

LECTURE-11

ACTIVATED CARBON

➤ INTRODUCTION

- **Activated carbon**, also known as activated charcoal, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions.
- It has high degree of microporosity.
- The word '*active*' is also sometimes used for '*activated*'.
- The surface area may vary greatly depending upon precursor (raw material) and the condition of carbonization for making active carbon
- As determined by gas adsorption, people (Dillon Jr. et al., 1989) used activated charcoals having surface area like 1500 and 3,000 m²/g in their research work.
- An activation level sufficient for useful application may be obtained solely from high surface area.
- Chemical treatment has been found to enhance the adsorption properties of activated carbon.
- AC is usually derived from charcoal.
- When derived from coal, it is referred to as activated coal.
- Activated coke is derived from coke.
- Therefore activated carbon, activated charcoal, activated coke, active carbon may be said to perform the same function.
- Chemical or physical activation methods and microwave radiation methods are the commonly used techniques adopted for preparation of activated carbon.
- They are used as an adsorbent by the separation and purification industries.
- They are composed of a microporous, homogenous structure with high surface area and show radiation stability.
- Their adsorption capacity depends on porosity and its surface chemistry
- activated carbon available in different forms have been shown in **Figure-1**



Figure-1: Activated carbon powder, granules and pellets.

➤ SWITCHING OVER FROM THE TRADITIONAL FEEDSTOCK (FOSSIL ORIGIN) TO THE BIORESOURCES

- Usually the activated carbon in the market were made from coal, lignite, peat, petroleum residue, wood which are expensive and exhaustible
- In recent years, the interest has developed for utilization of AC made from agricultural, municipal, industrial and forestry bio-wastes.
- These bioresources are cheap, easily available, renewable and ecologically suitable.
- Moreover, the prepared carbon material from the biomass has shown excellent surface properties with the high degree of porosity and the high specific surface area
- Agricultural wastes are palm shells, fruit shell, groundnut shell, coconut shell and *Ricinus communis* seed shell etc.
- The parts of the plant such as root, stem, bark, flower, leaf, fruit peel, husk, shell and stone are included in the biowaste
- These wastes are classified into woody and non-woody resources
- Woody resources are mainly composed of cellulose, hemicellulose and lignin
- Whereas non-woody resource are composed of cellulose, hemicellulose, lignin, lipids, protein, sugar, water, hydrocarbon, starch and many functional groups
- In general, selection of raw material depends on seven important criteria:
 - i. High carbon content.
 - ii. Low inorganic matter content for low ash result
 - iii. High density and volatile matter content.
 - iv. Abundant so that the raw material is always in very low cost.
 - v. Potential extent of activation
 - vi. Low degradation rate upon storage.
 - vii. Possibility of producing an activated carbon with high percent yield.

In real practice, it is not possible to have all of the seven features in a feedstock. Most of the biomass contains lower carbon contents than the coals, and gives lower yield. Due to the environmental concerns, high cost and non-renewability, they cannot be the permanent choice. On the other hand, the cheap cost, the ease of availability and environmental compatibility have made the bioresource feedstock logically more acceptable.

Nowadays, there is a great interest in finding inexpensive and effective alternatives to the existing commercial activated carbon. Exploring effective and low-cost activated carbon may contribute to environmental sustainability and offer benefits for future commercial applications. The cost of activated carbon prepared from bioresources is very low compared to the cost of commercial activated carbon. Therefore the bio resources need to be given due weightage and attention for AC synthesis.

➤ BIOMASS FEEDSTOCK

- Sunlight is used by the biomass to synthesize nutrients for growth and also for synthesis of important compounds, like carbohydrates, lipids and proteins.
- These components may be converted to biofuels and various products in the frame of a biorefinery concept.
- Biomass covers all forms of organic material, including plants both living and in waste form, and animal waste products.
- It can be divided into two different categories: (i) waste materials or (ii) dedicated energy crops .

- Biomass waste materials include agricultural and forest residues, municipal solid waste (MSW), food processing waste and animal manure, among others.
- The value that can be obtained from these wastes cannot be ignored as an important bioenergy source.
- If effectively harnessed, biomass wastes can be used as raw material for the synthesis of high-value solid products and/or chemicals, as well as for reducing the energy consumption from non-renewable fossil fuel sources.
- Furthermore, the use of solid waste materials would also save landfill space and increase the value of the biomass resources.
- The different types of biomass feedstocks are summarized in **Figure-2** and briefly described below:

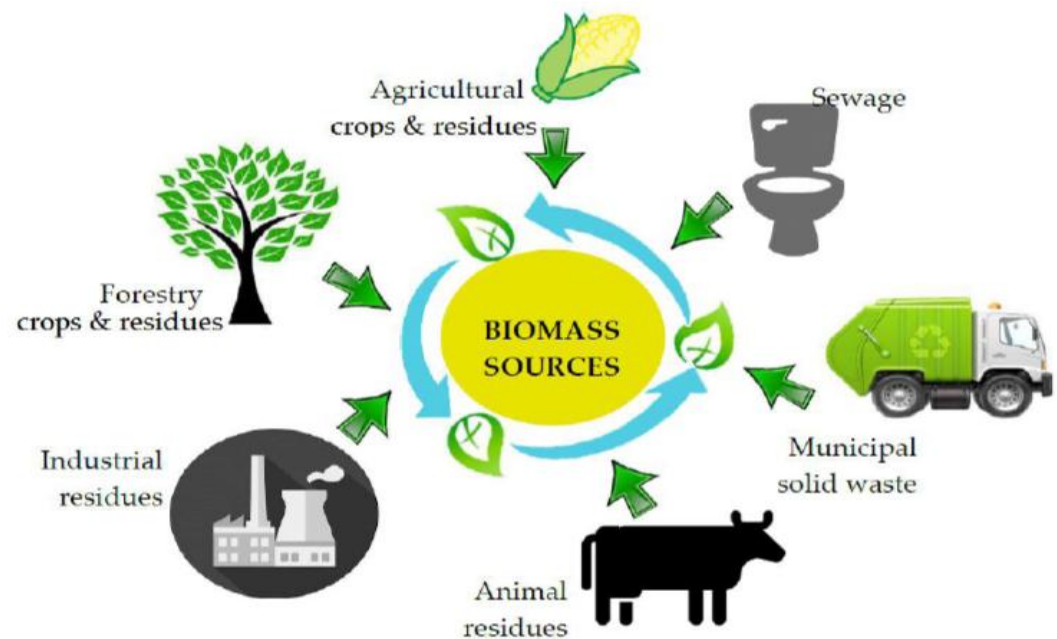


Figure 2. Different types of biomass feedstocks.

- **Dedicated Energy Crops**
 - ✓ The lands which are less arid, not fertile enough for traditional crops can be used to grow dedicated energy crops.
 - ✓ There exist two main types of dedicated energy crops: herbaceous and woody.
 - ✓ The former are grasses annually harvested including bamboo, wheatgrass, and sorghum, among many others.
 - ✓ The latter are constituted by fast-growing hardwood trees, such as poplar, willow, maple, walnut and so on.
- **Forest Residues**
 - ✓ Forest residues are obtained after logging timber or complete trees grown specifically for biomass collection.
 - ✓ Forest residues can be also obtained from the excess biomass in high-extension forests.
 - ✓ This action reduces the risk of fire and pests, and enhances the forest vitality, productivity and resilience.

- Agricultural Crop Residues
 - ✓ The use of agricultural biomass residues to produce biofuels, energy and value-added materials can achieve interesting environmental and socio-economic benefits.
 - ✓ Agricultural crop residues, which include wheat, barley, rye, oat, maize, rice, rapeseed and sunflower, are abundant, diverse, and widely distributed.
 - ✓ The benefits of the sale of these residues can produce complementary incomes supporting a local economy.
- Algae
 - ✓ Algae as feedstocks include the different biomass that grows in aquatic environments, covering microalgae, seaweed and even cyanobacteria.
 - ✓ Algae can grow in different types of waters including fresh, saline, brackish water and even in wastewater from different sources, such as agricultural water, treated industrial wastewater, aquaculture wastewater, water from oil and gas drilling operations, and so on.
 - ✓ Due to this, they can be considered a very promising biomass feedstock with very interesting growth potential in the near future.
- Municipal Solid Wastes (MSW)
 - ✓ Municipal solid wastes (MSW) are the materials discarded in urban areas, including predominantly household wastes.
 - ✓ MSW is a heterogeneous biomass feedstock mainly composed of food wastes, paper, wood trimmings and some textiles.
 - ✓ A significant proportion of MSW is derived from fossil resources, such as rubber, plastics, and some fabrics. The use of MSW as raw materials for bioenergy can reduce the huge volume of residential and commercial waste addressed to landfills.
- Wet Waste
 - ✓ Wet waste biomass includes food wastes, sewage sludge from municipal wastewater treatment plants, manure slurries, different organic wastes from industrial processes and the biogas obtained by the decomposition of organic matter in the absence of oxygen of any of the above feedstock resources.
 - ✓ The transformation of this waste into energy or value-added products can generate additional incomes for rural areas, besides reducing waste-disposal problems.

