THE UNIVERSITY OF CALGARY

Preparation and Characterization of Activated Carbon From Western Canadian Coals

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Preparation and Characterization of Activated Carbon From Western Canadian Coals" submitted by Jian Liu in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

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Abstract

Three Canadian coals, namely, Bienfait lignite A, Montgomery sub-bituminous C and Coal Valley bituminous C were activated in a fixed-bed reactor in the presence of steam to prepare activated carbons. Atmospheric pressure and temperatures between 650 and 750°C were used while varying activation time from 0.5 to 4.5 hours. Steam activation with and without chemical additives was employed. The quality of the product characteristics was determined using BET surface area, iodine number, ash content, product yield and methylene blue number measurements. The results were used to determine the optimum activation temperatures and times, the effects of particle size and preferred chemical reagents for preparing activated carbons.

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I dedicate this thesis

to Chengyan who has supported and stands by me, more than a wife, through all climactic changes besetting our life.

to my father and mother: Liu Zhengxian and Gu Yazhen to my father-in-law and mother-in-law: Wu Shulai and Liu Kezhen

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NOMENCLATURE

- D iodine number correction factor
- △H heat of the reaction kJ/mol
- I_n iodine number
- k reaction rate constant h⁻¹
- m mass g

- p pressure atm
- S_g specific surface area m²/g
- t time h
- T temperature °C
- W weight of activated carbon product g
- W_o weight of coal load g
- X conversion wt%

Chapter 1.

Introduction

Activated carbon may be defined as a processed carbonaceous material with a highly developed porous structure and large internal specific surface area. Due to the special structure, activated carbons are commonly used to remove a great variety of contaminants from air, gases, water and other liquids. Other applications include its use as a catalyst support, in the purification of sugar and in the preparation of alcoholic beverages. It is generally accepted that activated carbons have surface areas greater than 400 m²/g and pore volumes that are typically above 0.2 mL/g [Hassler,1970. Jankowska, 1991. Sousa, 1993].

1.1 History of Activated Carbon

Unlike the other 'advanced' carbon materials such as synthetic diamonds, activated carbons have a surprisingly long history. As reported in Hassler's book "Purification with activated carbon" [1970], the utilization of activated carbon goes back to 1550 B.C., Wood char, the forerunner of modern activated carbon was used for medicinal purposes by ancient Egyptians. It was not until 1773 that the sorptive properties of charcoal for gases were first described by the Swedish chemist, Karl Wilhelm Scheele. A dozen years later(1785) the Russian academician, Lowitz, from Saint Petersburg found that charcoal,

when immersed in tartaric acid solution, decolorised it by absorbing the organic contaminants present. This discovery lead to the first industrial application of charcoal in the sugar industry in England in 1794. Kehl, in 1793, discussed the use of char for removal of odours from gangrenous ulcers.

During the 19th century, many studies were made to develop decolorizing carbons from other raw materials such as bone, flour, tar and paper mill wastes. The development of modern, commercial, activated carbons is attributed to Ostrejko in 1793 who patented the first industrial process for making activated charcoal from carbonaceous materials i.e. from vegetable materials using metal chlorides [Hasslar, 1970]. The early interest in the development of activated carbons was stimulated by a large potential market which existed in the refining of sugar from sugar cane and beets. This led to the manufacture of powdered activated carbons in Europe as an effective substitute for bone char in established operations. However, major development of activated carbon began during World War I when the preparation of hard granular activated carbon was developed for use in gas masks. Today, activated carbons are widely used as adsorbents for pollutants in waste gases and liquids such as the removal of CS₂ from air, the treatment of potable and waste waters, in air conditioning devices and in vacuum technology. Recent studies on activated carbons have been concentrated on obtaining higher surface area and larger pore size to reach higher sorptive capacity.

The annual global production of activated carbons amounted to about 500,000 tons[Wilson, 1981] in 1991 compared with 200,000 tons in 1981 [Jankowska,1991], a large proportion of which came from Europe and North America. The commercial

preparation of activated carbons falls into two categories. Under the "physical activation" approach, the raw material is first carbonized and then partially oxidized with steam, air or carbon dioxide at high temperatures in the range about 600-1000°C. Activation using chemical additives, called "chemical activation", carbonize the raw material in the presence of an activating agent such as phosphoric acid, sodium, potassium and caustic soda [Hassler,1970].

Commercial processes to make activated carbons utilize a variety of raw materials including bones, peat, wood, coal, coconut shell, coke and other carbonaceous materials. Coal as a relatively cheap source material, which has a price between 55 Cdn \$/tonne and 70 Cdn \$/tonne comparing the price of activated carbon approximately 4.00 Cdn \$/kg, has created significant interest. Since 1981, studies on the use of coal to make activated carbon have been conducted in the Department of Chemical and Petroleum Engineering at the University of Calgary. Today, since only one small facility for the production of activated carbon is being operated in Canada, most of the activated carbons used are imported from other countries. In 1973, Aqua Tech Ltd, started to produce activated carbon in Lethbridge using semi-anthracite coal from Canmore Mines. Because of the difficulties encountered in activating this raw material, there was low throughput resulting in the commercial failure of the company. The search for suitable coals and activation methods which could produce commercially satisfactory activated carbon products was therefore one of the main reasons for undertaking this research.

1.2 Objectives

There is a variety of source materials which may be used to produce activated carbons. Among these, coal is the most widely used, about 60% of the activated carbon being produced coming from this material. Canada has large reserves of coal. It was estimated in 1979 that the coal reserves (mineable coal) in Canada were approximate 16 gigatonnes [Fung,1982]. The use of coal as an raw material to prepare activated carbon is widely reported. Although both low and high ranking coals are used in various parts of the world for production of activated carbons, it is considered that certain advantages might be derived from the use of softer, low ranking coals which have higher porosities and reactivities.

In this investigation, a fixed-bed reactor was used to produce activated carbon. The raw materials employed were: Bienfait coal (lignite A) from Saskatchewan, Montgomery coal (Sub-bituminous C) and Coal Valley coal (bituminous C) both from Alberta. Steam activations with and without chemical additives were studied. While steam reacts with the carbon during activation, it is not considered to be a "chemical additive".

The main objectives of this work included: 1) determining effects of coal of different ranks have on the sorptive properties of the activated carbon; 2) optimizing the activation parameters for preparation of activated carbon; 3) comparing the effect of particle size on product quality; 4) determining the properties of the activated carbons produced from those different coals ; 5) selecting the best chemical reagent for making activated carbon and 6) determining the effects of the impregnation ratio employed on

the product quality. After a careful study on the preparation and characteristics of activated carbons to obtain ideas on the selection of starting materials, on the ways in which activation conditions might be employed and on which of various chemical reagents is preferable as a catalyst, some theoretical guidance on the preparation of activated carbon from coal has been be extricated from this investigation.

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Chapter 2.

Literature review

Although many patents have been issued describing the use of coal as a source material for the production of activated carbon [Yehaskel,1978], there are relatively few books published on this subject. This literature survey is divided into three broad sections. The first deals with the properties of activated carbon; the second is a survey of various methods for the preparation of activated carbon and effects of various parameters in activation processes; the third describes analytical methods which are used to characterize activated carbon.

2.1 The Properties of Activated Carbons

Activated carbon has many methods of preparation and applications as discussed above. However, traditionally, it is still considered as a substance that is used mainly in water and waste treatment industry. Usually, its use depends on its general sorptive properties rather than on its physical or chemical structure.

2.1.1 Physical and Chemical Structure of Activated Carbon

Activated carbon is a porous material, widely used in adsorption and catalytic processes. Most uses and applications of activated carbon are based on its structural properties. X-ray studies [Prober, 1974] have shown that activated carbon has a microcrystalline structure that is similar to that of graphite. Graphite consists of large planes of flat molecules stacked rather loosely on one another. This property gives it softness and permits it to act as a lubricant. In graphite, the carbon atoms are arranged hexagonally in flat parallel planes. Carbon atoms in activated carbon are also arranged in planes in a hexagonal form. However, its structure differs from that of graphite in many ways. For example, the carbon planes of activated carbon have a random angular displacement. Disorganized tetrahedrally-bonded carbon and foreign atoms can be found to varying extent either incorporated into the planar faces or on the planar edges. It is reported that the microcrystallites range from 10 to 100 Å in diameter and from 3 to 30 carbon layers in thickness [Faust, 1989]. Microcrystallites are formed during the carbonization of the raw materials and continue to develop throughout the activation process. The size of the microcrystallite is influenced by the temperature of carbonization and the structure of the source materials [Singla,1983]. Faust states that planar surfaces of the micropores, which contribute most of the surface area, are responsible for most of the sorptive properties of activated carbon.

A conceptual model of the chemical structure of activated carbon has been gleaned from available sources. Prober and his co-workers [Prober,1974] suggested that activated carbon can be considered to be a relatively inert extended lattice of carbon atoms in a "chickenwire" arrangement with an occasional oxygen or nitrogen atom altering the lattice pattern. It is presented the Figure 1 shown as below.

CHEMICAL MODEL OF ACTIVATED CARBON



Figure 1. Chemical model of activated carbon [Prober, 1974]

Various functional groups are shown to illustrate the diversity of possible chemical reactions. The figure does not imply that any real activated carbon has exactly the same structure. However, it explains the importance of the functional groups. The groups containing oxygen (e.g.,-C=O, -COOH) are particularly important and occur for the most part at the edges of microcrystallites. They are very reactive . Unless special provision is made to exclude oxygen, surface oxides form the most abundant group on the carbon surfaces. The surface oxides strongly influence the properties of the carbon such as acidity, wettability and redox behaviour. They also have a strong effect on the sorptive properties.

The oxygen content of activated carbon ranges from 2 to 25% by weight and has been shown to vary considerably with the activation temperature. Both electron microscope and electron spin resonance studies have shown that the oxygen on the activated carbon surface is almost entirely attached at the edges of the layer planes, i.e., at the most reactive sites. Those surface sites associated with the functional groups constitute only a small portion of the total surface area of activated carbon. However, they can influence the characteristics of the carbon by participating in chemisorptive interactions or forming "specific adsorption" sites.

2.1.2 Sorptive Properties of Activated Carbon

Sorption results when a component becomes attached to the surface of the activated carbon causing an increase in concentration of a particular component at the surface or interface between two phases. The process may be classified as "physical" or "chemical", depending on the nature of the forces involved. Physical sorption on the solid phases is attributed to forces of interactions between the solid surface and sorbate atoms or molecules that are similar to the Van der Waals forces between atoms. Chemisorption is characterized mainly by large interaction potentials that lead to high heats of sorption approaching the values of chemical bonds.

Usually, the adsorptive capacity of the solid material is influenced not only by the sorbent itself, but is also affected by the sorbate. For example, on the sorbate side, the adsorptive capacity can be affected by several physical and chemical properties that include the solute's solubility, polarity, the molecular weight and size, temperature and even sometimes the ring structure of aromatic compounds [Faust, 1989]. The sorbent is generally influenced by 1) surface area; 2) pore structure; 3) particle size and 4) chemistry of the surface. Since our research goal is to produce a better activated carbon, in this review we will focus on the sorbent's properties exclusively.

Surface area and pore structure

Since the sorptive process results in the condensation of solutes at the sorbent surface, it is apparent that the surface area is one of the principal characteristics affecting the sorptive capacity of activated carbon. The sorptive capacity of activated carbon generally is proportional to the specific surface area [Smith,1970]. However, the specific surface area alone is frequently inadequate to explain the adsorptive capacity of porous solids such as activated carbon because the pore size distribution in activated carbon indicates that micropores contribute a major portion of the specific surface area. Also, many of the micropores possess molecular dimensions. It is, therefore, reasonable to expect that a solute molecule will readily penetrate into a pore having a certain critical diameter and will be excluded from pores smaller than this size. That means the surface area accessible to the sorbate will be affected by its molecular size, and only those that are accessible to the sorbate will contribute to the effective surface area.

Surface area and pore structure of activated carbon are developed by the process of carbonization followed by activation of the initially carbonaceous material. The product of the carbonization process has a relatively low sorptive capacity with a specific surface area of several m^2/g . During activation, the reaction between the carbonized material and

the oxidizing agent occurs with a loss of carbon and with the consequent modification of the textural parameters of the material. The pore size changes with an increase in the specific surface area as well as the macroporous and microsporous networks. As a result, the accessibility of molecules to the whole solid bulk is improved. Different activated carbons can have surface areas ranging from 400 to 2500 m²/g [Yehaskel,1978]. The pore sizes of activated carbon can usually be divided into three major groups. The first group is called the "macropores" which have radii between 5,000 and 20,000 Å, and they are formed mainly by removal of the hydrocarbon radicals on carbon plane edges and serve as distribution arteries for the adsorbate. The second group is the "micropores" which have radii less than 20 Å and they are formed by reaction causing removal of microcrystalline planes and provide almost all of the sorptive sites of the carbon. The third group is the "transition" pores which have radii from 20 to 5,000 Å and comprise less than five percent of the total surface area of activated carbon [Smisek, 1970]. Prober [1974] gave the same classification on pore sizes. However, Jankowska [1991] presented a very different definition of pore structure. He stated that pores with radii below 2 nm are called "micropores", with radii between 2 and 50 nm are called "mecropores" and with radii greater than 50 nm are called "macropores".

Particle size

The surface area of nonporous adsorbents increases considerably with a decrease in particle size. Consequently, the sorptive capacity should increase with reduction in particle diameter. However, for a highly porous material such as activated carbon, most of the surface area resides in the internal pore structure and the sorptive capacity is expected to be independent of the particle size. This conclusion was reached by several researchers. Zogorski [1975] showed that crushing activated carbon to particle sizes ranging between 0.66 and 1.4 mm had no effect on the nitrogen BET surface area and that the sorptive capacity for 2,4-dichlorophenol and 2,4-dinitrophenol was independent of the particle size.

Chemistry of the surface

The chemical nature of the surface of activated carbon is regarded as one of the important factors that determines the sorptive capacity. The role of its influence on sorptive capacity in the presence of functional groups on the surface is still under investigation by many researchers [Schafer, 1979]. Faust [1989] states that the formation of polar surface groups with chemisorbed oxygen during the activation process of the carbon, affects the sorptive capacity for many solutes. Surface oxides consisting of acidic functional groups reduce the capacity of carbon for adsorption of many organic solutes such as oxalic and succinic acids [Puri,1980] from aqueous solutions. Coughlin [1970] has reported the influence of surface oxides on the adsorption of various pollutant-type molecules from aqueous solution. The results show that increasing the concentration of surface oxides lowers both the capacity for and rate of adsorption of phenol, sodium benzenesulfonate and dextrose. Prober [1970] suggested that oxygen on the activated carbon surface may increase surface polarity. In aqueous solution, adsorption requires that a stronger solvent-activated carbon bond must be broken on the oxidized carbon than the

unoxidized carbon. Thus the adsorption of a nonpolar species could be more difficult on oxidized activated carbon than on unoxidized activated carbon.

