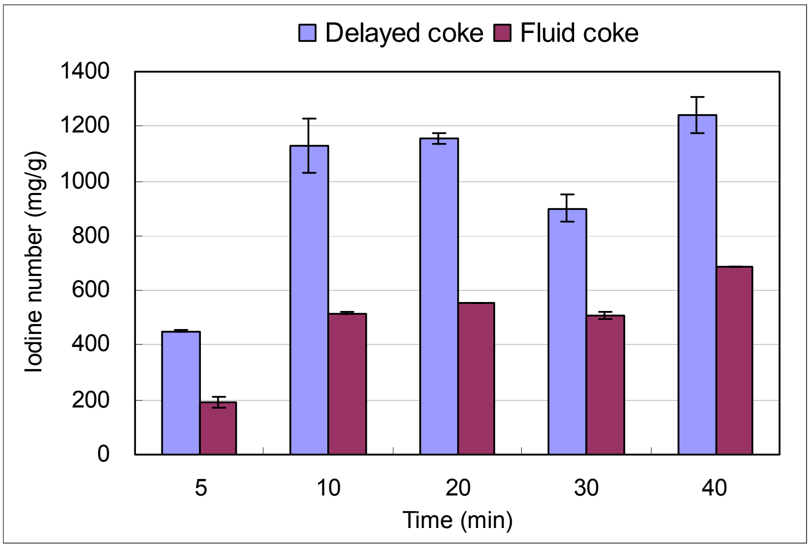


Figure 4-18 Iodine number as a function of microwave heating time (Particle size is III, KOH/coke ratio is 1, nitrogen with humidity, power level is medium)

As expected, the yield in Figure 4-19 decreased with the heating time. Fluid coke had a higher yield than delayed coke, which agreed with the results of iodine number tests. However, the yield of delayed coke was still high (above 70%) in comparison with values reported for KOH activation with conventional heating. (63% for KOH activation and 29% for KOH-steam activation) (Wu et al., 2005).

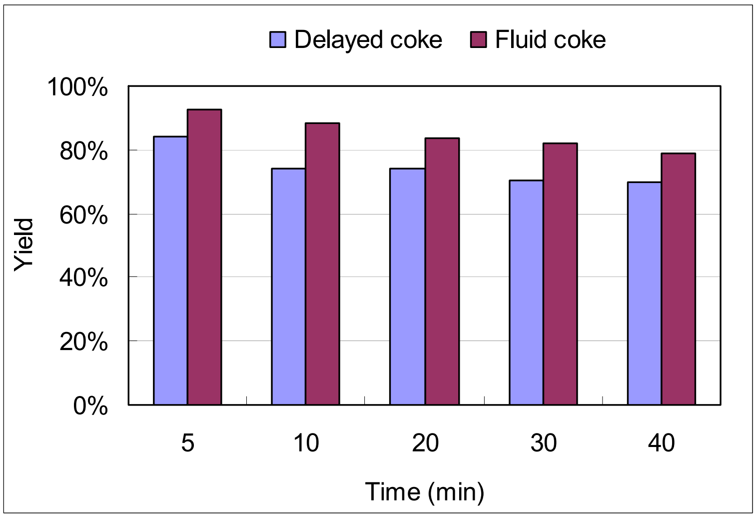


Figure 4-19 Activation yield as a function of microwave heating time (Particle size is III, KOH/coke ratio is 1, nitrogen with humidity, power level is medium)

4.3.8 Surface area pore size distribution

Table 4-4 lists the surface area of activated carbon under different activation conditions. The activation condition is simply stated by the form "*number1-letter-number2*". The *number1* indicates the ratio of KOH/Coke, the *letter* indicates the power level and whether it is with humidity or not, and the *number2* indicates the microwave heating time. For instance, "0.5-L-30" means the KOH/Coke ratio at 0.5, low power level and 30 minutes microwave irradiation; "1-MH-10" means the KOH/Coke ratio at 1, medium power level and 10 minutes microwave irradiation. Because all these activations used the same particle size (size III, 0.43-0.3mm), the particle size is not mentioned in the brief form.

Table 4-4 BET surface area and iodine number of raw and activated coke

	Delayed coke		Fluid coke	
	BET surface area (m^2/g)	Iodine number (mg/g)	BET surface area (m^2/g)	Iodine number (mg/g)
Raw	2.7	21.8	27.3	28.4
0.5-L-30	240.7	394.1	136.9	191.6
0.5-LH-30	348.9	462.7	142.2	198.8
1-MH-30	891.2	900.9	409.1	509.0
1-MH-10	1131.0	1129.1	440.0	517.1
1-MH-40	1163.0	1240.0	657.8	685.8

The BET surface of raw coke is very low which makes it ineffective for adsorption. The BET surface area is higher for raw fluid coke than raw delayed coke, which is consistent with the iodine number results. After activation, the surface area of both cokes increased significantly. The presence of humidity increased the BET area surface of activated delayed coke by about 45%, which means that steam was beneficial to the activation of delayed coke.

When the KOH/Coke ratio increased from 0.5 to 1 and the power level increased from low to medium for a 30 minute activation time, the surface area of activated coke increased from 348.9 m^2/g to 891.2 m^2/g for delayed coke and from 142.2 m^2/g to 409.1m^2/g for fluid coke. A similar trend was observed for the iodine number. This change demonstrated that the power and ratio had a critical effect on the activation for both delayed coke and fluid coke.

Compared with heating time, the BET surface area of activated delayed coke with 10 minutes microwave heating was 1131.0 m^2/g, then it decreased to 891.2 m^2/g with 30 minutes heating, and increased again to 1163.0m^2/g with 40 minutes heating. As for the activated fluid coke, the BET surface had the same trend, which dropped from 440.0 m^2/g with 10 minutes heating to 409.1 m^2/g with 30 minutes heating, and then increased again to 657.0 m^2/g with 40 minutes. This trend is similar to that observed for the iodine number. The reason why the BET surface area is not changed monotonically can be explained by pore size distribution in section 4.3.9.

Figure 4-20 shows that the relationships between surface area and iodine number are linear and that the coefficient is close to 1, which indicates a strong correlation between BET area and iodine number. (Mianowski et al., 2007) In addition, the slopes for the regression lines are close to each other: 0.946 of delayed coke and 0.877 for fluid coke. The iodine number measures how much iodine can be adsorbed on the surface of carbon; therefore, it is reasonable to conclude that the iodine number has a linear relationship with surface area.

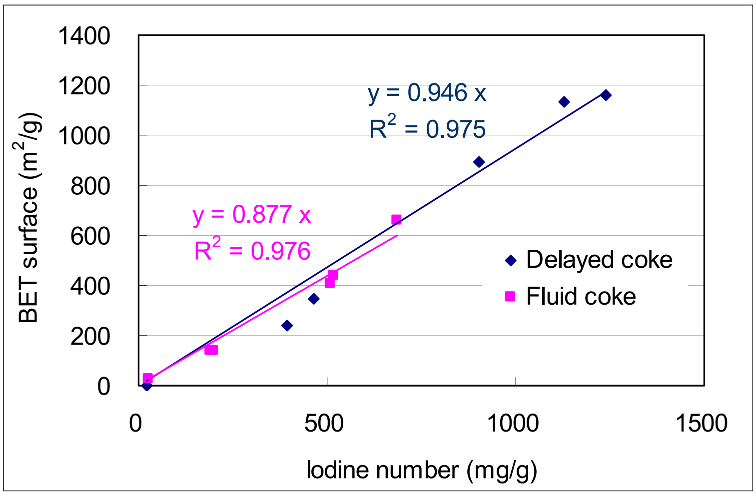


Figure 4-20 BET surface area Vs. Iodine number

4.3.9 Pore volume and pore size distribution

During activation, there are two effects on the formation of pores. One is to create new pores based on the reaction between the coke and the activation agent. The other is to enlarge or merge the existing pores, because the carbon skeleton around a pore or separating two pores can be burned away. If the carbon skeleton continues to be burned away, it will eventually result in the elimination of pores. Therefore, the iodine number, surface area, pore volume and pore size distribution of activated coke are the combined results of these two effects.

Table 4-5 depicts the impact of activation time on the structural properties of activated coke. As for the micropore volume case, both delayed coke and fluid coke had the same trend with the total pore volume. The decrease of the micropore volume is because a longer heating time would enlarge the micropores in the activated carbon, which might cause the pore wall between adjacent small micropores to disappear and merge into a large mesopore. If microwave irradiation was continued, then new micropores would be generated to enhance the micropore volumes.

For both delayed coke and fluid coke, the total pore volume was slightly reduced as the microwave heating time was increased from 10 minutes to 30 minutes, and then the total pore volume increased to more than the initial with 40 minutes of microwave heating. After some micropores were generated, the pore merger and elimination would affect the pore structure of activated coke with the increase in microwave heating time. This would have caused the total volume to decrease with the time. So the pore volume did not increase monotonically with the microwave heating time.

Table 4-5 Effect of activation time on the structural properties of activated coke

	Delayed coke			Fluid coke		
	1-MH-10	1-MH-30	1-MH-40	1-MH-10	1-MH-30	1-MH-40
Iodine number (mg/g)	1129.1	900.9	1240	517.1	509	685.8
BET area (m^2/g)	1131	891.2	1163	440	409.1	657.8
Total pore volume (cm^3/g)	0.4596	0.3818	0.4754	0.2247	0.2011	0.2942
Micropore volume (cm^3/g)	0.4224	0.3265	0.4475	0.1405	0.1399	0.2504
Mesopore volume (cm^3/g)	0.0372	0.0553	0.0279	0.0842	0.0612	0.0438
Micropore volume (%)	92%	86%	94%	63%	70%	85%

Figure 4-21 illustrates the pore size distribution of the activated delayed coke. For activated delayed coke, the micropore distribution of the 10 minutes activation sample is very similar to that of the 40 minute activation samples. On the other hand, the mesopores volume of the 30 minute activation sample was higher than that for the 10 or 40 minute activation samples, and the micropore volume proportion of it was lower than others. These results would explain why the iodine number and BET surface area dropped with a 30 minute microwave heating and increased again with a 40 minute microwave heating.

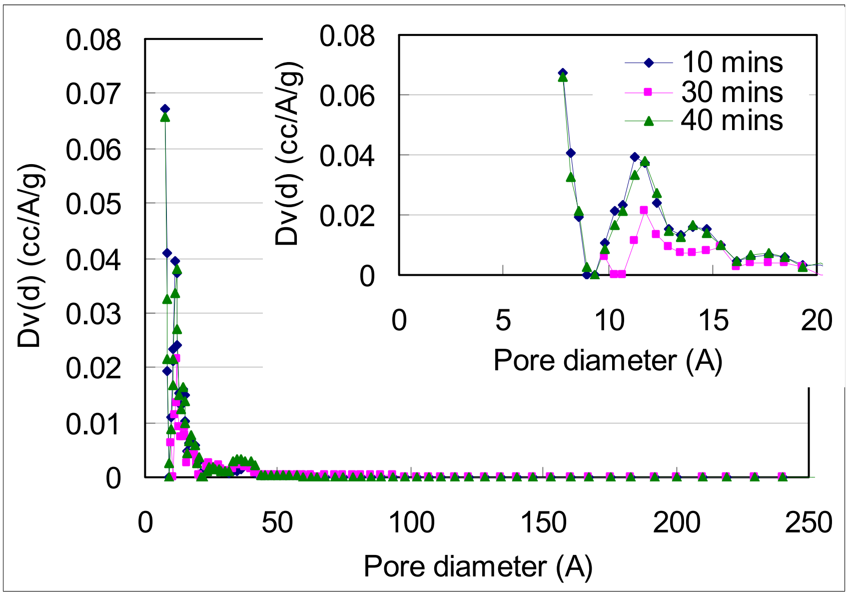


Figure 4-21 Pore size distribution of activated delayed coke with different microwave heating time

As shown in Figure 4-22, the pore size distributions of activated fluid coke with different microwave heating times varied. However, the micropores volume was the lowest in the 30 minute activation sample and it was the highest in the 40 minute activation sample. The mesopore volume of activated fluid coke kept decreasing as the heating time increased. As the unique onion structure made it hard for the activation agent to diffuse into the core of the particle, the reaction would mostly occur at the outer layers. Therefore outside pores kept growing larger to form macropores. If the reaction continued, the carbon skeleton forming the outside pores would be burned away, resulting in the elimination of pores. Therefore, the mesopore volume decreased with the increase of microwave heating time.

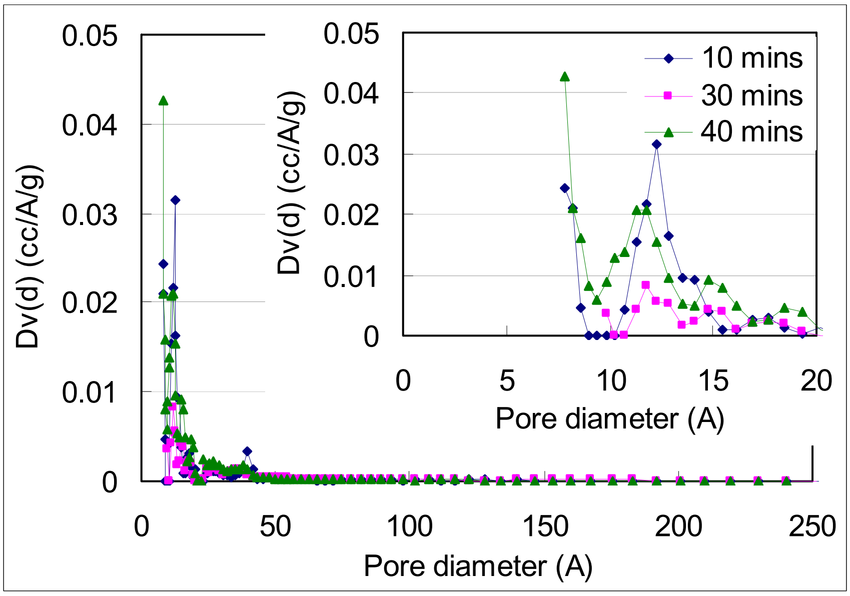


Figure 4-22 Pore size distribution of activated fluid coke with different microwave heating time

Figure 4-23 illustrates the pore size distributions of activated delayed and fluid coke at the same activation condition. Most pores of both activated coke were micropores and activated fluid coke had more mesopores than activated delayed coke. From the zoom-in figure, more micropores were obtained in activated delayed coke, which could explain why activated delayed coke had a higher iodine number than activated fluid coke.