➤ TYPES OF ACTIVATED CARBON

- Depending on the source material, and the processing methods used to produce activated carbon, the physical and chemical properties of the end product can differ significantly. This creates a matrix of possibilities for variation in commercially produced carbons, with hundreds of varieties available. Because of this, commercially produced activated carbons are highly specialized to achieve the best results for a given application. Despite such variation, there are three main types (**Figure-1**) of activated carbon produced:
 - (1) Powdered Activated Carbon (PAC)
 - (2) Granular Activated Carbon (GAC)
 - (3) Extruded Activated Carbon (EAC)

- **Powdered Activated Carbon (PAC)**
 - ✓ Powdered activated carbons generally fall in the particle size range of 5 to 150 Å, with some outlying sizes available.
 - ✓ PAC's are typically used in liquid-phase adsorption applications and offer reduced processing costs and flexibility in operation.
- **Granular Activated Carbon (GAC)**
 - ✓ Granular activated carbons generally range in particle sizes of 0.2 mm to 5 mm and can be used in both gas and liquid phase applications.
 - ✓ GACs are popular because they offer clean handling and tend to last longer than PACs.
 - ✓ Additionally, they offer improved strength (hardness) and can be regenerated and reused.
- **Extruded Activated Carbon (EAC)**
 - ✓ Extruded activated carbons are a cylindrical pellet product ranging in size from 1 mm to 5 mm.
 - ✓ Typically used in gas phase reactions, EACs are a heavy-duty activated carbon as a result of the extrusion process.

- **Additional Types**

Additional varieties of activated carbon include:

- ✓ **Bead Activated Carbon (BAC)**

- ✚ Bead shaped activated carbon (BAC) is a highly spherical activated carbon with petroleum pitch as its raw material

- ✚ In addition to intrinsically having the absorption performance of activated carbon, BAC has various features: Small particle, high fill capability, high flowability, high purity, low dust, high strength, high wear resistance, narrow particle size distribution

- ✚ Applications: Solvent recovery, gas treatment of filters, water treatment etc.



- ✓ **Impregnated Carbon**

- ✚ To further improve the action of activated carbon, we can **impregnate** the activated carbon **with selected chemicals**. Impregnation of activated carbon gives the activated carbon additional properties such as chemisorption properties which reinforces the adsorption or can result in bacteriostatic properties by controlled, low silver leach in point of use (POU) or point of entry (POE) home water appliance filters.

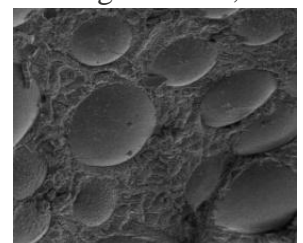
- ✚ Applications: Mercury removal from natural gas, purification of waste odours, removal of chemicals, desulphurisation of biogas; removal of mercury during the production of hydrogen gas; fume purification in laboratory fume cabinets; home water treatment in bacteriostatic water filters; removal of war gases from NBC filters and gas masks; ammoniac and amines removal from air



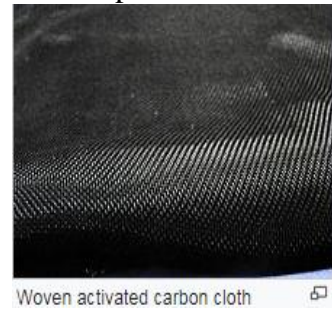
- ✓ **Polymer Coated Carbon**

- ✚ This is a process by which a porous carbon can be coated with a biocompatible **polymer** to give a smooth and permeable coat without blocking the pores.

- ✚ The resulting carbon is useful for **hemoperfusion**.



- ✚ Hemoperfusion is a treatment technique in which large volumes of the patient's blood are passed over an adsorbent substance in order to remove toxic substances from the blood.
- ✚ Early use of haemoperfusion through uncoated charcoal particles in patients with barbiturate over dosage was accompanied by the loss of formed elements from the blood stream and also by the formation of charcoal emboli. The use of the polymer coating 'polyhema' has shown to reduce the risk of both these complications.
- ✓ Activated Carbon Cloths
 - ✚ Activated Carbon Cloth (ACC) was originally invented by the British Ministry of Defence for inclusion in chemical warfare suits.
 - ✚ Today it has been developed for use in many odor control situations including industrial, medical, and domestic applications.
- ✓ Activated Carbon Fibers
 - ✚ Fibrous adsorbents have the advantages of fast adsorption rate and ease of handling when compared with granular adsorbents and powdered adsorbents.
 - ✚ Activated carbon fiber (ACF) is a promising microporous material with a fiber shape and well-defined porous structure. In general, production of ACF can be commercially manufactured from synthetic carbon fiber (CF) with providing an additional activation process.
 - ✚ Major application: Water filters (removal of chlorine, organic matter, etc.), surface treatment liquid cleaning, gas phase applications (deodorization/VOC adsorption)



➤ STRUCTURE OF ACTIVATED CARBON

- X-ray-diffraction studies have shown that the structure of thermally activated carbon is similar to that of graphite 9, 10 as shown in Figure-3.

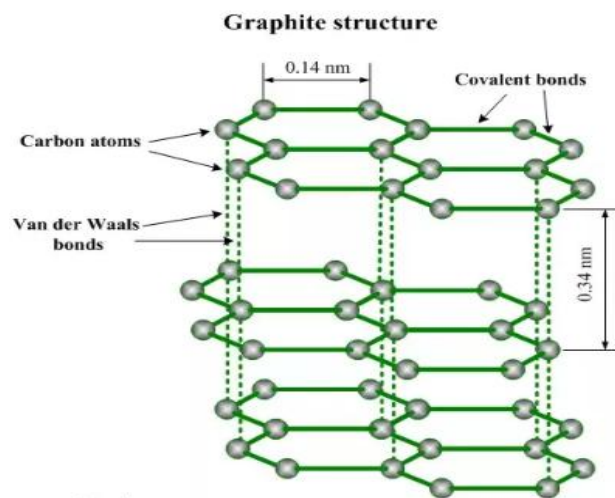


Figure-3: Schematic representation of the structure of graphite; the circles denote the positions of carbon atoms, while the horizontal lines represent carbon-to carbon bonds.

- Ideal graphite, consists of layers of fused hexagons held approximately 0.34 nm apart by Van der Waals forces, so that the carbon atoms in anyone plane lie above the centres of the hexagons in the layer immediately below it.
- The lattice is of the ABAB type (Figure-4).

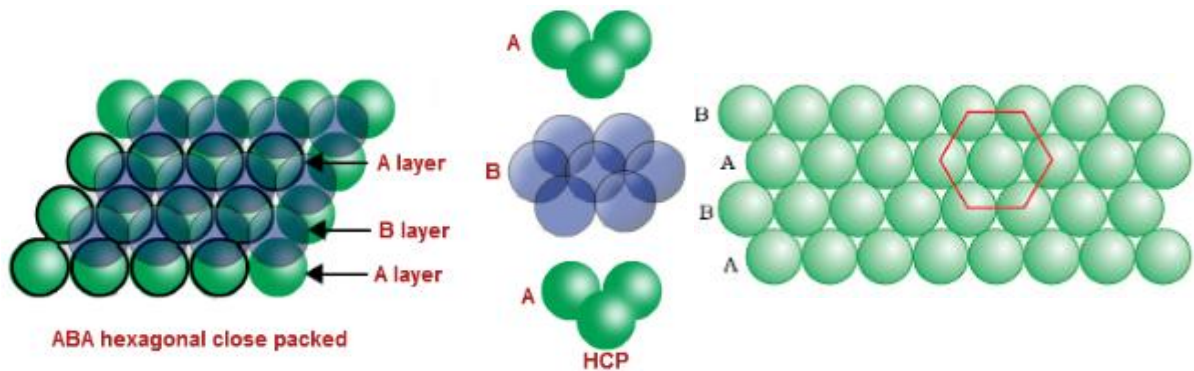


Figure-4: ABAB type lattice.

- The proposed structure of thermally activated carbon is depicted in **Figure-5**.
- The carbon is believed to be composed of tiny graphite-like platelets, only a few carbon atoms thick and 20 to 100 Å in diameter, which form the walls of open cavities of molecular dimensions, i.e. the pore system.
- However, the hexagonal carbon rings, many of which have undergone cleavage, are randomly orientated, and lack the directional relationship with one another that is present in single graphite crystals.
- The overall structure is therefore very disordered, and is often referred to as 'turbostratic'.
- Furthermore, the separation between the layers is greater than that found in graphite, viz 3.60 Å.
- Because of the high level of structural imperfections in activated carbons, there are many possibilities for reactions with carbon atoms at the edges of the planar layers.
- As a result, oxygen-containing organic functional groups, which are located mostly at the edges of broken graphitic ring systems, are present on the surface of the carbon.