2.2 Methods of Preparation of Activated Carbon

At the middle of this century, many factories were built in Europe and America to manufacture commercial brands of activated carbons [Wilson,1981]. Yehaskel's book [1978] "Activated carbon manufacture and regeneration" reported more than two hundred patents available on the preparation of activated carbon. Each specific method is quite unique and various materials are proposed for use as a source material. It is not reasonable to review each case. Therefore, in this chapter, the method of preparation will be focused on using coal as a source material exclusively to produce activated carbon. Some important parameters such as starting material selection and pretreatment, carbonization and activation conditions will be surveyed as well as some preparations using chemical additives.

2.2.1 Source material selection and pretreatment

Coals play an important role in the production of activated carbons. They are very cheap source materials with high mechanical strength. The popularity of coal as a raw material is partly due to the ease with which porous structures can be developed. Coals exhibit an initial porous structure of their own. According to Leon [1981] the area of these pores is in the range 100 - 400 m²/g for most American coals as measured by the sorption of carbon dioxide at room temperature, but is frequently smaller than 1.0 m²/g

as measured by the sorption of nitrogen at 77K.

Before carbonization and activation, the source material is usually pretreated. Depending on the final product shape desired, the raw material is first crushed and screened to reach relatively uniform particle sizes. To produce granular or pelleted activated carbon, it should undergo a granulation or a pelletization process, respectively. The raw material shape usually has no significant effect on product quality but, considering the shape factor itself, it may offer some advantages such as sphericallyshaped activated carbon. It has some advantages over cylindrical or irregularly shaped ones. The reason is that the spherical, activated carbon has no sharp edges nor protrusions which are liable to cause crumbling or abrasion. Furthermore, the packing of spherical grains guarantees the highest ordering.

One activated carbon preparation method is reported in which washing of the starting material improves the product quality. Jagtoyen and Derbyshire [1993] reported that acid washing reduced the ash content of coal and had a beneficial effect upon surface area development. Jagtoyen [1993] studied coals of three different ash contents. Two low ash content coals, after acid washing, showed that surface areas had been increased by 11 and 24%, respectively. For one with extremely high ash content, the surface area had been increased about three times from 156 to $625 \text{ m}^2/\text{g}$. The acids used were hydrochloric acid, nitric acid or sulphuric acid. The concentration of the acid is not considered critical less than 2.0% by weight is frequently used.

Pre-oxidation is another pretreatment used in the preparation of activated carbon. Slight oxidation prior to carbonization enhances the mechanical strength and the density of the carbonization materials [Hasslar, 1970]. The average residence times during the oxidation period ranging from 2 hours to 4 days are reported [Sousa, 1993]. Exposure to more severe temperatures during oxidation may result in destruction of the characteristic particle shape and may cause particle fusion.

Activated carbon properties are strongly dependent on those of the precursor materials. This is exactly the reason why people keep looking for more reliable and promising starting materials to obtain high quality activated carbon products. As reported from the book 'Activated Carbon Manufacture and Regeneration' by Yehaskel [1978] almost all kinds of coals can be employed to produce activated carbon. However, certain advantages and disadvantages of different coals as precursors have not been discussed. In the Department of Chemical and Petroleum Engineering at the University of Calgary, Tollefson and his co-workers reported [Tollefson,1981] that low ranking coals could been easily activated since they are relatively more reactive. Also, it is reported by Tollefson that high equilibrium moisture contents of the parent coals may imply the inherent initial porosity of the coals and suitability for large pore development. Other factors affecting activation could be the ash content of raw material, the alkali metal content and the potassium/sodium ratio. Some of these factors may be of importance in the activation process.

2.2.2 Carbonization

This is one of the most important steps in the production of activated carbons since it is in the course of carbonization that the initial pore structure is formed.

Carbonization is sometimes called "charring", which is the slow heating of the starting material in the absence of air. During the carbonization process, volatile pyrolysis products are removed from the starting materials which leaves a residue called "char" or "coke". Chars, frequently called "amorphous carbon", have been shown by X-ray studies to be composed of crystals of submicroscopic dimensions termed "microcrystallites" [Hasslar,1970]. Nitrogen and argon are sweep gases frequently used to carry away volatile products. Generally, carbonization consists of three consecutive steps: The first is a drying process in which the raw material is heated up to 170°C. The second is a decomposition process in which the material is heated up to 270-350°C and which forms considerable amounts of tar, methanol and other by-products. The final step is the completion of the carbonization process at temperatures of 400-600°C. However, this is not universal. Different temperatures can be used depending on the raw material's properties. Due to the evolution of volatile matters in the carbonization process, the material becomes richer in carbon and the initial porous structure is developed. Heat destroys the organic matters of the initial coal as well as of the binding material. The drying step removes the excess of the lower boiling fraction of the binding agent and gives the raw material the mechanical strength required in the further operations.

The relevant parameters of carbonization are the final temperature achieved and the rate of temperature increase. They are important to the initial pore development. For instance, the final temperature of coal carbonization is associated with the need to supply to the macromolecules of coal a significant amount of energy to cause splitting of the weaker chemical bonds and to enable the migration of the volatile products of thermal decomposition of the raw material from the structure. The significance of the influence of the final temperatures was also observed by Ludvig [1983]. when studying bituminous coals. The results showed that there is no increase in surface area upon heating to 500°C. However, significant surface area development $(10 \text{ m}^2/\text{g})$ was achieved by heating from 500 to 600°C. This indicates that micropores are developed in the later stages of coal carbonization. However, Merchant and Peterich [1992]. through a study on Illinois No.5 (bituminous) coal at different temperatures, found that temperature difference had no effect on char yield and char ash content. This result did not agree with findings that char yield decreases with increasing reaction temperature [Nsakala et al.,1978]. This may be explained on the basis that the disagreement between the two results is from the different materials they used which had different physical and chemical properties.

The heating rate is another factor affecting the final products, but the results from different authors show inconsistencies. Jankowska [1991] states that when the temperature is raised rapidly, the particular phases of the thermal decomposition of coal and secondary reactions of the pyrolysis overlap with each other. The reactivity of the carbonized products obtained in this way is greater than that of the products heated at a slow rate. This is due to the greater porosity and reduced ordering of the compact carbon material as compared with carbonized products obtained from the same raw materials but at a low rate of heating. However, Singla [1983], after having studied two bituminous coals, found that there was only a small influence on pore volume development as a result of a heating rate variation from 2 to 8°C/min. It is also reported by several researchers [Singla et al.,1983] that different heating rates during the carbonization process are another factor

which influences macropore development, but it had no effect on char yield and char ash content.

Another factor which might affect the char yield is a change in the residence time used in the carbonization process. It is generally agreed that a longer residence time is beneficial for completing the devolatilization process. But results from Merchant and Peterich showed, there was no difference in char yield. The writer thinks that this could be explained from the configuration of the reactor and from the flow rate of carrier gases because depending upon the conditions, the primary products would have more time to undergo secondary pyrolysis reactions such as char formation.

The effectiveness of carbonization can be enhanced when the source carbonaceous materials, e.g., wood, are impregnated with a solution of additives, such as zinc chloride or phosphoric acid. The products have considerably greater pore structures according to several patents [Yehaskel,1978].

2.2.3 Activation by mild oxidation

The activation process employed is a mild oxidation process with oxidizing gases such as air, steam and carbon dioxide. Although char prepared under appropriate carbonization conditions can be used successfully without further processing in many applications, chars from carbonization do not confer adequate sorptive capacity. Most of the sorptive properties of activated carbon are developed during the activation process.

Coal activation is a complex heterogeneous process encompassing the activating gas diffusing into the surface of the coal particle, chemisorption on the surface of the particle, the reaction between the activating gas and the carbon, desorption of the product gases and diffusion of these gases into the bulk stream. During the activation process, the oxidizing gases selectively attack portions of the char, transforming some of them into gaseous products while the resulting hollow pores are systematically developed and enlarged. Sometimes, the activation process is also called "a controlled oxidation process" in which the rate of the process is controlled by the temperature and the concentration of inlet oxidizing gas. It can fall into two categories. First, is the "physical activation" approach, in which the raw material is carbonized and then partially oxidized with oxidizing gas at a temperature between 600 and 900°C. The other involves "chemical activation" which uses chemical additives as catalysts during the activation to develop better or specific sorptive properties required for activated carbons.

Although air, carbon dioxide and steam are reported as activating gases, steam is considered to be the preferable one for the activation process [Hassler,1970]. Activation with carbon dioxide is usually conducted at temperatures ranging from 700 to 900°C. This kind of activation has some drawbacks as low yields are usually obtained and a long period of activation is required to attain high surface areas and porosities [Torregrosa, 1991]. Activation with air involves an exothermic reaction and measures must be taken to keep the temperature from rising above proper limits. The reaction of steam with carbon is endothermic and the reaction temperature can be easily controlled. With steam the temperature of the activation process must be high enough to provide a reasonable rate of oxidation, but temperatures above 1000°C are to be avoided because they impair sorptive powers [Hassler,1970]. Because of the complexity of the coal itself, the true mechanisms of the reactions between char and activating gases are not yet fully understood. The main reaction between char and carbon dioxide can be described as follows [Hasslar,1970. Juntgen, 1983]:

$$C + CO_2 \iff 2CO$$
 $\Delta H = 162 \text{ kJ/mol}$ (1)

The reaction between steam and char is more complicated. However, it is generally agreed [Hasslar, 1970. Juntgen, 1983. Jankowsla, 1991] that the main reactions can be represented by two stoichiometric equations:

(a) the carbon-steam reaction;

$$C + H_2O \iff CO + H_2$$
 $\Delta H = 119 \text{ kJ/mol}$ (2)

and (b) the water-shift reaction;

$$CO + H_2O \iff H_2 + CO_2$$
 $\Delta H = -42 \text{ kJ/mol} (3)$

The reaction of char with air (oxygen) yields simultaneously carbon oxide and carbon dioxide according to the following equations [Jankowsla, 1991]:

$$C + O_2 \iff CO_2$$
 $\Delta H = -387 \text{ kJ/mol}$ (4)
 $2C + O_2 \iff 2CO$ $\Delta H = -226 \text{ kJ/mol}$ (5)

It remains unknown whether carbon dioxide or carbon monoxide is the primary product of carbon activation. Current views are that both oxides are primary products [Jankowsla,1991] and that the CO/CO_2 ratio increases with an increase of reaction temperature.

Among the three activating gases discussed above, air shows the greatest and carbon dioxide the least activity. With steam and carbon dioxide, the reactions are endothermic so that the reaction temperatures of the activation process can be easily controlled. Air is seldom used as an activating agent because it causes several difficulties. Since the reaction with air (oxygen), is exothermic, it is not easy to control the temperature in the reactor at the required level. Being an aggressive reagent, the high reactivity can lead to two major problems: one is that it is difficult to avoid local overheating in the activation process; the other is that the carbon oxidation process proceeds chiefly at the surface of carbonized carbon, producing high losses of material. Therefore, activation with air is seldom practicable except for certain chars.

Various parameters reported have effects on the activation process. Hasslar [1970] concluded that the quality of activated carbon produced is determined by the chemical nature of the source material, the activation temperature, the extent of the activation conducted and the amount and kinds of mineral ingredients in the char. These are the most active areas in recent research on the activation of carbon.

Although a variety of different ranks of coal reported can be used to produce activated carbon, Tollefson and his co-workers [1981] confirmed that low rank coals have certain advantages in steam activation because they are more reactive and have better initial pore structures. In fact, most recent published papers describe the use of low rank coals such as bituminous, sub-bituminous and lignite coals. As examples, bituminous coals were studied by Sousa [1993] and Louisiana lignite coals were investigated by Merchant [1992]. However, it does not mean that only low rank coals give activated carbon better sorptive capacity. On the other hand, there are many patents which describe the use of high rank coals. Moreover, many industrial processes have used high rank
anthracite coal as a feedstock [Wilson, 1981].

The development of sorptive capacity activated carbon during the activation process usually is determined by two relatively important parameters, the activation temperature and time. This follows because the activation temperature is a critical factor controlling the activation rate and activation time directly contributes to the extent of activation. Therefore, most reported optimum activation conditions were represented by temperatures and times. For example, an investigation by Rist [1985] showed that maximum surface area of 460 m²/g could be obtained from lignite coal using steam for activation at 850°C for three hours. Similarly, Leon [1981] indicated that a maximum surface area of 110 m²/g was obtained for bituminous coal using air activation at 450°C for four hours. The effect of temperature was studied by Jankowska [1991]. He stated that a low activation temperature brought a low rate of the chemical reaction of carbon with the activating gas and that this slow reaction limited the overall rate of the process. This results in a relatively long activation time to achieve better sorptive properties. At a suitable activation temperature, the activation process yields a homogeneous product with a uniform distribution of the pores throughout the whole volume of carbon particles. At very high temperature, the oxidation reaction rate becomes so high that the reactions only occurred at the external surface of the char. In this situation, significant losses of the material occurred and porous structures were not formed.

2.2.4 Chemical activation

The preparation of activated carbons from coals by the chemical activation method

has been studied very little. As a potential route to produce activated carbon, it has some advantages in that it requires a relatively low activation temperatures, short activation times and some special sorptive capacities can be easily developed. Although few patents on the chemical activation process were reported, there is a limited fundamental understanding of the chemistry of the conversion processes. The initial ideas on the chemical activation method were introduced by some famous catalytic gasification studies. Massive evidence has supported the belief that chemical reactions between coal and steam in the presence of catalysts can increase the reaction rate dramatically. For example, a comparison of the behaviour of anthracite char and a char prepared from Illinois No.6 bituminous coal, in the presence and absence of added K₂CO₃ catalyst was conducted by Mckee[1983]. The results showed that non-treated anthracite char was quite unreactive (K=1.8*10E-6 min⁻¹) at 700°C and non-treated Illinois No.6 char (bituminous) was considerably more reactive (K=2.6*10E-5 min⁻¹). However, in the presence of 5 wt% added catalyst the reactivities of both chars were similar(K=2.6*10E-4 min⁻¹) at the same temperature. From the result two conclusions were drawn: One is that high rank coals can reach the same reactivities as those of low rank coals. The other is that even the low rank coals with relatively higher reactivities still have the potential to be catalyzed to obtain even higher reactivities.