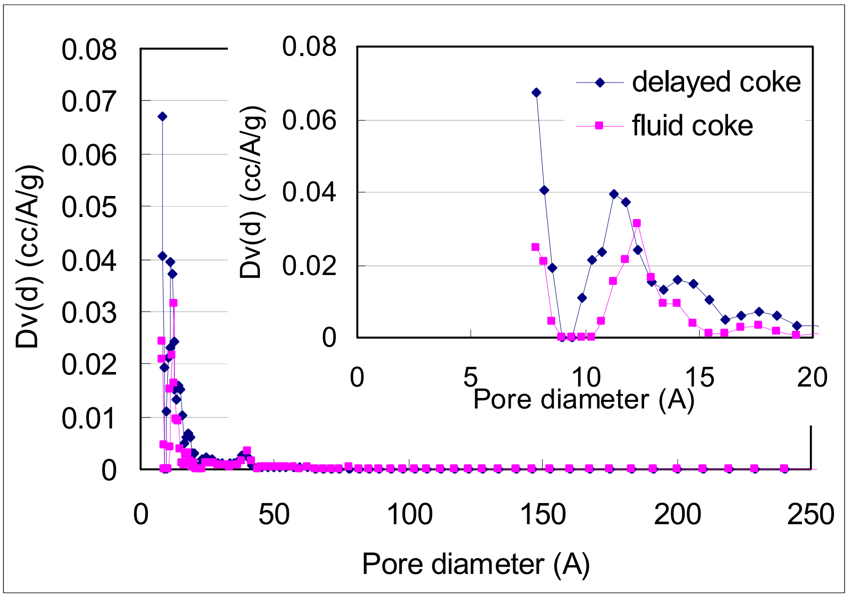


Figure 4-23 Pore size distribution of activated delayed and fluid coke (Particle size is III, KOH/coke ratio is 1, nitrogen with humidity, power level is medium, microwave heating time is 10 minutes)

4.3.10 Elemental analysis

Figure 4-24 to Figure 4-27 list the change of weight proportion after the activation process of four elements: C, N, H, and S after the activation process. The exact values are listed in Appendix F. In these figures, all the samples are labeled in the same format as described in section 4.3.8.

Raw delayed coke has less N and S, but more C and H proportions than fluid coke, which indicates that more volatile components are in the delayed coke. Table 4-3 confirmed the volatile components of delayed raw coke (8.3-11.0%) are almost twice those of the raw fluid coke (4.9-6.2%) (Scott and Fedorak, 2004).

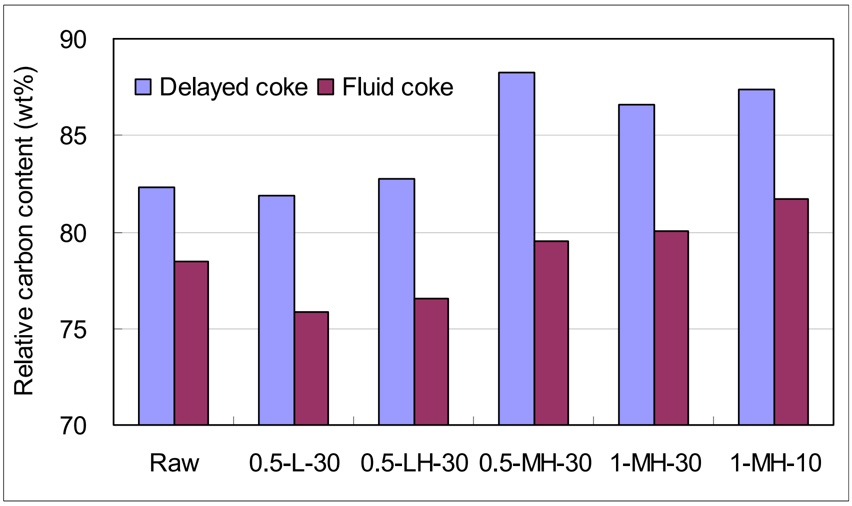


Figure 4-24 Relative carbon content of raw coke and activated coke under different activation conditions

(The x axis means the activation condition: the first number (0.5 or 1) means the ratio of KOH/Coke, the letter (L or M) is the power level and H means with humidity, and the second number (30 or 10) indicates the microwave heating time)

Compared to raw coke, the activated coke 0.5-L-30 has lower carbon content (% by weight). It is caused by two reasons: an increase in the proportion of oxygen and the potassium deposition on the carbon surface during activation. The surface functional groups, such as carbonyl and carboxyl group, will increase the oxygen content of activated coke. Since the pores in activated coke are mostly generated by the reaction between the coke and the activation agent, KOH, the potassium will cover all the surface of the activated coke. The washing after activation could not remove all the potassium from the surface, which made the relative carbon content lower than in raw coke.

In comparison with activated coke 0.5-L-30, the humidity was able to increase the relative carbon content in 0.5-LH-30. Comparing activated coke 0.5-LH-30 with 0.5-MH-30, the relative carbon content increased from 82.7% to 88.3% for delayed coke and from 76.6% to 79.5% for fluid coke. The huge jump of the carbon content indicates that the power level has a significant effect on coke activation.

It is also found that the relative carbon content increases with the KOH/Coke ratio for the activated fluid coke, but decreases a little for the activated delayed coke. Delayed coke reacts more easily with KOH than fluid coke does, which is confirmed by a lower yield of delayed coke. As for delayed coke, a higher KOH/Coke ratio results in more carbon being burned away. However, the layered structure of fluid coke prevents the activation agent from penetrating the core of the fluid coke particle, and blocks more reactions between coke and KOH. Therefore, the higher KOH/Coke has little effect on the relative carbon content for fluid coke.

Comparing activated coke 1-MH-30 and 1-MH-10, the longer microwave heating time reduces the relative carbon content. This suggests that 10 minutes is good enough to activate coke since a longer heating time will cause more carbon to burn away and finally reduce the carbon content.

Compared to raw coke, the relative nitrogen content of activated coke decreased (Figure 4-25). It is obvious that the microwave heating time has critical effect on the nitrogen content. Activated coke of 30 minutes heating has lower relative nitrogen content than that of 10 minutes heating. Additionally, power level also has an obvious effect on nitrogen content. The nitrogen content of activated coke 0.5-MH-30 is lower than that of 0.5-LH-3, especially for delayed coke. The small change of nitrogen proportion in fluid coke from 0.5-LH-30 to 0.5-MH-30 also results from the layered structure of fluid coke, which blocks the reaction of KOH or water vapor with the carbon in the core of a fluid coke particle. The humidity and KOH/Coke ratio have less effect on nitrogen content compared to heating time and power level.

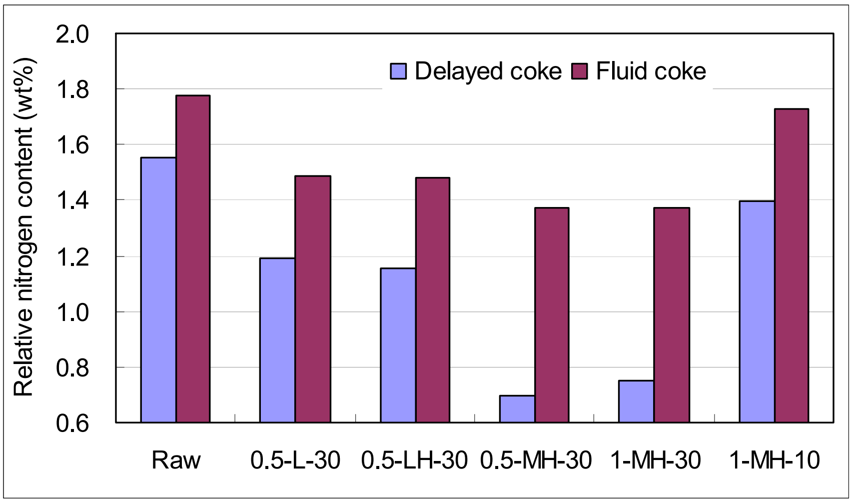


Figure 4-25 Relative nitrogen content of raw coke and activated coke under different activation conditions

Compared to raw coke, the hydrogen content and sulfur content of activated coke also decrease (Figure 4-26 and Figure 4-27). It is obvious that the power level has the most critical effect on the hydrogen and sulfur content.

Coke activated at a medium power level has lower H and S content than that which is activated at a low power level. Microwave heating time is also important to both H and S content, but the humidity and KOH/Coke ratio have less effect compared to power level and heating time.

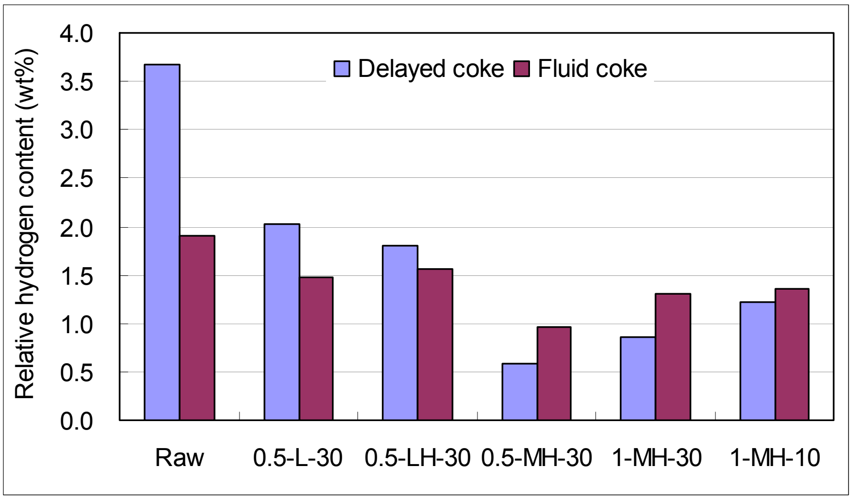


Figure 4-26 Relative hydrogen content of raw coke and activated carbon under different activation conditions

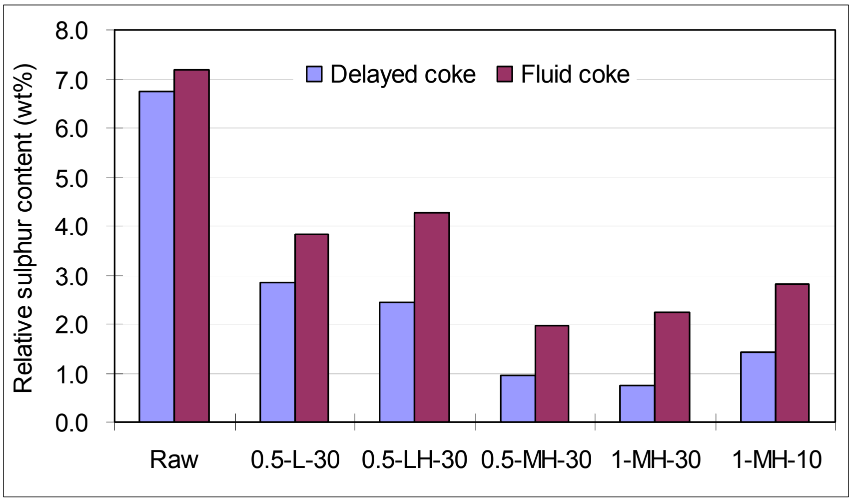


Figure 4-27 Relative sulfur content of raw coke and activated carbon under different activation conditions

In comparison with raw coke, the carbon content (% by weight) of activated delayed coke 1-MH-10 increased by 5.10%, while N, H and S decreased by 0.16%, 2.46% and 5.32%, respectively. The carbon content (% by weight) of activated fluid coke 1-MH-10 increased by 3.23%, while N, H and S decreased by 0.04%, 0.55% and 4.38%, respectively, as compared to raw coke. The higher carbon content and fewer impurities also demonstrate the fact that delayed coke is better activated than fluid coke.

4.3.11 XPS

Figure 4-28 illustrates the wide scan XPS spectra of raw delayed coke and activated delayed coke with 10 minutes and 40 minutes microwave heating. The other activation conditions of activated coke are: particle size is III; KOH/coke ratio is 1; activation atmosphere is humidified nitrogen; and power level is medium. Figure 4-29 shows the XPS spectra of fluid coke. The elements of C, N, O, S and K can be found from the spectra. The weight percentages of these elements are illustrated in Figure 4-30 and Figure 4-31.

