A study in The Production of Carbon Molecular Sieves and Its Uses.

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Declaration

I declare that no part of the work referred to in this thesis has been submitted in support of an application for another degree or qualification from this or any other University or Institution.

ABSTRACT

Carbon Molecular Sieving (CMS) is a carbonaceous adsorbent, with uniform super-micro pores of 10 angstrom or less pore diameter. The most common application of CMS is to be used as an adsorbent for gas separation technology.

The production of high economical value (CMS) from lignocellulosic agriculture waste such as bagasse and corncobs (for the first time), has been successfully achieved. CMS samples were prepared through heat treatment processes, including carbonization, with the use of traditional furnace; physiochemical activation and **chemical vapor deposition (CVD) (using LPG for the first time).**

Moreover, trials to precipitate carbon from hydrocarbon gas (LPG) on carbonaceous samples from bagasse and corncobs were made to reduce the pore-diameter of carbonaceous materials, in which LPG was pyrolyzed to deposit fine carbon on the pore mouth of the activated carbon to yield CMS.

Experimental studies has shown the effects of different treatment parameters (temperature of activation and the time during carbonization stage) on average pore-diameter, total pore volume and average pore density of products obtained from bagasse and corncobs. The change, which took place in surface characteristics of CMS, is measured by Scanning Electron Microscope (SEM) and a Gas Sorption System using Brunauer-Emmett-Teller (BET) method.

The effect of carbonization temperature and carbonization time, as two important process parameters on microporosity development of CMS, is examined at (350, 750, 850 ^{o}C) and carbonization time of 4 and 12 hours.

The Scanning analysis of the CMS samples explored the successful deposition of LPG on pores of corncobs and bagasse-derived activated carbon and was found to yield a microporous CMS with a narrow pore size distribution.

The final products were microporous Carbon Molecular Sieving of successfully developed surface area with an average pore diameter of corncobs (0.41 μm x 10^{-2}) and bagasse (0.58 μm x 10^{-2}). In addition, the total pore volume for corncobs (6.76 cm^3 g^{-1}) has better capacity than for bagasse (2.76 cm^3 g^{-1}). **The results obtained in this study have proved that a suitable choice of the activation procedure for corncobs and bagasse permits the production of cheap adsorbents with high sorption capacity toward gases.**

The economics of producing CMS from agricultural waste showed that the r**eturn on investment (ROI),** on using bagasse and corncobs for CMS production **is around 63%**. Thus, a high value CMS was obtained from a low value agricultural waste.

SUMMARY

Sugar cane bagasse is a byproduct of sugarcane industries obtained after the extraction of juice for the production of sugar. In Egypt about 600 thousand tons of bagasse produces 4.6% of the total annual agriculture waste in Egypt. In addition to 3450 thousand tons of corncobs which are produced annually. Bagasse and corncobs are usually used as fuel for boilers or supplied as raw material for the manufacturing of pulp and paper while corncobs are used for animal feeding. Approximately one third of the bagasse and corncobs is considered as waste material which is considered to have low economic value.

The major constituents of biomass of bagasse and corncobs are cellulose (a polymer glucosan), hemicellulose (a polysaccharide producing sugars), and lignin (a multi-ring organic compound).

The scope of this work is to prepare Carbon Molecular Sieves (CMS) from bagasse and corncobs as a waste lignocellulosic biomass. The crushed precursor is subjected to pyrolysis at different temperatures in inert gas and next to chemical activation by KOH then a trial is carried out to precipitate carbon from hydrocarbon gas (LPG) on micropores of bagasse and corncobs samples. The study includes; investigating the effect of the preparation parameters time of carbonization (4 and 12 hr) and temperature (350, 750 and 850 °C) on the average pore diameter, pore volume and average pore density of products.

Additionally, using carbon vapor deposition (CVD) technology using LPG; which was not used before for developing micropore porosity and control on, the average pore size, average pore density and total pore volume of samples to improve its adsorption selectivity for the application of gas separation. Moreover, studying the yield from both wastes (bagasse and corncobs) and evaluating the economics from these yields produced form bagasse and corncobs.

All samples are characterized in terms of surface area, micro-pore volume and pore size distribution by N_2 adsorption at 77 K in a gas sorption system. Brunauer-Emmett-Teller (BET) equation was used to measure the apparent surface area. The surface characteristics of the activated carbon was analyzed using Scanning Electron Microscope (SEM).

The experiments started with the insertion of pretreated samples from bagasse and corncobs in a stainless steel heater cylinder. Then, a hot inert gas was passed for a certain time followed by chemicals and physical treatments. Facilities to control the heater pressure, flow rate and temperature are used, in addition to a gas preheater tube to increase the degree of gas flow up to 850 ^{o}C.

The experiment show the following results:

1. A decrease in average pore diameter of bagasse and corncobs at low temperature, but this effect was lower in bagasse than corncobs as a sequence from different percentage of lignin and hemicellulose in bagasse and corncobs.
2. There is an increase in holes' density at higher temperatures (≥ 350 °C) which can be attributed to the rupture of the biomass structure resulting from the release of more volatile species as the heat treatment temperature is increased.
3. The pore diameter and holes' density increased sharply after being chemically treated as a result of the stronger effect of physicochemical treatment (using KOH) on lignin and hemicellulose of corncobs and bagasse.
4. By using carbon vapor deposition (CVD) technology for treatment of samples (corncobs and bagasse) with LPG gas at high temperature (850 °C), the average pore diameter and holes' density decreased due to the precipitation of carbon on sample holes.
5. Increasing the carbonization time, the average pore diameter of corncobs and bagasse decreased.
6. The pore characteristics of the products were evaluated by N_2 adsorption–desorption isotherm 77.00 K of the bagasse and corncobs samples, after the carbon depositions step. The shape of the isotherm was similar to the International Union of Pure and Applied Chemistry (IUPAC) Type I. The total pore volume of the activated samples increased when the activation time was increased from 4 hours to 12 hours.

The final products were microporous Carbon Molecular Sieving of successfully developed surface area with an average pore diameter of corncobs (0.41 μm x 10^{-2}) and bagasse (0.58 μm x 10^{-2}). Additionally, the total pore volume for corncobs (6.76 $cm^3\ g^{-1}$) which shows a better capacity than for bagasse (2.76 $cm^3\ g^{-1}$). Furthermore, the net yield results from bagasse is 11.62 %, and the net yield results from corncobs (11.05%).

The most admirable result is the successful conversion of agricultural waste materials (corncobs and bagasse) into high economic value product. As well as, the average return on investment (ROI) for CMS production is around 63% (±15%) from bagasse and corncobs at a production rate of 365 tons/year.

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NOMENCLATURE

p/p^0 : Relative pressure (p^0 is saturation pressure of the adsorptive at measurement temperature.)

ρ : kPa, Torr Absolute pressure

RH : % Relative humidity

V_a : cm^3(STP) g^{-1} Specific amount adsorbed expressed in the gas volume at the standard state (STP: T=273.15 K, 101.3 kPa) on 1 g of adsorbent

m_a : mg g^{-1} Specific mass adsorbed on 1 g of adsorbent

n_a : mol mol^{-1} Amount adsorbed on 1 mol of adsorbent expressed in mol

n_a : mol g^{-1} Amount adsorbed on 1 g of adsorbent expressed in mol

wt : % Amount adsorbed on 1 g of adsorbed expressed in percentage

α_s : A value obtained by dividing an adsorption amount at arbitrary equilibrium pressure by adsorption amount Va (p/p^0 = 0.4).