Among the catalysts surveyed were carbonates of alkali metals and transition metals of Group VIII and nickel. They were found to be particularly effective [Sams, 1983. Ono, 1984. Suzuki, 1984]. A study was made of activated carbons prepared from coals using phosphoric acid as a catalyst. The result was that the product had a

dominantly microporous sorptive capacity according to Derbyshire [1991]. The result also showed that chemical activation has a beneficial effect on sulphur removal.

2.3 Analytical Methods

The quality of activated carbons can be determined by standard analytical techniques. A variety of methods is discussed in several books [Sheffler,1956. Hasslar,1970. Jankowska 1991]. These measurements are of vital important to investigators studying the preparation of activated carbons. Sheffler [1956] divides different methods into three groups which include 1). fundamental properties tests, 2). sorptive capacity tests and 3). checking specifications. Jankowska [1991] also divided them into three categories. They are a) physical properties b) sorptive capacity and c) chemical and physicochemical tests. The techniques presented in this chapter are not exhaustive because there are more than twenty techniques mentioned. This survey will focus on the methods used in our research. Two groups of analytical methods are involved. One introduces physical testing, the other is sorptive capacity testing. Details of experimental procedures are discussed in the next chapter.

2.3.1 Physical Test

Bulk Density

The definition of bulk density is the mass per unit volume of the activated carbon sample in air including both the porous particle system and the voids between the particles. The measurement of bulk density of activated carbon should also consider the shapes, sizes and densities of the individual particles.

Moisture Content

Moisture content is a measure the percentage of water by weight in activated carbon. The "oven drying" method was used in this study. When water is the only volatile present in the activated carbon, the sample is dried in an oven at 110°C for two hours. The dry mass of the sample divided by original sample mass time 100 equals the moisture content.

Ash Content

Total ash content in activated carbon is measured to determine the amount of the inorganic matter present. This test is accomplished by a combustion process, The weighed sample is put into an oven at 650°C for four hours. The organic matter present is converted into carbon dioxide and water. Upon cooling to room temperature, the mass of the residual ash is determined. This mass divided by that of the original sample times 100 equals the percentage ash in the sample.

2.3.2 Sorptive Test

Sorptive capacity is paramount for both gas-phase and liquid-phase activated carbons. The sorptive properties of activated carbon are generally estimated by determining the isotherms of sorption from gas or liquid phase. The determination of the sorption of one test substance from a solution is often insufficient for characterizing the sorption properties of activated carbon. Thus the properties of activated carbons are estimated by comparing the results of measurements for different sorbates, e.g. by comparing the sorptive capacities of fairly large molecules such as methylene blue.

Specific Surface Area

The surface area of activated carbon has a profound effect on the amount of gas adsorbed. Smith [1970] stated that the standard method of measuring a porous substance's surface area is based on the physical adsorption of a gas on its surface. It can be achieved by the famous BET (Brunauer, Emmett and Teller) method. This method utilizes gas adsorption for the evaluation of the monolayer capacity which is defined as the volume of gas in cubic centimetres at standard temperature and pressure that would be required to cover the adsorbent with a monolayer. The specific surface area (m²/g) can be calculated by determining the area of monolayer of the gas corresponding to the volume of gas adsorbed. In this research, the High Speed Surface Area Analyzer (Model 2200) was employed. The gas used was nitrogen at liquid nitrogen temperature (-195.8°C). At this temperature the gas molecules are strongly attracted to the solid surface.

According to Smith [1970], the BET equation for obtaining the gas volume for monolayer coverage may be written in a linear form as shown below:

$$\frac{P}{V(P_o-P)} = \frac{1}{V_m c} + \frac{(c-1)P}{cV_m P_o}$$

where

P = equilibrium pressure

 P_o = saturation pressure of nitrogen at the temperature of the experiment

 V_m = volume of nitrogen adsorbed as a monolayer

C = constant characteristic of the gas-solid system

A straight line is obtained by plotting $P/V(P_o - P)$ against P/P_o and the value of V_m can be calculated from the slope (C-1)/ V_m C.

If the area covered by one adsorbed molecule is α , and V is the volume per mole of gas at the conditions under which V_m is determined, then the specific surface S_g is obtained by:

$$S_g = (\frac{V_m N_o}{V}) \alpha$$

where

 $N_o =$ the Avogadro's number

and α can be calculated from:

$$\alpha = 1.09 (\frac{M}{N_o \rho})^{2/3}$$

where

M = the molecular weight and

 ρ = the density of the adsorbed molecules

Usually the gases used surface area measurement are nitrogen and carbon dioxide. Since the minimum dimension of a nitrogen molecule (0.365 nm) is larger than that of carbon dioxide molecule (0.33 nm), the reported data of nitrogen surface areas are less than those of carbon dioxide surface areas.

Iodine Sorption

Sorption of iodine from an aqueous solution has been used to indicate the liquid sorptive capacity of activated carbon. The iodine number is defined as the number of milligrams of iodine adsorbed by one gram of activated carbon from an aqueous solution in which the iodine concentration of the residual filtrate is 0.02N. If the final values are not in the appropriate range a correction chart is necessary to obtain the number.

The specific surface areas of activated carbon with highly developed microporous structures as determined by the iodine number method are low. This is because iodine is absorbed chiefly on the surface of pores much larger than 1.0 nm [Jankowska, 1991]. In activated carbon with large specific surface area, the proportion of very fine pores inaccessible to iodine molecules is quite significant.

Although several standard methods are available, the method of determining the iodine number used in this study is the one from the book "U.S Environmental Protection Agency Technology Transfer" [1972]. The amount of iodine solution absorbed by activated carbon is determined by titrating with a standard sodium thiosulphate solution (0.10N). The iodine number may be calculated from the formula:

$$I_n = \frac{X}{m}D$$

where

 $I_n = iodine number$

X = the quantity of iodine adsorbed by the carbon in mg

m = the mass of activated carbon in grams

 $D_{.}$ = a correction factor depending on the residual normality of the standard iodine solution which is also given by the book

and $X = 12.693N_1 - 279.246N_2V$, where N_1 is the normality of the iodine solution, N_2 is the normality of the solution of the sodium thiosulphate solution and V is the volume of the thiosulphate solution in mL.

Methylene Blue Sorption

Methylene blue has a relatively larger molecular size than that of iodine. Thus only large pores are accessible to methylene blue solution. The methylene blue number gives an indication of the sorptive capacity of an activated carbon which results from the existence of pores of dimensions greater than 1.5 nm. The methylene blue molecule has linear dimensions greater than 1.5 nm, but sorption experiments on silica gels with a laminar structure of the lattice have shown that molecules of this dye are adsorbed in pores of exactly these dimensions. i,e. as if the molecules were a flat plate [Jankowska,1991]. The methylene blue number is defined as the number of milligrams of methylene blue adsorbed by one gram of activated carbon at an equilibrium concentration of 1.0 mg of methylene blue per liter of solution. According to Sheffer [1956], the methylene blue number can be obtained by a simple experiment described as follow: Aqueous methylene blue solution of 1.0 g/L concentration is added from a burette in small increments to a 1.0 g activated carbon sample. The mixture is agitated for approximately one minute after each addition. The residual methylene blue concentration in solution is observed by placing a drop on a filter paper and matching the intensity of the blue spot to a series of spots produced from drop of known methylene blue concentration. Methylene blue number is then calculated by the definition. However, Hall and Tollefson [1981], when analysing activated carbon, found that there is considerable uncertainty in this endpoint. Therefore, a method was developed in which the endpoint was checked spectrophotometrically and the residual methylene blue concentration was corrected by a known correction table from a Freundlich isotherm.

Chapter 3.

Apparatus and Procedure

3.1 Materials

Three coals varying in rank from bituminous to lignite were used as feedstocks in this research. Coal Valley, high volatile, bituminous coal was supplied by Luscar-Sterco Ltd., Edmonton. Montgomery coal, sub-bituminous C was by Manalta Coal Ltd while Bienfait, lignite coal from Saskatchewan was provided from the Bienfait Coal Company Ltd. The important properties of these coals are summarized as proximate and ultimate analyses in Table 1. The source of these data is a CANMET report (82-13E, 1982). Other properties such as bulk density and calorific value were also available, but are considered to be less important. However, for the sake of completeness, these data are presented at the bottom of the table:

Table T. Coal characteristic	Table	le 1. Co	oal charac	teristic
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Coal name	Coal Valley	Montgomery	Bienfait	
Coal rank	bituminous C	sub-bituminous C	lignite-A	
Proximate analysis (wt%)				
Moisture content	6.9	23.3	29.8	
Ash content	10.9	12.8	10.0	
Fixed carbon content	49.1	36.1	30.1	
Volatile content	33.1	27.8	30.1	
Ultimate analysis (wt%)				
Carbon content	69.44	66.90	64.70	
Hydrogen content	3.08	1.67	4.40	
Nitrogen content	0.79	1.96	1.20	
Sulphur content	0.34	0.53	0.50	
Oxygen content	15.10	14.64	17.30	
Ash content	11.25	14.64	11.90	
Bulk density (g/cm ³)	0.78	0.70	0.67	
Calorific value (MJ/kg)	24.75	17.93	15.28	

The coal preparation procedure was done by A.K. Dalai. A schematic diagram of the devices used in the process is shown in Figure 2. Initially, the dried coals were ground using an attrition mill to produce small particles of the coals. The product coals from the mill was sieved using a Gilson Test Master sieve equipped with 10, 5, 2.5, and 1.25 mm screens [Dalai, 1992]. The particles in the range from 0-1.25 mm were called "fines" while those in range from 1.25-2.5 mm were called "granular". Both fine and granular materials are suitable for activation to obtain "powdered" and "granular" activated carbons. It was found that the product from the attrition mill contained more "fines" than "granular" material. Furthermore, as expected, many difficulties in handling fines were reported. To avoid these difficulties, another form of coal particle was developed. It is produced by a process called "pelletization" which, simply involves a series of steps in which fines are convert to pellets. As shown in Figure 2 about 4.0 mass% wheat bran was added to the fines and fed to the tumbling mill. It was then mixed with water and the mixture was sent to an extruder to produce pellets. All three forms of the product coals were stored separately in 1.0 L screw-cap, wide mouth bottles.



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3.2 Experimental Set up

The apparatus used in this research consisted essentially of three parts; a feed section, a fixed-bed reactor, and a gas collection and analysis section. Figure 3 shows a schematic flow diagram of the experimental apparatus.

In the feed section, nitrogen serves as a carrier gas and distilled water is supplied at a constant rate to an electrically-heated boiler for generating steam. Nitrogen flow was controlled using a Matheson 601 rotameter while steam flow was controlled by metering water from a burette into the boiler using a Beckman Model 746 solution metering pump. The boiler consists of a 3/8-inch stainless steel tube inserted into a hole through a cylindrical insulated aluminum block that was heated by an electrical resistance heater. A Type K thermocouple was inserted into the block so that the boiler temperature could be monitored.

The fixed-bed reactor was constructed from a section of stainless steel tubing with an I.D of 22 mm and a length of 67.5 cm, the thickness of the tube wall being 1.2 mm. The reactor was surrounded by an electric furnace (Lindberg SB Hevi-Duti) mounted vertically on a steel frame support. To monitor the reactor bed temperature, a 1/4-inch (nominal) stainless steel tube was installed along the axis of the reactor. Three thermocouples were inserted into this axial well and were evenly spaced from the bottom to the top, the bed being about 6 cm in depth. The temperatures were monitored by a multi-point temperature recorder. The reactor was heated by an electric furnace constructed from an electric resistance coil forming a cylindrical heating chamber. The



Figure 3. Apparatus for conducting the coal-steam reaction

furnace temperature was controlled manually by regulating the voltage supplied to the resistance elements. Samples of coal undergoing activation were supported on a ceramic fiber pad held on a steel web welded to the wall of the reactor about 25 mm below the centre of the reactor. The temperatures reported in the activation process were mean temperatures taken between the top and bottom of the bed.

The produced gases and unreacted steam went through a water-cooled condenser and the water produced was collected in an ice-cooled trap. The volume of collected water inside the trap was measured so as to calculate the steam conversion. Noncondensible produced gas flows along with nitrogen were monitored by a wet test meter. Gas samples were taken from a gas holder by means of a syringe, then injected into a gas chromatogram for analysis.

3.3 Procedure

In preparing for a run, a previously prepared coal sample of approximately 22 g was initially weighed, then loaded into the reactor without drying. After sealing and pressure testing for leaks, the system was flushed with nitrogen at a flow of 150 mL/min. At the same time, the reactor and boiler were heated by setting the electrical power transformer regulators at predetermined levels. The coal sample was carbonized in the fixed-bed reactor at a heating rate of about 11°C/min. Carbonization was continued until the system achieved the desired activation temperature. It took about one hour for carbonization which converted the raw coals to "chars".

Instead of two separated stages, the carbonization and activation processes were combined as a single operation. When the carbonization step was completed and thermal equilibrium, which usually took 5 to 10 minutes, had been achieved, the steam carbon activation process was followed immediately. Activation was performed at 650, 700 and 750°C, respectively. The nitrogen flow was then reduced to 30 mL/min and water introduced at a controlled and predetermined flow rate by setting a pump rate of 0.9 mL/min. The durations of the activation times were again predetermined. Activation was conducted at atmospheric pressure. At the end of activation, the steam flow was terminated instantaneously and the nitrogen flow was increased to 340 mL/min. The furnace was opened and power supplies to the reactor and boiler were stopped. The reactor was cooled rapidly with a nitrogen atmosphere. After the system reached room temperature, the nitrogen flow was turned off and the produced activated carbon in the reactor was discharged, weighed and transferred to a sealed glass bottle for further physical and sorptive tests. At the exit of the reactor, unreacted steam was condensed and the product gases were passed through a wet test meter to measure the cumulative product gas volume.

During the course of a run, process gas samples were taken at regular intervals and were analyzed by gas chromatography. The temperature distribution along the length of the reactor and the surface temperature of the boiler were monitored continuously.