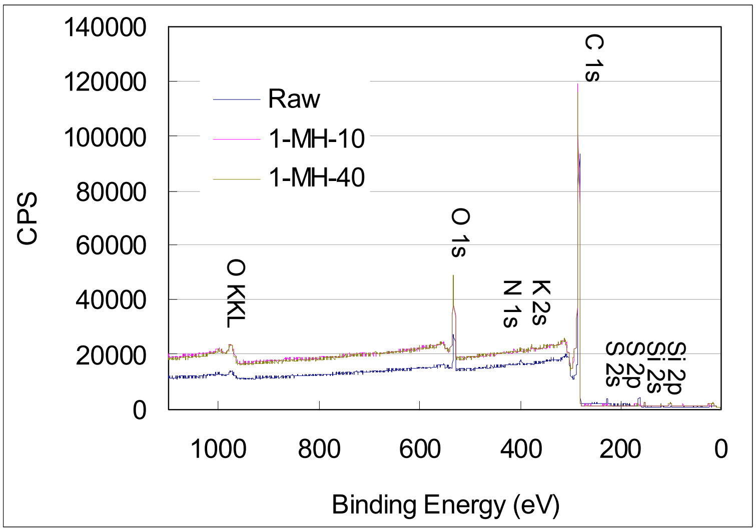


Figure 4-28 Wide scan XPS spectra of delayed coke

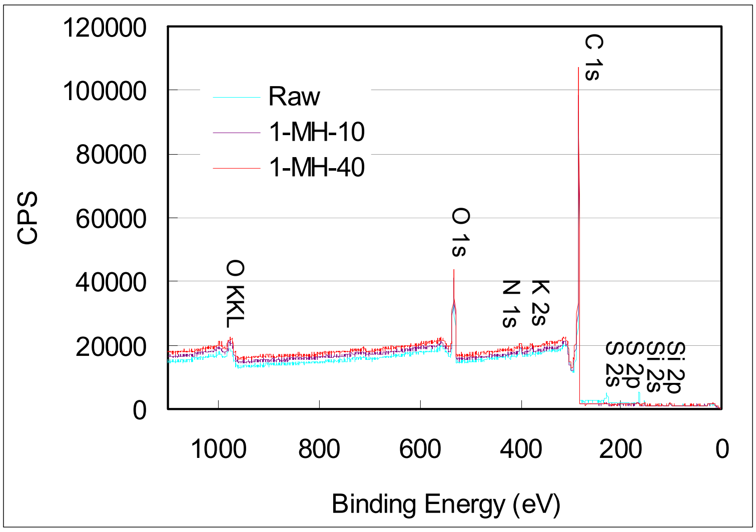


Figure 4-29 Wide scan XPS spectra of fluid coke

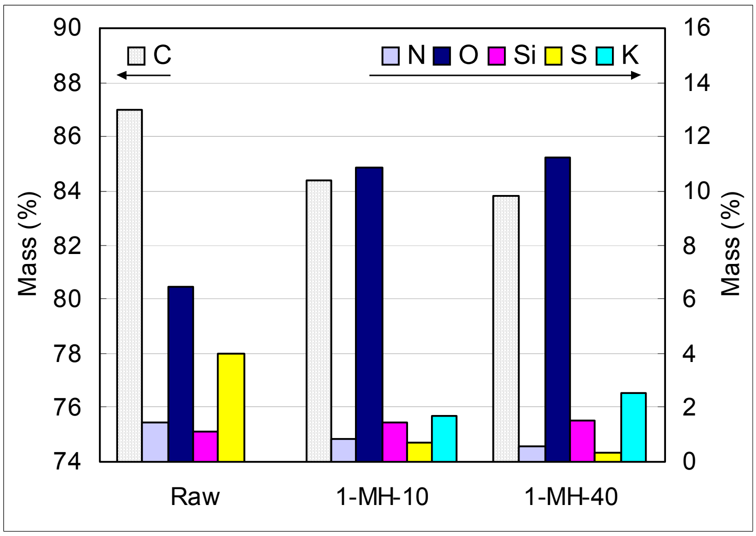


Figure 4-30 Mass percentage of elements on the delayed coke surface

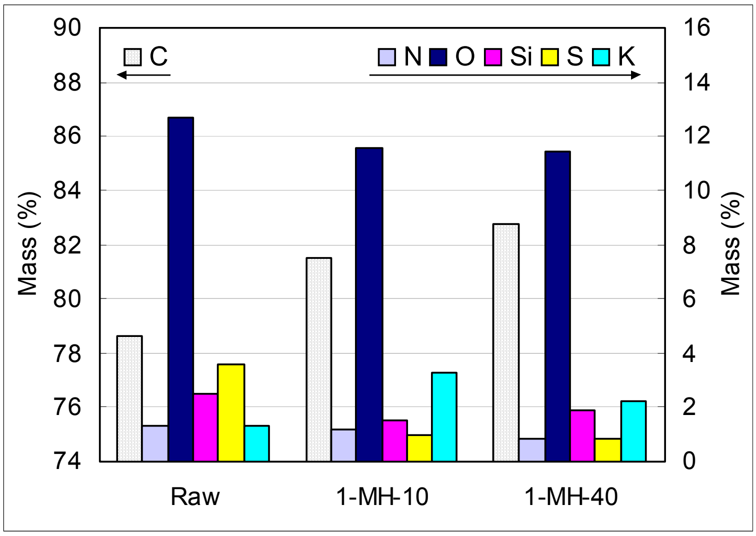


Figure 4-31 Mass percentage of elements on the fluid coke surface

For both delayed and fluid coke, the N and S contents have decreased after activation, which agrees with the results from the bulk elemental analysis. The carbon content of fluid coke has increased after activation, whereas it decreased a little for delayed coke. Oxygen content of delayed coke increases a lot after activation, which means that the activation introduces more surface oxygen groups. The fluid coke keeps almost the same oxygen content after activation. Potassium content is zero in the raw delayed coke and very small in the raw fluid coke, but it increases after activation, which means that the washing can't remove all activation agent. The silicon is related to the ash content of the coke, and originates in the exaction of bitumen from oil sands.

High resolution XPS spectra were performed for the element C, O, S and K. Figure 4-32 shows the C 1s peaks and its deconvolutions for 6 coke samples. It is found that deconvolution of the carbon 1s peak could be fitted to three curves with binding energies at 284.5-284.6eV, 285.3-285.9eV, 288.0-289.3eV. The binding energy peaks were identified as graphitic carbon or C-H at 284.5-284.6eV, C-O in phenol, alcohol or ether at 285.3-285.9eV, and C=O or O–C=O at 288.0-289.3eV (Dekanski et al., 2001; Kumar et al., 2010; Lee and Reucroft, 1999; Moulder et al., 1992; Sundberg et al., 1987). Both delayed coke and fluid coke have more C=O or O–C=O groups after activation, and the longer the microwave heating time, the more the C=O or O–C=O groups. A similar trend is observed for the C-O group in the fluid coke. However, the raw delayed coke has more C-O groups than the activated delayed coke, but the amount of C-O group of activated delayed coke also increases with the microwave heating time. These results show that the activation is able to introduce oxygen functional group at the surface of coke and longer microwave heating times can introduce more oxygen functional groups.

Figure 4-33 shows the high resolution O 1s spectra of the coke. The deconvolution of the whole peak can also be fitted to three curves: 531.6-532.2eV for hydroxide, hydroxyl, or ethers; 533.4-533.8eV for anhydride, lactone, or carboxylic acids; and 535.2-535.9eV for adsorbed H_2O or O_2 (Moulder et al., 1992; Valdes et al., 2003; Xu and Liu, 2008). Activation of delayed coke can increase the relative proportion of the C-O-H or C-O-C group, and reduce the relative proportion of O=C-O group; whereas activation of fluid coke has the reverse effect. The reason why the oxygen groups of delayed coke and fluid coke have different change after activation is not clear till now.

Figure 4-34 shows the spectra of sulfur of the coke. The peak at 163.7-163.9eV is identified as the sulfur $2p_{3/2}$, the peak at 164.9-165.1eV is sulfur $2p_{1/2}$, and the peak at 168.0-168.4eV is identified as sulfate (Moulder et al., 1992). Less sulfur is found after activation, which agrees with the bulk element analysis. In addition, more amount of sulfate is found after activation, reflecting that the activation is an oxidation process.

Figure 4-35 shows the spectra of potassium of the coke. The raw delayed coke has no potassium at the surface. The peak at 293.1-293.2eV is identified as the potassium $2p_{3/2}$, and the peak at 295.9-296.1eV is potassium $2p_{1/2}$. After activation, potassium is found in both delayed coke and fluid coke. It demonstrates that potassium is not completely removed by washing.

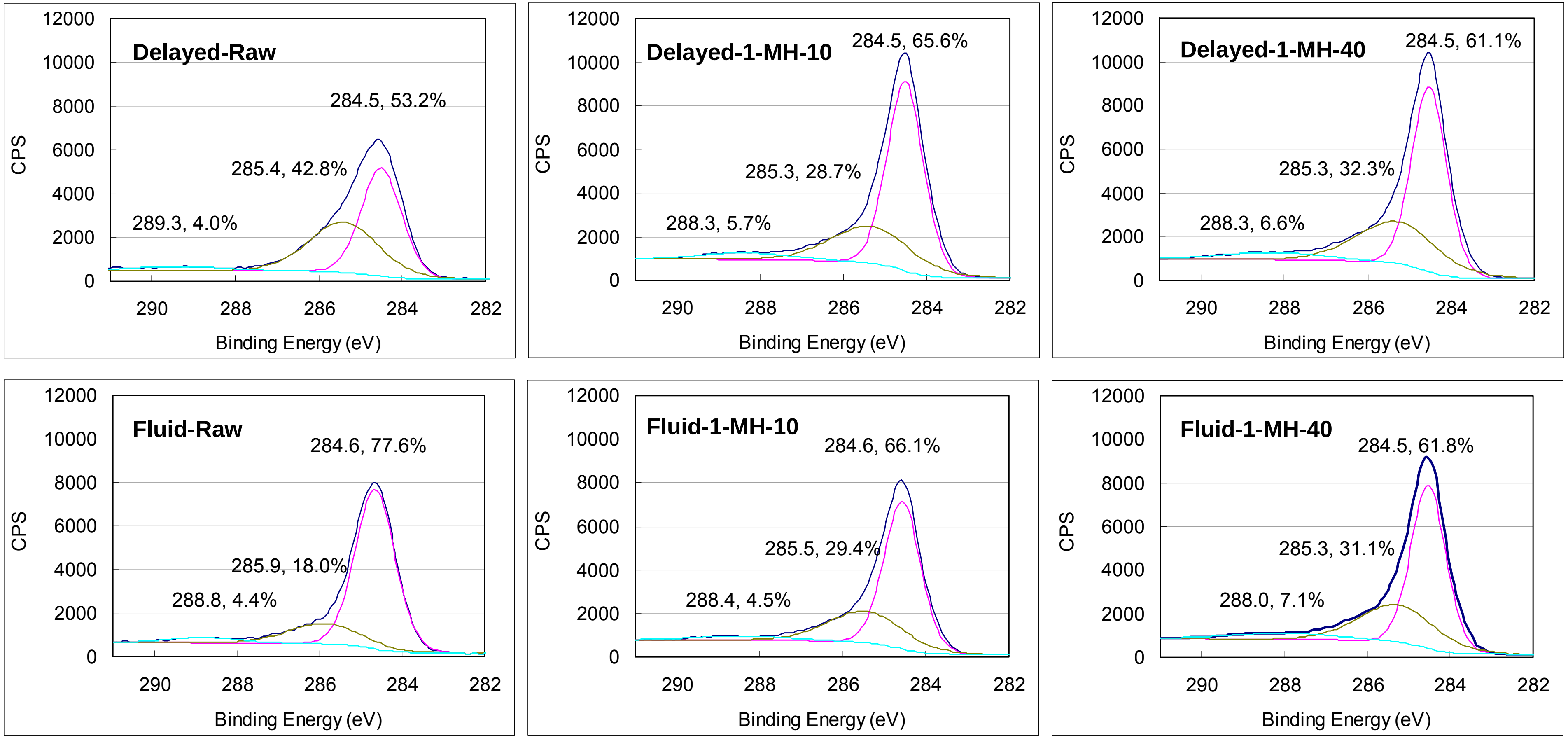


Figure 4-32 Narrow scan and deconvolution of C 1s peak (numbers are the peak position and the count area percentage of the deconvolution)