V_m : cm^3(STP) g^{-1} Monolayer volume

a_{sBET} : m^2 g^{-1} BET specific surface area

C : Energy constant (the first layer)

σ : nm^2 Cross section area of an adsorptive area

M_g : Molecular weight of adosorptive

L : Avogadro number

ρ_a : g cm^{-3} Dencity of adosorptive

ρ_s : cm^{-3} Dencity of sample

V_p : cm^3 g^{-1} Total pore volume

d_p : nm Mean pore diameter

l : nm Mean particle size

S_{DR} : $m^2\ g^{-1}$ micropore surface area

S_{BET} : $m^2\ g^{-1}$ BET surface area

V_{mic} : $cm^3\ g^{-1}$ microporous fraction

V_t : $cm^3\ g^{-1}$ total pore volume

LIST OF ABBREVIATION

AC:	Activated Carbon
MSC:	Molecular Sieving Carbon
CMS:	Carbon Molecular Sieves
BET:	Brunauer-Emmett-Teller
SEM:	Scanning Electron Microscope
IUPAC:	International Union of Pure and Applied Chemistry
HL:	Hysteresis loops
LPG:	Liquefied Petroleum Gas
CRT:	Cathode Ray Tube
LCD:	Liquid crystal displays
PID:	A proportional–Integral–Derivative controller
EDXA:	Energy-dispersive X-ray spectroscopy or energy dispersive X-ray analysis

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INTRODUCTION

Carbon molecular sieves (CMSs) are porous skeletal structures, which are able to select molecules based on their size and shape. They are a special category of activated carbon with a substantial number of micro-pores. However, a narrow pore-size distribution is not the only distinction between activated carbon and CMS, as the production of micro-porous activated carbon has been numerously reported. The main difference between them may refer to their adsorption kinetics. The essential feature of activated carbon is the molecules separation, based on differences in the adsorption equilibrium constant; meanwhile, CMS separates molecules through differences in the adsorption rate of molecules. Furthermore, carbon molecular sieves have remarkable sieving properties and they have certain advantages over inorganic oxide molecular sieves. For example, carbon molecular sieves' has stability over high temperature ranges (more than 300 ^{O}C), they are also inert toward acid media and they are hydrophobic materials which means that they could be used in high humidity environments.

A typical application of CMS in oil and gas industry is in gas separation technology. For example, in nitrogen production units and Carbon dioxide units that separate molecular gas using Pressure Swing Adsorption (PSA) technology(1-5).

Adsorption is the formation of a gaseous or liquid layer by molecules in a fluid phase on the surface of a solid, by the molecular attraction of the Van Der Waals. Atoms at the surface of solids like active carbons have imbalanced forces compared to those within the solids and in order for foreign molecules in a bid to satisfy this imbalance, they get attracted to the surface. These molecules (adsorbates) form a monolayer on the surface of the solid (adsorbent). Therefore, the adsorption capacity of activated carbon depends on the type of pores and the total surface area available for adsorption. Activated carbons molecular sieves are characterized by their strong adsorption capacity, which can be as high as 0.6–0.8 cm^3/gm, which occurs mostly in cavities of molecular dimensions called micro-pores (1-8).

Adsorption is a dynamic process in which some adsorbate molecules are transferred from the fluid phase onto the solid surface while some are released again to the fluid state. These processes are functions of partial pressures. When the rates of two processes become equal, an Adsorption Equilibrium or Adsorption Isotherm is obtained (1-8).

There are many researches related with the production of CMS which could be produced by a carbonization stage followed by an activation process then an additional process could be added to improve micropore, such as the deposition of carbon molecules(1-8).

A broad classification of carbon molecular sieves which is based on their physical characteristics is as follows:

a. Powdered forms; which form as powders or fine granules and hence present a large internal surface with a small diffusion distance.

b. Granulated activated carbon; which has a relatively larger size of particles compared to powdered activated and consequently, presents a smaller external surface.

c. Spherical activated carbons; this type is shaped as small spherical balls. the spheres have high mechanical strength and excellent SO_2 and NO_2 adsorption capacity.

d. Impregnated carbons; which are porous carbons containing several types of inorganic impregnate such as iodine, silver, caution such as Al, Mn, Zn, Fe, Li, Ca; which have also been prepared for specific application in air pollution control especially in museums and galleries. Impregnated carbons are also used for the adsorption of H_2S and mercaptans.

e. Polymers coated carbon; which are porous carbons coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for homoperfusion (4-10).

Crystalline or amorphous carbons which are are widely used nowadays for the separation and purification of gases as well as several such applications. For example, one of the most typical applications of CMS is nitrogen separation from Oxygen using PSA (Pressure Swing Adsorption) technology, Hydrogen from Methane, Hydrogen from Ammonia, Hydrogen from CO, SO_2 from Off gas and Olefins from Isoprene(6-7). Moreover, the performance of PSA is largely affected by the property of Molecular Sieving Carbon such as pore diameter, surface area, and total pore volume (5, 7).

Carbon Molecular Sieves could be produced from Coal by the following different processes:

1. The gas activation process which is the standard method of making carbon molecular sieves from coal which include heating in nitrogen at 800-900 °C then cooling to 400 °C then Exposure to air, Then are reheated in nitrogen up to 900 °C.

2. Chemical Activation process which includes mixing coal with $ZnCl_2$, H_3PO_4 followed by heating in nitrogen at 900 °C.

3. Gas Activation and Hydrocarbon Cracking that includes; heating and treatment of coal as in process 1 then cracking propylene at 400-500 °C. Finally, reheating to 800-900 °C

4. Melt spinning which includes dissolving coal in solvent, then evaporating solvent followed by Spin melting and finally reheating to 800-900 °C

In addition to that, Carbon Molecular Sieves (CMS) could be produced from polymers by the following different processes:

1. Gas Activation which includes nitrogen treatment at elevated temperatures (300~400 °C) , then Oxidation at lower temperature and finally reheating in nitrogen gas.

2. Chemical Activation which includes increasing polymer temperature to 800 °C then heating to 800 °C in nitrogen gas (5-14).

Furthermore, Carbon Molecular Sieves could be produced from other materials such as coal coke, petroleum coke or their mixtures, however, petroleum cokes are the preferred feedstock because of their low ash content. Moreover, particular carbon molecular sieves are produced by controlled chemical activation. The quality of carbon molecular sieves is independent of the starting material where consistently is reproducible with little variation in adsorptive and physical properties. In contrast, most of the properties of most other activated carbons based on thermal activation strongly depend on the starting material (5-15).

The purpose of the present study is to investigate the possible use of bagasse and corncobs, which were not used before, as carbon molecular sieves materials. The study includes studying and investigation of the parameters such as the time of carbonization and the effect of temperature on the average pore size, pore volume and average pore density of products. Additionally, a trial to precipitate carbon from hydrocarbon gas (LPG) on micropores of bagasse and corncobs samples to develop micropore porosity and control the average pore-size, average pore density and total pore volume of samples to improve its adsorption selectivity for application, such as gas separation.

CHAPTER I

I. THEORETICAL PART

I.1.ACTIVATED CARBON

Activated carbon is an amorphous solid that has an extraordinarily large internal surface area and porous volume. The term *"activated carbon"* defines a group of materials with highly developed internal surface area and porosity and hence large capacities for adsorbing chemicals from gases and liquids. Activated carbons are extremely versatile adsorbents of major industrial significance and they are used in a wide range of applications, concerned principally with the removal of species by adsorption from the liquid or gas phase, in order to affect the purification or the recovery of chemicals (1,2).

The structure of activated carbon is best described as a twisted network of defective carbon layer planes, cross-linked by aliphatic bridging groups. Activated carbon is mostly non graphitic, remaining amorphous; a randomly cross-linked network inhibits reordering of the structure (1,2).

Activated carbon (AC) filtration is the most effective process in removing organic contaminants from water. Organic substances are composed of two basic elements: carbon and hydrogen. Because organic chemicals are often responsible for taste, odor, and color problems, AC filtration can generally be used to improve aesthetically objectionable water. AC filtration also removes chlorine (1-5).

AC filtration is effective with some contaminants and not effective at all with others. AC filtration does not remove microbes, sodium, nitrates, fluoride, and hardness. Only a very specific type of AC filter removes lead and other heavy metals (1-4).

Some researches were carried out for the removal of heavy metal particles by using activated carbon produced from cotton stalks to utilize agricultural waste. The highest adsorption capacity was for lead, followed by copper and then cadmium. Multi-component metal adsorption experiments indicated a competition for the available surface sites. Adsorption capacities in the mixture were reduced from their single-solute values for all metals (1-10).

I.1.1. Raw Materials for Preparation of Activated Carbon.

For the selection of an appropriate raw material to prepare a porous carbon, several factors are taken into consideration. On the industrial level, inexpensive materials with high carbon and low inorganic (i.e. low ash) content are preferred as raw materials for the production of activated carbon. High density of the precursor and sufficient volatile content are of considerable importance. Evolution of volatiles during pyrolysis results in porous char, essential for making activated carbons, while high density contributes to enhanced structural strength of the carbon, which is essential to withstand excessive particle crumble during use, table (1) shows characteristics of various conventional raw materials used for making activated carbon(2-10).