In investigating the effects of chemical additives on the activated carbon preparation process, solutions of five chemical reagents were prepared. These reagents were K₂CO₃, ZnCL₂, P₂O₅, HCL and Na₂CO₃ and were high purity (99.7%) chemical reagents obtained from Fisher Scientific Company. In all cases, the carbonization and activation procedures were exactly the same except that there were some differences in the raw sample preparation. In preparing the chemically-activated carbons from the coals of three different ranks were prepared by thoroughly mixing 20 g of the raw coal pellets with a solution of additives at a particular strength. The mixture was then slowly heated in an oven to a temperature of 120°C and held at this temperature for 24 hours. The reason for such a long heating period was to prevent pellets prepared from coals breaking into fines. Another reason was that a low heating rate was required to avoid reaching the coal ignition temperature in the oven. In some of the initial runs, we had found that the pellets became deformed and many fine particles were generated during the drying process due to the rapid evaporation of the water. In the later runs, we reduced the drying temperature to 120°C and extended the drying time to 24 hours. The first 15 runs in the chemical activation program were designed to search out suitable chemical additives while the last 10 runs were conducted to study the temperature and impregnation ratio on carbon activation.

3.4 Product Characterization

The quality of the activated carbon products was determined by measuring physical and sorptive properties of the final products. For instance, the physical tests consist of a number of analytical measurements such as specific surface area, mercury porosity, ash content, moisture content, bulk density and product yield. The sorptive capacity tests used in this research were for iodine number and methylene blue number. The detailed theories and definitions of these tests are described in Chapter 2. The following is a discussion of some of the general procedures employed.

Bulk density

The bulk density of the activated carbon products was accomplished by weighing the sample and measuring the volume occupied in a graduated cylinder. The determined mass divided by the sample volume gives bulk density.

Moisture content

The moisture content of activated carbon can be achieved by weighing approximately one gram of sample in a dry crucible, then placing the crucible in the oven and allowing it to dry for two hours at 140°C. The dried sample is cooled in a desiccator and weighed. The moisture content of the activated carbon sample can be calculated from the mass difference between the oven dried sample and the original sample mass.

% moisture content =
$$\frac{M_1 - M_2}{M_1} * 100$$

where

 $M_1 = mass of initial sample$

 $M_2 = mass of final sample$

Ash content

The ash content of activated carbon can be obtained by weighing the dried sample from the moisture content test, putting it in an evaporating dish in an electrically-heated furnace for six hours at 650°C, then cooling it in a desiccator and weighing it. The mass difference divided by the original sample mass times 100 is the ash content in percent.

Specific Surface Area

The surface areas of activated carbons were measured with the High Speed Surface Area Analyzer, Model 2000, by determining the quantity of nitrogen gas required to form a single layer of gas molecules on the sample surface. Since the operating manual suggests that testing was best accomplished with 50 to 140 m² of surface, and the surface areas of our products are usually between 250 to 550 m²/g, only about 0.2 g sample was

weighed out to do a test. Initially, the sample inside the test tube was connected to a suction tube and was flushed with nitrogen for five minutes. Next, the sample was heated to 250°C and held at this temperature for one hour for degassing. Before the sample was evaluated, the test tube was immersed in liquid nitrogen to cool the temperature down to that of liquid nitrogen (-198.5°C), then a test was started. Nitrogen gas contacted the solid (activated carbon) surface, the adsorption process started and a "counter" began to count the number. The final number indicated by the counter was the specific surface area. The true specific surface area per gram activated carbon was calculated using a pressure correction factor given in the operating manual. This is known as the "single point method" of determining the surface area. Normally the surface area of two samples of the same product were run and the average of the two used were recorded.

Iodine number

The iodine number determination was accomplished as described in the Process Design Manual for Carbon Adsorption, U.S. Environmental Protection Agency Technology Transfer [1972]. About 2.0 grams of activated carbon sample was ground to pass a 325-mesh sieve to produce approximately 1.0 g pulverized carbon. The product was put into a flask. To the flask was added 10 mL of 5.0 mass% HCL solution. The flask was put on a hot plate to bring the contents to a boil and allowed to boil for about 30 seconds. When the flask and contents cooled to room temperature, 100 mL of standardized 0.10 N iodine solution was added to the flask. The flask was immediately stoppered and the contents shaken vigorously for 30 seconds. After filtration, the iodine remaining in solution was determined by titration with 0.10 N sodium thiosufate. Since the capacity of an activated carbon for the adsorbate is dependent on the concentration of the adsorbate in the medium contacting the carbon, the concentration of the residual titrate must be determined so that appropriate factors may be applied to correct the concentration to agree with the iodine number according to its definition. To meet that requirement, an iodine number correction factor was obtained from a table given in the Manual. At the beginning of a series of analyses, these portions of a sample were weighed and iodine numbers on each were determined. The results showed little variation (less than 1.0% variation in iodine number), so the method was considered to be satisfactory.

Methylene Blue Number

The experimental procedure to obtain the methylene blue number was also available in the Process Design Manual for Carbon Adsorption [1972]. A similar method described by Sheffler [1956] was more suitable for the small amounts of activated carbon used for the test. For this reason, Sheffler's method was applied in this study. Another reason for using Sheffler's method was to be consistent with the work of previous researchers. The test was performed by adding a solution containing 1.0 g/L of aqueous methylene blue from a burette in small increments to a 1.0 g sample of activated carbon. The mixture was agitated for approximately one minute after each addition. The residual methylene blue concentration in solution was determined by placing a drop on a filter paper and matching the intensity of the blue spot to a series of spots produced from drops spectrophotometrically and corrections applied where necessary using a Freundlich isotherm from the Process Design Manual for Carbon Adsorption [1972].

To a 1.0 g sample of activated carbon small increments of methylene blue standard solution (1.00 g/L) were slowly added, shaking for few minutes after each addition (2-5 mL). When a blue colour was slightly visible in the residual liquid, the sample was filtered through a Buchner funnel. The filtrate concentration was determined using a Bausch and Lomb Spectronic 20 spectrophotometer and used in combination with the sorption isotherm to correct the observed sorption levels to the methylene blue number, defined as the number of milligrams of methylene blue adsorbed by one gram of carbon at an equilibrium concentration of 1.0 mg of methylene blue per litre of solution.

To obtain standard a isotherm curve, first a methylene blue solution containing 0.4 to 5.0 mg per liter was prepared. Ten points throughout the concentration range were chosen and solutions were recorded as peak heights determined by means of the spectrophotometer. Then based on different heights an X-Y diagram was prepared by plotting concentration against peak heights.

Chapter 4.

Results and Discussion

The objectives of the present investigation were to study a) the effects of particle size of the original coals, b) various process parameters such as activation time and temperature and \dot{c}) the use of chemical additives during the preparation on the quality of the activated carbon. A total of 70 runs was completed.

The activated carbon products were characterized by determining bulk density, ash content, product yield, specific surface area as well as iodine and methylene blue numbers. The first 40 runs were preformed using steam without chemical additives. The experiments were designed to study the effects of activation parameters such as coal rank, coal particle size and operating conditions in order to obtain the optimum steam activation temperature and time at the same time producing commercially acceptable activated carbon products. Another 30 runs were conducted using chemical additives. The first 15 runs were designed to investigate the effectiveness of each of the five additives including HCL, P_2O_5 , Na_2CO_3 , $ZnCL_2$ and K_2CO_3 . It was found that the products obtained from Coal Valley coal using K_2CO_3 as an additive were of better quality. Therefore, several runs were conducted with Coal Valley coal containing only one additive K_2CO_3 . The chemical additive impregnation ratio for the parent coal, the activation temperature and the effects of time were also studied.

In this section, all runs deal with the pelleted form of the activated carbon products. In the beginning is a brief discussion of coal rank and selection. Next some characterization results will be presented as a function of activation time and temperature, the objectives being to obtain an optimum temperature and time for the different coals. A comparison of the activated carbon produced from pellets and from two other forms of coal was completed by A. K. Dalai while investigating the influence of particle size on the product quality [Dalai, 1992]. Although the activation process was not designed to study the chemical kinetics of coal-steam activation, a short study of the kinetics of coal activation was included to gain some insight of the reactions between coal and steam.

4.1 Coal Rank and Selection

Coals varying in rank from anthracite to lignite have been used to manufacture activated carbons. As some of the most often used feed materials, coals have certain advantages. They are inexpensive, readily available and have high mechanical strength. However, the most important aspect is that coals exhibit initial porous structures of their own. These unique properties directly favour the development of the principal properties of activated carbon. The characteristics of manufactured activated carbon depend on the type and the properties of the raw coal used. Therefore, the selection of the type of coal is an important step in the preparation of activated carbon. The initial work in searching for preferable starting materials was conducted by Tollefson and Hall [Tollefson, 1981] at the University of Calgary. Six coals, ranging in rank from semi-anthracite to lignite A, were investigated. These coals were Wilson Creek (semi-anthracite), Highvale (sub-bituminous B), Whitewood (sub-bituminous B), Roselyn (sub-bituminous C), Forestburg (sub-bituminous C) and Bienfait (lignite A). The coal rank analyses were given in the Analysis Directory of Canadian Coals [1980]. The ranks were determined on the basis of calorific values on a moist-feed and mineral-free basis. By comparing the qualities of produced activated carbons under the same preparation conditions, Tollefson and Hall concluded that low ranking coals had consistently better qualities, and they recommended that low ranking coals were preferred raw materials.

In this research, coals with a relatively low rank and high volatile matter content were employed for the production of activated carbons. They were Bienfait, Montgomery and Coal Valley coals. The properties of the selected coals are listed on Table 2 (see Table 2). One advantage of using low rank coals is that they exhibit a wide distribution of pore size, and, more importantly, low rank coal has a greater fraction of large pores which can be further enlarged during the coal activation process. Large pores are extremely important for activated carbon used in waste water treatment.

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Table 2. The r	nain ch	aracteristics	of th	ne coals.	their	surface	areas	and	iodine	numbers
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Coals Rank	moisture	fixed carbon	volatiles	ash	surface area	iodine number
Coal Valley Bituminous C	6.9	49.1	33.1	10.9	364	449
Montgomery Sub-bituminous C	23.3	36.1	27.8	12.8	506	585
Bienfait Lignite A	29.8	30.1	30.1	10.0	441	522

* surface area and iodine number presented are for coals conditioned at 700°C for 2 hours.

It is important to note that the moisture content of Coal Valley coal is 6.9% which is significantly lower than that of the other two coals (see Table 2). The relationship between moisture content and specific surface area or iodine number suggests that high moisture content benefits the development of the sorptive properties of the activated carbon product. The initial moisture content of the coal implies an inherent porosity. This initial porosity can provide access for steam to the interior of the coal particles during the activation process. Importantly, this initial porosity will not be lost by coal shrinkage during the drying or carbonization process[Tollefson, 1981]. Also, the initial porosity can be further enlarged during the activation stage. This contributes to the increase in activated carbon throughput and reduces the activation time. Larger micropores not only contribute higher surface area, but also help to produce larger pore volume in the activated carbon product.

The fixed carbon contents of the coals(as listed in Table 2) show that Coal Valley coal has profoundly higher fixed carbon content, 15% higher than Montgomery coal and 20% higher than Bienfait coal. Usually, high carbon content represents large calorific value. Table 2 indicates that, as the fixed carbon content increases, the specific surface area and iodine number of the activated carbon obtained decreases. Furthermore, high fixed carbon contents imply higher activation temperatures to achieve the same activation rate as lower rank coals permit. The reason is that the endothermic steam-carbon reaction requires that sufficient heat be supplied to drive the activation process. This conclusion will be verified in later discussion.

It is of interest to note that the volatile contents of the selected coals are similar.

The loss of volatile matters during the carbonization process can have a considerable effect on offgas content. Their effects on porosity and pore size distributions of the char are not well understood. Chowdhury [1985] states that high volatile content may be undesirable since during the carbonization process devolatilization of organic components can cause pore plugging especially when processed under conditions of rapid gas production which will lead to the development of internal pressures which may cause swelling or fracturing of the pores. Coking of these volatile components in the neck of the pores can cause blocking referred to as "bottlenecking" which traps gas in the pores causing the product to float in water.

The ash contents of the coals to be studied were in the range 10% - 12.9% on an equilibrium moisture basis. Since the ash contents of the three coals are so close, it seems unwise to say that ash content has significant impact on specific surface area and iodine number development. However, it is an active research field for the fuel industry to understand the roles which the components of the ash play in the coal gasification process. In later studies on the effects of ash contents on produced activated carbons, as expected it was found that the ash contents of activated carbons are substantially higher than those of the parent coals. The reason for this is that the carbonization and the activation processes remove carbon from the coal and thereby substantially increase the ash content of the activated product. Therefore, the high initial ash contents of raw material coals are undesirable because they are expected to impose restrictions on the development of high specific surface areas.

4.2 Characterization of the Activated Carbons Produced

This section presents the studies of the characteristics of activated carbon products obtained from various coals as a function of activation temperature and time.

4.2.1 Product Yield

The effects of activation temperature on the yield of activated carbon product for the three different coals tested are shown in Figure 4a,4b and 4c. The general trends of these results are similar, an increase in activation temperature and time causing product yields to decrease.

In calculating the yield the following quantities were defined:

 W_o =weight of the original dry coal sample; g W_a = weight of ash in the original sample; g W= weight of product after activation; g W_{a1} = weight of ash in the product; g % yield = $(W-W_{a1})/(W_o-W_a)*100$

In testing for reproducibility, yields were determined with five samples of the product and \cdot the reproducibility was found to be $\pm 0.76\%$.

Data from Figure 4a and Figure 4b show that, for short activation times, Bienfait and Montgomery coals have similar product yields at low activation temperatures. For example, at an activation temperature of 650°C and after 1-2 hours of activation, Bienfait gives product yields of 53% to 57% while Montgomery gives similar results from 54% to 59%. Figure 4c shows that Coal Valley coal has the highest product yield in coals tested. The results shown in Figure 4d are in good accordance with those of other researchers [Solano,1979. Fung, 1983. Dutta,1977]. The low rank coals are more reactive than the high rank coals. However, higher product yield can be achieved from a relatively short activation time. Furthermore, product yield is an important parameter in selecting a preferred coal source as it relates to the output from a given activated carbon production facility. The product yield, however, has to be balanced against other important characteristics of the activated carbon produced such as the specific surface area and the iodine number.