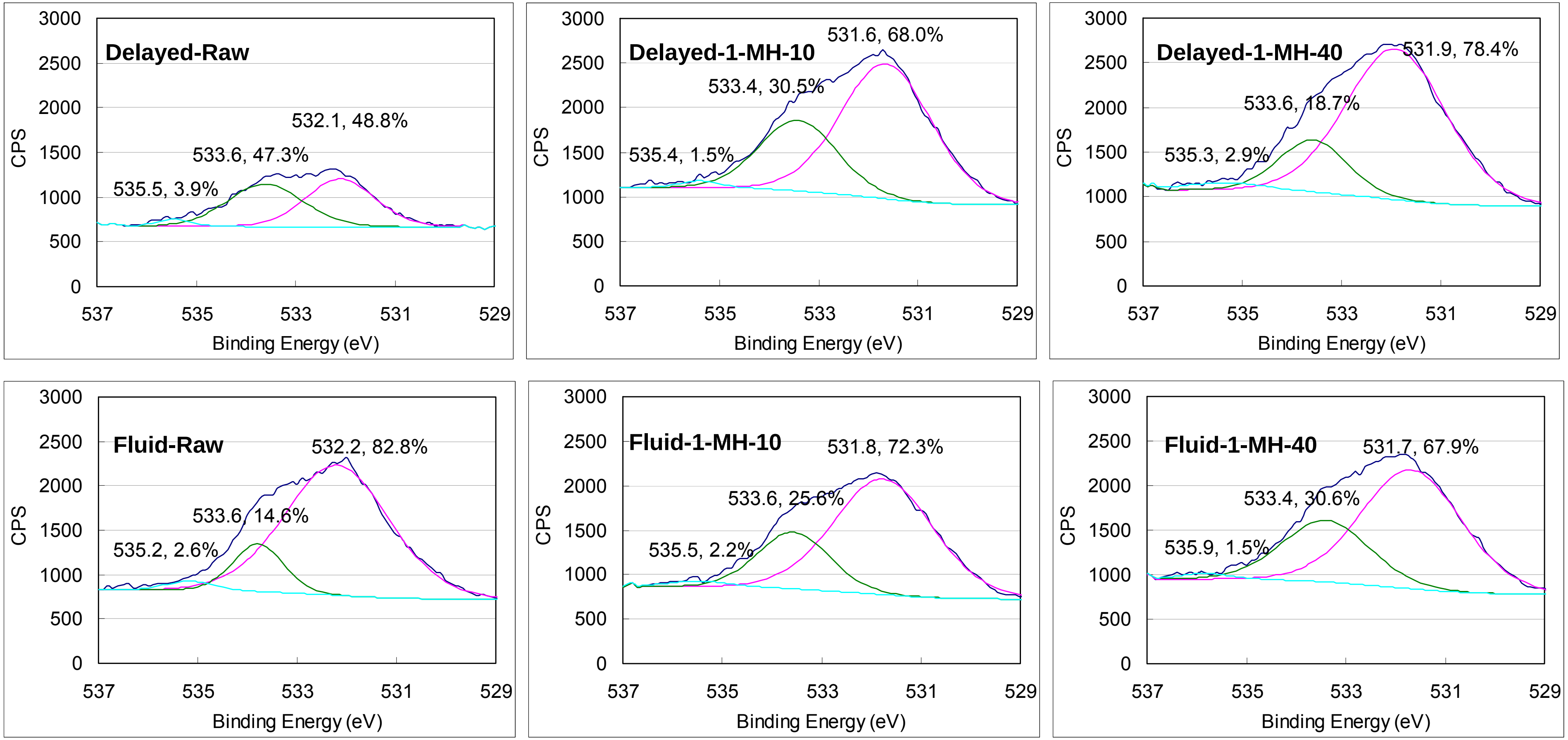


Figure 4-33 Narrow scan and deconvolution of O 1s peak

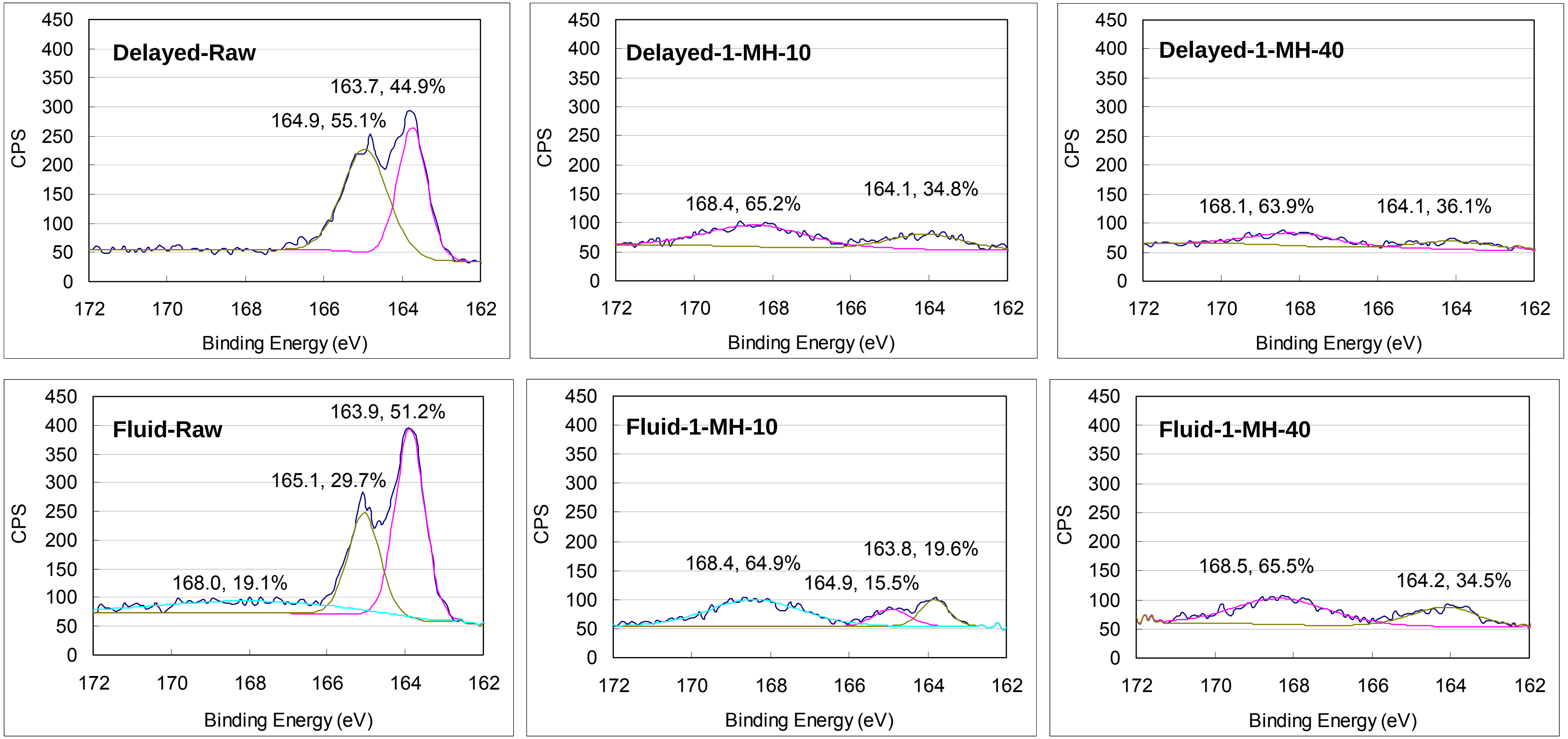


Figure 4-34 Narrow scan and deconvolution of S 2p peak

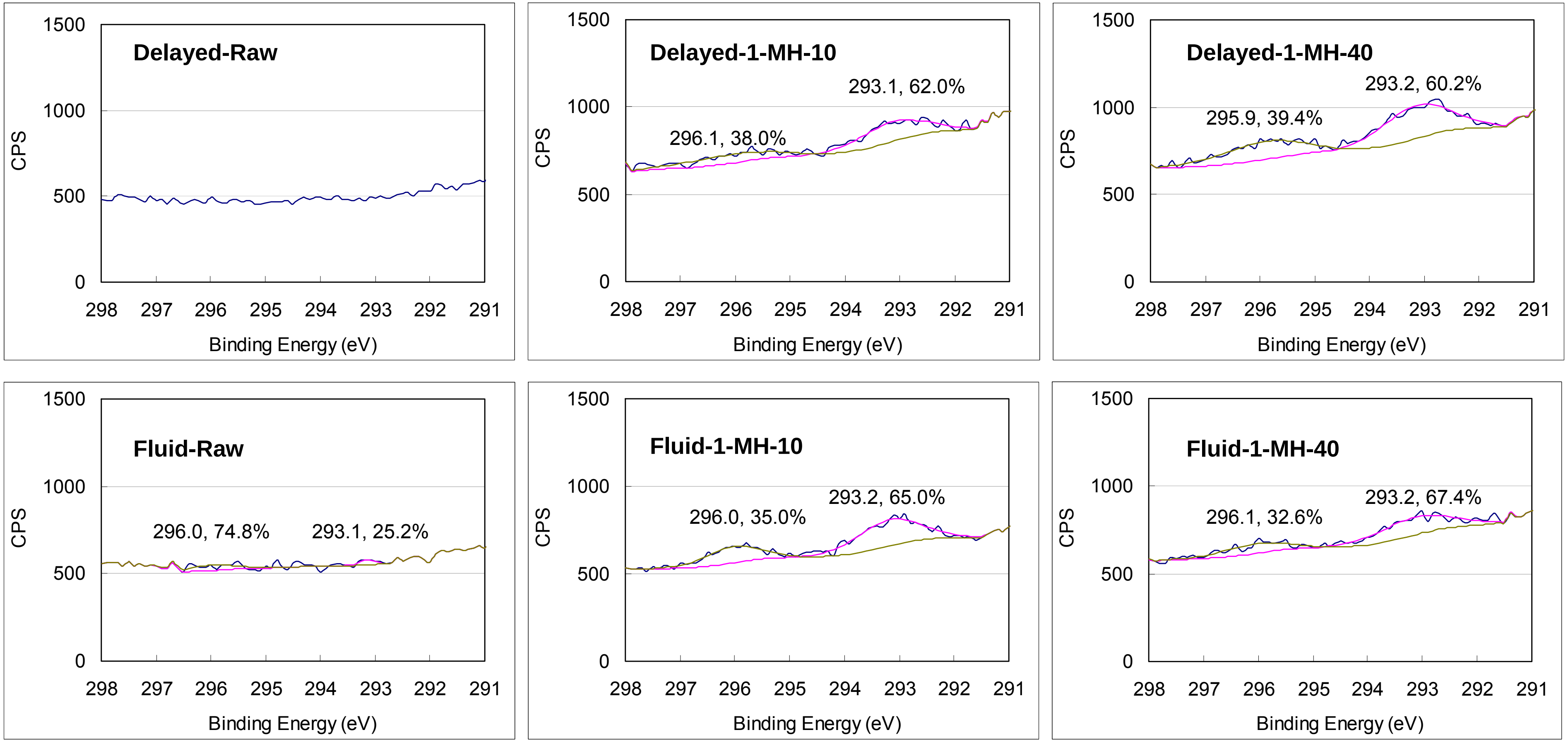
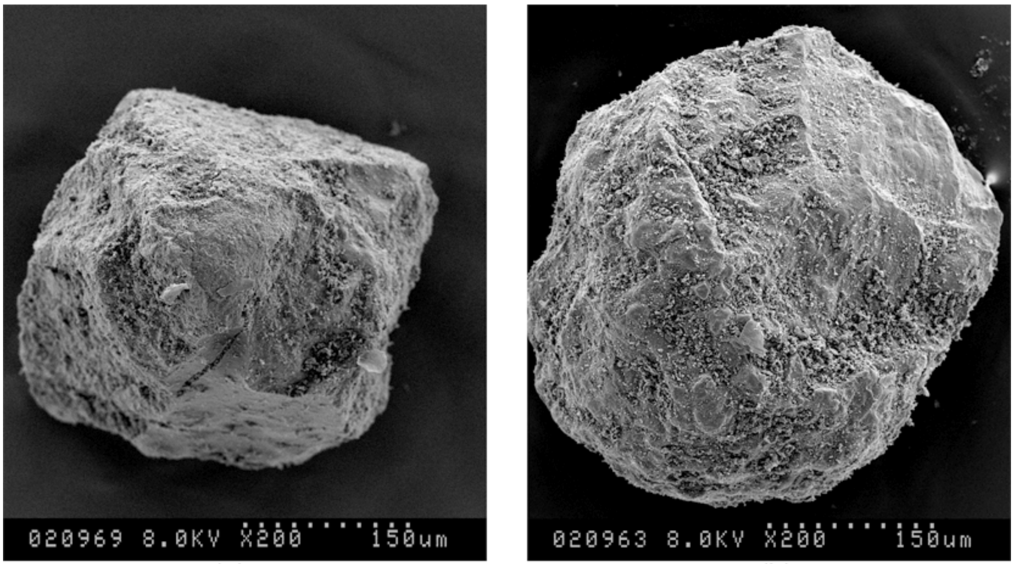


Figure 4-35 Narrow scan and deconvolution of K 2p peak

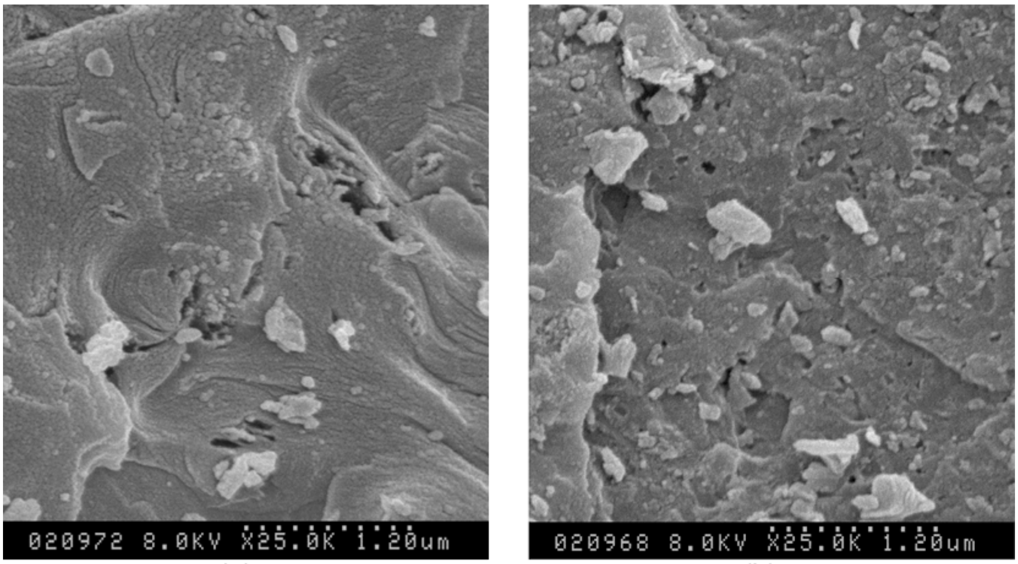
4.3.12 SEM micrographs

The morphology of activated delayed and fluid coke obtained after 10 minutes of microwave heating is illustrated in Figure 4-36. The views of particles are almost the similar at a 200X magnification. Both of them look like a big particle with many fine powders attached to the surface. In comparison with Figure 4-8a, it is clear that the surface of activated fluid coke is not as smooth as the surface of raw coke. Figure 4-37 provides 25000X magnification of the surface of the activated delayed coke and fluid coke, respectively. The shape of these pores is random. The surface of activated fluid coke has more but shallower pores than activated delayed coke. Since the fluid coke has a layered structure, it is hard to make a deep interconnected pore structure, whereas delayed coke has the potential to develop such a porous structure. Compared with the raw coke, it is easy to find that the number of pores in both activated carbons is much more than it in the raw coke. Although these pores are in the macropore range, they are very important because they increase access of the adsorbates to the inner micropores.



(a) (b)

Figure 4-36 Morphology of activated carbon (X200) from delayed coke (a) and fluid coke (b)



(a) (b)

Figure 4-37 Morphology of activated carbon (X25,000) from delayed coke (a) and fluid coke (b)

5 SUMMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and Conclusion

Microwave heating can be a promising method in adsorption applications based on its high energy efficiency and heating selectivity. This study investigated two applications of microwave heating: adsorbent regeneration and the preparation of activated carbon.

For the purpose of adsorbent regeneration, various adsorbents and solvents were selected to cover a wide range of microwave absorption and polarity. Adsorbents consisted of activated carbon, zeolite, ETS10 and silica gel. Solvents included water, heptane and acetone. Thermal behaviors of dry or solvent saturated adsorbents were investigated, from which the following conclusions can be obtained.

1. Based on the difference in the dielectric property between the adsorbent and adsorbate, microwave heating can be selective to preferentially heat either adsorbent or adsorbate.
2. Among the common adsorbents, activated carbon is a strong microwave-absorbing material, while silica gel is a weak microwave-absorbing material. Others like ETS10 and zeolite are among these two.

3. Chemical treatment of adsorbents can greatly change the dielectric property of adsorbents. For instance, silver exchanged ETS10 (Ag-ETS10) depicted a substantially reduced susceptibility for microwave heating compared to ETS10.
4. A strong polar solvent, such as water and acetone, can be quickly heated in microwaves. A trace amount of polar solvent has a strong effect on the thermal behavior during desorption of a weak microwave-absorbing adsorbent with non-polar adsorbate.
5. In addition to the polarity of the adsorbate, the heat of adsorption can influence the temperature profiles and heating rate during the regeneration of an adsorbent.

The use of microwave energy to prepare activated carbon from petroleum coke by chemical activation was also studied. Two different types of petroleum coke, delayed coke and fluid coke were used, and KOH was selected as a chemical activation agent in the study. The properties of activated coke as well as factors influencing these properties were investigated. Based on the work completed, the following conclusions are obtained.

1. Oil sands coke can be a suitable precursor for activated carbon based on its high carbon content. Since it is the product of thermal treatment, it has a low volatile component so that the carbonization process can be ignored during preparation.

2. Delayed coke with a particle size less than 0.85mm is good for activation, while fluid coke has a better activation result with a smaller particle size.
3. Adding some humidity to nitrogen instead of an inert environment (pure nitrogen) during the activation process can bring a positive effect to the activation, especially for delayed coke.
4. The higher the KOH/Coke ratio is, the higher the adsorptive property of activated coke will be. The iodine number of activated coke increased significantly when KOH/Coke ratio increased from 0.25 to 0.5, and kept increasing when the ratio was from 0.5 to 1.
5. Microwave heating can activate petroleum coke in a short duration resulting in activated coke with a high adsorption capacity. For instance, the iodine number was 1129.1 mg/g for delayed coke and 517.1 mg/g for fluid coke activated in 10 minutes of microwave heating, and the activation yield is 74% for delayed coke and 88% for fluid coke.
6. The adsorption capacity does not increase monotonically with the microwave heating time. 30 minutes of microwave heating reduced the iodine number, whereas 40 minutes of heating increased it again. This can be explained by the net effect of new pores creation and the pores mergence and elimination during activation.

