

THE GENERATION AND CHARACTERIZATION OF ACTIVATED  
CARBONS FROM THE PYROLYSIS OF CEREAL GRAINS

by

ANANTHAKRISHNAN VENKATARAMAN

B. Tech. Chemical Engineering, Indian Institute of Technology, Madras, 1989

M.S. Chemical Engineering, Kansas State University, 1992

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A DISSERTATION

submitted in partial fulfillment of the  
requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

College of Engineering

KANSAS STATE UNIVERSITY

Manhattan, Kansas 66506

August, 1996

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**UMI Number: 9704772**

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## ABSTRACT

Whole grain kernels of hard red winter wheat (HRW) and corn are potentially viable feedstocks for producing activated carbons with high surface areas and pore volumes. These activated carbons have been obtained by the physical activation, i.e., reaction, of grain charcoals generated by a single-stage as well as a two-stage pyrolytic process, at 850° C in an atmosphere of CO<sub>2</sub>. The single-stage process involved direct pyrolysis of the kernels at the temperature of interest while the two-stage process comprised pyrolysis at a low temperature of 275° C followed by that of the resultant charcoals at the temperature of interest. For both kernels, the terminal yield of charcoals generated by the two-stage process at various temperatures and the BET nitrogen surface areas and total pore volumes of the corresponding activated carbons (which ranged from 500 to 1750 m<sup>2</sup> / g and 0.3 to 0.7 cm<sup>3</sup> / g, respectively) are appreciably higher than those by the single-stage process.

The pore structures and the fractal nature of the pore-solid interfaces of charcoals obtained from both corn and HRW were investigated through small-angle X-ray scattering on length scales from approximately 10 to 10,000 Å. The scattered intensity,  $I(q)$ , for either type of charcoal is proportional to  $q^{-\alpha}$  for  $q$  between 0.0006 and 0.04 Å<sup>-1</sup>. [Here,  $q = \{ 4\pi \sin(\theta) \} / \lambda$ ;  $2\theta$  is the scattering angle;  $\lambda$ , the X-ray wavelength; and  $\alpha$ , a positive constant]. For samples of unpyrolyzed corn kernels,  $\alpha$  is 4.0, or the surface fractal dimension ( $d_{SF}$ ) is 2.0, and hence, their pore-solid interfaces are smooth on length scales from about 100

to 5000 Å. For corn charcoals obtained at 540, 720 and 820° C,  $\alpha$  is approximately 3.6, and therefore, on the aforementioned length scales, the pore-solid interfaces are fractal with a  $d_{SF}$  of 2.4. The samples of unpyrolyzed corn and those of chars retrieved at 370 and 540° C exhibit broad minima for Bragg spacings of about 12 Å, thus indicating order in these samples. Similar studies on pore structure and surface irregularity were also carried out for some wood charcoals. Furthermore, the fractal properties of non-carbon porous materials, such as mesoporous calcium hydroxide sorbents and microporous silica-gels, were analyzed with the aid of a thermodynamic method and a modified molecular tiling method.

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## ACKNOWLEDGEMENTS

I thank Dr. W. P. Walawender, my major advisor for the last seven years, for his guidance, encouragement, and patience throughout my graduate program at Kansas State University. I appreciate his support and the genial atmosphere he induced at work. I wish him a speedy recovery from his by-pass surgery.

Special thanks are extended to Dr. L. T. Fan, my co-major advisor, for invoking my interest in fractal geometry. I appreciate his valuable criticisms, suggestions, and meticulous editing of several of my journal articles.

I would like to acknowledge Drs. R. O. Fox, L. E. Erickson, A. Chakrabarti, C. M. Sorenson, and Dr. R. M. Hammaker, Chairperson, for their expedient review of my dissertation and for serving as members of my supervisory committee.

Appreciation is also extended to Drs. Sajan Thomas, Paul Schmidt, and Tom Riecker for their assistance in obtaining the small-angle X-ray scattering data at various laboratories. The financial support of the Kansas Agricultural Experiment Station at Kansas State University is duly acknowledged.

I am greatly indebted to my family for their unconditional love and support. In fond memory of my late father, I dedicate this dissertation to him.



## CHAPTER 1. INTRODUCTION

The term "activated carbon" is a generic name for a family of carbonaceous materials with highly developed internal surface area and porosity and hence, a large capacity for adsorbing chemicals from gases or liquids. Activated carbons are extremely versatile adsorbents of major industrial significance and are utilized in a wide range of gas-phase and liquid-phase applications that involve either purification or recovery of chemicals. They also serve as catalysts or catalyst supports. The unique properties and low cost of activated carbon adsorbents relative to those of competing adsorbents have enabled the former to dominate the market for adsorbents over the last two decades.