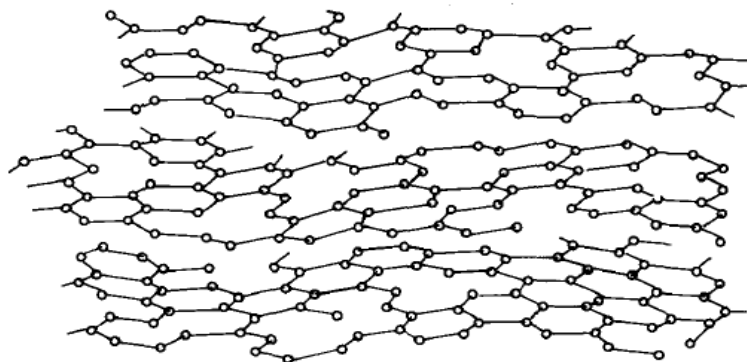


Figure-4: Schematic representation of the proposed structure of activated carbon; oxygen containing functional groups are located at the edges of broken graphitic ring systems.

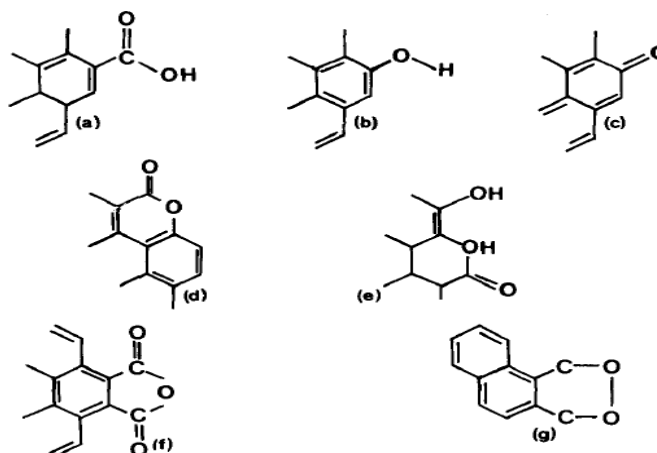


Figure-5: Structure of some surface oxides: (a) carboxylic acid (b) phenolic hydroxyl (c) quinone-type carbonyl groups (d) normal lactone (e) fluoreacein-type lactones (f) carboxylic acid anhydrides (g) cyclic peroxides

- Although the exact chemical structures of these surface oxides are not known with certainty, it has been suggested that the surface oxides depicted in **Figure-5** are the oxides most often present in thermally activated carbons.
- Basic surface groups have also been identified, and it appears that the nature of the surface groups depends upon conditions during and after manufacture.

➤ **PROPERTIES OF ACTIVATED CARBON**

- The physical and chemical properties most often employed by manufacturers of activated carbon to characterize their products are listed in Table-I, below:

Table-1: Physicochemical Properties of Activated Carbon

Physical Properties	Chemical Adsorption Characteristics
Particle density	Surface area
Bulk density	Iodine number
Pore volume	Carbon tetrachloride number
Ball-pan hardness	Benzene Number
Particle size distribution	
Ash content	
Moisture content	
Carbon Content	

- Some of the properties are discussed below:

✓ **Pore Structure (Figure-6)**

Activated carbon can be defined as a crude form of graphite with a random or amorphous structure, which is highly porous over a broad range of pore sizes, from visible cracks and crevices to cracks and crevices of molecular dimensions. Activated carbon purification is primarily based on a phenomenon called adsorption, in which molecules of a liquid or gas are trapped by either an external or internal surface of a solid. The phenomenon is somewhat similar to iron filings being held by a magnet. Activated carbon has a very high internal surface area (up to 1500 m²/g) and is thus an ideal material for adsorption.

Activated carbon can be manufactured from a wide variety of raw materials containing a high percentage of carbon. The production process of converting the raw

material into the finished adsorbent can be divided into chemical and thermal processes both of which require the use of elevated temperatures.

The pore structure of activated carbon varies and is largely as a result of the source material and the method of production. The pore structure, in combination with attractive forces, is what allows adsorption to occur.

The volume of the pores in activated carbons is generally defined as being greater than 0.2 ml/g, and the internal surface area is generally larger than 400 m²/g as measured by the nitrogen BET method.

According to the IUPAC (International Union of Pure and Applied Chemistry), three groups of pores are distinguished, according to the pore size:

Macropores:	(> 50 nm diameter)
Mesopores:	(2-50 nm diameter)
Micropores:	(< 2 nm diameter)

Micropores generally contribute to the major part of the internal surface area. Macro and mesopores can generally be regarded as the highways into the carbon particle, and are crucial for kinetics.

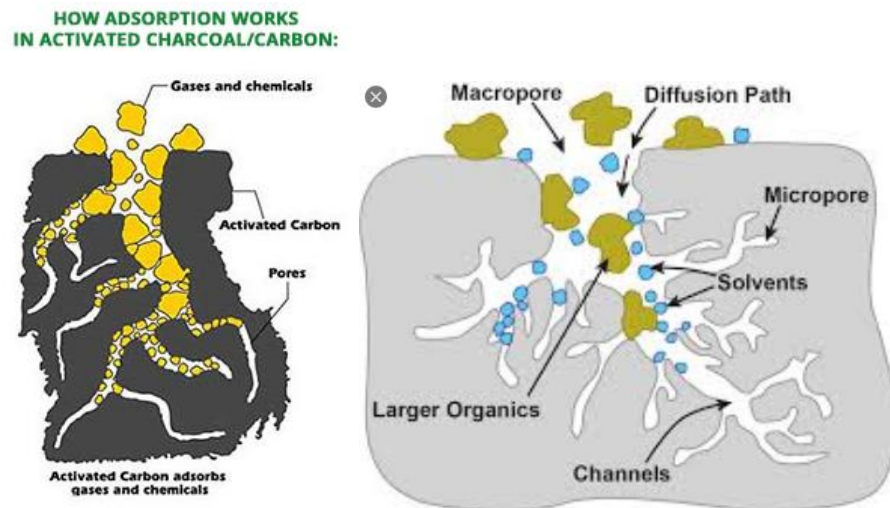


Figure-6: Pore structure of activated carbon.

✓ **Hardness/Abrasion**

The Hardness number (DSTM 20) measures the external integrity against wearing along exterior and breakage of small points of activated carbon. It is expressed as a percentage of loss on a particular sieve after shaking granules under certain conditions.

The abrasion number (AWWA B604) measures the structural strength of granular activated carbon. It is a measure of the ability of the particle to stand up to shear forces caused by particles rubbing together or particles rubbing against another surface such as a column wall or supporting screen. It is measured by shaking granules with steel balls in a container under certain conditions and expressed as a percentage reduction in Mean Particle Diameter (mpd).

Hardness/abrasion is also a key factor in selection. Many applications will require the activated carbon to have a high particle strength and a resistance to attrition (the breakdown of material into fines). Activated carbon produced from coconut shells has the highest hardness of activated carbons.

✓ **Adsorptive Properties**

The process by which a solid surface concentrates fluid molecules by physical forces is known as adsorption (whereas, absorption is a process whereby fluid molecules are taken up by a liquid and distributed throughout that liquid).

The elemental force causing physical adsorption on activated carbon is the London dispersion force, a form of Van der Waals force, resulting from intermolecular attraction.

In the case of adsorption, carbon and the adsorbate are thus chemically unchanged. However, in the process known as chemisorption, molecules chemically react with the carbon's surface (or an impregnant on the carbon's surface) and are held by chemical bonds that are much stronger forces compared to London dispersion forces.

The London dispersion force is an intermolecular interaction that exists between all molecules (both polar and non-polar), but it is extremely short-ranged. It is responsible for condensation of most gases to liquids, and the reason higher-molecular-weight gases have higher boiling points. London forces are:

Additive: The observed London force is the sum of all the individual interactions of the adsorbate molecule and the neighbouring graphite plates composing the carbon structure. The magnitude of the adsorption force will be related to the number of carbon plates, or density of carbon, within the vicinity of the adsorbate molecules.

Nonspecific: London forces exist between all molecules. Therefore, all molecules adsorb on activated carbon to some extent, depending on their vapour pressure and solubility at the carbon temperature.

Temperature-independent: The London forces are unaffected by temperature, and thus the adsorption force field will be constant with temperature. (The carbon adsorption capacities will still be sensitive, however, to the changes with temperature in vapour pressure or solubility of the adsorbing molecules).