7. The BET surface area shows a linear relationship with the iodine number. The pore size distribution demonstrated that more micropores could be found in activated delayed coke than in fluid coke. These results show that the activated delayed coke has more adsorption capacity than activated fluid coke.
8. The relative carbon content of coke increases after activation compared to that of the raw coke. Elemental analysis showed that 10 minutes of microwave heating time resulted in the highest relative carbon content. Longer microwave heating can reduce the relative content of N, H and S, but at the same time it also will burn away more carbon.
9. Activation introduces more oxygen groups such as carboxyl groups at the surface of coke. In addition, XPS confirmed that the sulfur was greatly reduced after activation and some potassium was left after washing of activated coke.

5.2 Recommendation

The above results demonstrate that microwave heating has great prospects for environmental applications. However, further studies are required.

As for the adsorbent regeneration by microwaves, the mass balance of solvent needs to be studied for the real application. The power consumption is also an important factor that needs to be measured. In addition, adsorption-desorption cycle should be completed to measure the efficiency of microwave regeneration and to evaluate the lifespan of adsorbent by microwave regeneration.

As for the oil sands coke activation, scaling up is the most important issue for the real industrial application. Pilot scale testing is necessary to confirm the feasibility of commercializing this novel technology. More studies are needed to further reduce cost, for instance, by optimizing the KOH/water vapor ratio or using physical activation with steam to reduce the consumption of KOH. Additionally, adsorption capacity in real applications, such as removal mercury from flue gas or organic pollutants from water, is also critical for marketing the activated coke.

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APPENDICES

Appendix A. Temperature Profile of Raw Fluid Coke during Low Power Level Microwave Heating

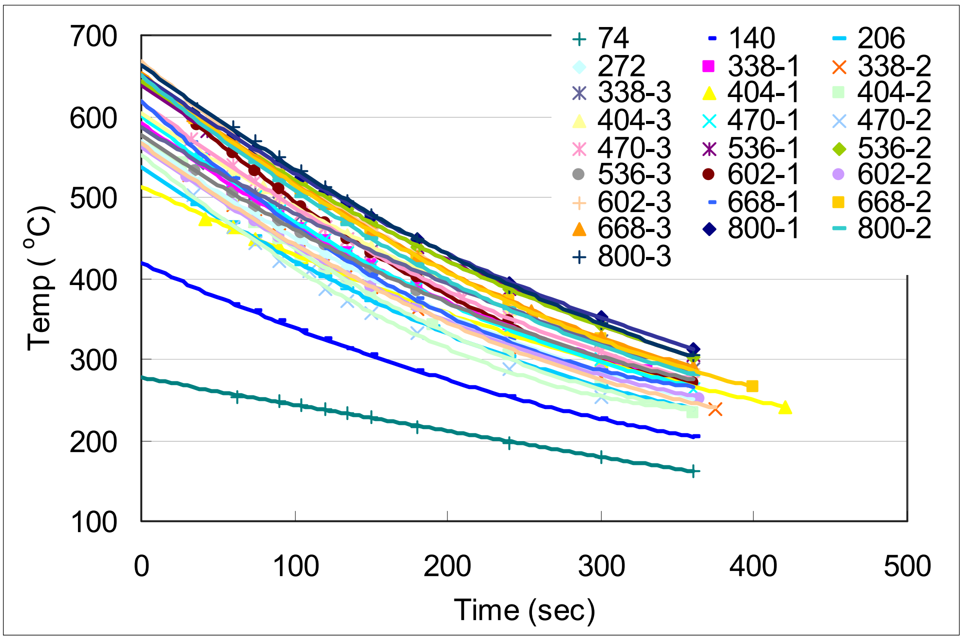

Figure A-1 Measured temperature of raw fluid coke as a function of time after shutdown

(The number in the label is in the format a-b, the number a means the microwave heating time, and the number b is the test number)

Table A-1 Temperature of raw fluid coke immediately after shutdown as a function of microwave heating time

Heating time	(sec)	0	74	140	206	272	338
	(min)	0	1.2	2.3	3.4	4.5	5.6
Temp	(^{o}C)	22.0	277.1	418.2	537.1	568.0	581.2
Heating time	(sec)	404	470	536	602	668	800
	(min)	6.7	7.8	8.9	10	11.1	13.3
Temp	(^{o}C)	564.3	590.3	619.0	626.6	640.8	654.0

Appendix B. Results of Iodine Number Tests

Table B-1 Iodine number of the raw coke and commercial GAC

Sample	Raw delayed coke	Raw fluid coke	GAC
1#	22.9	29.9	1178.8
2#	23.8	27.6	1136.1
3#	16.7	28.9	
4#	23.6	27.3	
Average	21.8	28.4	1157.5
Standard deviation	3.4	1.2	30.2

Note: The iodine number of raw coke was tested four times.

Table B-2 Iodine number of Figure 4-9

Particle size	I (4.76-2mm)		II (0.85-0.6mm)		III (0.42-0.3mm)	
	Delayed	Fluid	Delayed	Fluid	Delayed	Fluid
1#	142.5	105.9	395.1	129.9	391.3	195.3
2#	132.5	77.7	397.4	155.2	397.0	187.9
3#			371.2			
4#			394.7			
Average	137.5	91.8	389.6	142.5	394.1	191.6
Standard deviation	7.1	20.0	12.3	17.9	4.0	5.3

Note: The activation of delayed coke (size II) was duplicated and the iodine number test was completed twice for each activation.

Table B-3 Iodine number of Figure 4-11

Humidity influence	No humidity		Humidity	
	Delayed	Fluid	Delayed	Fluid
1#	391.3	195.3	465.0	204.8
2#	397.0	187.9	460.5	192.9
Average	394.1	191.6	462.7	198.8
Standard deviation	4.0	5.3	3.2	8.4

Table B-4 Iodine number of Figure 4-14

Power level	Low		Medium	
	Delayed	Fluid	Delayed	Fluid
1#	465.0	204.8	824.9	465.9
2#	460.5	192.9	783.0	467.4
Average	462.7	198.8	804.0	466.7
Standard deviation	3.2	8.4	29.6	1.0

Table B-5 Iodine number of Figure 4-16

KOH/Coke Ratio	0.25		0.5		1.0	
	Delayed	Fluid	Delayed	Fluid	Delayed	Fluid
1#	115.0	98.2	824.9	465.9	848.8	500.0
2#	134.6	69.3	783.0	467.4	869.2	517.9
3#		99.0			941.1	
4#					944.7	
Average	124.8	88.8	804.0	466.7	900.9	509.0
Standard deviation	13.8	17.0	29.6	1.0	49.2	12.6

Note: The iodine number for fluid coke with KOH/Coke ratio at 0.25 was based on triplicates. The activation of delayed coke with KOH/Coke ratio at 1 was duplicated and the iodine number test was completed twice for each activation.

Table B-6 Iodine number of Figure 4-18

Time (min)	5		10		20		30		40	
	Delayed	Fluid	Delayed	Fluid	Delayed	Fluid	Delayed	Fluid	Delayed	Fluid
1#	452.7	204.0	1044.5	518.9	1174.7	555.8	848.8	500.0	1185.7	685.7
2#	450.8	177.7	1043.1	515.3	1171.8	554.5	869.2	517.9	1182.0	685.9
3#			1192.0		1141.3		941.1		1296.6	
4#			1237.0		1141.3		944.7		1295.7	
Average	451.7	190.9	1129.1	517.1	1157.3	555.2	900.9	509.0	1240.0	685.8
Standard deviation	1.4	18.6	100.2	2.6	18.5	0.9	49.2	12.6	64.8	0.1

Note: The activation of delayed coke with 10, 20, 30 and 40 minutes microwave heating was duplicated and the iodine number test was completed twice for each activation.

Appendix C. Nitrogen Adsorption Isotherms

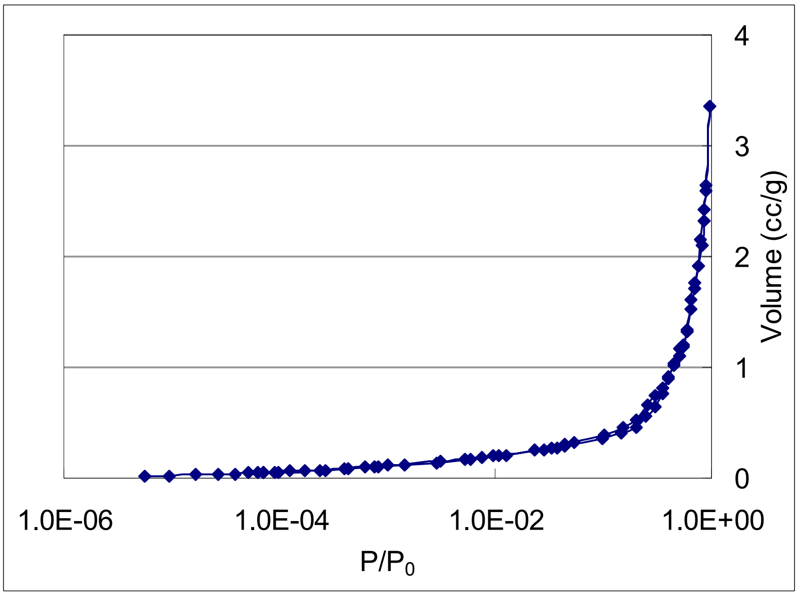

Figure C-1 Isotherm of raw delayed coke

Table C-1 Data of isotherm of raw delayed coke

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
5.65E-06	0.0154	1.05E-02	0.207	7.52E-01	1.9237	2.48E-01	0.5631
9.47E-06	0.0234	2.28E-02	0.2489	8.02E-01	2.1007	1.98E-01	0.4523
1.64E-05	0.0308	3.30E-02	0.2756	8.51E-01	2.3255	1.48E-01	0.4014
2.69E-05	0.037	4.32E-02	0.2984	9.01E-01	2.6414	9.74E-02	0.3489
3.91E-05	0.0421	5.30E-02	0.3155	9.52E-01	3.3526	4.37E-02	0.2812
5.09E-05	0.0459	1.03E-01	0.3946	8.97E-01	2.5918	3.70E-02	0.2685
6.16E-05	0.0488	1.53E-01	0.4617	8.47E-01	2.4212	2.81E-02	0.2499
7.06E-05	0.051	2.03E-01	0.5259	7.99E-01	2.1573	1.28E-02	0.2087
9.63E-05	0.0563	2.52E-01	0.6531	7.48E-01	1.9195	5.90E-03	0.1735
2.31E-04	0.0734	3.02E-01	0.7386	6.98E-01	1.7125	2.80E-03	0.1432
4.02E-04	0.0864	3.52E-01	0.8216	6.48E-01	1.522	1.42E-03	0.1188
6.06E-04	0.0972	4.02E-01	0.9164	5.98E-01	1.3463	7.55E-04	0.1027

8.18E-04	0.1059	4.52E-01	1.0086	5.48E-01	1.1879	4.30E-04	0.0875
1.01E-03	0.1124	5.02E-01	1.1063	4.96E-01	1.1683	2.63E-04	0.0755
3.05E-03	0.1497	5.52E-01	1.21	4.48E-01	1.0263	1.73E-04	0.0659
5.20E-03	0.1718	6.02E-01	1.3229	3.98E-01	0.8928	1.22E-04	0.0594
7.33E-03	0.1882	6.50E-01	1.6064	3.48E-01	0.7659	8.98E-05	0.0549
9.46E-03	0.2002	7.02E-01	1.7601	2.98E-01	0.6512	6.93E-05	0.0507

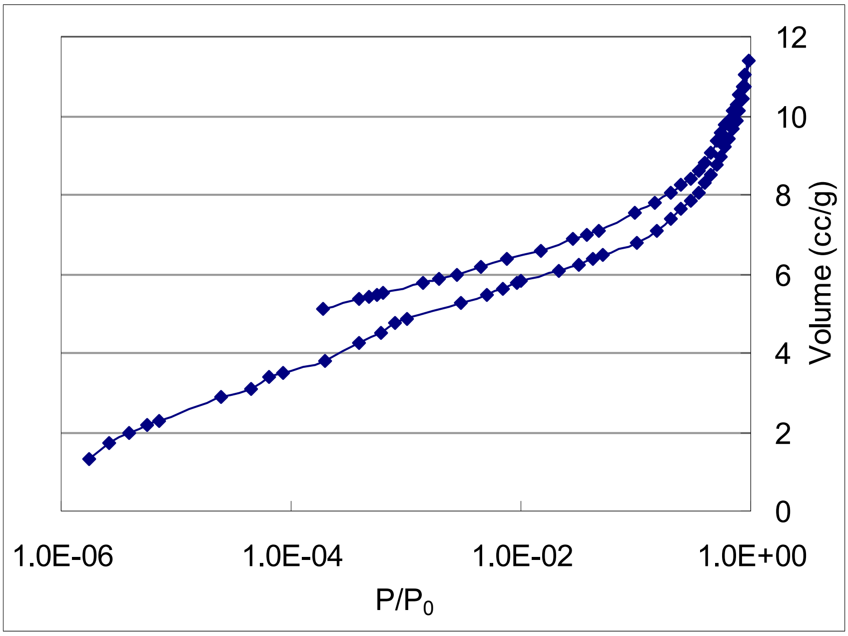

Figure C-2 Isotherm of raw fluid coke

Table C-2 Data of isotherm of raw fluid coke

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
1.74E-06	1.2948	1.02E-02	5.8275	7.51E-01	9.8847	2.49E-01	8.263
2.59E-06	1.7273	2.15E-02	6.0735	8.01E-01	10.1372	1.99E-01	8.0498
3.87E-06	1.9993	3.20E-02	6.2378	8.51E-01	10.4125	1.49E-01	7.8147
5.60E-06	2.1927	4.23E-02	6.3631	9.00E-01	10.7374	9.96E-02	7.5437
7.00E-06	2.2963	5.24E-02	6.4688	9.52E-01	11.404	4.73E-02	7.0959
2.48E-05	2.8717	1.00E-01	6.8034	9.00E-01	11.014	3.79E-02	6.9932
4.49E-05	3.0848	1.51E-01	7.0793	8.49E-01	10.7539	2.88E-02	6.8745
6.45E-05	3.3801	2.00E-01	7.3786	7.99E-01	10.5125	1.48E-02	6.561
8.48E-05	3.5139	2.51E-01	7.6214	7.49E-01	10.28	7.61E-03	6.3651
1.96E-04	3.8215	3.01E-01	7.85	6.98E-01	10.1234	4.42E-03	6.1626
3.97E-04	4.2589	3.51E-01	8.0743	6.49E-01	9.8973	2.80E-03	5.9965
6.00E-04	4.5247	4.01E-01	8.2983	5.98E-01	9.794	1.93E-03	5.8611

