

# Chapter 2

## Activated Carbons

An activated carbon is mostly made from a carboneaceous material, such as wood, peat, coconut shell, coal, etc. Generally, activated carbons, cokes and chars are termed amorphous. X-ray studies have shown that the amorphous substances have crystalline characteristics but they may not show the certain features such as crystal angles and faces. An amorphous structure may be composed of crystals of submicroscopic dimensions, so called crystallites in which carbon atom are arranged in hexagonal lattice as shown in Figure 2.1 [23].

At the excited state, an electron in 2p orbital of the L shell is excited from the 2s orbital of the same shell, as shown in Table 2.1. Each carbon atom, excepting

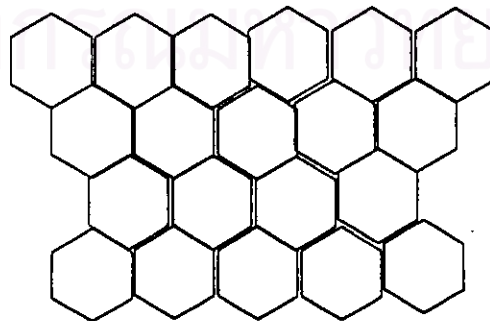


Figure 2.1: Arrangement of carbon atoms in a single-layer plan of crystallines formed a different temperatures.

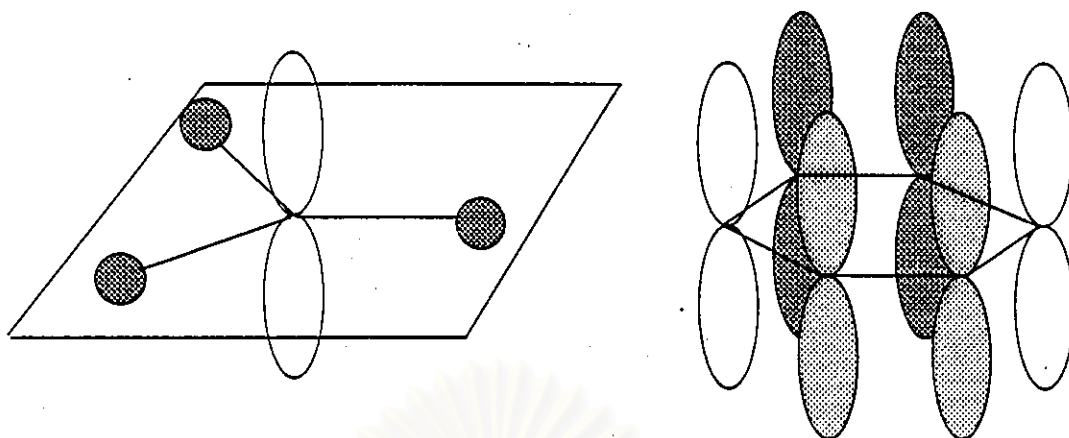


Figure 2.2: Carbon atom in the triangle.

the atom at the edge, uses one electron from 2s orbital and 2 electrons from 2p orbital to create a sigma bond with the adjacent carbon atoms in the triangle flat plan. The remaining electron will localize above and below the plan to create Phi bond. Finally, 6 carbon atoms will form a stable aromatic structure with delocalizing electrons of the layer plan as shown in Figure 2.2.

Table 2.1: The electron orbitals of carbon atom in excited state.

Electron shell	K		L		
Orbital	1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>
Electrons	↑↓	↑	↑	↑	↑

This crystallites resemble to a large graphite but differ in the size exit. The graphite, the plates are more closely together than the carbons do. The size of crystallites depend on the temperature of carbonization and the structure of the raw material. During carbonization, the original organic substances are split into fragments which regroup to form the stable aromatic structure shown in Figure 2.3 [24].