Raw materials used for the preparation of activated carbons vary in their application. Conventional raw materials; in order of their importance as porous carbon production capacity, characteristics and market; are: wood, coal, lignite, coconut shell, peat and others (2-10).

Commercially activated carbon is produced from bituminous or lignite coal. The long-term availability of coal, environmental impacts and potentially increasing cost have encouraged researchers to find other alternatives, which may be cost effective and equally with high potential. Activated carbon can be manufactured from any material that has reasonable elemental carbon content. Any lignocellulosic material can be converted to an activated carbon (5,6).

Table 1. Characteristics of various conventional raw materials used for making activated carbon$^{(5)}$.

Raw materials	**Carbon (%)**	**Volatile (%)**	**Density (Kg/m^3)**	**Ash (%)**	**Texture of activated carbon**	**Application carbon n of activated**
Softwood	40–45	55–6	0·4–0·5	0·3–1·1	Soft, large pore volume	Aq. phase adsorption
Hardwood	40–42	55–60	0·55–0·8	0·3–1·2	Soft, large pore volume	Aq. phase adsorption
Lignin	35–40	58–60	0·3–0·4	–	Soft, large pore volume	Aq. phase adsorption
Nut shells	40–45	55–60	1·4	0·5–·6	Hard, large multi pore volume	Vapour phase adsorption
Lignite	55–70	25–40	1·0–1·35	5–6	Hard small pore volume	Waste water treatment
Soft coal	65–80	25–30	1·25–1·50	2·12	Medium hard, medium micropore volume	Liquid & vapour phase adsorption
Petroleum coke	70–85	15–20	1·35	0·5–0·7	Medium hard, medium micropore volume	Gas–vapour adsorption
Semi hard coal	70–75	1–15	1·45	5–15	Hard large pore volume	Gas–vapour adsorption
Hard coal	85–95	5–10	1·5–2·0	2·15	Hard large pore volume	Gas–vapour adsorption

I.2. CARBON MOLECULAR SIEVES

Molecular Sieving Carbon (MSC) or Carbon Molecular Sieves (CMS) is defined generally as a carbonaceous adsorbent with uniform super-micro pores smaller than 10 angstrom in pore diameter (1-15).

Carbon molecular sieves (CMS) are a special type of activated carbons. Although, pore size distribution of these materials is not always strictly discrete and molecules are not hard spheres; they can sometimes squeeze into narrow pores. The difference between activated or porous carbons and carbon molecular sieves is not clearly know. Carbon molecular sieves have most of the pores in the molecular size range but some conventional activated carbons also have very small pores (5-7).

The main difference is that activated carbons separate molecules through differences in their adsorption equilibrium constants. In contrast, an essential feature of carbon molecular sieves is that they provide molecular separations based on rate of adsorption rather than on the differences in adsorption capacity (7).

Carbon molecular sieves are non-crystalline or amorphous and quite differ from inorganic oxide molecular sieves which have a well-ordered crystalline structure. A hypothetical structure of a carbon molecular sieve crystallite is shown in Figure 1b. Disordered graphitic platelets of carbon are separated by interstitial spaces. The size of the gaps are determined by several factors, such as the presence of foreign atoms between the layers, hanging side groups, and cross-linking chains of carbon atoms. Also influencing the pore structure is the presence of capping groups on the edges of the layers. Additionally, shown in Figure 1a is a well-ordered structure of graphite for comparison purposes. The surface area, dimensions, and distribution of the pores depend on the precursor and on the conditions of the carbonization and activation (2-9).

Despite the amorphous nature of carbon molecular sieves, they show remarkable sieving properties and as such, they have certain advantages over inorganic oxide molecular sieves. These properties are as follows:

- Stability at high temperature.
- Stable in acid media.
- Carbon molecular sieves materials are hydrophobic and can be used to ensure accurate sampling in high humidity environments.

Note: Inorganic oxide molecular sieves (Zeolite molecular sieves) have extremely high-adsorption attraction for water. This affinity is so strong that water will normally displace any other material that is already adsorbed (properties of co-adsorption and affinity for water), to further enhance this selectivity toward water, the temperature of the adsorbent bed is raised.

- The pore sizes can be controlled by the method of preparation (1, 5-9).

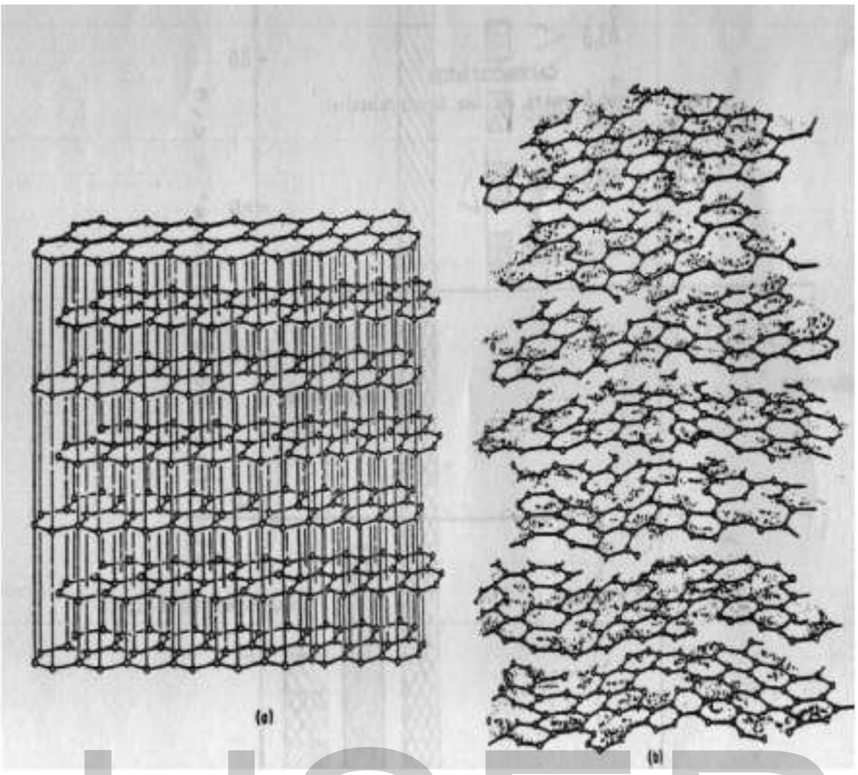


Figure1: hypothetical structure of a carbon molecular sieve crystallite (2).

I.2.1 Structure of Porous Carbons.

The pores in activated carbons are dispersed over a wide range of size and shape. The pores are classified by their sizes usually into three groups: (i) macropores; having average diameter more than 50 nm, (ii) mesopores; with diameter 2–50 nm, and (iii) micropores; having average diameter less than 2 nm. Micropores are further divided into supermicropores (0.7–2.0 nm) and ultramicropores of diameter less than 0.7 nm. The pore structure in wood derived carbons is a memory of the texture of the precursor wood and hence differs based on the type of wood/plant (see figure 2). They basically consist of slit-like voids and macropores (6, 9, 10).

In some woods like pine, these are of similar shape and size and are equally distributed, whereas in bagasse, Babool, castor (see figure 2), pores are of very different shapes and sizes and are organized in circular fashion. These macropores are in turn connected to mesopores and micropores. This is shown in figure 3. Figure 3 also includes the structure of activated carbon fibers, which in contrast to wood-based activated carbon, predominantly consists of micropores directly exposed to the surface of the fibers. Different techniques have been used to determine pore size distribution in porous carbons. These are mercury porosimetry and gas adsorption isotherms and recently, the scanning tunneling microscopy (10-16).