8.03E-04	4.7432	4.51E-01	8.5176	5.49E-01	9.5796	1.42E-03	5.75
1.00E-03	4.8596	5.01E-01	8.7393	4.99E-01	9.3642	6.32E-04	5.5294
3.03E-03	5.2618	5.51E-01	8.9639	4.50E-01	9.0745	5.49E-04	5.4809
5.09E-03	5.4738	6.01E-01	9.2186	3.99E-01	8.8314	4.85E-04	5.4372
7.09E-03	5.62	6.51E-01	9.4329	3.49E-01	8.6194	3.89E-04	5.3627
9.27E-03	5.7644	7.01E-01	9.6593	2.99E-01	8.4154	1.91E-04	5.1223

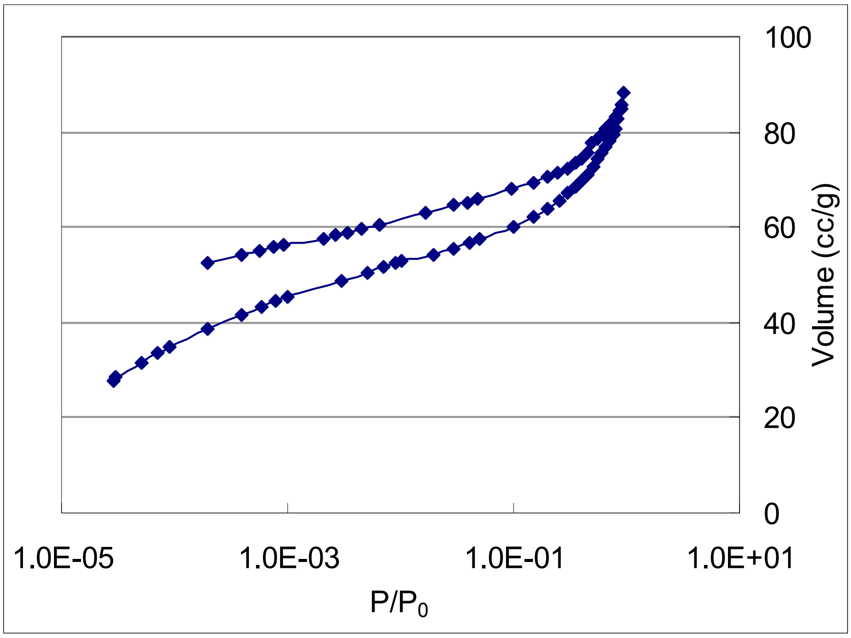

Figure C-3 Isotherm of activated delayed coke 0.5-L-30 (Activation condition is explained in chapter 4.3.8)

Table C-3 Data of isotherm of activated delayed coke 0.5-L-30

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
2.86E-05	27.8561	4.03E-02	56.57	8.49E-01	82.9824	2.00E-01	70.5308
3.00E-05	28.3971	5.04E-02	57.4243	9.01E-01	85.03	1.51E-01	69.3716
5.01E-05	31.6022	9.91E-02	60.1684	9.50E-01	88.028	9.72E-02	67.8737
7.01E-05	33.6426	1.50E-01	62.291	8.97E-01	85.7478	4.86E-02	65.8547
9.01E-05	34.9514	2.00E-01	64.042	8.51E-01	84.4024	3.85E-02	65.211
1.99E-04	38.7843	2.51E-01	65.5649	8.00E-01	83.1927	2.95E-02	64.5082
3.99E-04	41.5986	3.01E-01	67.1745	7.50E-01	82.0976	1.64E-02	63.0551
6.00E-04	43.4486	3.52E-01	68.5498	7.00E-01	81.1067	6.50E-03	60.4773
7.99E-04	44.3627	4.02E-01	69.8865	6.49E-01	80.5188	4.54E-03	59.57
9.99E-04	45.3651	4.52E-01	71.2002	6.00E-01	79.5588	3.37E-03	58.8208
3.00E-03	48.838	5.02E-01	72.4986	5.50E-01	78.6088	2.62E-03	58.1941

5.01E-03	50.3884	5.50E-01	74.2112	5.00E-01	77.6769	2.12E-03	57.66
7.03E-03	51.4724	6.02E-01	75.5069	4.49E-01	75.5	9.06E-04	56.1418
9.20E-03	52.3855	6.52E-01	76.8	4.01E-01	74.3114	7.66E-04	55.7798
1.00E-02	52.7622	7.02E-01	78.0312	3.50E-01	73.3314	5.72E-04	55.1251
1.92E-02	54.3902	7.52E-01	79.3327	3.00E-01	72.4157	3.95E-04	54.28
2.96E-02	55.6127	8.02E-01	80.7551	2.50E-01	71.5794	1.99E-04	52.5624

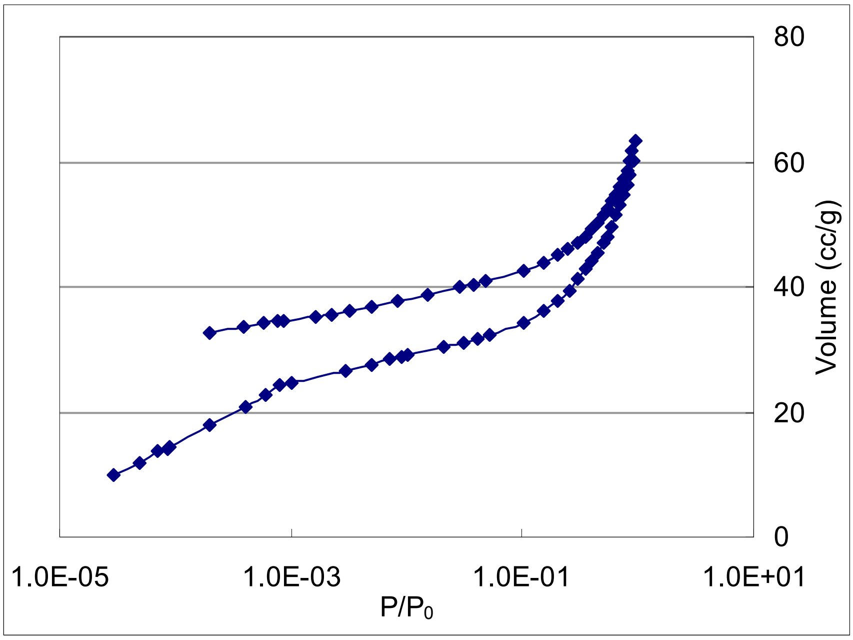

Figure C-4 Isotherm of activated fluid coke 0.5-L-30

Table C-4 Data of isotherm of activated fluid coke 0.5-L-30

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
2.98E-05	9.9264	4.15E-02	31.7184	8.52E-01	58.0328	2.00E-01	44.973
4.98E-05	11.7446	5.16E-02	32.3191	9.02E-01	60.1274	1.51E-01	43.8598
6.96E-05	13.7491	1.01E-01	34.3302	9.50E-01	63.487	1.01E-01	42.6147
8.48E-05	14.124	1.51E-01	36.1635	8.95E-01	61.6742	4.86E-02	40.8677
9.02E-05	14.2906	2.02E-01	37.83	8.47E-01	60.0412	3.82E-02	40.3612
2.00E-04	17.9752	2.52E-01	39.4081	8.01E-01	58.6514	2.92E-02	39.8495
3.99E-04	20.9206	3.01E-01	41.2605	7.51E-01	57.2981	1.51E-02	38.7786
6.00E-04	22.7711	3.52E-01	42.8084	7.01E-01	56.033	8.45E-03	37.6523
7.99E-04	24.2588	4.02E-01	44.286	6.50E-01	54.844	5.01E-03	36.83
1.01E-03	24.5514	4.49E-01	45.4474	6.00E-01	53.7067	3.22E-03	36.1716
3.02E-03	26.6502	5.02E-01	46.9428	5.50E-01	52.6226	2.23E-03	35.6453
5.01E-03	27.5877	5.49E-01	48.1258	5.00E-01	51.5702	1.65E-03	35.2084

7.08E-03	28.3651	6.02E-01	49.6123	4.50E-01	50.3567	8.64E-04	34.68
9.08E-03	28.9323	6.51E-01	51.6095	4.01E-01	49.1872	7.61E-04	34.5281
1.00E-02	29.2723	7.02E-01	53.1488	3.50E-01	48.1156	5.85E-04	34.1765
2.08E-02	30.2814	7.52E-01	54.6979	3.00E-01	47.0681	3.83E-04	33.6514
3.11E-02	31.0884	8.02E-01	56.3079	2.50E-01	46.0353	1.96E-04	32.7649

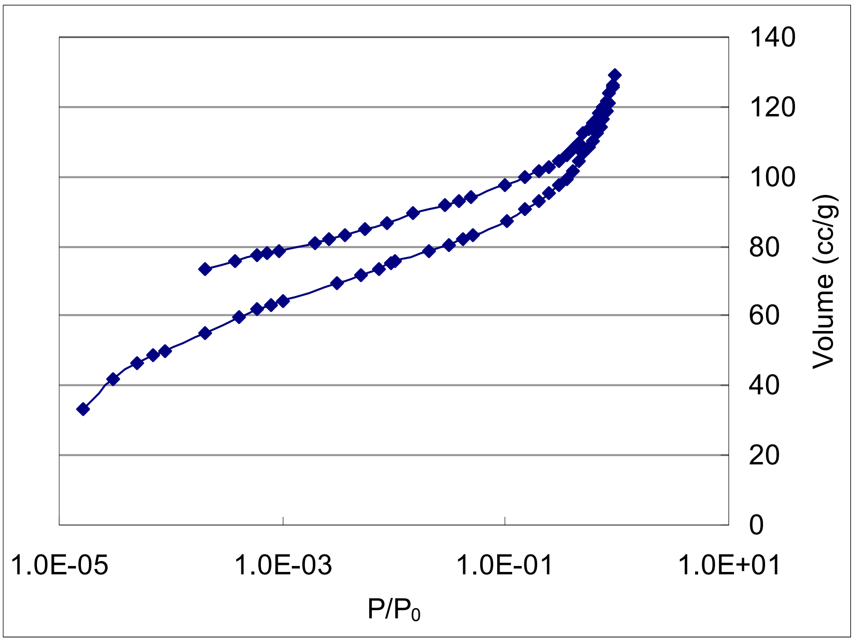

Figure C-5 Isotherm of activated delayed coke 0.5-LH-30

Table C-5 Data of isotherm of activated delayed coke 0.5-LH-30

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
1.64E-05	33.469	4.11E-02	81.9106	8.49E-01	121.0566	1.99E-01	101.4712
3.00E-05	41.9956	5.14E-02	83.1783	9.02E-01	125.4699	1.49E-01	99.5686
5.00E-05	46.2252	1.01E-01	87.3686	9.52E-01	129.019	9.97E-02	97.3341
7.02E-05	48.6712	1.52E-01	90.7894	9.00E-01	126.1234	4.80E-02	93.8761
9.03E-05	49.9642	1.99E-01	93.0102	8.50E-01	123.7522	3.77E-02	92.8655
1.99E-04	55.3571	2.49E-01	95.2203	7.99E-01	121.6553	2.88E-02	91.765
4.01E-04	59.469	3.00E-01	97.3788	7.49E-01	119.7872	1.51E-02	89.2735
5.99E-04	61.996	3.50E-01	99.396	6.99E-01	118.0124	8.82E-03	86.6969
8.00E-04	63.3159	4.00E-01	101.377	6.48E-01	116.7177	5.42E-03	84.8367
1.00E-03	64.5186	4.52E-01	104.5168	5.98E-01	115.6133	3.62E-03	83.3261
3.07E-03	69.3588	5.00E-01	106.4509	5.49E-01	113.8916	2.61E-03	82.0699
5.06E-03	71.5704	5.50E-01	108.4336	4.99E-01	112.215	1.98E-03	81.0456

7.20E-03	73.6416	6.00E-01	110.3434	4.50E-01	109.6049	9.24E-04	78.715
9.27E-03	75.0212	6.50E-01	112.3252	3.99E-01	107.8013	7.19E-04	77.896
1.02E-02	75.6987	7.00E-01	114.3398	3.49E-01	106.1009	5.86E-04	77.1978
2.05E-02	78.5942	7.50E-01	116.4173	2.99E-01	104.4836	3.80E-04	75.6071
3.08E-02	80.4708	8.00E-01	118.6398	2.49E-01	102.8584	2.00E-04	73.2018

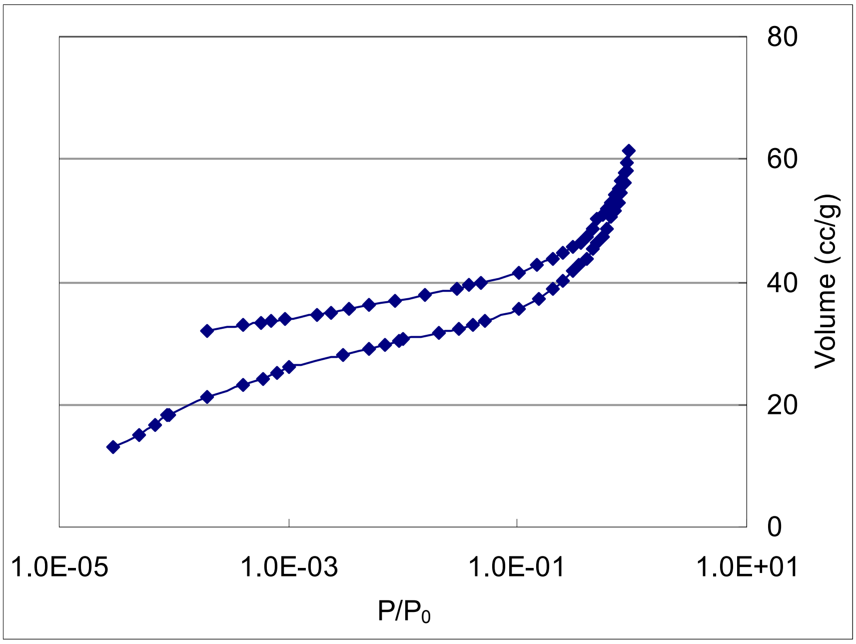

Figure C-6 Isotherm of activated fluid coke 0.5-LH-30

Table C-6 Data of isotherm of activated fluid coke 0.5-LH-30

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
2.99E-05	12.9676	4.13E-02	33.0967	8.52E-01	56.1296	2.00E-01	43.6822
4.96E-05	15.0096	5.15E-02	33.6756	9.02E-01	58.141	1.50E-01	42.6592
6.95E-05	16.6368	1.01E-01	35.5909	9.50E-01	61.4532	1.01E-01	41.5795
8.87E-05	18.1903	1.51E-01	37.2402	8.95E-01	59.4909	4.84E-02	39.894
9.03E-05	18.2409	2.02E-01	38.707	8.47E-01	57.8238	3.83E-02	39.4238
1.99E-04	21.1099	2.52E-01	40.112	8.01E-01	56.5035	2.93E-02	38.9288
4.00E-04	23.1667	3.02E-01	41.6478	7.51E-01	55.2379	1.53E-02	37.8805
6.02E-04	24.3215	3.49E-01	42.7329	7.01E-01	54.0648	8.52E-03	36.8667
8.00E-04	25.2549	3.99E-01	43.8723	6.50E-01	52.9801	5.10E-03	36.087
1.00E-03	26.0064	4.52E-01	45.242	6.00E-01	51.9313	3.34E-03	35.4524
3.01E-03	28.0497	4.99E-01	46.2971	5.50E-01	50.9352	2.34E-03	34.9449
5.04E-03	29.1017	5.49E-01	47.4064	4.99E-01	50.3335	1.75E-03	34.5234