Short-ranged: The magnitude of the London force is very sensitive to the separation of the adsorbate molecule from the graphite plate. The London force can be considered negligible with a separation greater than about two molecular layers. Therefore, the adsorption forces will only be significant if the gaps or voids within the carbon structure (pore widths) are less than four or five molecular layers.

The first three characteristics of London forces are shared by another familiar force: gravity. London forces, and consequently the carbon adsorption forces, are analogous to gravitational forces. However, London forces are much shorter-ranged, and operate on a molecular scale instead of an astronomical scale.

The adsorptive properties of the activated carbon encompass several characteristics, including adsorptive capacity, the rate of adsorption, and the overall effectiveness of activated carbon. Depending on the application (liquid or gas), these properties may be indicated by a number of factors, including the iodine number, surface area, and CTC.

✓ **Carbon Tetrachloride Activity (CTC)**

The Carbon Tetrachloride Activity (ASTM D3467) measures the loading of carbon tetrachloride, weight percent on carbon, at concentrations close to saturation in the air. The method is basically a measure of the pore volume of the activated carbon and is primarily used as a quality assurance test for the production of activated carbon.

The Carbon Tetrachloride Activity has been replaced by the Butane Activity (ASTM D5742) test due to the ban on carbon tetrachloride.

$$\text{CCl}_4 \text{ activity} = 2.55 \times \text{the Butane Activity.}$$

✓ **Apparent Density**

The apparent density, sometimes called the bulk density of activated carbon, or volumetric density is defined as the mass of many particles of the activated carbon divided by the total volume they occupy. The total volume includes particle volume, inter-particle void volume, and internal pore volume.

While apparent density does not affect the adsorption per unit weight, it affects the adsorption per unit volume.

✓ **Moisture**

The moisture content of activated carbon (ASTM D2867) is measured as weight loss after heating at 150°C and allowed to dry to a constant weight (usually after 3 hours). The moisture content of packed activated carbon will usually increase during transport and storage.

Ideally, the amount of physical moisture contained within the activated carbon should fall within 3-6%.

✓ **Ash Content**

Total ash is a measure of the mineral oxide content of activated carbon on a weight basis. It is measured by converting the mineral constituents to the respective oxides at 800°C. The ash consists mainly of silica and aluminium and the amount is dependent on the base raw material used to produce the product. Typical values are 2-3% W/W for coconut shell based activated carbon, 5% W/W for wood based activated carbon, and 8-15% W/W for coal based activated carbons.

Total ash analyses are also a good indicator for the spent carbon quality used in groundwater sanitation or drinking water applications. High ash content can be an indication of calcium, aluminium, manganese or iron deposition on the activated carbon or the presence of sand.

The ash content of activated carbon is a measure of the inert, amorphous, inorganic, and unusable part of the material. The ash content should ideally be as low as possible. The quality of the activated carbon increases as ash content decreases.

✓ **pH Value**

The pH value of activated carbon is a measure of whether it is acidic or basic. Coconut shell based activated carbon is normally specified for a pH of 9 – 11.

The method chosen for activation and the reagent used also effects the pH of the activated carbon.

The pH has a very significant effect on adsorption processes in the liquid phase. The pH indeed has an influence on surface chemistry and on surface charge. For instance, at low pH, the surface is positively charged, so the performances for adsorbing cations will be low because of the corresponding electrostatic repulsion.

The pH value is often measured to predict potential change when activated carbon is added to liquid.

✓ **Particle Size**

Particle size has a direct effect on adsorption kinetics, flow characteristics, and filterability of the activated carbon.

The finer the particle size of an activated carbon, the better the access to the surface area and the faster the rate of adsorption kinetics. In vapour phase systems this needs to be considered against pressure drop, which will affect energy cost. Careful consideration of particle size distribution can provide significant operating benefits.

However, in the case of using activated carbon for adsorption of minerals such as gold, the particle size should be in the range of 3.35–1.4 millimetres (0.132–0.055 in). Activated carbon with particle size less than 1 mm would not be suitable for elution (the stripping of mineral from an activated carbon).

The size range of granular activated carbon (GAC) is usually expressed as the sieve sizes, expressed in mm or US Mesh, between which most of the GAC is retained.

It is measured by shaking a sample of granular activated carbon through a defined series of sieves. In metric units it is the width between the sieves wires expressed in mm. In the US Mesh system the sieve size number refers to the openings between the sieves wires per inch.

For example; a 8×30 US Mesh activated carbon means at least 93% of the granules by weight are larger than 30 Mesh (0.60mm) and at least 90% of the granules by weight are smaller than 8 Mesh (2.36mm). 12×40 US Mesh (0.42 to 1.70mm), 6×16 US Mesh (1.18 to 3.35 mm).

✓ **Iodine Number**

The iodine number (or “iodine value”) (ASTM D4607) is an indication of the available surface area in m^2/gram of virgin carbon. Although the Iodine number has become synonymous with the “activity” of activated carbon and it is widely used as a quality control (QC) parameter in production and reactivation of activated carbon, it does not necessarily provide a measure of the carbon's ability to adsorb other species.

The iodine number is defined as the milligrams of iodine adsorbed by one gram of material when the iodine residual concentration of the filtrate is 0.02N (0.01 mol/l) according to ASTM D4607 standard, which is based on a three-point isotherm.

✓ **Pore, Porosity, Pore volume, Pore diameter**

A pore is small opening in the surface of the activated carbon leading to the interior in tortuous manner as depicted in the **Figure-6**. Also means the tiny hole or opening that allows the passage of liquid.

Porosity or void fraction is a measure of the void spaces in the activated carbon. It is a fraction of the volume of voids over the total volume, between 0 and 1, or as a percentage between 0% and 100%.

Activated carbons are porous materials of great importance for several processes. AC is characterized by several physical parameters such as surface area and pore volume. In the development of these materials it is very important to satisfy such physical properties, because they will directly influence the performance of the material in its application.

For the pore volume determination, the procedure more commonly used also uses nitrogen adsorption isotherm data. The total pore volume is estimated from the

amount of nitrogen adsorbed at the highest relative pressure and the micropore volume is calculated from the nitrogen adsorption isotherms using the Dubinin-Radushkevich equation. The unit is ml/g of AC.

Due to varying methods of preparation, the pore sizes of the activated charcoal can be categorized as being micropores (width < 2 nm), mesopores (width = 2–50 nm), or macropores (width > 50 nm); the differences in the size of their width openings being a representation of the pore distance.

✓ **Surface Area**

The surface areas of activated carbons are usually measured using the Brunauer-Emmett-Teller (BET) method, which employs the nitrogen adsorption at different pressures at the temperature of liquid nitrogen. The unit of AC area is m²/g.

➤ **PRODUCTION OF ACTIVATED CARBON**

- The most important step in the production of activated carbon is activation.
- This is the process by which the chosen raw material or carbonized raw material is converted into a finely crystalline form of carbon that is permeated by the greatest possible number of randomly distributed pores of various shapes and sizes.
- These pores give rise to the extended internal surface area.
- In the manufacture of activated carbon, it is desirable to develop the maximum accessible surface area that is commensurate with economic viability and product application.
- The products of simple coking or carbonizing (such as that used in the early days) do not meet present-day standards.
- This can be attributed to the fact that the available surface area of pulverized charcoal, which is essentially external surface area, is only 2 to 4 m²/g -as against typically 1000 m²/g or more for a granular activated-carbon product-measured by the nitrogen BET method.
- Activated carbon is produced through two main processes: carbonization and activation.

✓ **Carbonization**

- Literal meaning of carbonization is 'formation of carbon'.
- In bioresource engineering/bioresource technology, carbonization is a process in which a carbonaceous materials like biomass is heated in the absence of air to leave solid porous carbon.
- Coke is produced commercially by carbonization of coal, either at high or low temperatures.
- It is the conversion of organic matters like plants and dead animal remains into carbon through destructive distillation.
- It is a pyrolytic reaction, therefore, is considered a complex process in which many reactions take place concurrently such as dehydrogenation, condensation, hydrogen transfer and isomerization.
- During carbonization, the raw material (bioresource) is thermally decomposed in an inert environment, at temperatures below 800 °C.
- Through gasification, elements such as oxygen, hydrogen, nitrogen, and sulfur, are removed from the source material and biochar is left behind as a solid product.

✓ **Activation**

- The carbonized material, or char, must now be activated to fully develop the pore structure.