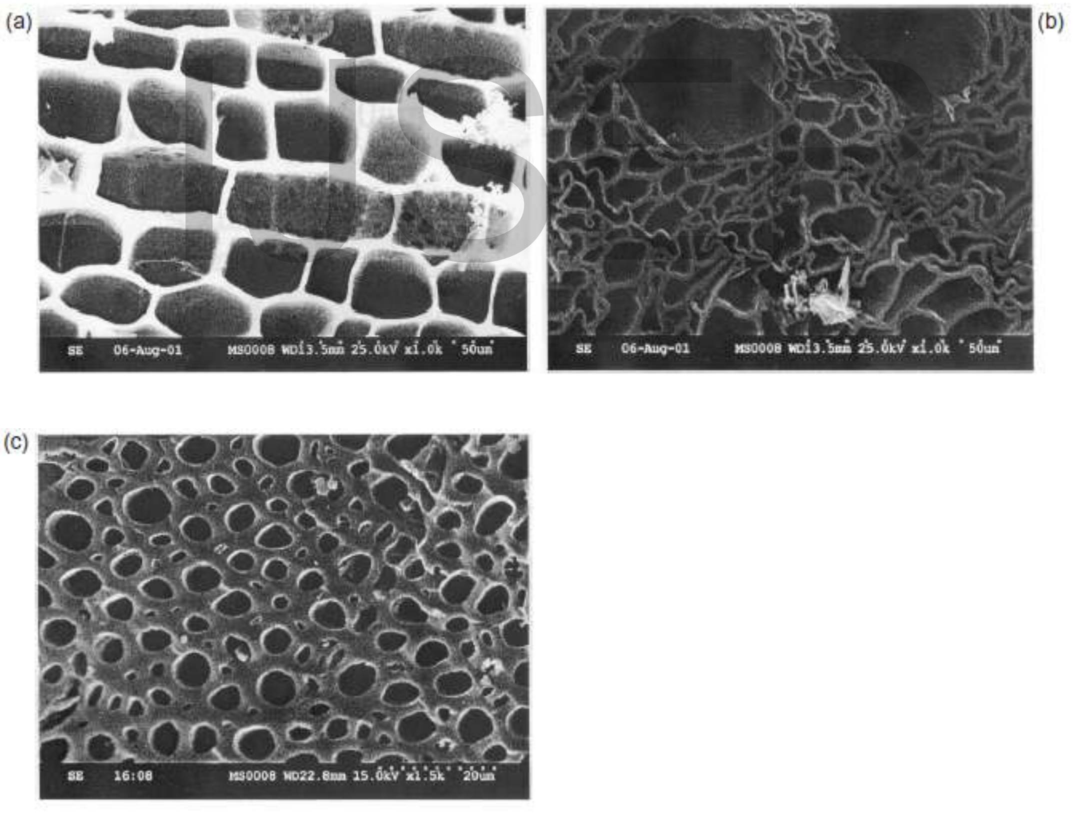


Figure 2. SEM micrographs of porous carbons: (a) castor wood, (b) bagasse, and (c) bamboo wood (10).

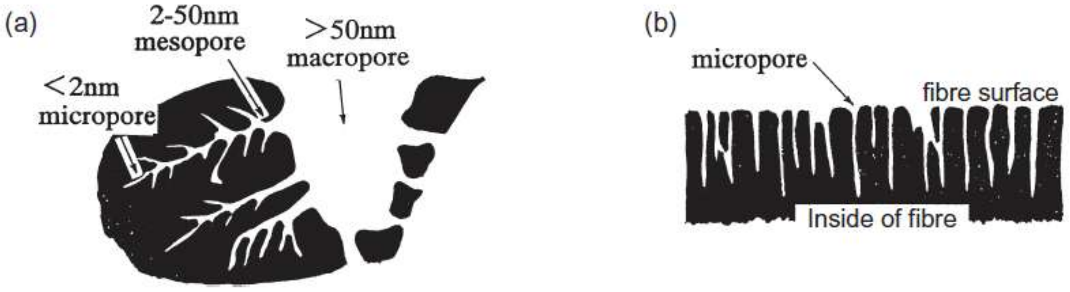


Figure 3. Pore structure of activated carbon: **(a)** granular and **(b)** fibrous (16).

I.3. THE ADSORPTION PHENOMENON

I.3.1. Pore size and Adsorption Potential

The shape of sorption isotherms of pure fluids on planar surfaces and porous materials depends on the interplay between the strength of fluid–wall and fluid–fluid interactions as well as the effects of confined pore space on the state and thermodynamic stability of fluids confined to narrow pores. The International Union of Pure and Applied Chemistry proposed to classify pores by their internal pore width (the pore width defined as the diameter in case of a cylindrical pore and as the distance between opposite walls in case of a slit pore). For example: Micropore; pore of internal width less than 2 nm; Mesopore: pore of internal width between 2 and 50 nm; Macropore; pore of internal width greater than 50 nm. The sorption behavior in macropores is distinct from that of Mesopores and Micropores. Whereas, Macropores are so wide that they are considered as nearly flat surfaces figure 4(a) the sorption behavior in micropores is dominated almost entirely by the interactions between fluid molecules and the pore walls. In fact the adsorption potentials of the opposite pore walls are overlapping. Hence, the adsorption in micropore filling is distinct from the adsorption phenomena occurring in mesopores. As illustrated in figure 4(b), the pores. Hence, the adsorption behavior in mesopores does not depend only on the fluid –wall attraction, but also on the attractive interactions between fluid molecules, which may lead to the occurrence of pore condensation. Pore condensation represents a phenomenon whereby gas condenses to a liquid – like phase in pores at a pressure less than the saturation pressure p^0 of the bulk fluid. It represent an example of a shifted bulk transition under the influence of the attractive fluid–wall interaction(10-16).

I.3.2. Classification of Adsorption Isotherms

Adsorption is the formation of a gaseous or liquid layer by molecules in a fluid phase on the surface of a solid, by the molecular attraction of the Van Der Waals. Atoms at the surface of solids like active carbons have imbalanced forces as compared to those within the solids and, consequently, foreign molecules in a bid to satisfy this imbalance get attracted to the surface (1,4, 13, 18).

These adsorbates form a monolayer on the surface of the solid adsorbent. Figure 5 illustrates the adsorption process showing transfer of adsorbate molecules through the bulk gas phase to the surface of the solid and diffusion onto the internal surfaces of the pores in the solid adsorbent. Therefore, the adsorption capacity of activated carbon depends on the type of pores and the total surface area available for adsorption. Activated carbons are characterized by their strong adsorption capacity, which can be as high as 0.6–0.8 cm^3/gm, which occurs mostly in cavities of molecular dimensions called micro-pores. Adsorption is a dynamic process in which some adsorbate molecules are transferred from the fluid phase on to the solid surface while some are released again to the fluid state. These processes are functions of partial pressures. When the rates of two processes become equal, an adsorption equilibrium or so-called adsorption isotherm is obtained. This expresses the amount of adsorbate adsorbed as a function of gas phase concentration measured by equilibrium partial pressure p/p^o at constant temperature (5, 13, 16, 17).

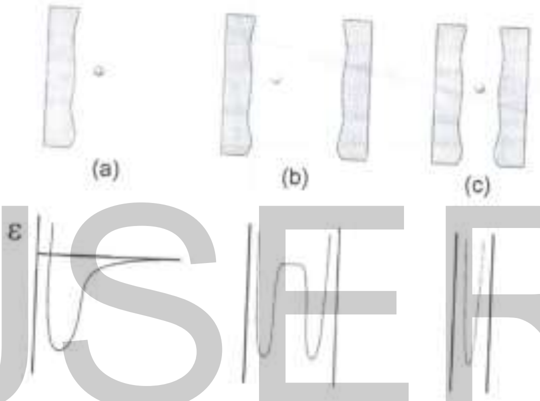


Figure 4: Schematic illustration of adsorption potential, on (a) planar, nonporous surface; (b) mesopores; (c) micropore(15,16).