7.07E-03	29.8081	5.99E-01	48.5406	4.48E-01	48.5242	9.34E-04	34.0089
9.06E-03	30.3433	6.50E-01	50.476	4.00E-01	47.4928	7.18E-04	33.6706
1.00E-02	30.6545	6.99E-01	51.6549	3.50E-01	46.5176	5.73E-04	33.3636
2.05E-02	31.6646	7.52E-01	53.0306	3.00E-01	45.5749	4.00E-04	32.889
3.09E-02	32.4526	8.02E-01	54.5257	2.50E-01	44.6393	1.98E-04	31.9398

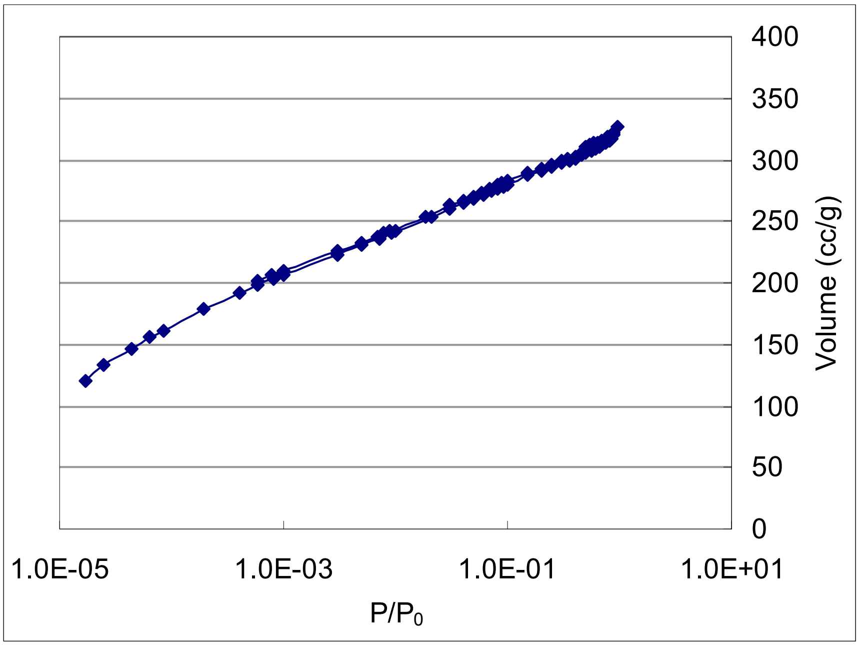

Figure C-7 Isotherm of activated delayed coke 1-MH-10

Table C-7 Data of isotherm of activated delayed coke 1-MH-10

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
1.68E-05	119.7212	6.06E-02	271.666	8.49E-01	317.8838	1.01E-01	282.7676
2.47E-05	133.4942	7.11E-02	274.4357	9.00E-01	321.0809	8.83E-02	280.5622
4.44E-05	147.0058	8.15E-02	276.7863	9.50E-01	327.0208	8.05E-02	279.0104
6.45E-05	155.6602	9.17E-02	278.8153	8.99E-01	322.7054	6.86E-02	276.3506
8.47E-05	161.6805	9.96E-02	280.2407	8.48E-01	320.2863	5.86E-02	273.7116
1.95E-04	178.7077	1.51E-01	287.0394	7.97E-01	318.4792	4.91E-02	270.6639
3.97E-04	191.4232	2.00E-01	291.2946	7.45E-01	317.4357	3.97E-02	267.0166
5.98E-04	198.2114	2.51E-01	294.6618	7.01E-01	316.1432	3.07E-02	262.6307
7.99E-04	202.8521	3.01E-01	297.3506	6.47E-01	314.5705	1.87E-02	254.1784
1.00E-03	206.3066	3.51E-01	299.6079	5.97E-01	313.1307	8.88E-03	242.1411
3.01E-03	222.805	4.02E-01	301.5581	5.47E-01	311.6847	7.71E-03	239.9253
5.02E-03	230.6162	4.52E-01	303.3071	4.97E-01	310.1784	6.79E-03	237.944

7.07E-03	235.9647	5.01E-01	305.3382	4.50E-01	305.529	4.96E-03	233.1846
9.05E-03	239.8983	5.52E-01	306.9647	3.98E-01	303.0623	2.98E-03	225.6058
1.01E-02	241.8174	6.02E-01	308.4938	3.48E-01	301.0726	9.90E-04	210.0083
2.10E-02	253.4398	6.52E-01	310.0104	2.98E-01	298.9025	7.92E-04	206.7438
3.03E-02	259.666	7.02E-01	311.5809	2.47E-01	296.4792	5.94E-04	202.1261
4.10E-02	264.8589	7.52E-01	313.249	1.98E-01	293.307		
5.04E-02	268.444	8.02E-01	315.1058	1.49E-01	289.0332		

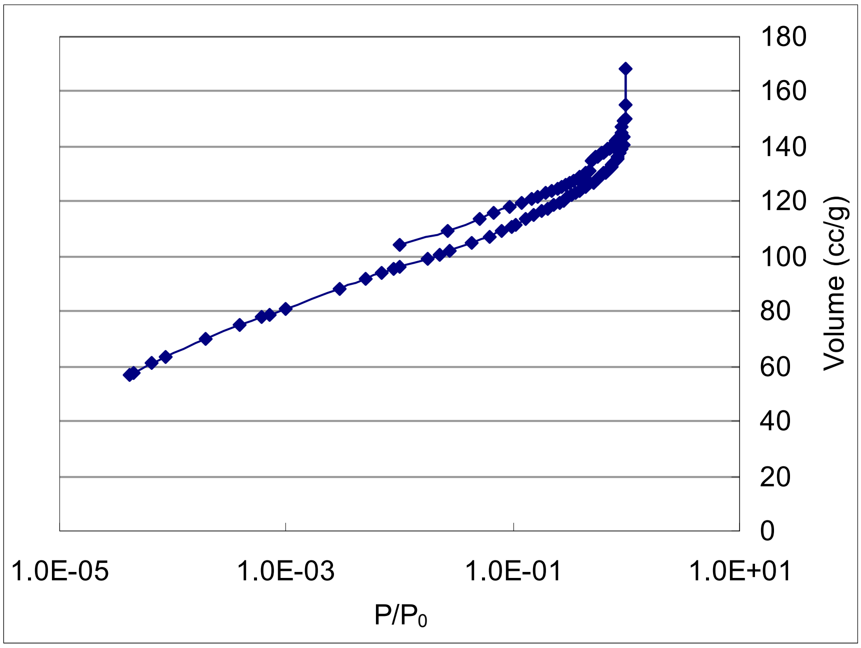

Figure C-8 Isotherm of activated fluid coke 1-MH-10

Table C-8 Data of isotherm of activated fluid coke 1-MH-10

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
2.43E-05	52.5257	1.81E-01	116.3108	8.07E-01	134.8086	5.68E-01	136.3871
4.17E-05	56.9737	2.06E-01	117.5387	8.32E-01	135.5968	5.42E-01	136.0301
4.44E-05	57.8295	2.31E-01	118.6387	8.55E-01	136.4817	5.17E-01	135.671
6.45E-05	60.9682	2.56E-01	119.6387	8.81E-01	137.6011	4.95E-01	134.4871
8.48E-05	63.332	2.82E-01	120.5613	9.06E-01	139.0043	4.74E-01	131.4968
1.94E-04	69.9423	3.07E-01	121.4301	9.29E-01	140.8688	4.46E-01	130.1236
3.95E-04	75.0418	3.32E-01	122.2355	9.51E-01	143.6183	4.19E-01	129.3376
5.96E-04	77.8219	3.56E-01	123.1774	9.75E-01	150.1656	3.93E-01	128.6656
7.18E-04	78.943	3.82E-01	123.9151	9.95E-01	168.3312	3.67E-01	128.1591
9.97E-04	80.9589	4.07E-01	124.6	9.77E-01	155.2925	3.42E-01	127.6054
3.00E-03	88.4354	4.32E-01	125.2473	9.44E-01	149.3172	3.18E-01	126.9667
5.01E-03	91.8102	4.57E-01	125.8678	9.23E-01	147.0936	2.93E-01	126.2731

7.01E-03	93.8487	4.82E-01	126.4634	8.96E-01	145.1957	2.68E-01	125.5376
9.01E-03	95.4035	5.07E-01	127.0527	8.71E-01	143.8376	2.43E-01	124.7516
1.01E-02	96.1348	5.32E-01	127.6054	8.45E-01	142.7366	2.18E-01	123.9
1.77E-02	99.0627	5.56E-01	128.2398	8.20E-01	141.8247	1.93E-01	122.9634
2.21E-02	100.4329	5.82E-01	128.9978	7.93E-01	141.0097	1.68E-01	121.9591
2.72E-02	101.7382	6.07E-01	129.5699	7.70E-01	140.3172	1.44E-01	120.7935
4.28E-02	104.6809	6.32E-01	130.1172	7.42E-01	139.9613	1.19E-01	119.429
6.31E-02	107.4092	6.57E-01	130.6656	7.18E-01	139.4667	9.48E-02	117.8301
8.01E-02	109.2656	6.83E-01	131.2344	6.94E-01	138.9022	6.83E-02	115.657
9.58E-02	110.7323	7.07E-01	131.8054	6.68E-01	138.3785	5.07E-02	113.7355
1.07E-01	111.728	7.32E-01	132.3806	6.43E-01	137.8839	2.60E-02	109.6043
1.30E-01	113.4194	7.56E-01	133.0065	6.18E-01	137.3721	9.89E-03	104.1803
1.55E-01	114.9537	7.80E-01	134.0591	5.93E-01	136.8634		

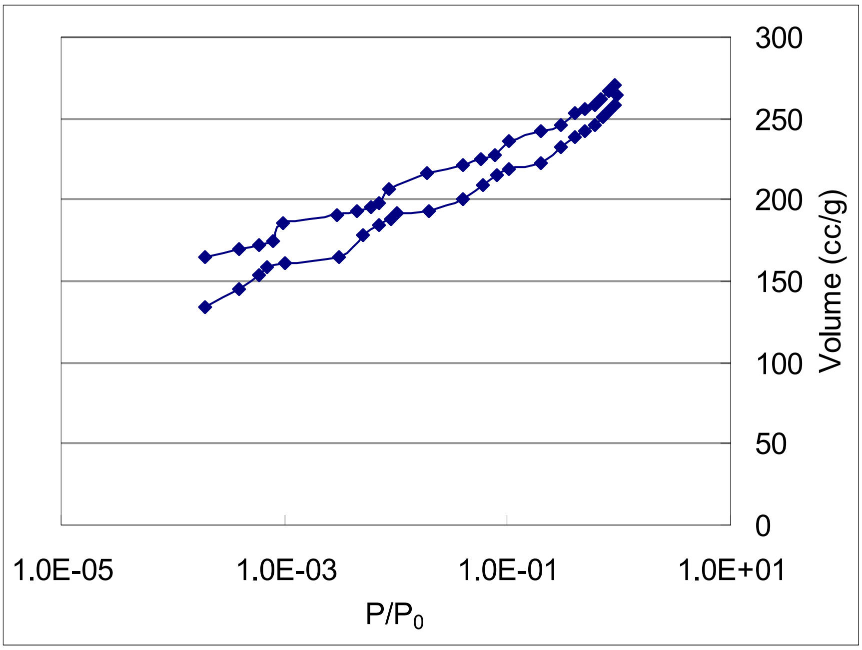

Figure C-9 Isotherm of activated delayed coke 1-MH-30

Table C-9 Data of isotherm of activated delayed coke 1-MH-30

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
9.50E-05	133.4533	4.02E-02	209.5362	9.50E-01	270.2723	4.00E-02	216.0769
1.95E-04	144.4962	5.94E-02	214.7889	8.96E-01	266.3181	1.93E-02	207.1289
3.97E-04	154.0147	8.01E-02	218.9227	7.98E-01	261.988	8.70E-03	197.8602
5.97E-04	159.0166	1.01E-01	222.1882	6.97E-01	258.7807	7.13E-03	195.5993
7.02E-04	160.8921	2.00E-01	231.9759	5.97E-01	255.8916	5.99E-03	193.6398
1.00E-03	165.2831	3.02E-01	238.3123	4.97E-01	253.0771	4.48E-03	190.4499
3.03E-03	178.0622	4.00E-01	242.5904	3.98E-01	245.9735	2.93E-03	185.8562
5.03E-03	184.0364	5.01E-01	246.3566	2.98E-01	241.8386	9.92E-04	174.8429
7.02E-03	188.2357	5.99E-01	250.3928	1.98E-01	236.4615	7.81E-04	172.2764
9.12E-03	191.4576	7.01E-01	254.1133	1.01E-01	227.7092	5.98E-04	169.2988
1.00E-02	192.7906	8.00E-01	258.3928	7.84E-02	224.5024	3.96E-04	164.5316
2.01E-02	200.7834	9.01E-01	264.5494	5.88E-02	220.9152	1.97E-04	155.7366