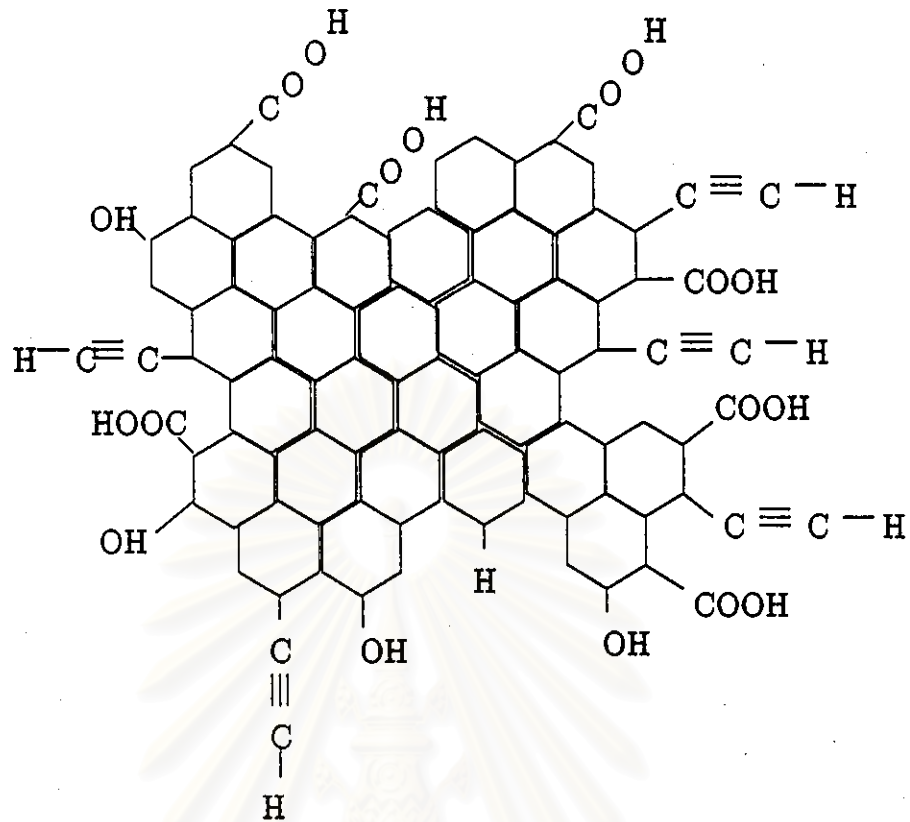


Figure 2.3: Theoretical structures of crystallines.

The transformation is seldom complete. The residual chains, which cannot be extracted with solvents or removed by degassing, are attached by the chemical bonds to the border atoms of the crystallites. The theoretical structure of crystallites are shown in Figure 2.3.

## 2.1 Manufacturing Processes

A process of manufacturing activated carbon can be divided into 3 steps:

### Raw Material Preparation:

Raw materials are crushed and screened to yield the desired size of particles in order to achieve uniform properties of activated carbons.

### Carbonization:

The prepared raw materials are charred in oxygen-free atmosphere in order to eliminate volatile matters. The operating temperature is in a range below  $600^{\circ}\text{C}$  [25]. The heating rate also affects the properties of carbonized materials, i.e. the high heating rate yields large pore sizes. The carbonized materials are usually uniformly black and shiny.

### Activation:

The carbonized materials are, then activated to improve porosity and specific surface area. The activation can be divided into 2 approaches; i.e. chemical activation and physical activation.

#### 1. Chemical Activation Approach

This approach uses the chemicals, such as  $\text{ZnCl}_2$ ,  $\text{CaCl}_2$  and  $\text{H}_3\text{PO}_4$ , to activate the surface. The activation temperature is in a range of  $400$ - $600^{\circ}\text{C}$ . Some chemicals tend to remain the surface after the complete activation.

#### 2. Physical Activation Approach

The surface of the carbonized materials is activated with some oxidizing gases, such as  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  etc. For instance, the structure of activated carbons activated by steam is shown in Figure 2.4. The C-O bond at the first position is decomposed with water at  $800$ - $900^{\circ}\text{C}$  lead-

ing to elimination a phenol molecule from the surface. Consequently, hydrogen atoms at position 2 and 3 in Figure 2.4 are removed from the surface to create the benzene ring.