- This is done through oxidizing the char at temperatures between 800-900 °C in the presence of air, carbon dioxide, or steam.
- Depending on the source material, the process of producing activated carbon can be carried out using either thermal (physical/steam) activation, or chemical activation.
- In either case, the charcoal or biochar obtained during gasification, pyrolysis or hydrothermal gasification are subjected to further treatment for improvement of surface area and activity of the biochar in order to obtain active biochar or carbon.
- A general method for preparation of activated carbon from bioresource may be represented by the following **Figure-7**.
- Although the general outlines of the various manufacturing processes are well known, the exact details of the procedures employed by the manufacturers are jealously guarded secrets.
- In general, the methods most commonly employed for the manufacture of activated carbon are of two main types: the wet-chemical process (basically a single-stage process), and the physical or thermal-gas process (essentially a two-stage process).
- As would be expected, chemical methods use chemicals for activation, whereas thermal processes use gases (usually carbon dioxide and air), vapours (steam), or mixtures of gases and vapours.
- Any bioresource such as coconut shells, peach and apricot stones, wood, sawdust, cellulose, walnut shells, almond shells, tree leaves, bark, bamboo, rice husks, corn cobs, sugar, bones, etc. may be used as raw material.
- After proper cleaning, sizing and upstream processing, the feedstock is impregnated with some reagent, i.e. reagent-1.

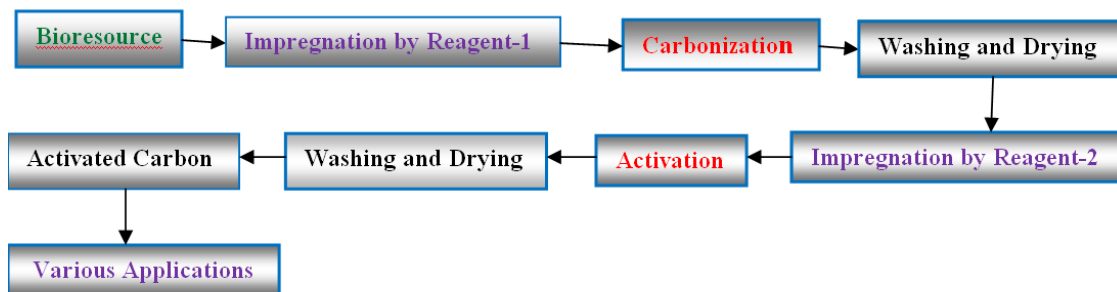


Figure-7: General flow diagram for manufacturing of activated carbon from bioresource feedstock.

- Carbonization is carried out under specified condition in order to obtain the charcoal which has certain degree of porosity.
- After carbonization the biochar is, washed and dried, and impregnated with reagent-2.
- The impregnated biochar is subjected to activation which is carried out by physical /chemical method under specified conditions.
- After washing and drying the activated carbon is ready for desired application.

➤ **PREPARATION OF ACTIVATED CARBON FROM RICE HUSK (RH)**

- RH-derived AC via physical and chemical activations is shown in **Figure-8**.
- **Physical Activation**
 - ✓ Physical activation comprises the carbonization of RH to eliminate organic matters and followed by activation (two steps process).

- ✓ The precursor RH is normally washed with de-ionized (DI) water to remove dust and attached particles, followed by drying process.
- ✓ The carbonization process is carried out at temperatures of 500 to 900 °C under the nitrogen or argon gas atmosphere and followed by subsequent activation.
- ✓ During the activation, the carbonized RH is gasified by CO₂, steam or their mixture at high temperature ranging from 800 to 1000 °C.
- ✓ These activating agents eliminate carbon atoms from the carbonized RH as CO to ease the pores development.
- ✓ The activation route using two different activating agents CO₂ and steam would result in AC with significantly porous structure and improved physical properties.
- ✓ CO₂ activating agent creates pore openings, followed by the widening of narrow microporosity which eventually result in AC with larger micropore volume but narrower micropore size distribution.
- ✓ Steam activating agent widens the micropores in biochar from the early stages of the activation process and thus produces AC with a wider pore size distribution (micropores and mesopores).
- ✓ CO₂ is a preferable activating agent for activation process due to its inherent cleanliness and ease of handling.
- ✓ Moreover, CO₂ gas also facilitates in controlling the activation process due to the slow reaction rate at temperatures around 800 °C.

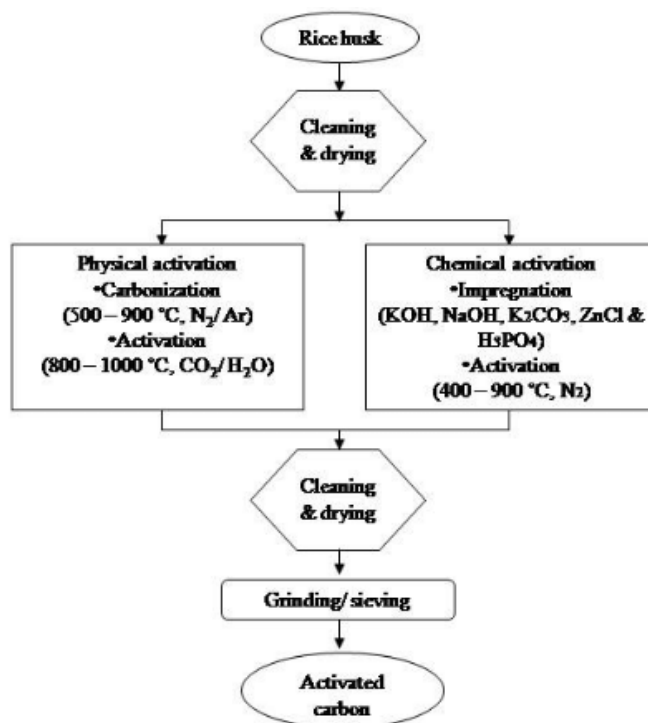


Figure-8: RH-derived AC via physical and chemical activation.

- **Chemical activation**

- ✓ Chemical activation of RH-derived AC involves both carbonization and activation being performed in a single step using chemical agents such as KOH, NaOH, H₃PO₄ and ZnCl₂.
- ✓ A cleaned RH is impregnated with activating agent in the form of concentrated solution to remove the cellulosic materials.

- ✓ The chemical impregnated RH precursor is then pyrolyzed at temperatures ranging from 400 to 900 °C in the absence of air.
- ✓ The use of chemical activating agent inhibits the formation of tar and other byproducts (methanol and acetic acid), resulting in a better yield of RH-derived AC.
- ✓ The impregnation ratio between chemical activating agent and precursor is one of the major factor that greatly influences the yield and pore characteristics of RH-derived AC.
- ✓ Based on studies done by various researchers, the impregnation ratio (weight of chemical activating agent to weight of precursor) varies from 0.25 to 4 is normally applied on raw materials.
- ✓ The yield of AC decreases when the impregnation increases.
- ✓ Large amounts of organic matter would be burnt off when more chemical activating agents are used to treat the precursors.
- ✓ Studies have shown that the increase in impregnation ratio resulted in better porosity development and widening of porous structure of the AC.
- ✓ Besides impregnation ratio, activation temperature is another factor which influences pore development, physical properties and yield of the AC.
- ✓ Activation at high temperatures could enhance the pores development of the RH-derived AC.
- ✓ Study by Guo and co-workers shows that the increase in activation temperature enhanced the pore characteristics of ACs derived from RH.
- ✓ The increase in activation temperature from 650 to 800 °C increased the BET surface area (from 2110 to 3014 m² g⁻¹) and micropore volume (from 0.14 to 0.44 cm³ g⁻¹) of the RH-derived ACs.
- **Advantages and Disadvantages of Chemical Activations Over Physical Activation in AC Production from RH**
 - ✓ For the preparation of RH-derived AC with good porosity, chemical activation offers several advantages over the physical activation.
 - ✓ These advantages are single step activation process, higher yield obtained and better pores development in AC.
 - ✓ A single step activation process could cut down on AC manufacturing time and energy required.
 - ✓ Furthermore, the use of chemical activating agent could lower the activation temperature, shorten the activation time and enhance the porosity development in final RH-derived AC obtained.
 - ✓ However, there are certain drawbacks of using chemical activation for the RH-derived AC production.
 - ✓ Additional cleaning step is required subsequent to the activation process to remove the residual chemicals. KOH and NaOH are hazardous, corrosive and expensive, while ZnCl₂ is unfriendly to the environment and creates waste disposal problem.
 - ✓ The use of chemical activating agents in treatment also increases the processing cost.
 - ✓ Handling of the chemical activation agents might cause threat to health.
 - ✓ Therefore, extra precautions are required to minimize the safety and health risk.

➤ SELF ACTIVATION

- Self-activation is a process that takes advantage of the gases emitted from the pyrolysis process of biomass to activate the converted carbon, which saves the cost of activating agents and decreases the environmental impact, compared with conventional activation processes.
- An activation model was developed to describe the mechanism of the activation process, and it was examined by the self-activation experiments using the kenaf core as a raw material.
- The relationships among the parameters, yields, specific surface areas, and specific pore volumes were quantified.
- The results showed that the ideal temperatures for the self-activation process of the kenaf core were found between 970–1090 °C.
- The yield of 9.0% for the activated carbon from the kenaf core provided the highest surface area per gram of biomass, while the yields of 5.5–13.8% could achieve 90% of the highest.
- The developed activation model (**Figure-9**) can be used to explain the relationship between the yields, specific surface areas, and specific pore volumes, effectively.