The properties of activated carbons depend to a large extent on the nature of the feedstock or precursor and the particular processing technology utilized during production. Little pertinent information exists in the open literature on the fundamental relationships between the carbon product and the structure of the feedstock or the process chemistry. Although the manufacture of activated carbons is a long-established industry, most of the world production is confined to a relatively small number of manufacturers. Each one of them utilizes different feedstocks and/or different process methods, the result of which is that the properties of commercial activated carbons are very different. This implies that there are only a few market segments where there is serious competition; consequently, the incentives for research and development over the last decade have been minimal. The position has begun to change, however, with the advent

of more diverse applications and increased demand for high-performance adsorbents. Nonetheless, much remains to be investigated in the areas of renewable and cost-effective feedstocks for activated carbon production.

Chapter 2 of this dissertation provides a perspective on the structure, history, emerging applications, and current market trends for activated carbons. This chapter is followed by a detailed discussion in Chapter 3 on the salient features of activated carbon production such as the types of feedstocks, the processing routes, and state-of-the-art techniques of production. Chapter 4 reviews traditional physisorption methods for determining the surface area, pore volume, and pore-size distributions of porous solids. The chapter also focuses on the volume-filling phenomenon in microporous solids and discusses the Dubinin approach for estimating the total micropore volume of a carbon.

Chapter 5 reports in detail the generation of activated carbons from the pyrolysis of kernels of whole grain corn and hard red winter wheat in a tubular reactor and the subsequent characterization of the carbons through physisorption. The essential concepts of small-angle X-ray scattering (SAXS) are reviewed in Chapter 6; this chapter also reports its application to the analysis of the fractal nature of pore-solid interfaces of wood charcoals that were pyrolyzed for various retention times in a reactor operating at a fixed temperature. Chapter 7 presents the results of SAXS investigations on the changes in the surface morphology of corn charcoals with the temperature of pyrolysis.

Chapter 8 deals with the determination of the surface fractality of porous solids through physisorption. The salient features and limitations of various

models of adsorption on a fractally rough surface are discussed; the complexity involved in probing the fractal nature of microporous materials is also delineated in this chapter. Chapter 9 describes the non-ideality correction factors for adsorbates in physisorption experiments, that have been obtained by employing accurate equations of state. Chapter 10 recapitulates conclusions drawn in each chapter in the context of the entire dissertation. Moreover, recommendations for future work are made.

## CHAPTER 2.

### ACTIVATED CARBONS : AN OVERVIEW

#### 2.1 Introduction

Various aspects of activated carbons including their structure, historical development, recent advances in applications, and prospects for further growth and penetration of the adsorbent market are the focus of this overview. The history of the technology of activated carbon synthesis and the industrial requirements that essentially provided the driving force are particularly relevant to considering modern practice, as many of the current processes employed have their origins in earlier discoveries.

#### 2.2 Structure

All carbon materials can be divided into two main groups: the anisotropic graphitic carbons and the isotropic non-graphitic carbons, depending on the degree of crystallographic ordering. Graphite is basically a lamellar structure in which each lamellae is composed of carbon atoms arranged in six-membered rings as shown in Figure 2.1. The term, graphitic, is applied to carbons whose structures resemble that of graphite, i.e., with the three-dimensional symmetry and anisotropy (Marsh, 1986; Wigmans, 1986). On the other hand, the term, non-graphitic, refers to carbons that do not possess the aforementioned structure of graphite.

Porous carbons are a non-graphitic form of carbon composed of carbon atoms in spatial arrangements which roughly resemble a short-range, layered lamellar structure as shown in Figure 2.2. Some of these layers are stacked approximately parallel to each other up to a distance of a few nanometers (Marsh, 1986). Frequently, the structure of porous carbons is described in terms of "elementary crystallites" (Hassler, 1974). It should be emphasized, however, that the concept of such a fundamental building block is hypothetical, and that the crystallite does not exist as such within these structures. Very often it can be a misleading name for an *amorphous* non-graphitic material (Byrne and Marsh, 1995).

The non-graphitic carbons can further be divided into two classes - the graphitizable and non-graphitizable carbons. The former are carbons which can be converted into graphite by heat treatment, and are usually termed cokes. The degree of graphitization depends on the temperature of heat treatment and the time allowed to anneal the structure. The non-graphitizable carbons, also known as chars, are those that cannot be transformed into graphite solely by heat treatment under inert conditions up to temperatures of 3500 K under atmospheric or lower pressures (Byrne and Marsh, 1995). Examples of chars are the products derived from the pyrolysis of wood, lignites, brown coals, and others. A schematic of the above classification of all carbon materials is presented in Figure 2.3.