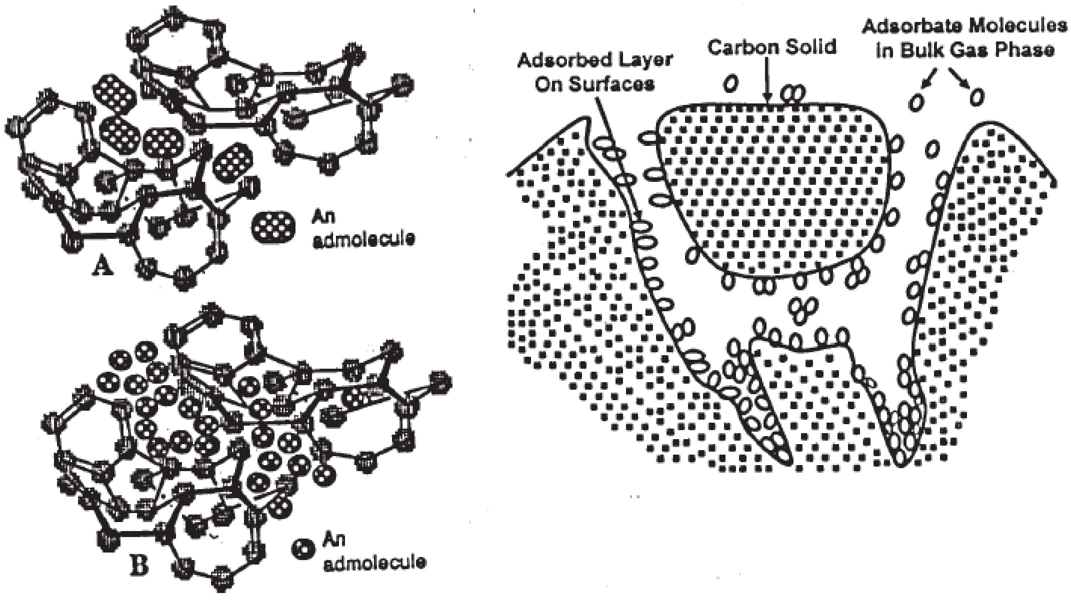


Figure 5: Adsorption processes in activated carbons: Transfer of adsorbate molecules to adsorbent (5).

Adsorption isotherms are used to estimate surface area, pore volume in various porosity regimes, assessments of the surface chemistry of the adsorbent and fundamental information on the efficiency of industrial carbon employed in separation/purification techniques. Six general types of isotherms have been observed and the shapes of these characteristic isotherms are shown in figure 6 (10-19);

Type I isotherms are typical of microporus solids where only monolayer adsorption occurs. In these, micropore filling occurs significantly at relatively low partial pressure <0.1 p/p_o, the adsorption process being complete at 0.5 p/p_o. Example includes the adsorption of $N_2(g)$ on microporous carbon at 77K and ammonia on charcoal at 273K(10-19).

Type II isotherms describe physical adsorption of gases by nonporous solids. Monolayer coverage is followed by multilayer adsorption at higher p/p_o values (10-19).

Type III isotherms are obtained from carbons with mixed micro-and mesoprosity wherein the amount of material adsorbed increases without limit and its natural adsorption approaches unity. Type IV and type V isotherms are convex towards the relative pressure axis. These isotherms are characteristic of weak gas-solid interaction. Type IV isotherms describe a multilayer adsorption process, where complete filling of the smallest capillaries has occurred (10-19).

Type IV isotherms originate from both non-porous and mesoporous solids and type V isotherms originate from microporous or mesoporous solids. An example is the adsorption of water vapor on graphitized carbon black. The type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorptions on a uniform nonporous surface. The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers [(10-1)].

Amongst the examples of type VI isotherms are those obtained with argon or krypton on graphitized carbon black at liquid nitrogen temperature. Information concerning effective surface areas, pore size distribution, micropore volume etc., is incorporated within the isotherms. However, knowledge of adsorption mechanism in different sizes of porosity is necessary to explain the isotherms shape[(15-20)].

Adsorption process in micro porosity is quite difficult to describe accurately. The adsorption process occurring within mesopores is more easily understood. Macro porosity behaves in the same way as an open surface to adsorption, and accounts for <1% of the adsorption process within microporus carbons [(10-19)].

I.3.3.Adsorption Hysteresis

Classification of Hysteresis loops (HL): It is widely accepted that there is a correlation between the shape of the hysteresis loop and the texture (such as, pore size, distribution, pore geometry, connectivity) of a mesoporous adsorbent. An empirical classification of hysteresis loops was given by the International Union of Pure and Applied Chemistry (IUPAC); classification is shown in Figure 7[(20)].

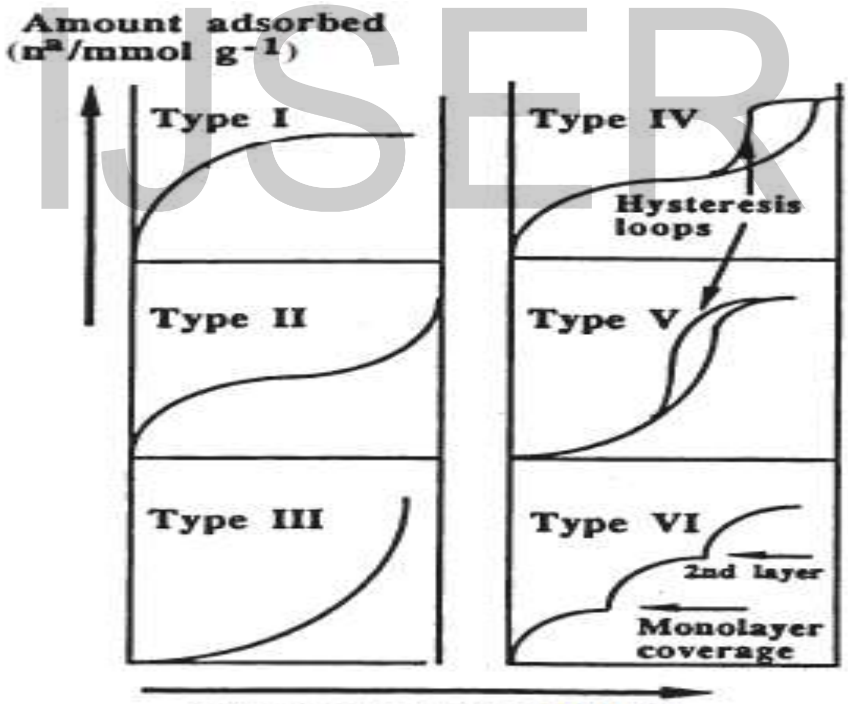


Figure 6: IUPAC Classification of adsorption isotherms [(17-18)].

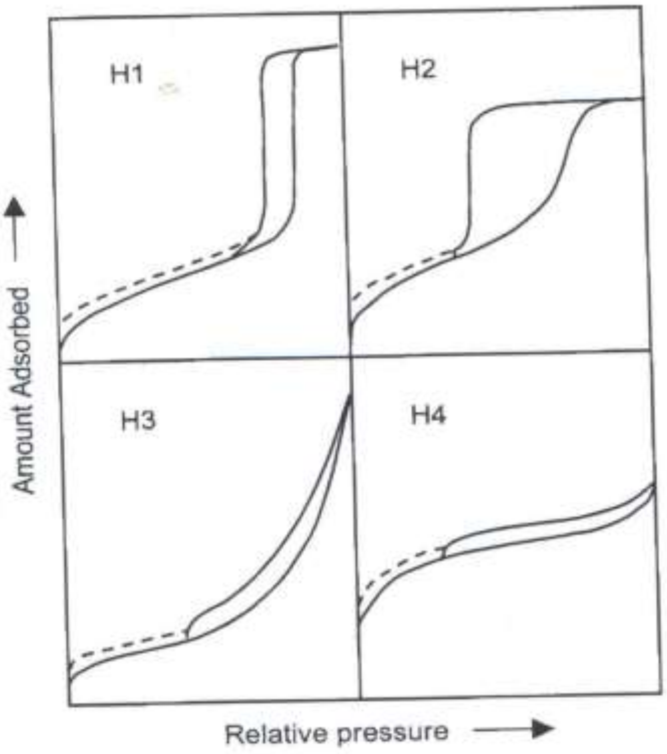


Figure 7: IUPAC Classification of Hysteresis loops (20)

According to the IUPAC classification type H1 is usually associated with porous materials consisting of well-defined cylindrical-like pore channels or agglomerates of compacts of approximately uniform spheres. That materials that give rise to H2 Hysteresis are often disordered and the distribution of pore size and shape is not well defined. Isotherms revealing type H3 hysteresis do not exhibit any limiting adsorption at high P/P0, which is observed with non-rigid aggregates of plate-like particles giving rise to slit-shaped pores. The desorption branch for type H3 hysteresis also contains a steep region associated with a {forced} closure of the hysteresis loop ,due to the so –called tensile strength effect. This phenomenon occurs for nitrogen at 77K in the relative pressure range from 0.4 -0.45. Similarly, type H4 loops are also often associated with narrow slit pores, but now includes pores in the micropore region. The dashed curves in the hysteresis loops shown in Figure 8 reflect low–pressure hysteresis, which may be observable down to very low relative pressure. Low–pressure hysteresis may be associated with the change in volume of the adsorbent, such as the swelling of non–rigid pores or with the irreversible uptake of molecules in pores of about the same width as that of the adsorptive molecule. Additionally, chemisorption also leads to such "open" hystereis loops. An interpretation of sorption isotherms showing low-pressure hysteresis is difficult and an accurate pore size analysis of the porous materials and the decision whether the adsorption or desorption branch should be taken for calculation of the pore size distribution curve depends very much on the reasons which caused the hysteresis (15,20-22).