Montgomery coal



Figure 4d. Effect of coal rank on product yield at an activation temperature of 700°C

4.2.2 Bulk Density

The variation in bulk densities as a function of steam activation time and temperature during steam activation period is shown in Figure 5a, 5b and 5c. Figure 5a and 5b show that low rank Bienfait and Montgomery coals exhibit similar patterns for the bulk densities. Moreover, comparing the results obtained at low temperature, 650°C, the bulk densities do not seem to change with increasing activation time. However, for low rank Bienfait and Montgomery coals, bulk density does decrease sharply with an increase in activation time at 700 and 750°C. For example, for Bienfait at 700°C, the bulk densities vary from 0.54 g/mL to 0.32 g/mL during activation times from 0.5 to 3 hours. Conversely, the data in Figure 5c indicate that the bulk density of Coal Valley coal does not change significantly with activation time at each of the temperatures tested.

A comparison of the bulk densities of the products from the three coals activated at 700°C is given in Figure 5d. It is interesting to note that Montgomery coal gives a product with lowest bulk density. Although it is not always true, low bulk density implies a larger pore volume of the activated carbon product.



Figure 5a. Bulk density as a function of steam activation temperature and time for Bienfait coal



Figure 5b. Bulk density as a function of steam activation temperature and time for Montgomery coal





Bulk density as a function of steam activation temperature and time for Coal Valley coal


4.2.3 Ash Content

Although the ash content of activated carbons probably has no significant effect on the sorptive capacities, it is quite possible that mineral matter composition and its distribution has a role to play in the variation of the relative reactivities of the steamcarbon reactions [Hippo,1979. Mahajan, 1979]. Data in Figures 6a, 6b and 6c show the ash contents of carbon products as functions of steam activation time at different activation temperatures. Generally, ash content increases with the activation time and temperature. For Bienfait and Montgomery coals, at longer activation times and especially at higher temperatures. the ash contents are considerably higher than those at low temperature. However, Figure 6c shows that the ash contents of Coal Valley coal are substantially lower and they are slightly affected by activation temperatures and times. The variation in bulk densities in the tested runs was less than 9%. The reason for this small difference is that Coal Valley coal is less reactive and has higher carbon content.

A comparison of ash contents for the products obtained at 700°C is given in Figure 6d. It can be seen that the effect of coal rank on ash content of the activated product is significant. For example, at the activation time of 2 hours, Coal Valley coal gave ash content of 20.6%, while Bienfait coal gave 43.2% which is more than double the lower value. A high ash content in the activated carbon produced is undesirable [Tollefson,1981] since high ash content can reduce the activated carbon mechanical strength and sorptive properties. Jagtoyen [1993] reported that reducing the ash content increases the specific surface area and pore volume. The changes in surface area and pore volume caused by lowering ash content might be attributed simply to the fact that ash has negligible porosity. Hence, reducing the ash content will increase the specific surface area and pore volumes. However, in this research, it was found that this is not always true. The reactions between coal and steam may be affected by the small amount of mineral matter present in the ash not by the ash itself. It is more likely that ash constituents block the pore structure of the coals and this may only have a significant effect on specific surface area and porosity in the subsequent activation period.

Coal with a high ash content can be purified by flotation, wet oxidation or other chemical treatments such as acid washing. For instance, coal which contains chiefly silicates can be upgraded with a solution of sodium hydroxide or sodium carbonate which removes the silicates [Jankowska,1991]. A unique process which deals with low ranking coals was reported by Jankowska [1991]. Coals, before carbonization and activation, could be mixed with an oil and water solution. The coal separates into the oil layer while the ash penetrates the water phase. In this method, the coal ash contents can be remarketly reduced.

Another interesting point about the ash content of the parent coals is that the mineral matter presented mainly by the ash may affect the reactivity of the carbon during activation of the coal. That mineral matter catalyses coal gasification has been widely reported by writers such as Jatoyen [1991] and Ehrburger [1988] who pointed out that ash constituents may catalyze unwanted reactions. Tollefon and Hall [1981] indicate that relatively high alkali metal content and high potassium/ sodium ratio may have an impact on the development of enhanced sorptive properties. However, it is still difficult to

ascertain the manner in which mineral matter correlates with pore size and surface area development. The results reviewed from the literature also are varied.

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Figure 6a. Ash content as a function of steam activation temperature and time for Bienfait coal



Figure 6b. Ash content as a function of steam activation temperature and time for Montgomery coal





Figure 6d.

Effect of coal rank on ash content at an activation temperature of 700°C

4.2.4 Specific Surface Area

High specific surface area is one of the most desirable parameter used in judging the quality of the activated carbon produced. The BET adsorption method was employed to measure the specific surface area of the activated carbon products. Figure 7a,7b and 7c show specific surface area as a function of activation temperature and time for each coal. The data show that low specific surface areas are developed during the initial stages of activation and later increase to maximum values in most cases.

For Bienfait coal, the results show in Figure 6a that the highest specific surface area of 490 m²/g was obtained for the products at 650°C after 4 hours of activation. It is important to note that most of the specific surface areas are above 400 m²/g which are in the region of surface areas of commercial activated carbons. The maximum surface areas for 700 and 750°C are approximately 450 and 420 m²/g respectively. At 650°C, the specific surface area data show a linear relationship with the increase in activation time. Although low temperature activation gives a higher specific surface area, a considerably longer activation time is undesirable from the stand point of plant operation especially for high temperature endothermic reactions.

Montgomery coal gave the highest specific surface area of 506 m²/g for material produced at 700°C in a two hour period. A rapid rise in surface area with increasing activation temperatures and times shown in Figure 7b indicates that specific surface area development for Montgomery coal is very sensitive to the activation conditions. However, the influence on specific surface area development only happens at relatively high temperatures. Surface areas development is almost independent of activation time as

observed at 650°C.

Figure 7c indicates that, for Coal Valley coal, to achieve a high specific surface area, a reasonably high activation temperature and long activation time are required. For example, at 650°C, even with a longer activation time of 3 hours, the specific surface area obtained was still considerably lower than expected at 300 m²/g. Even at a relative high temperature of 700°C, the results obtained show a value less than 400 m²/g.

The effects of coal rank on the development of specific surface area development are shown in Figure 7d. The results imply that Coal Valley coal as a source material to produce activated carbon is less desirable than the other coals since it gives products with lower surface areas.

Since specific surface area may be the most important characteristic of activated carbon, most research papers use it to indicate the quality of the activated carbon produced. It is worth comparing the specific surface areas obtained with those given by other researchers. Merchant [1992] studied the steam activation method to produce activated carbon using Illinois No.5 bituminous coal with a volatile content of 39.7% and an ash content of 9%. The specific surface area reported was in the range from 400 to 670 m²/g. Five Louisiana lignites coals were used to produce activated carbon, Rist reported the maximum surface area obtained was 460 m²/g at a steam activation temperature 850°C for three hours. Using the same steam activation method, Jagtoyen obtained a value of the specific surface area of 660 m²/g at an activation temperature of 550°C using bituminous high volatile C coal. The highest surface area reported in the literature review was that of Sousa[1993] which was about 1300 m²/g. However, it needed

the longest activation time of four days. The highest specific surface area from this research with the pellet form of activated carbon was 506 m²/g and with the granular form was 640 m²/g from Montgomery sub-bituminous C. For Bienfait lignite A, the maximum specific surface areas obtained were 490 m²/g for the pellet form and 510 m²/g for the granular form. Coal Valley bituminous C coal gave 426 m²/g for the pellet form and 300 m²/g for the granular form. They are in good agreement with the values of other researchers such as Rist [1985] and Merchant [1992].



Figure 7b. Specific surface area as a function of steam activation temperature and time for Montgomery coal



Figure 7c. Specific surface area as a function of steam activation temperature and time for Coal Valley coal



Figure 7d. Effect of coal rank on specific surface area at an activation temperature of 700°C

4.2.5 Iodine Number

High iodine numbers are generally regarded as a measure of sorptive properties of activated carbon. Effects of steam activation time at three different temperatures on iodine numbers are shown in Figure 8a, 8b and 8c for the products prepared from Bienfait, Montgomery and Coal Valley coals, respectively. It is interesting to note that the iodine numbers developed as a function of activation temperature and time show patterns similar to those obtained from specific surface areas (see Figure 8). Again, there is clear rank dependence of iodine adsorption on activation time shown in Figure 8d. For Bienfait coal, iodine number is highest in the initial stages of activation. For example, the iodine number data in Figure 8d show that, during the short time period from 0 to 1 hour, Bienfait coal has substantially higher iodine numbers than those of Montgomery and Coal Valley coals. More importantly, Figure 8d implies that the iodine number development of the three tested coals is different. The increase in iodine number generally indicates the generation of new pores from steam activation. It can be seen from Figure 8d that, at 700°C, the pore creation of Bienfait coal is in the 0 to 1.5 hour period, Montgomery coal is at 1 to 2 hour region. The high rank coal needs the longest activation time to reach its maximum sorptive properties. Again, it may be concluded that low rank coals can be easily activated. However, a larger iodine number is achievable for Coal Valley bituminous C coal. Figure 8c shows that development of the iodine number of Coal Valley coal requires relatively high activation temperature and longer activation time. In fact, the highest iodine number was obtained with Coal Valley coal which was 607 at a activation temperature of 750°C and with 3.5 hours activation time.



Figure 8a. Iodine number as a function of steam activation temperature and time for Bienfait coal



Figure 8b. Iodine number as a function of steam activation temperature and time for Montgomery coal



4.2.6 Methylene Blue Numbers

Methylene blue is a substantially larger molecule than iodine. Therefore, larger pore diameters are required to accommodate the methylene blue molecules than are required to allow access for iodine to the sorptive internal surface of a given activated carbon. Methylene blue number measures the extent of larger pores obtained with an activated carbon product.

Methylene blue numbers in Figure 9a, 9b, 9c and 9d also exhibit shapes similar to those demonstrated for iodine number and specific surface area. However, relatively longer activation temperatures are necessary for enlargement of the pore structure to obtain the larger methylene blue number which is observed. For example, Figure 9a shows Bienfait has the largest methylene blue numbers at temperature 750°C. A similar result is given by Coal Valley coal in Figure 9c. The maximum methylene blue numbers for the three coals tested were the range of 70 to 80. A comparison of the effect of coal rank on methylene blue number is given in Figure 9d which shows methylene blue number as a function of steam activation time at a fixed temperature of 700°C. The data show that larger methylene blue numbers can be obtained readily from Montgomery Coal.



Figure 9b. Methylene blue number as a function of steam activation temperature and time for Montgomery coal



Figure 9c. Methylene blue number as a function of steam activation temperature and time for Coal Valley coal



Figure 9d. Effect of coal rank on methylene blue number at an activation temperature of 700°C

4.3 Effects of Activation Temperature and Time

The steam-coal activation producing activated carbon is a complex heterogeneous process encompassing a series of steps such as steam transport to the coal surface, adsorption of steam, the reaction of steam with carbon at the coal surface and diffusion of produced gases to the surface. However, temperature has a great influence on each step and thus affects the activation process. Hassler[1974] stated that the sorptive properties of the activated carbon produced are determined by the temperature and the extent of activation. The effects of activation temperature and time on steam activation are two of the most important factors in the current investigation.

According to Jankowska [1991] the effect of temperature on the activation process occurs in three ways. At low temperature, the overall rate of the activation process is limited by the chemical reactions at the coal surface. In such a case, the process yields a homogeneous product with a uniform distribution of the pores. With an increase in the activation temperature, the overall rate can be mutually controlled by chemical reaction and mass transfer. However, it is also true that the rate of the chemical reaction increases much faster than that of diffusion in which case the overall rate of the activation process becomes limited by the rate of transport of steam to the carbon matrix. A very high temperature is undesirable because the reaction rate becomes so high that the steam reacts with the carbon on the external surface of the coal. In such a case, significant losses of the material occur due to superficial oxidation, and a porous structure is not formed.

To find the optimum activation time at a particular temperature during the

activation process, a relationship between iodine number, specific surface area and product yield was established. Product yield is an important parameter in reactor design. Moreover, considering the applications of activated carbon, its sorptive capacities in the liquid and gas phases are important characteristics, and may be represented by iodine number and specific surface area values. The increases in specific surface area and iodine number are directly related to pore development of the products. They could be affected by one or more of the following phenomena: 1) opening of previously closed pores; 2) creation of new pores; 3) enlargement of preexisting and/or newly developed pores; and 4) pore collapse by over rapid reactions. Owing to the carbonization of coal, an initial porous structure builds up inside the char. The pores of the carbonized coal (or char) are often filled with tar-like decomposition products and may be blocked with amorphous carbon [Jankowska, 1991]. This amorphous carbon reacts in the initial activation step and, as a result closed pores are opened and new ones are formed. During activation, the carbon of the elementary crystallites enters into reaction causing the existing pores to widen. With a large group of pores developed and more active sites becoming available, the rate of reaction between carbon and steam is dramatically catalyzed. Existing pores may also be destroyed by rapid surface reactions.

Bienfait lignite A coal, as discussed in previous sections, is the most reactive coal among the three coals tested. Figure 10 gives the iodine number and specific surface area values as functions of product yield from Bienfait coal at an activation temperature of 700°C. The figure indicates that in the initial stages of steam activation, the product yield is substantially higher in the range of 50%, and then on further activation, the product



Figure 10. Iodine number and specific surface area as a function of % product yield for Bienfait coal at 700°C

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yield is progressively decreased. In fact, with a sufficiently long reaction time, all carbon components could be converted to product gases. More importantly, with the decrease in product yield, the product specific surface area and iodine number increase to maximum values. It can be seen that the product yield corresponding to a maximum iodine number of 521 is about 33% and for a maximum specific surface area of 454 m²/g, the product yield is about 25%. Therefore, the data in Figure 10 show that the optimum activation time for the products obtained for Bienfait coal at 700°C is between 1.5-2.0 hours (see Figure 4a).

The relationship between the product yield and sorptive properties development for Montgomery Coal is given in Figure 11. The optimum product yield at 700°C is in the range of 33% which is at less than two hours of activation (see Figure 4b). The products obtained from Coal Valley coal in Figure 12 indicate that the optimum product yield is in the region 45-47% for an activation temperature of 750°C and reaction time of 3-3.5 hours (see Figure 4c).