The recently discovered fullerenes possess a structure that is either spherical or cylindrical based on the graphitic lattice (Chibante et al., 1993; Murry et al., 1993; Smalley, 1993). Fullerenes can be obtained by replacing the

six-membered ring systems of graphite with five-membered ring systems. When this is carried out, the lamellae adopt spherical shapes with about 70 carbon atoms per sphere. The discussion of this new and interesting development is beyond the purview of this work.

There exists today a wide variety of commercially available activated carbons that are derived from various sources. In terms of structure, they are classifiable as non-graphitizable, non-graphitic carbons. They can be visualized simply as being composed of imperfect sections of graphitic lamellae. One can envision constructing such a structure hypothetically from graphite by cutting the lamellae of the latter into pieces ranging in size from about 10 Å to 500 microns, and then merging them into a two-dimensional composite structure. This resultant structure will comprise crumbled pieces of various proportions with all kinds of defects (Byrne and Marsh, 1995). When several of these composite pieces are bonded together subsequently, a three-dimensional network will be created (Figure 2.4). Such a structure whose properties are isotropic approximates to that of porous activated carbons. Hence, on account of the crumpled, defective nature of the lamellar constituent molecules (LCM), the packing densities of these carbons are usually low, i.e., the apparent density is less than 1.0 g/cc as measured with mercury displacement (Marsh, 1986). The porosity in these carbons arise from the spaces or voids between the LCM.

The graphitizable carbons such as cokes, on the other hand, are composed of LCM's which are larger, less defective, and less crumpled than those in the porous carbons. Accordingly, they stack parallel to each other over distances of

the order of a few microns (McEnaney and May, 1989). Their apparent densities are consequently higher compared to those of the activated carbons, and are approximately 2.0 g/cc. Note that the true density of graphite is 2.26 g/cc. The graphitic carbons have little or no porosity at length scales comparable to those of molecules. Hence, cokes are not used as feedstocks for activated carbon production (Byrne and Marsh, 1995).

The differences in the packing arrangements of LCM's in non-graphitic carbons result in wide differences in their properties. In carbon blacks, the LCM's are arranged more or less parallel to each other thereby, imparting a low porosity and graphitizability. The glassy carbons are similar to the activated carbons but have a denser packing of LCM's to create a harder carbon with a narrower range of pore sizes (Mantell, 1968). The pyrolytic carbons formed from processes such as chemical deposition from the vapor phase (CVD) possess highly developed (in terms of crystallographic order) LCM's with a significant packing density and hence, are highly graphitizable (Byrne and Marsh, 1995). Thus, it is the extreme flexibility of the structural associations possessed by these LCM's that give rise to carbons with a wide range of structural, physical, and chemical properties. Furthermore, within one class of carbons, i.e., activated carbons, wide variations in properties are caused by differences in the detail of size, shape, deformation, and bonding together of the LCM's generated from the individual feedstocks during pyrolysis and carbonization (McEnaney and Mays, 1989). Extents of bonding or cross-linkages within the carbon are critical as they control the hardness or abrasability of the carbon, particularly after the activation process

in which internal carbon material is removed by gasification (Wigmans, 1986).

The sizes of pores present in activated carbons are distributed over a continuous interval; however, for practical purposes, the pores are classified into three distinct groups according to the IUPAC convention (Rodriguez-Reinoso, 1986). Pores whose widths are less than 20 Å are called micropores, while those with widths greater than 500 Å are termed macropores. The third group of pores whose dimensions lie between those of the micropores and macropores are known as mesopores. The surface areas of the macropores and mesopores are relatively small; as a result, their adsorptive capacities are negligible. These pores primarily serve as channels of transport for molecules of adsorbate to diffuse into the interior of the porous network through progressively finer passageways. In contrast, the surface areas associated with the micropores constitute almost 90% of the total internal surface area of an activated carbon; accordingly, most of the adsorption takes place within these pores.

### 2.3 History

The earliest known applications of activated carbons dates back to the time of the Egyptians and Sumerians at approximately 3750 BC (Faust and Aly, 1983). They employed wood charcoal as a smokeless fuel and as a reducing agent for producing bronze from the ores of copper, tin, and zinc. Later, in 1500 BC, the Egyptians utilized charcoals for medicinal purposes and to adsorb odours. In 450 BC, the inhabitants of the Indus valley civilization utilized charcoal filters to purify drinking water (Hassler, 1974).