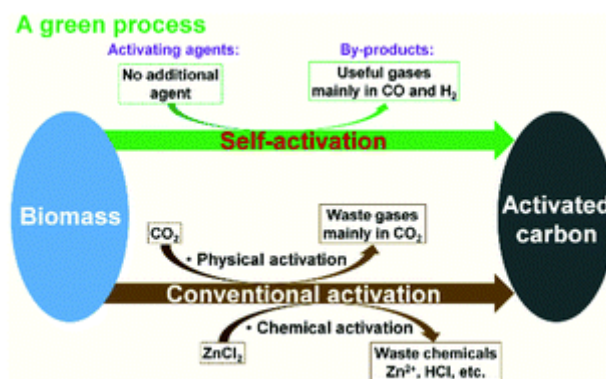


Figure-8: Model for self activation.

➤ DEPICTION OF VARIOUS POSSIBLE ROUTES FOR SYNTHESIS OF ACTIVE CARBON FROM BIOMASS

- In general terms, carbon-based adsorbents can be synthesized from any precursor with a high proportion of carbon in its composition.
- Therefore, biomass materials are ideal precursors for carbon-based adsorbents, i.e., biochars or activated carbons (AC).
- The difference between biochar and biomass-derived activated carbon is somewhat diffuse.
- The syntheses of carbon adsorbents from biomass agricultural waste, such as olive stones, rice husk, coconut husks or bamboo are available in the literature.
- Furthermore, many studies have also focused on the synthesis of carbon materials from biomass industrial wastes including lignin, (a by-product of the papermaking industry), Tara gum (generated in the food industry), wood waste or sawdust (from the furniture industry), and so on.
- The **Figure-9** schematizes the synthesis routes to biochars and activated carbons from biomass.

- Biochar is usually prepared upon carbonization, while activated carbons can be obtained in two well-known ways, namely physical and chemical activation, giving rise to a more developed porosity.
- In recent years, alternative procedures with the aim of energy and/or chemical savings have been proposed.

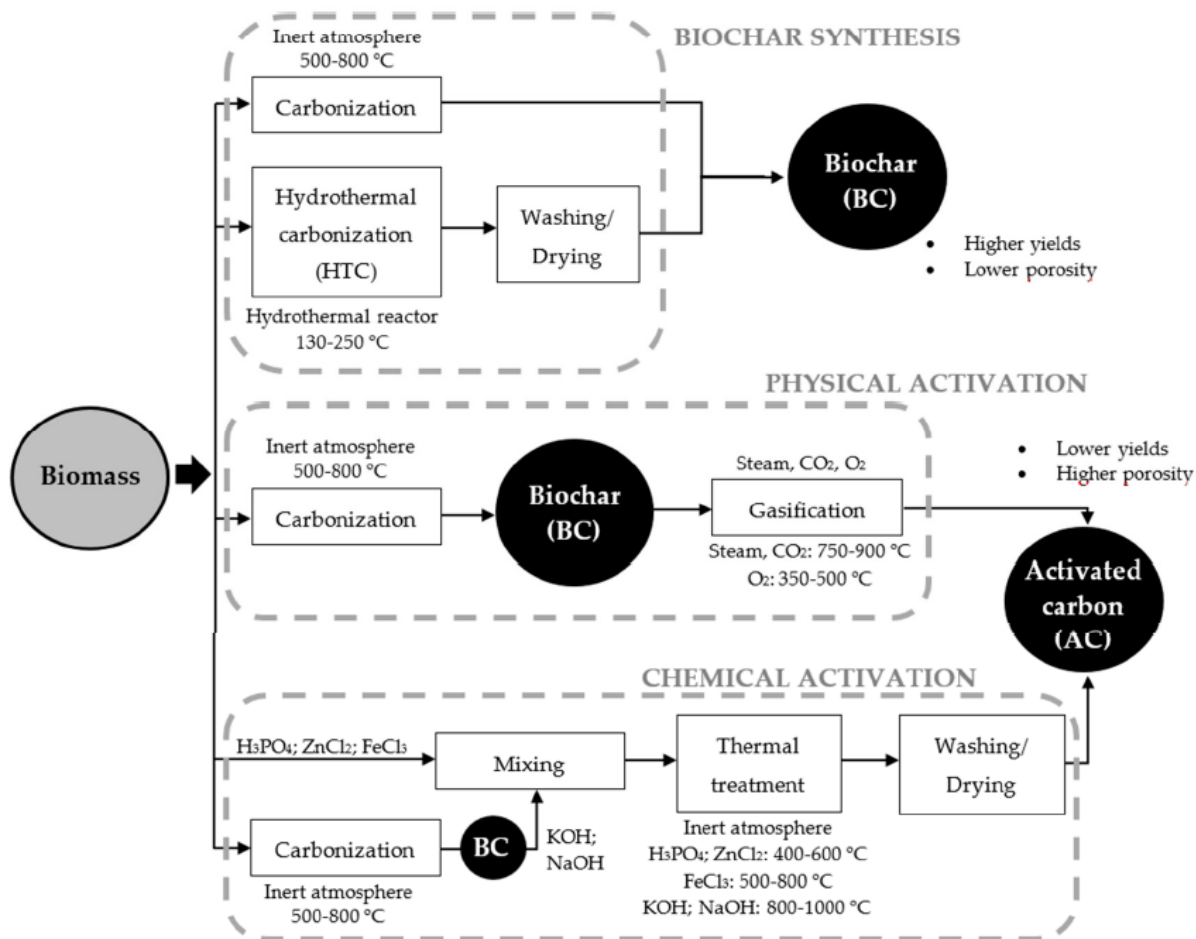


Figure-9: The synthesis routes to biochars and activated carbons from biomass.

- Thus, non-conventional methods, such as microwave heating and hydrothermal carbonization, are being analyzed for both biochars and activated carbons.
- It is worth mentioning that the porosity, surface chemistry and yields of the synthesized carbon-based adsorbents are highly dependent on the starting biomass composition and the operating conditions used in the synthesis.

➤ **FACTORS (PARAMETERS) AFFECTING AC PRODUCTION**

Factors affecting AC production are discussed below:

• **Raw materials**

- ✓ Most organic substances such as the biomass (bioresource) with high carbon content are potential raw materials for AC production.
- ✓ To produce a porous carbon structure, the under listed factors may be considered:
 - High carbon content
 - Low inorganic content (i.e. low ash)
 - Potential extent of activation

- iv. Low degradation upon storage
 - v. High density and sufficient volatile content
 - vi. Stability of supply in the countries
 - vii. Inexpensive materials
- ✓ Lignocellulosic materials are generally accepted as precursor for AC production and constitute about 45% of the total raw materials used.
 - ✓ **Table-2** shows the characteristics of some raw materials used in the AC production.
 - ✓ To produce AC with low ash content, it is important to get materials with low inorganic content.
 - ✓ Full control of the manufacturing process requires a moderately high volatile content.
 - ✓ Coconut shell and fruit stones are the most commonly raw materials.
 - ✓ This might be because of their hardness, volatile content, and relatively high density, their hardness, which make them most prepared for hard GAC production.
 - ✓ Moreover, other materials for example coconutshell, olive stones and peach waste are commercially utilised for micro-porous AC production and as well find usage for a variety of application.

Table-2: The Characteristics of Some Raw Materials used in the AC Production

Raw material	Carbon (mass %)	Volatiles (mass %)	Density (cm^3g^{-1})	Ash (mass %)	Texture of AC
Soft wood	40 – 45	55 – 60	0.4 – 0.5	0.3 – 1.1	Soft, large-pore volume
Hard wood	40 – 42	55 – 60	0.55 – 0.8	0.3 – 1.2	Soft, large-pore volume
Lignin	35 – 40	58 – 60	0.3 – 0.4	-	Soft, large-pore volume
Nutshells	40 – 45	55 – 60	1.40	-	Hard, large micro-pore volume
Lignite	55 – 70	25 – 40	1.0 – 1.35	5 – 6	Hard, small-pore volume
Soft coal	65 – 80	20 – 30	1.25 – 1.5	2 – 12	Medium-hard, medium-pore volume
Petroleum coke	70 – 85	15 – 20	1.35	0.5 – 0.7	Medium-hard, medium-pore volume
Semi-hard coal	70 – 75	10 – 15	1.45	5 – 15	Hard, large-pore volume
Hard coal	85 – 95	5 – 15	1.5 – 1.8	2 – 15	Hard, large-pore volume

Note: Materials with fossil origin have been included only for comparison.