Figure 11. Iodine number and specific surface area as a function of % product yield for Montgomery coal at 700°C



Figure 12. Iodine number and specific surface area as a function of % product yield for Coal Valley coal at 750°C

A comparison of the products obtained from the three coals shows that, in the optimum regions, the specific surface areas and iodine numbers are about 450 m²/g and 550, respectively. Bienfait coal gives the highest specific surface area values in the initial activation stages which are substantially higher than those of Montgomery and Coal Valley coals. This may be due to the fact that: 1) Bienfait coal is relatively more reactive and has more initial pores or 2) in the initial stage of the activation process, the closed pores are more easily opened by the steam-carbon reaction. Figure 11 indicates that for products from Montgomery coal, the iodine number and specific surface area developments increase more rapidly with decreasing of product yield. This implies that most micropores are created in the 35-40% product yield region. At the relatively higher activation temperature of 750°C, Coal Valley coal exhibits properties similar to Bienfait coal. However, it gives a considerably higher product yield. The high product yield has to be balanced with the activation time and product quality. Using optimum activation times and product yields, sample calculations of hourly output for the same feed rate among the three coals show that Bienfait and Montgomery coals have similar hourly output rates of 17% while Coal valley coal shows about 14%. So, high rank coal with longer activation time and a higher reaction temperature may not be desirable depending on the properties desired and the costs operating a plant.

4.4 The Effect of Particle Size

The effect of coal particle size was studied by comparing the characteristics of the three forms of activated carbons produced from the three coals employed. They were fines (0-1.25 mm), granular (1.25-2.5 mm) and pelleted (cylindrical, 3.18 in diameter and 7 mm long) products. For the sake of convenience, they will hereafter be referred to as "fines", "granular" and "pelleted". Conventionally, in industry, the products of these three are called "powdered", "granular" and "pelleted" activated carbon. Fines and granular are frequently used in the liquid phase while pellets are often used for gas phase adsorption. It should be mentioned here that the preparation of fines and granular forms of activated carbon used in this research was done by A.K.Dalai.

The effects of coal particle size on the product yields are given in Figure 12 which shows product yield as a function of activation time at a fixed activation temperature of 750°C. As expected, the data show that product yield decreases during steam activation. With the respect to coal rank, Coal Valley bituminous C coal, gives consistently high product yields whereas Bienfait lignite A coal gives the lowest product yields under the same conditions of activation.



Figure 13. Effect of steam activation time at 750°C on yield of solid products from coals having different particle sizes in a fixed-bed reactor

The data in Figure 13 show that, for Bienfait coal, product yields are only slightly changed as a result of the size difference of the feed coal, the data presented for Bienfait coal for three different particle sizes being very close. This implies that there is no effect of particle size on the rate of activation. In other words, the activation process is not diffusion controlled.

For Montgomery coal, the data in Figure 13 show that the product yields are affected by using different particle sizes. The activated carbons produced from fines give the highest yields, followed by granular and pelleted products. If the reaction is mass transfer controlled, the product yield will change with the different particle sizes. Interestingly, the product yield results for Montgomery coal are just the opposite in that product yield decreases with an increase of coal particle size. More interestingly, the product yield for Coal Valley coal shows that the yields from the granular form are higher than those from fines and pellets. Fines and pellets exhibit similar results. The exact mechanism behind, the steam-coal reactions is not understood. One possible reason used to interpret the irregularities of the product yields from Montgomery and Coal Valley coals using different particle sizes is that the overall process is not simply controlled by a single step during the entire activation period. The steam-carbon reaction is indeed a rather complicated process. At a given temperature, the process may be controlled by mass transfer in the initial stages of activation, and then, with the increase of activation time, a large surface area is developed, and the activation process becomes controlled by a chemical reaction. Later, with the loss of surface area during further activation, the reaction could return to being controlled by mass transfer. Because of the complexity of coal itself, the activation time period under a particular controlling behaviour could depend on coal rank, the particle size of the coal used, the development of pore structure, the activation temperature or some unknown factors. Moreover, they all may be important parameters which influence the yield of product.

In a manner similar to that employed in the previous section on the investigation of optimum activation temperature and time, the effect of particle size on the development of specific surface area and iodine number is also plotted. Iodine number and specific surface area are functions of product yield at a given activation temperature.



Figure 14. Iodine number and specific surface area as a function of % product yield from Bienfait coal at 700°C using a fixed-bed reactor

For Bienfait coal, Figure 14 shows that optimum product yields were 38%, 30% and 32% for fines, granules and pellets, respectively, while their corresponding activation times were 1.5, 1.0 and 2.0 hours. The development of optimum specific surface and iodine number are similar. For example, fines have a specific surface area of 400 m²/g, granules have a specific surface area of 460 m²/g and pellets show 411 m²/g. Different particle size curves indicate that the iodine numbers and specific surface area obtained from Bienfait fines are very sensitive to activation time. This may be explained on the basis that the pores developed by steam activation of fines are not like those of pellets or granules. They may be relatively fragile and may be easily collapsed by further activation.



Figure 15. Iodine number and specific surface area as a function of % product yield from Montgomery coal at 700°C using a fixed-bed reactor

Figure 15 shows the effect of coal particle size on the development of the iodine number and specific surface area of Montgomery coal. Unlike Bienfait coal, the curves show that it takes a relatively longer time to reach maximum values. The maximum iodine numbers and specific surface areas obtained are quite different. For example, the difference between the maximum specific surface areas for fines and granular activated carbons is more than 200 m²/g as shown in Figure 15. One thing which should be mentioned is that, for the granular product, this is a surprising result in that the iodine number value curve is lower than that of the specific surface area which has not happened in other cases. This may be due to a change in the pore distribution of the activated carbon produced. It is likely that only a small fraction of relatively large pores were developed.

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The effect of coal particle size on the iodine number and specific surface area development of Coal Valley coal is given in Figure 16. It can be seen that the shapes of the three specific surface area curves are almost identical. The fines and the pellets exhibit similar results whereas the granular material gave the lowest surface area and iodine number. Comparing the optimum iodine numbers obtained using different coal particle sizes, it is noted that they are in the range from 420 to 450. It seems that by using different particle sizes, there is no significant effect on iodine number development.



Figure 16. Iodine number and specific surface area as a function of % product yield from Coal Valley coal at 700°C using a fixed-bed reactor

The effect of coal particle size on methylene blue number development using the three coals is illustrated in Figure 17, 18 and 19. The methylene blue data in these figures show that the activated carbons from the fines of the three tested coals exhibit substantially higher methylene blue numbers than those from the granular and pelleted products. The figures also indicate that the pelleted forms are less favourable for methylene blue number development. Figure 17 shows that activated carbons from Bienfait coal using the granular form can achieve high methylene blue numbers under optimum conditions, but it usually needs a relatively longer activation time than the fines do. The methylene blue numbers in Figure 18 and 19 indicate that methylene blue number development for Montgomery and Coal Valley coals show somewhat similar results when using the granular and pelleted forms. Curves representing the data for the fines may be drawn according to a linear equation or according to a second order equation (hatched). The latter suggests that the results go through a peak and then decrease at lower yields. This is to be expected since the activated carbon structure will tend to disintegrate at high conversion levels.



Figure 17. Methylene blue number as a function of % product yield from Bienfait coal at 700°C using a fixed-bed reactor



Figure 18. Methylene blue number as a function of % product yield from Montgomery coal at 700°C using a fixed-bed reactor


Figure 19. Methylene blue number as a function of % product yield from Coal Valley coal at 700°C using a fixed-bed reactor

The influence of different coal particle sizes on ash content is given in Figure 20. The ash content results are plotted as a function of steam activation time. As expected, ash contents increase with the extent of activation. Most curves exhibit almost a linear relationship between ash content and steam activation time. Exceptions are observed with Bienfait fines and granular sizes. The curve of granular Bienfait coal shows a particularly steep slope. The reason is that both Bienfait fines and granular products need relatively short activation times at 700°C to reach the maximum specific surface area as discussed earlier. No data are presented from the later stages of the activation. The reactions takes place vigorously at the surface of the coal and the pores collapse faster than pore creation and enlargement and a rapid increase in ash is to be expected.



Figure 20. Effect of steam activation time at 700°C on ash content of solid products from coals having different particle size in a fixed-bed reactor

The effect of particle size on the densities of activated carbon produced is shown in Figure 21. The almost linear relationship implies that bulk densities are not greatly influenced by different particle sizes.



Figure 21. Effect of steam activation time at 700°C on bulk density in a fixed-bed reactor

4.5 Effect of Chemical Additives on the Preparation of Activated Carbon

The study of the effect of chemical additives on the preparation of activated carbon is another important objective of this research. The use of chemical additives to achieve a high quality activated carbon is highly attractive since it offers the possibilities of activation of the carbon in shorter activation times and at lower temperatures that are practicable in the absence of chemical additives. However, only a few researchers have investigated the effects of chemical additives on the preparation of activated carbon [Derbyshire, 1992]. Most studies are usually focused only on the carbonization process [Torregrosa,1991. Jagtoyen 1992]. In this study, the first 15 runs were conducted to investigate the effectiveness of the five selected chemical reagents used for coal activation process. The effectiveness of these activation reagents was determined from the characteristics of the activated carbon products such as specific surface area, iodine number, methylene blue number, product yield, ash content and bulk density. Also, the outstanding selected chemical additive was selected for further studies with respect to the effects of impregnation ratio, activation temperature and time.

4.5.1 Chemical Additive Selection

Five predetermined chemical reagents, namely, HCL, P_2O_5 , Na_2CO_3 , $ZnCL_2$ and K_2CO_3 were investigated. They were added to the coal by aqueous impregnation. Activation conditions were set at 700°C for two hours. For all runs, chemical loading was fixed at 1.0 percent. The results obtained are present in the Table 3.

Coal Soruce	Coal Rank (ASTM)	Catalyst	Surface Area (m ² /g)	Iodine Number	Methylene Blue Number	Yield (% dry basis)	Bulk Density (g/mL)	Ash Content (%W:W)
Bienfait	Lignite A	None HCl P_2O_5 ZnCl ₂ Na ₂ CO ₃ K ₂ CO ₃	441 452 420 446 428 426	522 501 447 433 480 488	32 66 51 47 59 54	30.8 44.1 43.1 41.3 34.0 37.3	0.34 0.43 0.44 0.42 0.38 0.37	38.4 26.8 27.4 28.6 34.8 31.8
Montgomery	Sub- bituminous C	None HCl P_2O_5 ZnCl ₂ Na ₂ CO ₃ K ₂ CO ₃	506 391 439 413 488 420	585 409 388 398 515 414	82 33 31 32 44 29	33.1 35.7 38.2 48.8 37.2 42.6	0.29 0.32 0.32 0.37 0.28 0.32	37.4 34.7 32.5 25.4 23.3 29.1
Coal Valley	Bituminous C	None HCl P_2O_5 ZnCl ₂ Na ₂ CO ₃ K ₂ CO ₃	364 297 318 326 386 465*	449 445 337 373 448 538	25 14 17 18 29 59	55.7 62.5 57.2 64.1 57.1 48.8	0.42 0.42 0.42 0.45 0.42 0.39	20.6 . 18.4 20.0 17.9 20.1 20.8

Table 3. The effect of various catalysts (% dry weight) on the properties of cylindrical pellets of activated carbon obtained from three western Canadian coals activated at 700°C for 2 hours.

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From Table 3, it is apparent that most tested chemical reagents have no effect or a negative effect on the product qualities. However, in general, chemical additives in use have been beneficial in improving the product yield, increasing bulk density and reducing ash content. Particularly, it has been observed that ash content can be reduced dramatically. For example, Table 3 indicates that the ash content is dropped more than 30% for the activated product from Bienfait coal using HCL and 37% for Montgomery coal using Na₂CO₃. Higher product yield and lower ash content are highly desirable because better yield represents more output and lower ash content implies better mechanical strength of the products. However, the changes in product yield and ash content must be balanced by the important characteristics such as iodine number, specific surface area and methylene blue number. In our studies on specific surface area and iodine number development, we found that almost all specific surface areas obtained from the chemical activation process are lower than those from blank runs except that of Bienfait coal using HCL and Coal Valley coal using K₂CO₃. However, only slight improvement of specific surface area of the product from Bienfait using HCL is observed. Furthermore, on comparing the surface area and the iodine number of the product (see Table 3) from Coal Valley coal using K₂CO₃, it is seen that the specific surface area increased from 364 m²/g to 465 m²/g and the iodine number went up from 449 to 538 from which it was concluded that K_2CO_3 is the most effective chemical additive among the tested chemical reagents.

The changes in methylene blue number in Table 3 show that use of chemical

additives has a different impact on each coal. It is interesting to note that methylene blue numbers developed from Bienfait coal by using chemical additives are substantially higher than those from the runs without chemical additives. At the other extreme, reduced methylene blue solution adsorptive capacities by using chemical additives is observed with Montgomery coal.

Methylene blue numbers from Coal Valley coal activation products show that only Na_2CO_3 and K_2CO_3 can be used to improve methylene blue number development. The addition of K_2CO_3 increases the methylene blue number from 25 to 59 which is more than 100% These results may be explained on the basis that chemical additives play an important role in enlarging existing pores. However, this role is rather dependent on the properties of coal itself. It should be mentioned that Bienfait coal using an HCL treatment shows a substantially higher product yield and a considerably lower ash content both of which are worthy of further investigation. Since specific surface area and iodine number are the most important parameters which are directly associated with sorptive capacities, only Coal Valley coal using K_2CO_3 as additive was studied further.

4.5.2 The Effect of Impregnation Ratio

The impregnation ratio is defined as the percentage by weight of the chemical additive added to the source material. The current study is concentrated on Coal Valley coal activation using K_2CO_3 exclusively as an additive. Table 4 shows the results obtained using different K_2CO_3 impregnation ratios from 1 to 10%. The activation conditions were fixed at a temperature 700°C for 2 hours.

Table 4. Investigation of the effect of different K_2CO_3 impregnation ratios on the Coal Valley coal activation process (T = 700°C, t = 2 hrs, pellets)

Impregnation ratio wt %	Surface Area (m ² /g)	Iodine Number	Methylene Blue Number	Yield (% dry basis)	Bulk Density (g/mL)	Ash Content (% W:W)
0	364	449	25.4	55.7	0.42	20.6
1	465	538	58.8	48.8	0.39	20.8
2	405	520	46.9	47.2	0.36	22.4
5	397	499	36.6	41.3	0.41	27.8
10	247	375	5.3	19.6	0.41	58.9

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Based on a screening study from Table 5, under the given activation temperature and time, the results show that product yields decrease with the increase in K_2CO_3 loading. In contrast, the ash contents increase, especially, at a K_2CO_3 loading at 10%. A rapid decrease in product yield means that the reaction rate of the coal-steam reaction is accelerated by the increase in chemical reagent loading. Although the bulk densities are not constant, they seem unaffected by different impregnation ratios.