I.4. PREPARATION OF CMS

Carbone Molecular Sieves are carbon produced from carbonaceous source materials. It could be produced by the following processes:

I.4.1.Carbonization

During carbonization, most of the non-carbon elements, hydrogen and oxygen for example, are first removed in gaseous form by pyrolytic decomposition of the starting materials, and the free atoms of elementary carbon are grouped into organized crystallographic formations known as Elementary Graphite Crystallites. The mutual arrangement of the crystallite is irregular, so that free interstices exist between them. Thus, carbonisation involves thermal decomposition of carbonaceous material, eliminating non-carbon species producing a fixed carbon mass and rudimentary pore structure. The process is usually, carried out at temperature below 800^{o}C in a continuous stream of an inert atmosphere. The important parameters that determine the quality and the yield of the carbonized product are: (i) rate of heating, (ii) final temperature and (iii) soaking time. The carbonization process involves various important stages that markedly determine the properties of the final product to be obtained. The basic microstructure of the char with micro-porosity is formed around 500^{o}C (17,20-25).

Some of these pores are blocked by the tarry products evolving during pyrolysis and could be available only when further heat treatment reaches about 800^{o}C. Further heat treatment to temperature of 1000^{o}C and above, normally lead to the hardening of the carbon structure due to partial alignment of graphitic planes and the decrease in porosity which de-accelerates activation (26).

I.4.2.Activation

Carbons are described as graphitic or non-graphitic depending upon the degree of crystallographic ordering. Graphitic carbons possess three-dimensional symmetry while non-graphitic carbons do not. As discussed above, during carbonization the free interstices present in the carbon become filled, or at least partially blocked by disorganized “amorphous” carbon, apparently because of deposition of tarry substances.

The resulting carbonized product has only a very small adsorption capacity. Presumably, at least for carbonization at lower temperature, a part of the tar remains in the pores between the crystallites and on their surfaces. Such carbonized materials can be then, at least partially, activated by removing tarry products by heating in steam or under inert gas or by extraction with a suitable solvent or by chemical reaction. Thus, activation is carried out to enlarge the diameters of the pores which are created during the carbonization process and to create some new porosity thus resulting in the formation of a well-developed and readily accessible pore structure with very large internal surface area. Activation is carried out by two ways as in the following sections (20-29).

I.4.2.1. Chemical activation.

Chemical activation is carried out with wood as the starting material. In the beginning, wood is infused by a concentrated solution of activating agents. It results in degradation of cellulosic material. Chemical-impregnated material is then pyrolysed between 400°C and 600^{o}C in the absence of air. Pyrolysed product is cooled and washed to remove activating agent, which is later recycled. On calcination, impregnated and chemically dehydrated raw material results in charring and aromatization, and creation of porous structure. Various types of activating agents are used. Some of them are: phosphoric acid, zinc chloride, H_2SO_4; K_2S, alkali metal hydroxide, and carbonate and chlorides of CaC_2; MgC_2 and FeC_3. All activating agents are dehydrating agents, which influence the pyrolytic decomposition and inhibit the formation of tar. They also decrease the formation of acetic acid, methanol etc. and enhance the yield of carbon (29-32).

I.4.2.2. Physical activation.

It is a process, by which the carbonized product develops porous structure of molecular dimensions and extended surface area on heat treatment in the temperature range of 800°C –1000^{o}C, in presence of suitable oxidizing gases such as steam, CO_2, air. Gasification of the carbonized material with steam and carbon dioxide occurs by the following endothermic reactions: Activation is carried out by two ways as follows:

$$\begin{aligned} C + H_2O &\rightarrow CO + H_2 \ (29\ \text{kcal}), \\ C + CO_2 &\rightarrow 2CO \ (39\ \text{kcal}), \\ CO + H_2O &\rightarrow CO_2 + H_2 \ (10\ \text{kcal}). \end{aligned}$$

The H_2O molecule is smaller than the CO_2 molecule and diffuses faster into the pores of the carbon. Consequently, reaction with steam is faster than that with CO_2. Activation with CO_2 promotes external oxidation and development of larger pores as compared to activation with steam. The relative amounts of external and internal oxidation depends on how well developed the pores are in the carbonized material. Activation of chars without the development of significant pore structure only results in the decrease in carbon granule size. Activation is associated with carbon loss and hence with the decrease in weight of the host carbon. Weight loss increases linearly with activation temperature and time. Activation at lower temperature predominates in the development of mesopores and macropores. Efficient formation of pores, which have no adsorption ability, i.e. macropores, increases at higher activation temperature, while mean pore diameter decreases with increasing activation temperature (28-35).

In case of activation with oxygen, both the reactions are as follows:

$$C + O_2 \rightarrow CO_2 + 92{\cdot}4\ \text{kcal},$$

and

$$2C + O2 \rightarrow 2CO + 53{\cdot}96\ \text{kcal},$$

Since both reactions are exothermic, there is excessive burning and the reaction is difficult to control. Moreover, since there is always some local overheating, the product obtained is not uniform. As the reaction is very aggressive, burning is not restricted and occurs on the surface of the grains, causing excessive weight loss (28-35).

I.4.2.3. Mechanism of Activation

The structure of the pores and pore size distribution are largely dictated by the nature of the raw materials and the history of their carbonization. Carbon atoms differ from each other in their reactivity depending on their spatial arrangement. Activation eliminates the disorganized carbon, exposing the aromatic sheets to the action of activation agents and leads to the development of a microporous structure. Since activation is associated with weight loss of the host carbon, the extent of burn-off of the carbon material is considered as a measure of the degree of activation. At a particular temperature, weight loss increases linearly with activation time. Normally, in the first phase, the reorganized carbon is burnt preferentially when the burn-off is about 10%. This results in the opening of blocked pores. Subsequently, the carbon of the aromatic ring system starts burning, producing active sites and wider pores. In the latter phase, excessive activation reaction results in knocking down of the walls by the activated agents and a weight loss of more than 70%. This results in an increase in transitional pores and macropores. The volume of the micropores decreases and there is no significant increase in adsorption capacity or internal surface area (5,10,35-38).

At higher burn-off, the difference in porosity, created by different activating agents, becomes more pronounced. In a typical example, activation of a hard wood with water vapor results in progressive development and widening of all size pores until, at a burn-off of 70%, the activated product contains a well-developed porous system with wide pore size distribution. Activation with 50–70% burn-off causes an increase in the total adsorption volume from 0.6 to 0.83 cm^3/gm. Additionally, as it is associated mainly with the widening of pores, the surface area remains almost the same. Activation with carbon dioxide mainly develops microporosity over the entire range of burn-off. The micropores account for about 73% of the total adsorption pore volume and for over 90% of total surface area. Micropores contribute only 33% towards the total pore volume and 63% towards the surface area in the case of steam-activated carbon. Thus, carbon produced by CO_2 activation has lower total pore volume, 0.49 cm^3/gm, than those of corresponding samples obtained by the activation of steam. However, the effective surface area in both cases is almost the same. This is mainly due to the contribution of micropores to the surface area. Moreover, the carbon atoms, which are localized at the edges and the periphery of the aromatic sheets or those located at defect position and dislocations or discontinuities, are associated with unpaired electron or have residual valencies; these are rich in potential energy (5,35-39).

Consequently, these carbon atoms are more reactive and have a tendency to form surface oxygen complexes during oxidative activation. These surface chemical groups promote adsorption and are beneficial in certain applications. Alternatively, these surface oxygen complexes break down and peel off the oxidized carbon from the surfaces as gaseous oxides leaving behind new unsaturated carbon atoms for further reaction with an activating agent. Thus, activation mechanism can be visualized as an interaction between the activating agent and the carbon atoms, which form the structure of intermediate carbonized product resulting in useful large internal surface area with interconnected pores of desired dimension and surface chemical groups (35-40).