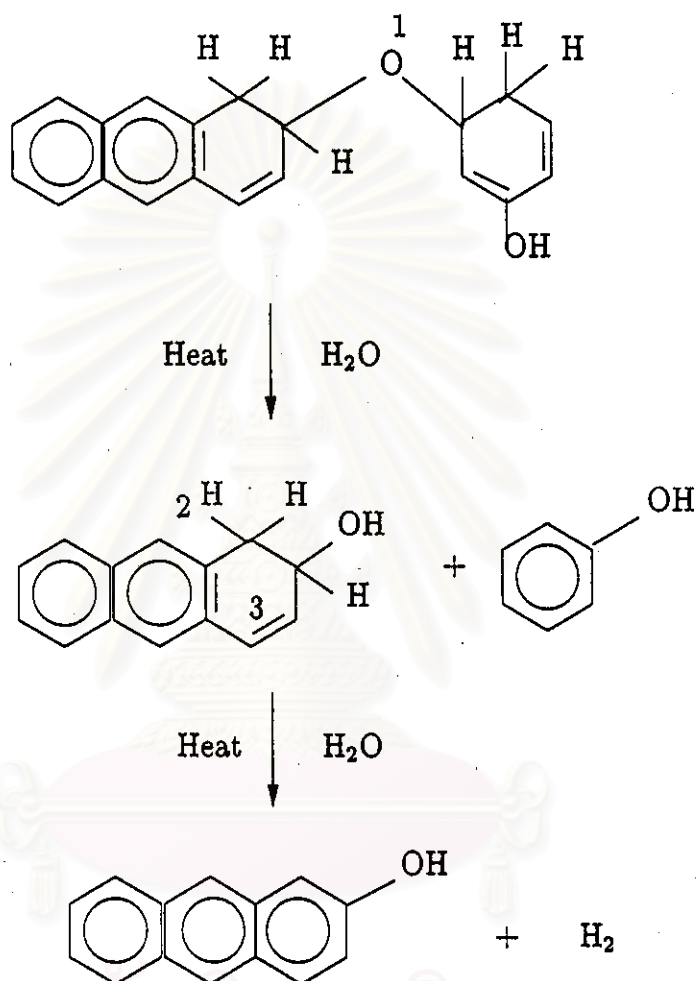


Figure 2.4: The structure of activated carbon after activation.

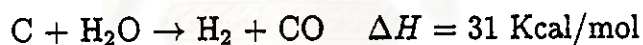
The advantages of steam activation are economic and no chemical remains on the surface. However, the optimum conditions are specific for each situation and depend on prior history of char. For many types of chars, steam is preferable to carbon dioxide and must be better than air. For using steam, the temperature of activation must be high enough to provide the rapid

rate of oxidation but the temperature above 1,000° C must be avoided because of impairing adsorptive powers. In activation by oxidation, the kind of adsorptive powers developed are determined by:

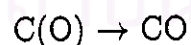
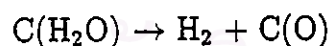
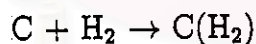
1. The chemical nature and concentration of oxidizing gas
2. The temperature of the reaction
3. The extent to which the activation is conducted.
4. The amount and kind of mineral ingredient in the char

#### Activation by steam

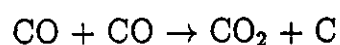
The reaction with steam is the endothermic reaction.



The mechanism of the reaction is following.



Mostly, H<sub>2</sub> and CO are released so the activated carbons are increased the porosity but CO will react and give CO<sub>2</sub> and C shown by the equation below.



## 2.2 Pore Structure

The desired pore structure and mechanical strength can be achieved by the controlling the conditions carbonization and activation. For adsorption in liquid phase, most of the pores are large than 30 Å in diameter in order to allow the liquid solvent to penetrate into the volume. While the pores of the carbon for adsorption are in a range from 10 Å to 25 Å in diameter [26].

According to the International Union of Pure and Applied Chemistry (IUPAC), the classification of pore size is summarized in Table 2.2 [27].

Table 2.2: Pore Sizes of Typical Activated Carbons<sup>†</sup>

	Micropore	Mesopore	Macropores
Diameter (Å)	<20	20-500	>500
Pore Volume (cm <sup>3</sup> /g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area (m <sup>2</sup> /g)	100-1000	10-100	0.5-2

<sup>†</sup> Particle density 0.6-0.9 g/cm<sup>3</sup>; porosity 0.4-0.6

## 2.3 Surface Properties

The surface of activated carbon might be divided into two parts. The major part, mostly of the surface, is nonpolar. Consequently, the activated carbons tend to be the hydrophobic and organophilic adsorbents. So they can adsorb the organic and nonpolar strongly and adsorb weakly polar compounds weakly, the other is slight polarity arising from surface oxidation under which some oxygen complexes are added on the surface leading to an increase in polarity, as shown in Figure 2.5 [28].