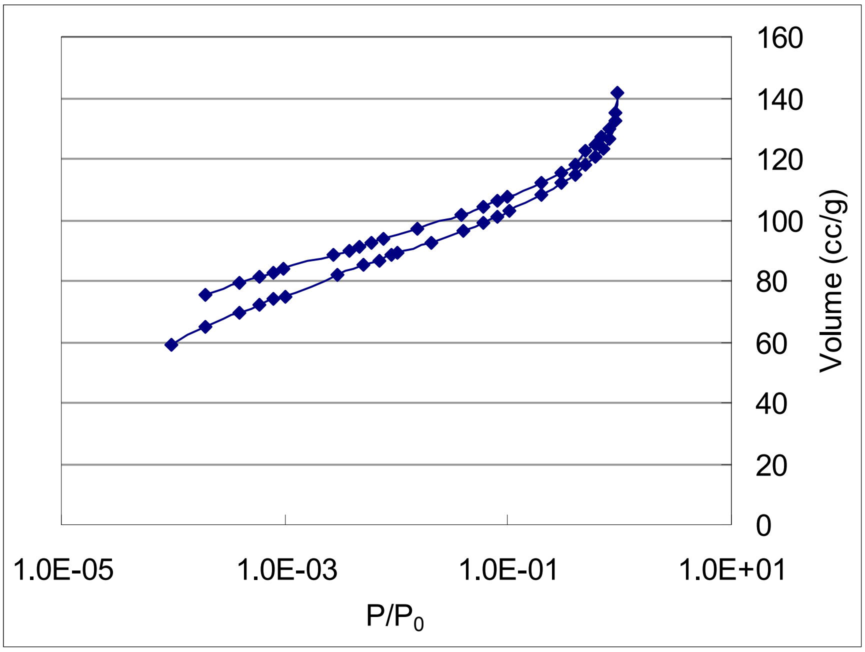

Figure C-10 Isotherm of activated fluid coke 1-MH-30

Table C-10 Data of isotherm of activated fluid coke 1-MH-30

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
9.49E-05	58.945	4.01E-02	96.319	9.52E-01	141.806	3.85E-02	101.9558
1.95E-04	64.746	6.12E-02	99.0246	8.98E-01	135.0942	1.55E-02	97.0662
3.97E-04	69.4069	8.16E-02	101.0575	7.98E-01	130.1304	7.71E-03	93.5452
5.97E-04	72.0354	1.02E-01	102.9956	6.97E-01	127.1021	5.88E-03	92.1946
7.98E-04	73.8017	2.02E-01	108.4363	5.97E-01	124.6477	4.67E-03	91.064
1.00E-03	75.0377	3.00E-01	111.9754	4.97E-01	122.3983	3.82E-03	90.1025
3.01E-03	81.7392	4.01E-01	114.9925	3.98E-01	118.0738	2.77E-03	88.5662
5.02E-03	84.9627	5.02E-01	118.3529	2.98E-01	115.38	9.86E-04	84.0137
7.03E-03	86.7902	6.02E-01	120.8133	1.98E-01	112.1712	7.87E-04	82.9352
9.07E-03	88.2654	7.01E-01	123.4998	9.88E-02	107.4877	5.93E-04	81.5308
1.01E-02	89.1152	8.01E-01	126.7837	8.02E-02	106.1775	3.92E-04	79.395
2.04E-02	92.5144	9.01E-01	132.4194	6.10E-02	104.5413	1.96E-04	75.6052

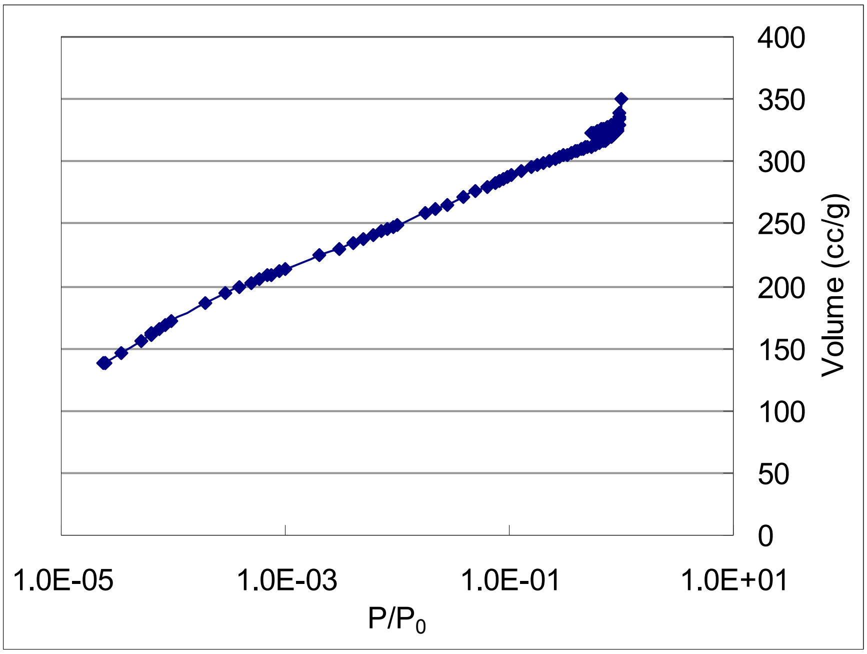

Figure C-11 Isotherm of activated delayed coke 1-MH-40

Table C-11 Data of isotherm of activated delayed coke 1-MH-40

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
2.41E-05	137.6013	7.06E-03	243.4237	3.56E-01	306.8645	9.53E-01	328.9461
2.43E-05	137.9276	8.06E-03	245.5526	3.82E-01	307.8474	9.74E-01	333.6618
2.47E-05	138.1697	9.07E-03	247.4382	4.07E-01	308.7237	9.94E-01	350.6855
3.44E-05	146.4737	1.01E-02	249.1224	4.32E-01	309.5329	9.76E-01	339.4816
5.16E-05	156.2355	1.78E-02	258.2987	4.57E-01	310.3053	9.50E-01	335.1447
6.25E-05	161.0658	2.22E-02	262.0829	4.82E-01	311.0184	9.22E-01	332.7355
6.45E-05	162.0434	2.74E-02	265.6974	5.07E-01	311.729	8.95E-01	331.2553
7.46E-05	165.4803	3.86E-02	271.675	5.32E-01	312.3842	8.69E-01	330.1895
8.48E-05	168.479	5.07E-02	276.4408	5.57E-01	313.0303	8.44E-01	329.3303
9.49E-05	171.0921	6.27E-02	280.1026	5.82E-01	313.6658	8.18E-01	328.571
1.94E-04	185.9553	7.41E-02	282.9895	6.07E-01	314.2711	7.93E-01	327.8974
2.94E-04	193.7579	8.15E-02	284.6158	6.31E-01	315.3382	7.68E-01	327.2763

3.95E-04	198.9158	8.74E-02	285.7934	6.57E-01	315.9855	7.42E-01	326.9276
4.95E-04	202.7421	9.65E-02	287.4171	6.82E-01	316.6237	7.17E-01	326.5526
5.96E-04	205.775	1.06E-01	289.0684	7.07E-01	317.2355	6.93E-01	325.9737
6.96E-04	208.2434	1.29E-01	292.0697	7.32E-01	317.8645	6.68E-01	325.4013
7.58E-04	209.5802	1.54E-01	294.804	7.57E-01	318.5395	6.43E-01	324.8198
8.97E-04	212.2171	1.80E-01	297.1013	7.83E-01	319.2382	6.18E-01	324.2408
9.98E-04	213.8842	2.05E-01	299.0447	8.07E-01	319.9619	5.93E-01	323.6382
2.00E-03	224.1697	2.31E-01	300.7	8.32E-01	320.7724	5.68E-01	323.0171
3.02E-03	230.3039	2.56E-01	302.1592	8.56E-01	321.6882	5.43E-01	322.3908
4.01E-03	234.5724	2.81E-01	303.4539	8.81E-01	322.7263		
5.02E-03	238.0842	3.07E-01	304.6316	9.05E-01	324.5697		
6.03E-03	240.925	3.32E-01	305.6987	9.30E-01	326.375		

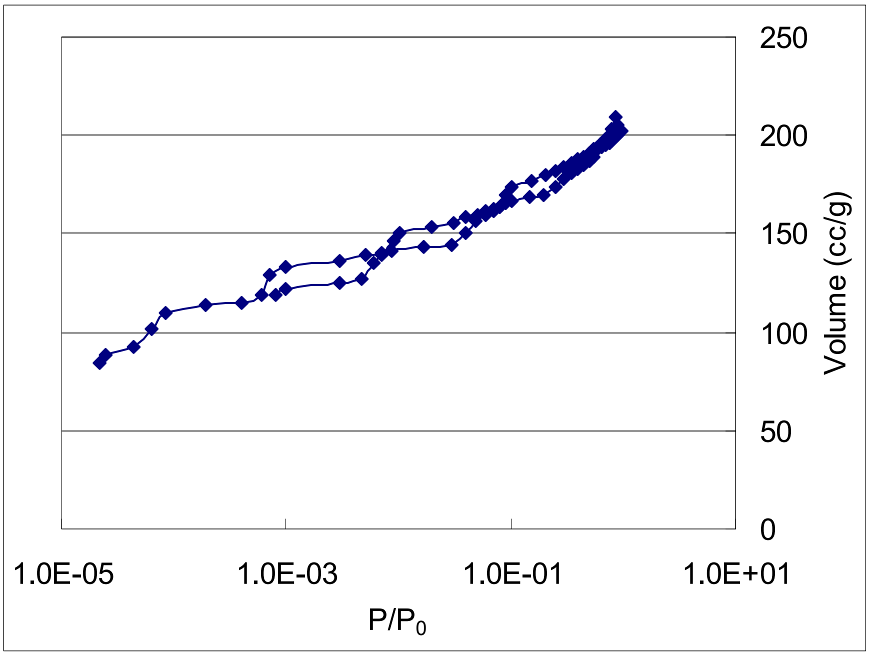

Figure C-12 Isotherm of activated fluid coke 1-MH-40

Table C-12 Data of isotherm of activated fluid coke 1-MH-40

P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)	P/Po	Volume (cc/g)
2.22E-05	74.0502	6.07E-02	158.0612	8.50E-01	200.1566	1.01E-01	169.5271
2.47E-05	75.9203	7.11E-02	159.9968	8.99E-01	203.0272	9.07E-02	168.2987
4.44E-05	83.8613	8.14E-02	161.6773	9.49E-01	209.0272	7.83E-02	166.5783
6.45E-05	88.7118	8.92E-02	162.885	9.00E-01	205.1709	7.05E-02	165.393
8.47E-05	92.0815	1.01E-01	164.5192	8.49E-01	202.5208	5.86E-02	163.393
1.95E-04	101.9294	1.51E-01	169.5607	7.98E-01	200.6166	4.87E-02	161.3834
3.97E-04	109.4417	2.01E-01	173.4377	7.48E-01	199.0192	3.91E-02	159.0914
5.98E-04	113.7664	2.52E-01	176.9345	6.97E-01	197.5863	3.00E-02	156.3994
7.02E-04	115.2307	3.00E-01	179.492	6.47E-01	196.2348	1.67E-02	150.7124
1.00E-03	118.5655	3.50E-01	181.8562	5.96E-01	195.2667	8.50E-03	144.577
3.02E-03	128.5759	4.00E-01	183.9601	5.47E-01	193.984	7.14E-03	143.0404

5.01E-03	133.312	4.51E-01	185.845	4.97E-01	192.6422	6.11E-03	141.7012
7.02E-03	136.5905	5.01E-01	187.5974	4.50E-01	189.3546	4.71E-03	139.4926
9.02E-03	138.9687	5.51E-01	189.2268	3.99E-01	187.0527	2.94E-03	135.5401
1.01E-02	140.1278	5.99E-01	191.2045	3.48E-01	185.0814	9.78E-04	126.707
1.95E-02	145.9711	6.51E-01	192.8307	2.98E-01	182.9697	7.96E-04	125.024
3.05E-02	150.4292	7.01E-01	194.4281	2.48E-01	180.6725	5.95E-04	122.4575
3.98E-02	153.2107	7.51E-01	196.1198	1.99E-01	177.8275	3.98E-04	118.8121
5.02E-02	155.8236	8.01E-01	197.9633	1.49E-01	174.2556		

Appendix D. Mass Percentage of Elements on the Surface of Coke Based on XPS Analysis

Table D-1 Mass percentage of elements on the surface of coke based on XPS analysis

Mass (%)	Delayed coke			Fluid coke		
	Raw	1-MH-10	1-MH-40	Raw	1-MH-10	1-MH-40
C	87.02	84.39	83.78	78.62	81.52	82.74
N	1.43	0.88	0.61	1.30	1.19	0.87
O	6.47	10.86	11.25	12.68	11.55	11.43
Si	1.11	1.43	1.49	2.47	1.50	1.87
S	3.97	0.75	0.31	3.59	0.97	0.86
K	0	1.69	2.56	1.33	3.28	2.22

Appendix E. Activation Yield Results

Table E-1 Activation Yield of Figure 4-10

Particle size	I (2-4.76 mm)	II (0.6-0.85 mm)	III (0.3-0.42 mm)
Delayed coke	92.1%	91.8%	91.5%
		89.2%	
Average	92.1%	90.9%	91.5%
Fluid coke	94.6%	93.5%	92.2%

Note: The activation of delayed coke (size II) was duplicated and the yield is the average of two activations.

Table E-2 Activation Yield of Figure 4-12

	No humidity	Humidity
Delayed coke	91.5%	85.2%
Fluid coke	92.2%	93.1%

Table E-3 Activation Yield of Figure 4-15

Power level	Low	Medium
Delayed coke	85.2%	76.8%
Fluid coke	93.1%	84.9%

Table E-4 Activation Yield of Figure 4-17

KOH/Coke ratio	0.25	0.5	1
Delayed coke	91.4%	76.8%	63.8%
			76.7%
Average	91.4%	76.8%	70.2%
Fluid coke	96.6%	84.9%	82.0%

Note: The activation of delayed coke with KOH/Coke ratio at 1 was duplicated and the yield is the average of two activations.

Table E-5 Activation Yield of Figure 4-19

Time (min)	5	10	20	30	40
Delayed coke	83.9%	74.8%	76.1%	63.8%	69.7%
		73.1%	71.8%	76.7%	70.5%
Average	83.9%	73.9%	73.9%	70.2%	70.1%
Fluid coke	92.6%	88.3%	83.5%	82.0%	78.9%

Note: The activation of delayed coke with 10, 20, 30 and 40 minutes microwave heating was duplicated and the yield is the average of two activations.

Appendix F. Elemental Analysis Results

Table F-1 Elemental analysis of the raw coke and activated carbon under different condition

	N (wt %)		C (wt %)		H (wt %)		S (wt %)	
Type	Delayed	Fluid	Delayed	Fluid	Delayed	Fluid	Delayed	Fluid
Raw	1.56	1.78	82.28	78.49	3.68	1.90	6.75	7.20
0.5-L-30	1.19	1.49	81.85	75.81	2.02	1.47	2.84	3.82
0.5-LH-30	1.16	1.48	82.76	76.59	1.81	1.56	2.44	4.29
0.5-MH-30	0.70	1.37	88.25	79.53	0.59	0.96	0.94	1.97
1-MH-30	0.75	1.37	86.60	80.08	0.86	1.31	0.74	2.23
1-MH-10	1.40	1.73	87.38	81.72	1.21	1.36	1.43	2.83