I.4.3. Coke Deposition by Organic Polymer Cracking

In order to reduce the pore size of initial CMS (carbonaceous substrate), a solution of organic polymer was used as the cracking agent for coke deposition. The aim of coke deposition is to reduce the pore opening to the required molecular range. The sieve character of the initial CMS was improved by impregnation with a 4% solution of polystyrene in benzene. The amount of polymeric impregnator used to block the substrate macropores will vary with the desired gas selectivity. The optional dosage may be determined by varying the dosage and identifying the impregnated sieve with the optional sieving properties (40-44).

I.4.4. Different Methods to Produce CMS:

I.4.4.1. Methods to produce Carbon Molecular Sieves from Coal.

Table (2) shows the different processes to manufacture CMS from coal and the procedure for these processes (45-48).

Table 2 Processes for production of CMS from coal (45).

Process	Procedure
1. The gas activation process is the standard method of making carbon molecular sieves from coal and from other materials also. (Fluidized)	Heat in nitrogen 800-900 °C Cool to 400 °C Expose to Air Reheat in nitrogen to 900 °C
2. Chemical Activation.	Mix with $ZnCl_2$/ H_3PO_4 Heat in nitrogen 900 °C
3. Gas Activation plus Hydrocarbon Cracking.	Heat and treat as in process 1 Crack propylene 400-500 °C Reheat 800-900 °C
4. Melt Spinning.	Dissolve coal in solvent Evaporate solvent Spin melt Heat and treat fiber

I.4.4.2. Methods to Produce Carbon Molecular Sieves from Polymers:

Table (3) shows the different processes to manufacture CMS from polymers and the procedure for these processes (45-49).

Table 3 Processes for production of CMS from polymers (45).

Process	Procedure
Gas Activation	Nitrogen treat at elevated temperatures Oxidation at lower temperature Reheat in nitrogen.
Chemical Activation	Char at 800 °C Granulate +15% sulfite waste Heat to 800 °C in nitrogen

I.5. COMMERCIAL FORMS OF CARBON ADSORPTIVE MATERIALS

Activated carbons are complex products, which are difficult to classify on the basis of their behavior, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics (48-55).

a. Powdered activated carbon

Traditionally, active carbons are made in particular form as powders or fine granules less than 100mm in size with an average diameter between 15 and 25µm. Thus, they present a large internal surface with a small diffusion distance (48, 49).

b. Granulated activated carbon.

Granulated activated carbon has a relatively larger size of particles compared to powdered activated and consequently, present a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapors as their rates of diffusion are faster. Granulated carbons are used for water treatment, deodorization and separation of components of flow system (48-54).

c. Spherical activated carbon

These are made of small spherical balls, wherein pitch is melted in the presence of naphthalene or tutoring and converted into spheres. These spheres are contacted with solution naphtha, which extracts naphthalene and creates a porous structure. These porous spheres are then heated at temperatures between 100°C and 400^{o}C in the presence of an oxidizing gas, containing about 30% of oxygen by weight. The oxidised spheres are then heated between 150°C and 700^{o}C in the presence of ammonia to introduce nitrogen into the spheres which are then activated in steam or CO_2. The spheres have high mechanical strength and excellent SO_2 and NO_2 adsorption capacity (48-55).

d. Impregnated carbon

Porous carbons containing several types of inorganic impregnate such as iodine, silver, caution such as Al, Mn, Zn, Fe, Li, Ca; have also been prepared for specific application in air pollution control especially in museums and galleries. Silver loaded activated carbon is used as an adsorbent for purifications of domestic water. Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and flocculating agent $Al(OH)_3$. Impregnated carbons are also used for the adsorption of H_2S and mercaptans (1, 5).

e. Polymers 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 homoperfusion (53-54).

I.7. APPLICATIONS OF CARBON MOLECULAR SIEVES (CMS)

The primary use of carbon molecular sieves is for the separation and purification of gases are show in Table (4) (45).

Table 4: Applications uses of CMS (45).

Separation	Possible Application	Type of Molecular Sieve
Nitrogen from Oxygen	Nitrogen production	CMS
Hydrogen from Methane	Off gas coke ovens	CMS
Hydrogen from Ammonia	Ammonia Plants	CMS
Hydrogen from CO	Ethylene production	Russian Carbon
Hydrogen from Product Gas	Refineries	RSM (Calgon)
Methane from carbon dioxide	Gases/Oil Wells/CO_2	RSM (Calgon)
Alcohol from water	Gasohol	Calgon
Methane from ethane ethane from propane propane from butane	Academic Studies(Japan)	MSC-5A
Butane from neopentane		(PVS + pitch) char
Olefins from Isoprene	Synthetic rubber	UOP Carbon
C_4 olefins from Isoprene	Synthetic rubber	UOP Carbon
Butane isomers	PET Chemical	(PVA-Phenol)
Polynuclear aromatics from hydrocrackate	Refinery	UOP Carbon
Pentane from carbon disulfide	Foamed Plastics	CMS
Hydrogen from stack gas	Power Station	Calgon CMS & $FeCL_2$
SO_2 from Off gas	Sulfuric Acid	CMS (B-F)

One of the most typical applications is nitrogen PSA (Pressure Swing Adsorption). Nitrogen PSA is classified into the PSA system using velocity separation, which makes use of the difference of adsorption velocity between nitrogen and oxygen. The performance of PSA is largely affected by the property of Molecular Sieving Carbon (5,55-58).

Because the difference of molecular sizes is very small between oxygen compound (0.28nm×0.40nm) and nitrogen compound (0.30nm×0.41nm), the effective difference for the velocity separation can be obtained only when you use Molecular Sieving Carbon, whose uniform supermicro pores are highly controlled as shown in figure 8. The best Molecular Sieving Carbon is controlled, to have slightly larger pores than nitrogen compound. This well control results in that the nitrogen compound is harder to adsorb and the oxygen compound is easier to adsorb (5,55-58).

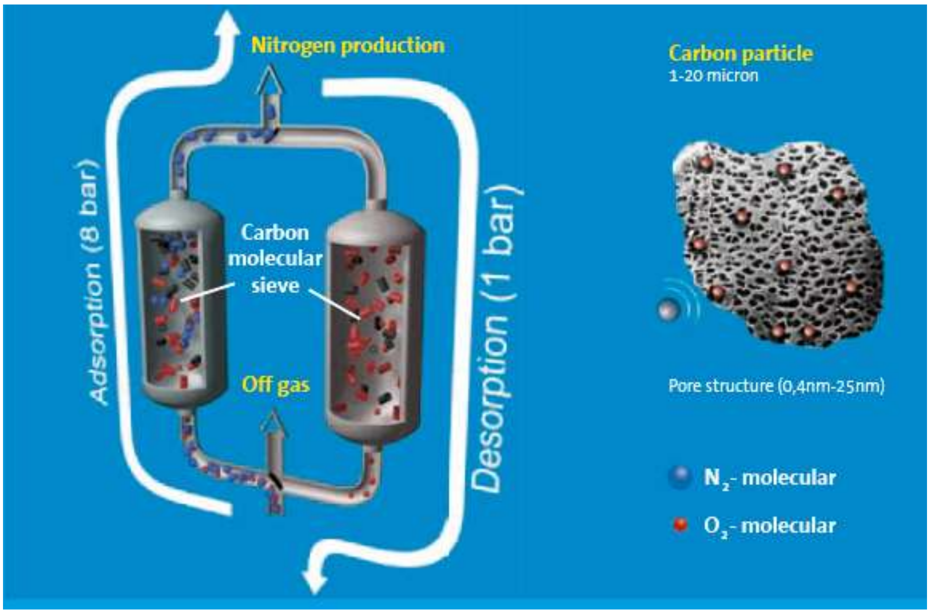


Figure 8: The Typical Application of CMS to Generate N_2(58).

I.8.BAGASSE AND CORNCOBS

Sugar cane bagasse is a byproduct of sugarcane industries obtained after the extraction of juice for the production of sugar. About 54 million dry tons of bagasse are produced annually all over the world. In Egypt about 600 thousand tons of bagasse (which contributes in about 4.6% of the total annual agricultural waste in Egypt) as well as 3450 thousand tons of corncobs are produced annually. Bagasse is presently used as fuel for boilers or supplied as raw material for the manufacturing of pulp and paper whereas corncobs are used for animal feeding (59-61).