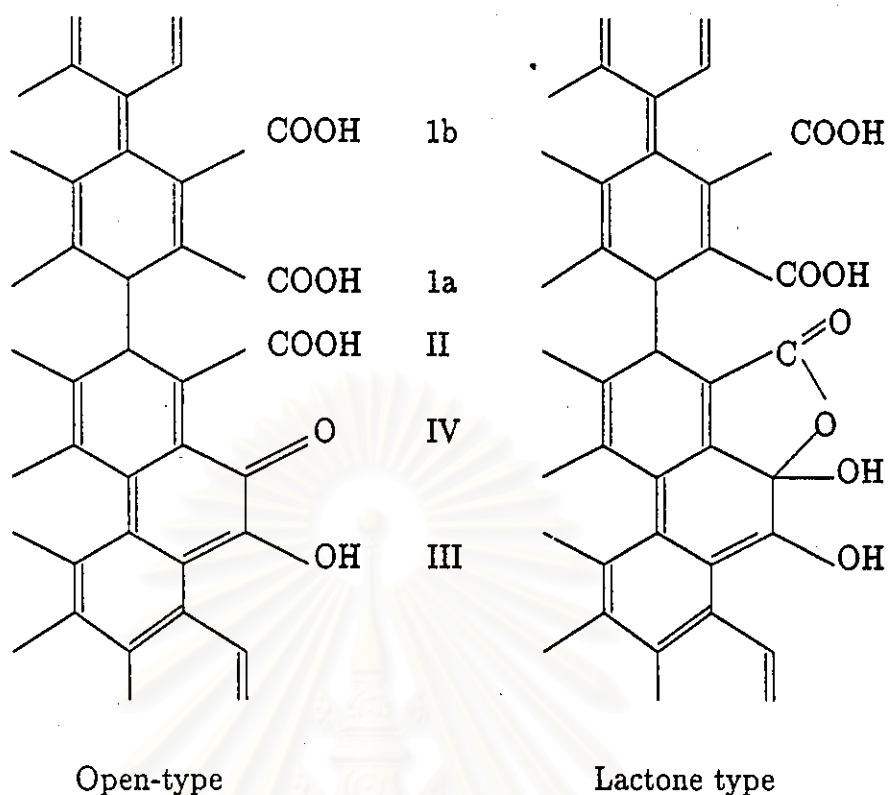


Figure 2.5: Surface oxides on carbon surface I: Carboxyl group, II: Carboxyl group which exists as lactol group, III: Phenolic hydroxyl group, IV: Carbonyl group

Generally, oxygen complexes exist in the form of oxide surfaces, i.e. strong carboxylic groups, weak carboxylic groups, phenolic groups and carbonyl groups. The amounts of oxide groups on the surface of activated carbons can be determined from the difference in titration values of the alkaline solutions as shown in

Table 2.3.

Table 2.3: Determine the amounts of surface oxide groups by titration with alkaline solutions

	Surface oxide group	Titration solution	pK <sub>a</sub>
1	Strong carboxylic groups	NaHCO <sub>3</sub>	6.37
2	Weak carboxylic groups	Na <sub>2</sub> CO <sub>3</sub>	10.25
3	Phenolic groups	NaOH	15.74
4	Carbonyl groups	NaOC <sub>2</sub> H <sub>5</sub>	20.58



These surface oxide groups may be removed by heat treatment under vacuum or in the inert atmosphere. The activated carbon can be classified by the following principle as shown in Table 2.4.

Table 2.4: Classification of activated carbons

Classification		Properties
1	Activation	Chemical activated carbon use the chemicals to activate the surface large pore size Physical activated carbon use the oxidizing gas to be the oxidant small pore size use for gas phase
2	Density	Low density use for liquid phase High density use for gas phase
3	Type of adsorbate	Gas adsorbents adsorb the toxic gas, odor and organic vapor Color adsorbents Metal adsorbents separate the metal

## 2.4 Carbon Molecular Sieves

A special type of activated carbons, of which the pore size distribution is narrow and almost uniform, is known as carbon molecular sieves (CMSs) or molecular sieve carbons (MSCs). In general, the average pore size of the CMSs is in a range about 4 - 9 Å and the pore volume does not exceed a value of 25 cm<sup>3</sup>/100 g [26]. Consequently, the separation with adsorption on the CMSs is usually based on shape or size selection. In addition, the separation can be achieved by diffusion

selection, as the case of air separation for nitrogen production.

Three approaches have been reported for the preparation of carbon molecular sieves.

1. Carbonization of polymers such as Saran(90/10 mixture of vinylidene chloride and vinyl chloride), poly(vinylidene)PVDC, cellulose, sugar and coconut shell.
2. Slightly carbonizing coals such as anthracite.
3. Coating of the pore mouths of the commercial activated carbon with carbonized or coked thermesetting polymer.

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