- **Temperature**

- ✓ In the AC production, the activation temperature plays a vital role in affecting the characteristic of the AC produced.
- ✓ As for commercial purposes AC, it is normally carried out in a mixture of steam and CO_2 at a temperature above 800°C .
- ✓ In recent times, researchers have been up-and-doing to optimize final activation temperature in order to reduce cost and period of AC production.
- ✓ Several studies have been reported which indicated that activation temperature has great influence on surface area and production yield of AC.
- ✓ The activation temperature is between 200 to 1100°C .
- ✓ However, a temperature range of 400 to 500°C was reported by previous researchers to be considered regardless of time taken and the impregnation ratio for a variety of raw materials.

- ✓ Therefore, increasing activation temperature always results in the reduction of AC yield during production, which at the same time results in increasing the volume of volatile substances released.
- ✓ Generally, it is inappropriate to prepare AC at a temperature above 800°C.
- ✓ This goes along with an increase of fixed carbon and ash content, which may be ascribed to the removal of volatile matter in the material during carbonization process.
- ✓ Thus, results in more stable carbon and ash-forming minerals.
- ✓ The Brunauer, Emmett and Teller (BET) surface area (Adsorption on the upper layer commences immediately after the first layer has completed) is suggested to be another important feature showing the influence of production temperature on the AC characteristics.
- ✓ As the BET surface area increases, the activation temperature also increases.
- ✓ This might be due to the advancement of new pores due to the release of volatile matter and the broadening of presence ones as the activation temperature goes high.
- **Activation time**
 - ✓ The activation time also has a greater influence on both the carbonization process and properties of AC in addition to the activation temperature.
 - ✓ Few decades earlier, it was established that the activation times widely used were range from 1 to 3 hours for palm-fruit bunch, banana peel, and coconut shell.
 - ✓ Previous studies have reported that as the activation time increased gradually, the BET surface area also increased while the AC percentage yields decrease.
 - ✓ These might be attributed to the volatilization of organic substances from raw agricultural waste residues.
 - ✓ Some other researchers observed that as excessive activation time occurs, it causes the reduction in product yield.
- **Type and Concentration** of the chemicals used during impregnation and chemical activation have also effect on the yield and characteristic of the activated carbon.

➤ **APPLICATIONS OF ACTIVATED CARBON**

- Activated carbon is an incredibly diverse material that lends itself to thousands of applications through its superior adsorbent capabilities.
- The availability of high surface area of particles possessed by AC as well its adsorptive ability makes it a significant constituent in many industries.
- Industries like; petroleum, fertilizer plants, nuclear, pharmaceuticals, cosmetics, textiles, automobile, and vacuum manufacturing all uses AC.
- AC has found to be good porous materials, which make it very effective in adsorption of solutes from aqueous solutions.
- This was suggested to be due to the possession of large specific surface area.
- Furthermore, it has been extensively used for; solvents recovery, separation of gases, dye removal from industrial wastewater and as a catalyst in the process of biodiesel production.
- **Metals Recovery**

Activated carbon is a valuable tool in the recovery of precious metals such as gold and silver.

- **Food & Beverage**

- ✓ Activated carbon is widely used throughout the food and beverage industry to accomplish a number of objectives.
- ✓ This includes decaffeination, removal of undesirable components such as odor, taste, or color, and more.

- **Medicinal**

- ✓ Activated carbon can be used to treat a variety of ailments and poisonings.

- **Air Emission Purification**

- ✓ Air emission control with respect to organic or inorganic components is becoming an ever-greater challenge in today's industrialised world.
- ✓ It can involve components that give rise to a pervasive **odour**, or that exceed the **VOC emission** directive in the manufacturer's operating permit.
- ✓ The sources of these emissions can vary widely: they can emanate from a waste storage building, a waste treatment centre, a water treatment plant, from venting storage tanks or reactors, manufacturing chemical intermediates and end-products such as polyester, from manufacturing furniture, windows and doors, paint and chemical/petrochemical products.
- ✓ The diversity of components is infinite, as are the areas of application.
- ✓ Systems developed with activated carbon can solve harmful effects of air emission.



- **Biogas Purification**

- ✓ Converting biogas into electric power, heat from renewable sources or biomethane requires the gas to be treated first.
- ✓ This prevents problems occurring in the gas engine while at the same time enabling gas quality in excess of 99% CH₄ to be achieved, which renders the gas suitable for feeding into the natural-gas grid.
- ✓ Components typically needing to be eliminated include H₂S and siloxanes from landfill gas for example or H₂S and terpenes from fermentation gas.
- ✓ To meet all these challenges mobile activated carbon filters are used.



- **Remediation**

- ✓ Soil and/or groundwater may be contaminated anywhere there is or has been industrial activity.
- ✓ It often involves historic contamination, which dates back long before there was any question of enforceable environmental legislation.
- ✓ These contaminated areas are treated step by step, making them suitable for re-use or change of use.
- ✓ This often requires complex remediation techniques.
- ✓ Mobile activated carbon filters are ideally suited for this and are therefore frequently deployed as part of the remediation process.
- ✓ The technologies developed with activated carbon filters clean up historic contamination, as well as clean up disasters on the spot, such as an overturned fuel oil tanker, a leaking petroleum pipeline or treating fire water following a conflagration on an industrial site.



- **Chemicals (Purification with mobile activated carbon filters)**

- ✓ Plants manufacture products.
- ✓ Certain reactions may occur during the manufacturing process that can give rise to undesirable contamination of the end-product.
- ✓ On the other hand, certain products may fail to meet the requirements of the manufacturing process.
- ✓ Malfunctions can also occur during the manufacturing process, which will result in a batch of products failing to meet specification.
- ✓ Moreover, certain products acquire increased sales value if they have a certain degree of purity, which can be achieved thanks to activated carbon.



- **Waste Water (Purification with activated carbon)**

- ✓ Water is often required when we want to manufacture something.
- ✓ This water will become contaminated during the production process: it results in wastewater that cannot be simply discharged back into the environment.
- ✓ Wastewater produced in this way will then require to be treated before it can be discharged into a sewer or surface water, or indeed re-used.
- ✓ On the other hand it may also be the case that the water supply for a factory requires to be treated before it can be used in the production process.
- ✓ Activated carbon is often the appropriate technology for treatment at source as well as in between the various production stages, and for end-of-pipe treatment (e.g. after upstream biological or physicochemical treatment).



- ✓ Parameters such as COD, BOD, TOC, BTEX, hydrocarbons, AOX, pesticides, cyanides, odour, colour, etc. hold no secrets for activated carbon.
- ✓ Even contaminated fire water can be treated by the activated carbon technology.
- ✓ To meet all these challenges, AC technology offers a viable solution.
- The following two figures have summarized the applications of activated carbon:



APPLICATION



Smelting Instrument



Textile Industry



Foundry Industry



Material Welding



Sewage Treatment



Electron Equipment



Chemical Industry



Machine Industry



Spaceflight Industry

➤ REACTIVATION OR REGENERATION

- With the continuous application, activated carbon lose the adsorption capacity.
- In order to restore this, reactivation is carried out.
- The reactivation or the regeneration of activated carbons involves restoring the adsorptive capacity of saturated activated carbon by desorbing adsorbed contaminants on the activated carbon surface.

The Reactivation Cycle

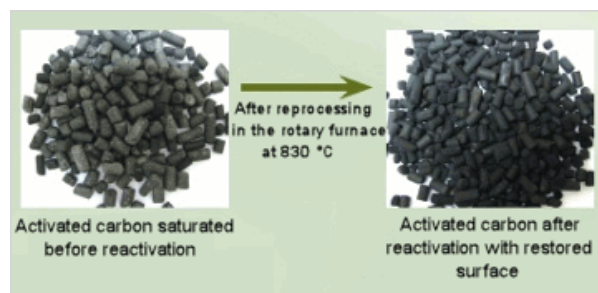
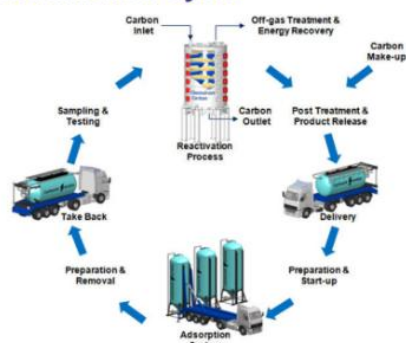


Figure-10: Regeneration cycle and activated carbon after reactivation with restored surface.

- One of the many advantages to activated carbon is its ability to be reactivated.