In order to study the effect of impregnation on the development of sorptive properties, the specific areas and iodine numbers obtained are plotted as a function of impregnation ratio in Figure 22.



Figure 22. Iodine number and specific surface area as a function of K₂CO₃ impregnation ratio

Figure 22 indicates that iodine numbers and specific surface areas increase rapidly to their maximum then decrease with the increasing impregnation ratio. It can be clearly seen that the maximum iodine number and specific surface area are obtained at an impregnation ratio of approximately 1.0% under the test activation condition.

The data in Table 4 show a similar result on the development of the methylene blue numbers,. A maximum methylene blue number is produced at an impregnation ratio of approximately 1%. In contrast, a considerably lower methylene blue number is obtained at a K_2CO_3 impregnation ratio of 10%.

Scanning electron microscope studies show that for activated carbon with high specific surface area and iodine number, or, in other words with the better sorptive capacities, its surface is more uniform and homogeneous as shown in Figure 23a. Figure 23b shows how pores grow in size and bigger cavities are formed by the collapse of the pores. Pore collapse in an over-reacted situation is clearly presented in Figure 23b. This further supports the contention that the activation action of the activating gas (steam in this case) does not consist of an indiscriminate removal of successive layers of atoms from the coal surface. Instead, steam activation selectively erodes the coal surface so as to increase the specific surface area and develop larger porosity. In the presence of an extremely high activation rate, the reactions between steam and carbon can destroy already existing pores. In general, the higher the activation rate, the more apt the system is to produce activated carbon. However, these results show that this is not necessarily true when considering the product from higher impregnation ratios such as at 10%. A suitable activation rate is a key factor in the activated carbon preparation process.



Figure 23a. Scanning electron microscope study on activated carbon produced from Coal Valley using K₂CO₃ impregnation ratio 1.0%



Figure 23b. Scanning electron microscope study on activated carbon produced from Coal Valley using K₂CO₃ impregnation ratio 10.0%

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4.5.3 Activation Temperature and Time

It has been known for many years that K_2CO_3 can catalyse the coal-steam reaction, but its effect on pore structure development is not understood. The possible reactions between coal and K_2CO_3 as proposed by Juntgen [1983] which are given as below:

$$K_2CO_3 \rightarrow K_2O + CO_2$$

 $K_2O + C \rightarrow 2K + CO$

The presence of elemental K was found by experimental study of the reactions between 500°C and 800°C. The reaction between coal and steam in the presence of K_2CO_3 was also studied by Kayembe [1976]. Studying on bituminous type of coal, the activation energy of the coal tested could be reduced from 254.2 to 144.5 KJ/mol by using 10% K_2CO_3 . Similar results are given in Table 4 which showed that product yields are decreased significantly by increasing impregnation ratio. One possible answer for the improved sorptive properties developed in the presence of K_2CO_3 is that a more energetic reaction occurs with Coal Valley coal which *r*esults in erosion of the carbon accompanied by an increase in sorptive power. It seems that a reasonable reaction rate is rather an important factor in the producing of activated carbon.

Further study on the effects of activation temperature and time on the coal chemical activation process was conducted at a fixed impregnation ratio of 1.0 % which is close to the optimum ratio for Coal Valley coal using K_2CO_3 . The activation temperatures, times and the obtained characteristics of the activated products are listed in Table 5.

Temperature (°C)	Time (hr)	Surface Area (m ² /g)	Iodine Number	Methylene Blue Number	Yield (% dry basis)	Ash Content (% W:W)	Bulk Density (g/mL)
650	1	277	342	10.4	60.34	19.04	0.36
	2	264	319	7.3	60.55	18.73	0.36
	3	360	417	23.6	48.31	21.53	0.38
700	1	382	414	21.3	53.52	21.47	0.38
	2	465	538	58.8	48.81	20.76	0.39
	3	429	533	72.5	47.75	24.06	0.36
·750	1	408	589	42.5	44.16	26.02	0.32
	2	481	588	71.2	42.13	26.83	0.35

Table 5. Investigation of the effect of activation temperature and time on Coal Valley coal using K_2CO_3 at a fixed impregnation ratio of 1.0%

The results show that, at a low activation temperature of 650°C, although it gives higher product yields and lower ash contents, the specific surface areas, iodine numbers and methylene blue numbers of activated products are substantially lower than those obtained at a higher activation temperature. However, it seems that bulk densities are not affected by the difference in temperatures. In order to obtain a higher sorptive capacity, higher activation temperature is necessary. The data in Table 5 show that, at a given activation time, a high temperature of 750°C obtains the highest specific surface areas, iodine numbers and methylene blue numbers. The development of sorptive properties also shows time dependence. The optimal surface area of 465 m^2/g is obtained at 700°C for two hours and the maximum surface area is given at 750°C for two hours. The reason why a relatively low temperature generally requires a longer activation time to reach a maximum value is that the low activation rate does not supply sufficient energy to generate new pores. It should be mentioned here that, in the absence of a chemical additive, it generally requires about four hours activation to achieve 480 m²/g surface area. In contrast, with the chemical additive, at the same activation temperature of 750°C, it only needs two hours of activation. That makes the chemical activation process more economic, because it can save energy consumption for generation of steam and heating the reactor at the same time the emission of carbon dioxide to the atmosphere from generating steam would be reduced. On the whole, it can be stated that chemical activation has made some important progress, however, its more detailed study is still an aim for the future.

4.6 Steam Activation Kinetics

Preparation of activated carbon by the reaction of coal and steam is a very complex process in which two kinds of processes overlap: a) carbonization of the coal and b) the reaction of the carbonized product with steam (activation). The activation process is complex comprising parallel and subsequent reactions of coal with steam and with reaction product gases (H₂, CO). The literature on the reaction of coal with steam is guite extensive and several reviews have been published [Kayembe, 1976. Solano, 1979, Fung, 1982, 1983. Kwon, 1989. Yang 1994]. The whole process is heterogeneous and therefore occurs in a series of steps involving diffusion and chemical reaction. They may be described as follows: 1) mass transfer and diffusion of steam through a relatively stagnant film to the coal surface; 2) chemisorption of steam on the carbon surface, coupled with reaction of chemisorbed steam with carbon to form products; 3) release of the surface reaction product gases; and 4) diffusion and mass transfer of the gases to the bulk gas stream. Thus, in a broad sense, the heterogeneous process comprises of parts including diffusion and chemical reaction. In the previous section, the rate of activation has been observed to be influenced by several parameters such as activation temperature, the coal type, coal particle size and chemical additive added.

Although product quality is dependent mainly on the activation stage, it is reasonable to have a brief discussion on the coal carbonization process. By periodically monitoring tail gas compositions, the results show that the carbonization process is composed of three stages: First, there is the drying stage during the initial heating period in which only a trace of water vapour is present and the temperature range is from room temperature to about 250°C. This period consumes most of the carbonization time (about 35 min). The second stage is the coal devolatilization process in which the excess of lower boiling fractions of organic matters are removed. This occurs at 250 to 600°C and lasts about 15 to 20 minutes. The third stage involves further devolatilization in which the production of light gases is found to decrease rapidly above 600°C. This observation supports the idea that the carbonization process is complete. The main aim of the carbonization process is to generate the initial pore structure and to give the coal the mechanical strength required during activation.

It is necessary to consider the chemistry of the activation process. According to Fredersdorff [1963] and Gadsby [1946], it seems to be generally agreed that the primary products of the reaction of steam with comparatively pure carbons at atmospheric pressure are carbon monoxide and hydrogen. The reaction can be written as:

$$C + H_2O = CO + H_2$$

It is also reported by other investigators [Fung 1983. Kayembe, 1976. Kwon,1989] that two other reactions may occur when steam contacts char (carbonized coal). These are the water-gas shift reactions

$$CO + H_2O \iff CO_2 + H_2$$

and the reaction of the carbon with steam to produce methane as follows:

$$2C + 2H_2O \iff CH_4 + CO_2$$

The latter reaction, however, is unimportant since according to tail gas analyses there is

almost no methane existing during the activation process.

Unfortunately at the present time insufficient data are available to make a more quantitative study of the kinetic investigation of the whole activated carbon preparation process. The experimental runs were designed to study the optimal activation temperature and time to obtain a better quality product. In this special situation, the kinetic study would focus only on the steam activation process in the absence of chemical additives. The experimental runs were conducted in a fixed bed reactor (see experimental section). The reaction temperature was from 650 to 750°C and the pressure was atmospheric essentially. The calculation of conversions of the feedstock, reactivities, reaction order and global activation energies will be presented.

4.6.1 Conversion

As has been mentioned earlier, the rate of carbonization is very rapid and can be assumed to be essentially complete when the temperature reaches 600°C. The remaining coal or char reacts slowly with steam which is termed "activation". For steam, a "nonchemical" additive in the activation of the three coals tested, the relationship between coal conversion and steam activation time is shown in Figure 24.



Figure 24. Coal conversion with time for steam activation at 700°C

The conversion X is based on the reactive portion of the char, which is mass of activated carbon produced. Due to the overall process a global conversion is thus defined as:

$$X = (W_o - W)/W_o$$

where

 $W_o =$ the weight of coal loaded into reactor

W = the weight of activated carbon product

It should be noted that the simple approach given above can not truly account for the real activation process. This approach can, however, represent the overall trends of the preparation process. Since a very small amount of trace inorganic matter still remains in the coal, the char contains only a small fraction of ash at the initial stage of activation [Dutta, 1977].

Figure 24 shows coal conversion versus steam activation time for the three tested coals. Each curve represents a least-squares fit to a polynomial of conversion data at 700°C. In general, the conversions increase with the activation time. It is to be noted that the difference in reactivity between Bienfait lignite A and Montgomery sub-bituminous C coals is small. Of the coals tested, Coal Valley bituminous C is least reactive as shown by lower conversions. As expected, at high conversions, all of the tested coals show that the reactions slow down markedly and the curves become flat since the reaction rates decrease with the decreasing fraction of char remaining during the activation process. From Figure 24, it can be clearly seen that the conversion curves are primarily affected by coal rank.

4.6.2 Reactivity

Following the suggestion of Solano [1979], the reactivity was calculated by the following equation:

$$R = -\frac{1}{W_o} \frac{dW}{dt}$$

The rate of coal conversion was determined by first fitting the Newton Interpolating Polynomial function to each set of conversion-time data, and then taking the first derivative. The experimental runs were conducted up to 3.5 hours for each coal. Figure 25 demonstrates changes in the reaction rate with coal conversion for each coal at 700°C. It clearly shows that each coal has its own characteristic rate-conversion curve. Obviously, the chemical reactivity of each coal depends on its rank. As expected from Figure 24, the rates increase to maximum and then decrease. The maximum reaction rate for the most reactive Montgomery coal is about two times that of the least reactive Coal Valley coal. The variety of rate-conversion curves is due to the fact that different coals vary greatly from one to another with respect to their pore structures and the changes of their surface areas during the activation process. To account for such phenomena, it is important to note that the highest specific surface areas and iodine number values are developed at the peaks of the reaction rates as shown in Figure 25 by comparing Figure 10, 11 and 12. Thus, the rapid decrease of reaction rates can be the explained by the decrease of carbon concentrations, and importantly the drastic changes in pore structures and specific surface areas. At the beginning of the reaction, the pore structure and surface area of the coal are not fully developed. A relatively small reaction rate is expected. During activation, the effect of the steam-coal reaction generates a large fraction of micropores which contribute to the specific surface area. The existing pores are further enlarged as a result of the effects of internal diffusion and chemical reaction on the overall rate. The reaction rate is significantly accelerated by the pore structures and coal surface area changes. The reaction rate reaches its maximum, but further drastic reaction between carbon and steam damages the existing pores. More importantly, the reaction may change so that it is concentrated at the surface of the coal which destroys the surface area being created. The reaction rate is thus significantly reduced.

It also should be noted that for all of the tested coals, the nature of the curves will change with temperature, coal particle size, coal rank or possibly some other unexpected side reactions between steam and trace matter within the coal.



Figure 25. Reaction rate versus activation time at 700°C

From Figure 25 and Figure 10, 11 and 12, it can now be concluded that the low rank coals have a higher concentration of active sites, a higher initial porosity and surface area and hence a greater utilization of the active sites. Thus the reaction rate is usually higher and it is easier to reach their maximum surface area. Thus, the sorptive capacities of low rank coals can be more readily developed.

4.6.3 The Reaction Order, Rate Constant and Apparent Activation Energy

In general, the rate of reaction depends on the coal reactivity and activation conditions. A previous study showed that Bienfait lignite A is more reactive than Montgomery sub-bituminous C and Coal Valley bituminous coals. After a series of runs on the preparation of activated carbons, it is possible to give global values in the calculation of reaction rate constants, activation energies as well as reaction order.

After testing several reaction models, it was found that the results concerning the activation rate could be correlated to obtain the reaction order and the rate constant using a model proposed by several investigators [Dutta, 1977. Leonhardt, 1983. Fung, 1983]. This model assumes that the activation rate depends only on the amount of coal present in the reactor and that the reaction is first order with respect to the solid phase. To be sure that the reaction is first order, several standard methods were employed. It uses an integration method which gives a good match with experimental data. The first order

reaction model for coal activation is given by

$$-\frac{dC}{dt} = kC$$

where C is the fraction of coal remaining in the reactor at time t, and k is the first order specific rate constant.

Integration of the equation for a given set of conditions gives:

$$\ln C = kt$$

Thus, a plot of the negative natural logarithm of C as a function of reaction time is a straight line with k as the slope.

The data for the tested coals for the runs made at 700°C are plotted against reaction time in Figure 26. A least-squares fit of the natural logarithm of C with time produced the straight lines. It can be seen from Figure 26, that the data correspond quite well to straight lines over a relatively large range. If the lines are extrapolated, they all pass almost exactly through the origin. From the study of the first order reaction between steam and char it can be concluded that, the rate constants at 700°C, as shown in Figure 26, obtained are 0.417(h⁻¹),0.378(h⁻¹) and 0.213(h⁻¹) for Bienfait, Montgomery and Coal Valley coals, respectively. However, reaction orders have been reported from 0.6 to 1.0 from different investigators [Fung, 1983. Kwon 1989]. The existence of different reaction orders from different researchers, may be explained on the basis that the different rank coals have their own characteristics.

Similarly, the apparent activation energies can also be calculated from different

reaction temperatures. An Arrhenius plot showing the exponential dependency of the rate constant on reaction temperature for 650, 700 and 750°C is given in Figure 27. For all three coals, straight lines were obtained by a least-squares fit of the natural logarithm of k plotted against the inverse absolute temperature. The apparent activation energies calculated from the Arrhenius equation gave 189.9, 198.81 and 224.83 kJ/mol for Bienfait, Montgomery and Coal Valley Coals, respectively. These values are in reasonable agreement with those of the researcher Kwon [1989] who studied bituminous coal and obtained an activation energy of 175.5 kJ/mol. The results also show that low rank coal has a smaller value of the activation energy and that it can be easily activated while producing activated carbon.



Figure 26. Integration method to investigate the reaction order



Figure 27. Arrhenius plot of the first-order rate constants for the steam-coal reaction

Chapter 5.

Conclusions and Recommendations

5.1 Conclusions

A detailed study of the preparation of activated carbon has been conducted. The effects of factors such as the coal rank, activation temperature, activation time, coal particle size, the chemical additive employed and its impregnation ratio on the product quality were investigated with a small scale, fix-bed reactor. The quality of the activated carbon produced was determined by testing bulk density, ash content, specific surface area, iodine and methylene blue numbers. On the basis of experimental data on product yields from 40 steam activation runs, a brief discussion on activation kinetics was completed to demonstrate the relationship between coal rank and reactivity.

After 70 successful runs, it can be concluded that all three of the coals tested are capable of producing activated carbons having a specific area in excess of 400 m²/g. This study also confirms that low rank Bienfait lignite A and Montgomery sub-bituminous C coals can be readily activated. Montgomery coal gave the highest specific surface area of 506 m²/g. A study of the effects of the properties of the parent coals on the development of product sorptive capacities suggests that a high moisture content in the parent coal accompanies a larger group of initial pores which is beneficial to further sorptive property development during the activation process. A high ash content in the parent coal

is undesirable because high ash concentrations may adversely alter the physical strength of the product and its specific sorptive capacity. It is also possible that ash constituents may block the pore structure.

It was observed that the temperature and activation time have a great influence on the quality of activated carbon produced. In fact, activation temperature and time are two critical parameters which control the product quality. They directly affect the rate and extent of the steam-coal reaction. Therefore, suitable reaction conditions are most important factors in the process of activated carbon preparation. A study on the effect of activation temperature and time concludes that, Bienfait lignite A and Montgomery subbituminous C coals have similar optimal activation conditions of temperature at 700°C and a time of 2 hours. Coal Valley coal requires a relatively higher activation temperature and longer time which are 750°C and 3 to 4 hours.

By comparing the results with those from previous researchers, it is apparent that the effect of coal particle size is complicated. Generally, granular size coal gave the best results in terms of specific surface area and iodine number values, the fines obtained consistently gave the highest methylene blue number.

The use of chemical additives on the steam-coal activation to produce high quality activated carbon was another main objective of this research. The results indicate that the presence of different chemical reagents can either facilitate or impede the coal activation rate. However, most chemical additives had no or a negative effect on the development of sorptive capacities of the activated carbon products. In contrast, K_2CO_3 showed its superiority in Coal Valley coal activation. Especially, at 700°C, in the activation of Coal

Valley coal using K_2CO_3 , the specific surface area was increased more than 100 m²/g from 365 to 467 m²/g. The effect of using K_2CO_3 appears to have been due to a considerable increase in the number of reaction sites as well as an increase in reaction rate which can be further confirmed by comparing the different product yields from non-chemical activation and chemical activation. The effect of the chemical additive impregnation ratio on the reaction was also investigated to search for a suitable chemical reagent loading. The optimal impregnation ratio of approximately 1.0% was obtained. Further, study on the activation temperature and time gave a maximum surface area of 481 m²/g at 750°C for 2 hours.

After 40 runs of steam activation, it is possible to report on the results of a brief kinetic study. A first-order reaction between steam-coal was found. The activation energies for the activation in the absence of chemical additives were found to be 189.9 kJ/mol for Bienfait coal, 198.8 kJ/mol for Montgomery coal and 224.8 kJ/mol for Coal Valley coal. The reaction rate, could be a vital factor influencing the quality of products. As expected at lower temperatures the reaction rate was quite slow. Although Coal Valley coal gave a higher product yield, the sorptive capacities obtained were considerably lower. In contrast, higher activation temperature gave a rapid reaction. Care needs to be taken to avoid drastic surface reactions which could possibly destroy the created pore structure. Therefore, a mild, suitable reaction temperature is necessary. Finally, this study has demonstrated the applicability of the fixed-bed reactor in the kinetic studies of the steam-coal reaction.

5.2 Recommendations

From this study it is recommended that the following items be considered for possible future research.

- 1. That the reaction kinetics and mechanism of the steam-coal reaction in the presence of K_2CO_3 be further investigated by performing additional activation runs.
- 2. That acid washing studies be extended to determine whether mineral matter of the coal has an effect on the development of the sorptive properties of the product.
- 3. That activation be conducted with relatively low ash content coal to study the effect of ash content of parent coal on the development of the sorptive properties of activated carbon.
- 4. That more studies on coal carbonization such as heating rate (rate of temperature rise), final carbonization temperature and residence time during carbonization on the development of activated carbon quality be investigated.

References

- 1. Chowdhury, A.I., Hall, E.S., and Tollefson, E.L., 1988, Preparation of activated carbon from coal, research report.
- Coughlin, R.W., 1970, Effect of surface groups on adsorption of pollutants, Environ. Sic. Tech., (2), 291-298.
- 3. Dalai, A.K., Zaman, J., Hall, E.S., Tollefson, E.L., 1992, Preparation of activated carbon from western Canadian coals, Research report.
- 4. Derbyshire, F.J., Jagtoyen, M., McEnaney, B., Sethuraman, A.R., Stencel, J.M., Taulbee, D. and Thwaites, M.W., 1991, The production of activated carbons from coals by chemical activation, *Am. Chem. Soc. Fuel Div. prep.*, **36(3)**, 1072 - 1080.
- Derbyshire, F.J., Jagtoyen, M., McEnaney, B., Sethuraman, A.R., Stencel, J.M., Taulbee, D. and Thwaites, M.W., 1991, The production of activated carbons from coals by chemical activation, Am. Chem. Soc. Fuel Div. prep., 36(3), 1072 - 1080.
- 6. Douchannov, D. and Angelova, G., 1983, Effect of catalysis and inlet gas on coal
gasification, Fuel, 62, 231 - 233.

- 7. Dutta, S. and Wen, C.Y., 1977, Reactivity of coal and char. 1. in carbon dioxide atmosphere, *Ind. Eng. Chem. Prod. Res. Dev.*, **16(1)**, 20 30.
- 8. Dutta, S. and Wen, C.Y., 1977, Reactivity of coal and char. 2. Oxygen Nitrogen atmosphere, *Ind. Eng. Chem. Prod. Res. Dev.*, **16(1)**, 31 37.
- 9. Ehrburger, P., Addoun, F. and Donnet, J.B., 1988, Effect of mineral matter of coals on the microparasite of charcoals, *Fuel*, **67**, 1128 1231.
- 10. Faust, S.D., and Aly, O.M., 1989, Chemistry of water treatment, 193 199.
- 11. Fredersdorff, V., and Elliott, M.A., 1963, Kinetics of gasification reactions, Chemistry of Coal Utilization, supplementary volume.
- Fung, D.P.C., 1982, Laboratory gasification of five Canadian coals, *Fuel*, **61**, 139 144.
- Fung, D.P.C. and Kim, s.D., 1983, Laboratory gasification of study of Canadian coals, 2. chemical reactivity and coal rank, *Fuel*, 62, 1337 - 1340.

- 14. Gadsby, J., Hinshelwood, C.N., and Sykes, K.W., 1946, The kinetics of the reactions of the steam-carbon system. *Proc. Roy. Soc (London)*, **187A**, 129 151.
- 15. Hasslar, J.W., 1970, Purification with activated carbon, Chemical Publishing Company, Inc.
- 16. Hippo, E.J., Jenkins, R.G. and Walker Jr, P.L., 1979, Enhancement of lignite char reactivity to steam by cation addition, *Fuel*, **58**, 338 344.
- Jagtoyen, M., Groppo, J. and Derbyshire, F., 1993, Activated carbons from bituminous coals by reaction with H₃PO₄: the influence of coal cleaning, *Fuel Processing Technology*, 34, 85 - 96.
- Jankowska, H., Swiatkowski, A., and Choma, J., 1991, Active Carbon, Ellis Horwood Limited, 9 - 74.
- 19. Juntgen, H., 1983, application of catalyst to coal gasification processes, incentive and perspectives, *Fuel*, **62**, 234 238.
- 20. Kayembe, N. and Pulsifer, A.H., 1976, Kinetics and catalysis of the reaction of coal char and steam, *Fuel*, 55, 211 216.

- 21. Kwon, T.W., Kim, J.R., Kim, S.D. and Park, W.H., 1989, Catalytic steam gasification of lignite char, *Fuel*, 68, 416 421.
- 22. Leon, s., Klotzkin, M., Gard, G. and. Emmett, P.H., 1981, Enlargement of the micropores of a caking bituminous coal by controlled oxidation, *Fuel*, **60**, 673 676.
- 23. Leonhardt, P., Sulimma, a., Heek, K.H.V. and Juntgen, H., 1983, Steam gasification of German hard coal using alkaline catalysts, *Fuel*, **62**, 200 204.
- 24. Linares-Solano, A., Mahajan, O.P. and Walker Jr, P.L., 1979, Reactivity of heattreated coals in steam, *Fuel*, **58**, 327 - 332.
- 25. Ludvig, M.M., gard, G.L. and Emmett, P.H., 1983, Use of controlled oxidation to increase the surface area of coal, application to a bituminous and a semi-anthracite coal, *Fuel*, **62**, 1393 1396.
- 26. Mahajan, O.P. and Walker Jr, L., 1979, Effect of inorganic matter removal from coals and chars on their surface areas, *Fuel*, **58**, 333 337.
- 27. Mckee, D.W., Spiro, C.L., Kosky P.G. and Lamby, E., 1983, Catalysis of coal char gasification by alkali metal salts, *Fuel*, **62**, 217 220.

- Merchant, A.A. and Petrich, M.A., 1992, Preparation and characterization of activated carbons from scrap tires, almond shells and illinois coal, *Chem. Eng. Comm.*, 118, 251 263.
- Nsakala, N.Y., Essenhigh, R.H. and Walker Jr, P.L., 1978, Characteristics of chars produced from lignites by pyrolysis at 808 °C following rapid heating, *Fuel*, 57, 605 - 611.
- Ono, T., Haga, T. and Nishiyama, Y., 1984, Studies on catalytic gasification of coal chars . Part I. Development of pores during gasification, *Fuel Processing Technology*, 9, 265 - 278.
- 31. Prober, R., Pyeha, J.J., Helfgott, T., and Rader, B.B., 1974, Chemical implications in activated carbon regeneration, *AIChE symposium series*, 339 351.
- 32. Puri, R.P., 1980, Activated carbon adsorption of organics from the aqueous phase, Ann Arbor Science Publishers, Inc, 353.
- Rist, L.P. and Harrison, D., 1985, Surface area and pore development during lignite activation, *Fuel*, 64, 291 - 296.

- 34. Rulz Bevla, F., Prats Rico, D., and Marclla Gomis, A.F., 1984, Activated carbon from almond shells. Chemical Activation. 1. Activating reagent selection and variables influence, *Ind. Eng. Chem. Prod. Res. Dev.*, 23, 266 - 269.
- 35. Rulz Bevla, F., Prats Rico, D., and Marclla Gomis, A.F., 1984, Activated carbon from almond shells. Chemical Activation. 2. Z_nCl₂ activation temperature influence, *Ind. Eng. Chem. Prod. Res. Dev.*, 23, 269 - 271.
- Sams, D.A. and Shadman, F., 1983, Catalytic effect of potassium on the rate of char - CO₂ gasification, *Fuel*, 62, 880 - 882.
- 37. Schafer, H.N., 1979, Pyrolysis of brown coals. 1. Decomposition of acid groups in coals containing carboxyl groups in the acid and cation forms, *Fuel*, 58, 667 672.
- Schafer, H.N., 1979, Pyrolysis of brown coals. 2. Decomposition of acidic groups on heating in the range 100 - 900 °C, *Fuel*, 58, 673 - 679.
- 39. Sheffer, G.H., 1956, Carbon, Activated, Snell-Ettra Encyclopedia of Industuial Chemical Anlysis, 8, 139 161.
- 40. Singla, P.K., Miura, S., Hudgins, R.R. and Silveston, P.L., 1983, Pore development

during carbonization of coals, Fuel, 62, 645 - 648.

- 41. Smith, K.M., 1970, Chemical Engineering Kinetics, McGraw Hill Book Company, 2rded., 282 318.
- 42. Sousa, J.C., Mahamud, M., Parra, J.B. and Pajares, J.A., 1993, Effect of operation variables in the obtention of tailored active carbons from coals, *Fuel Processing Technology*, **36**, 333 339.
- 43. Suzuki, T., Mishima, M., Kitaguchi, J., Itoh, M. and Watanabe, Y., 1984, The catalytic steam gasification of one Australian and three Japanese coals using potassium and sodium carbonates, *Fuel Processing Technology*, **8**, 205 212.
- 44. Tollefson, E.L., and Hall, E.S., 1981, Preparation of activated carbon from subbituminous Alberta coals, research report.
- 45. Torregrosa, R. and Martin-Martinez, M., 1991, Activation of lignocellulosic materials: a comparison between chemical, physical and combined activation in terms of porous texture, *Fuel*, **70**, 1173 1180.
- 46. Wilson, J., 1981, Active carbons from coals, *Fuel*, **80**, 823 831.

- 47. Yang, Y. and Watkinson, A.P., 1994, Gasification reactivity of some Western Canadian coals, *Fuel*, **73**, 1786 - 1791.
- Yehaskel, A., 1978, Activated carbon manufacture and regeneration, Noyes Data Corporation.
- 49. Zogorski, J.S., 1975, The adsorption of phenols onto granular activated carbon from aqueous solution, PhD Thesis, Rutgers University, New Brunswick, NJ.