- While not all activated carbons are reactivated, those that are cost savings in that they do not require the purchase of fresh carbon for each use.
- Regeneration is typically carried out in a rotary kiln and involves the desorption of the components that had previously been adsorbed by the activated carbon.
- Once desorbed, the once saturated carbon is again considered active and ready to act as an adsorbent.
- Thermal reactivation
 - ✓ The most common regeneration technique employed in industrial processes is thermal reactivation.
 - ✓ The thermal regeneration process generally follows three steps:
 - Adsorbent drying at approximately 105 °C (221 °F)
 - High temperature desorption and decomposition (500–900 °C (932–1652 °F)) under an inert atmosphere
 - Residual organic gasification by a non-oxidising gas (steam or carbon dioxide) at elevated temperatures (800 °C (1470 °F))
- Other regeneration techniques
 - Chemical and solvent regeneration
 - Microbial regeneration
 - Electrochemical regeneration
 - Ultrasonic regeneration
 - Wet air oxidation



Figure-11: Continuous carbon activation furnace rotary kiln.



World's Largest Reactivation Plant Located in Feluy, Belgium

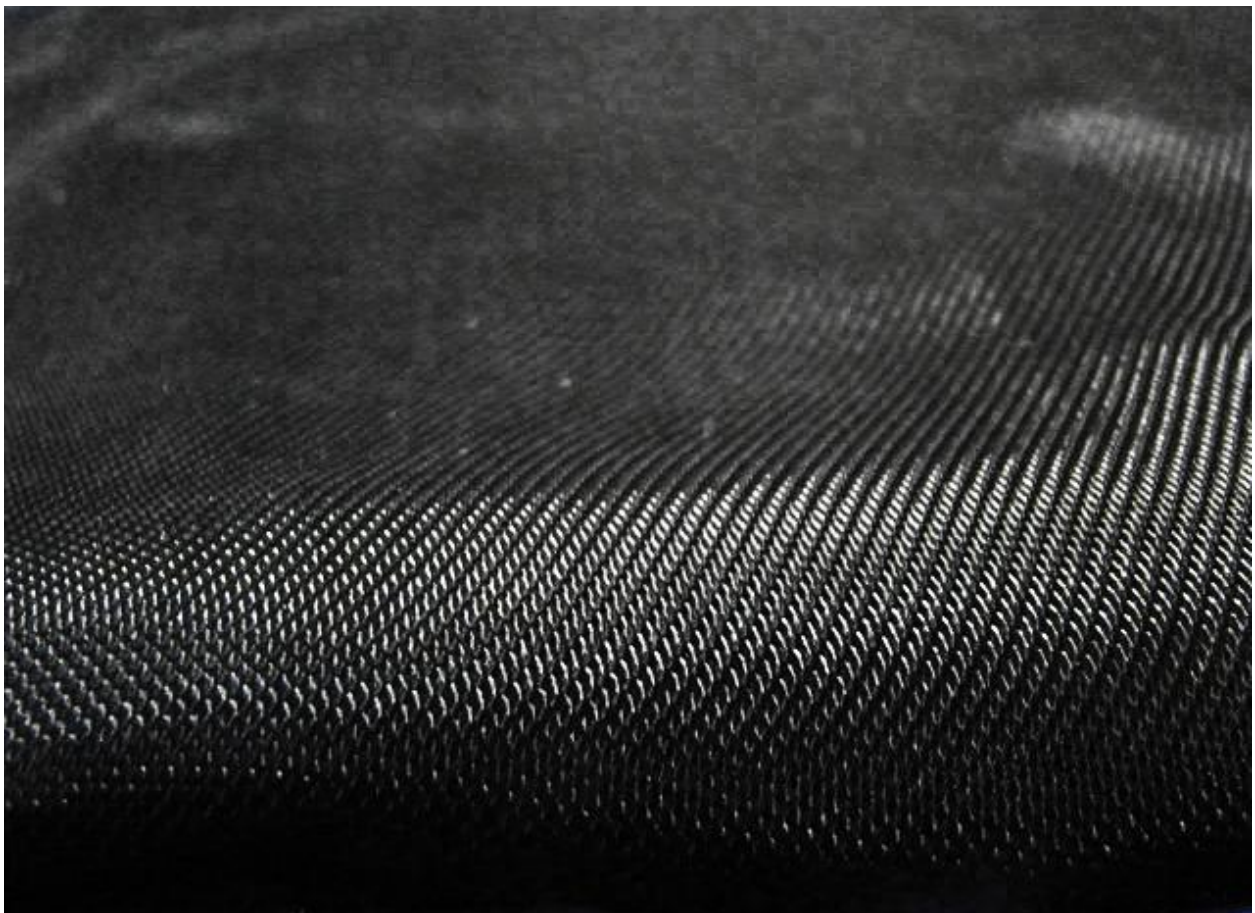


MSW GASIFICATION PLANT

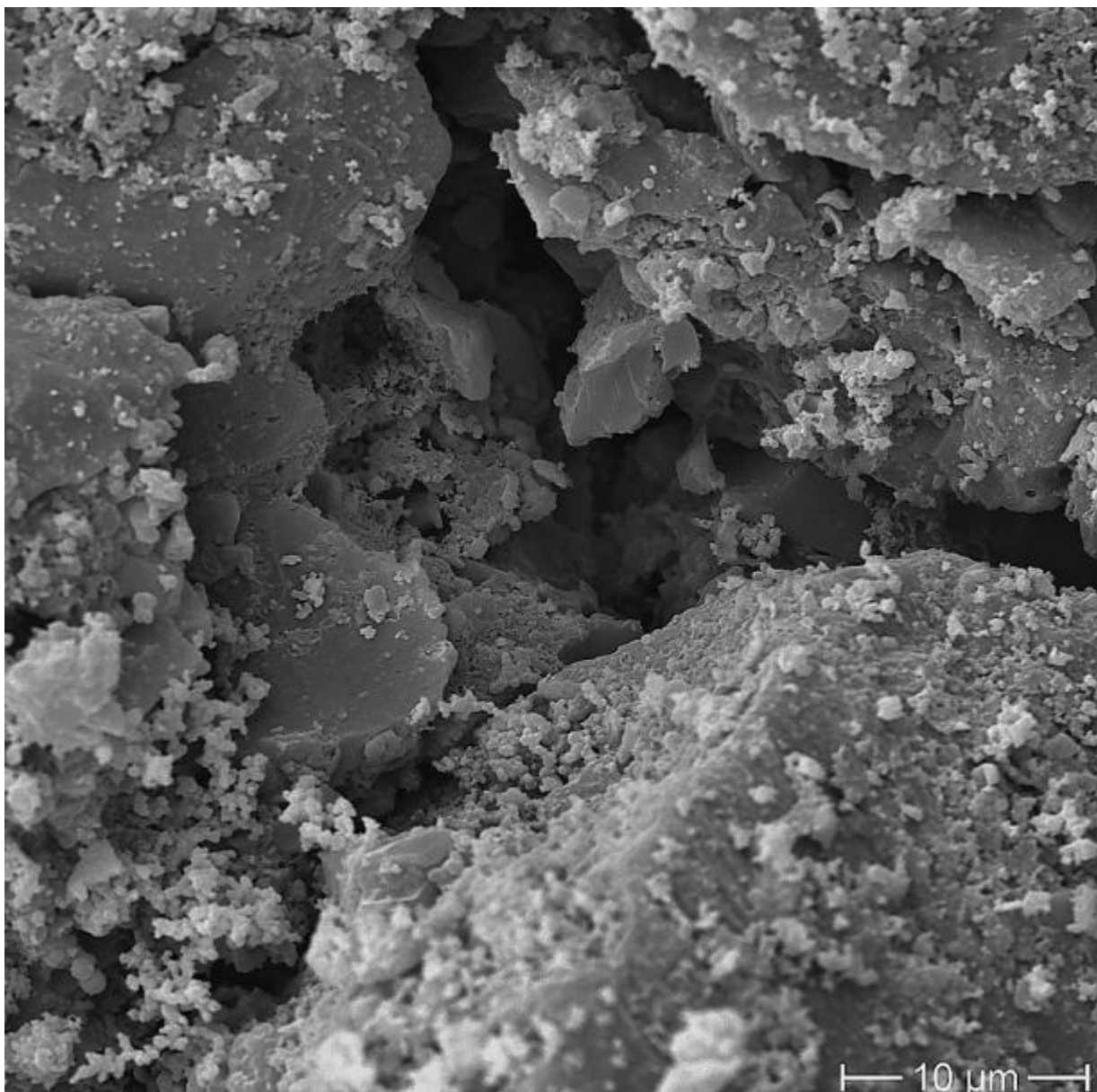


**BIOMASS OR TYRE
TO ACTIVATED CARBON PLANT**

MULTIPLE HEARTH KILN | CHINA



Woven Activated Carbon Cloth



A micrograph of activated charcoal (GAC) under scanning electron microscope.