I.8.1.Uses of Bagasse and Corncobs as Raw Materials for Production of CMS

Sugarcane bagasse and corncobs in their natural state are a poor adsorbent of organic compounds such as sugar colorants and metal ion. Bagasse and corncobs should be modified physically and chemically to enhance their adsorptive properties towards organic molecules or metal ions, routinely found in water and wastewater. This is effectively accomplished by converting bagasse and corncobs to CMS. Bagasse and corncobs are considered as a suitable economic resource for preparation of CMS (61-65).

I.8.2. Bagasse and Corncobs Composition

The major constituents of biomass of bagasse and corncobs are cellulose (a polymer glucosan), hemicellulose (a polysaccharide producing sugars), and lignin (a multi-ring organic compound). There is some variation in the relative abundance of these constituents in different species of biomass (60-66).

In addition to this, Bagasse and Corncobs are a kind of hard lignocellulosic biomass with lignin content of around (18 - 24 % in bagasse and 11 -14 % in corncobs). Lignin is a natural aromatic polymer found in the cell wall of woody biomass whose function is to cement the cellulosic structure of plants. Conventional physical or chemical activation process may not effectively convert it to highly porous activated carbon. Thus, in this study a combination of chemical and physical activation processes are implemented to obtain activated carbon with large micropore surface area and high micropore volume before deposition step (61-65).

I.8.3. The Process Of Pyrolysis Of Organic Materials

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. It involves the simultaneous change of chemical composition and physical phase, and it is irreversible.

I.8.3.1.The physical process:

The basic phenomenon that takes place during pyrolysis is the heat transfer from a heat source leading to the release of volatiles and the formation of char (61-66).

I.8.3.2.The chemical process:

The chemistry of pyrolysis is strongly influenced by the chemical composition of the biomass (62-66).

The reaction products of pyrolysis are a combination of the products expected from the separate pyrolysis of each of the three major constituents as follows:

1. Cellulose

At temperatures less than 300°C, the dominant process is the reduction in degree of polymerisation. In the second stage, at temperatures above 300°C, there is formation of char, tar and gaseous products. The major component of tar is laevoglucosan that vaporizes and then decomposes with increasing temperature (62-67).

2. Hemicellulose

It is of much lower molecular weight than cellulose. Hemicellulose is thermally the most sensitive element and decomposes in the temperature range 200°C to 260°C. This decomposition may occur in two steps;

- Decomposition of the polymer into soluble fragments and/or conversion into monomer units that further decompose into volatile products.
- As compared to cellulose, hemicellulose gives rise to more volatiles, less tar and char. The components of tar are organic acids such as acetic acid, formic acid. Figure 10 shows pathways of pyrolysis reactions (62-67).

3. Lignin

Lignin decomposes when heated between 280°C and 500°C. Char is the most abundant constituent in the products of lignin pyrolysis with a yield of 55% (62-67).

A typical chemical analysis of bagasse (50-65)

- Cellulose 45–55%
- Hemicellulose 20–25%
- Lignin 18–24%
- Ash 1–4%
- Waxes <1%

Control of products by heating rate;

- Slow pyrolysis, with heating rates of order of 10°C /min. observation suggests that it yields char.
- Rapid/fast/flash pyrolysis, with heating rates approaching 1000°C /min. observation suggests that the yield of volatiles increases remarkably (62-67).

Heat of reaction;

- The pyrolysing region can be divided into three zones:
- An endothermic primary decomposition zone at T < 250°C.
- An exothermic zone at 250°C < T < 340°C;
- An endothermic surface char zone at 340°C < T < 520°C.
- The overall mass weighted effective heat of reaction is endothermic at -613.2 kJ/kg, as shown in figure 9.

I.8.4.The Pyrolysis of Bagasse and corncobs

Bagasse and corncobs undergo pyrolysis reaction during heat treatment. This pyrolysis is a thermal decomposition of biomass, hemicellulose, cellulose and lignin in inert nitrogen atmosphere. It was found that this decomposition proceeds through three stages of weight loss:

I. The first stage is allocated to water evaporation in the range up to 160°C.

II. In the second stage, the mass loss is a consequence of thermal decomposition of biomass compounds from 160°C to 430°C.

III. The last and third stage represents a slow and long decomposition of lignin up to 900°C (65-69).

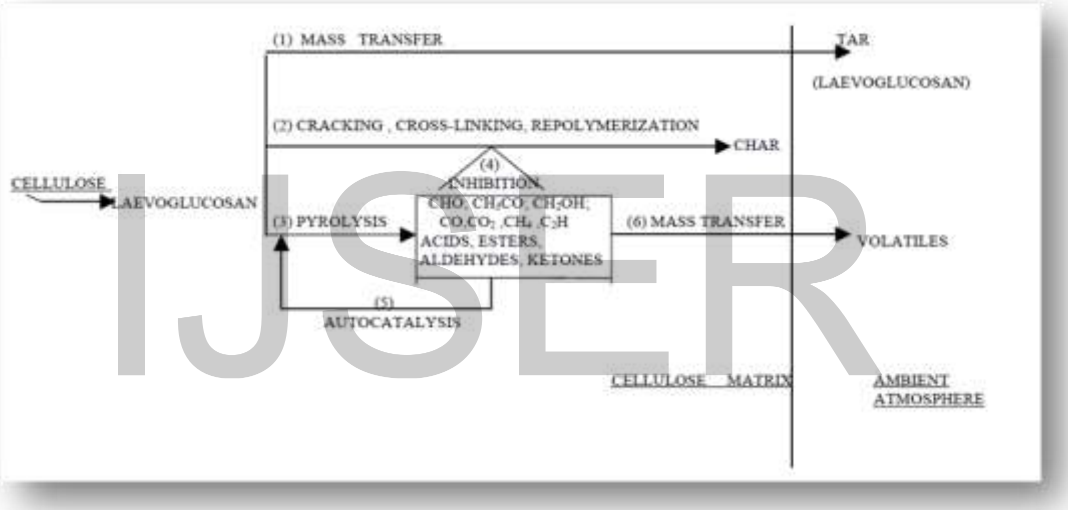


Figure 9: Pathways of Pyrolysis Reactions (66).

I.9.REVIEW OF LITERATURE

The Previous research could be classified according to materials' source and technology of preparation as the following:

I.9.1. MATERIALS

The Previous works according to materials' source are summarized in table (5).

Table (5) Summary of the previous work according to materials.

Title	Summary	Years	Reference
Production of Carbon Molecular Sieves from Illinois Coal.	Chars were prepared from coal under various pyrolysis and activation conditions in a horizontal tube fixed-bed reactor.	1992	70
Carbon Molecular Sieve from Poly (Vinylidene Chloride-Co-Vinyl Chloride).	A carbon membrane was prepared by coating it with a polymeric solution. The carbonization temperature had a marked influence on gas adsorbed. The carbon membrane obtained by carbonization at a temperature of 700°C exhibited better balance between permeance and selectivity.	2000	71
Novel Method to Synthesize Carbon Molecular Sieves from Petroleum Cokes.	Petroleum cokes were feasible to be the starting material for producing carbon molecular sieves.	2002	72
Carbon Molecular Sieves Produced from Palm Shell by Carbon Deposition.	Preparation of CMS from palm shell was investigated through some consequent heat treatment processes including carbonization, char activation and CVD from methane. The effect of methane flow rate and deposition time as two important process parameters on micro porosity development of CMS was examined.	2011	73

Carbon Molecular Sieves Produced from Walnut Shell.	Carbonized walnut shells were impregnated with a small amount of potassium hydroxide (KOH) followed by pyrolysis. The produced samples were further modified by a carbon deposition to form the final CMS.	2012	74
Physical and Chemical Analysis of Activated Carbon Prepared from Sugarcane Bagasse and Use for Sugar Decolorisation	Sugarcane bagasse was mixed with molasses, in the binder, and compressed into moulding press to make homogenized pellets at high pressure. The sample was then pyrolyzed at high temperature in an inert atmosphere then activated carbon was obtained.	2008	75
Synthesis of Activated Carbon and MCM-41 from Bagasse and Rice Husk and their Carbon Dioxide Adsorption Capacity	Three adsorbents; activated carbon synthesized from bagasse (BAC) and from rice husk (RAC), and Mobil Composition of Matter number 41 (MCM-41) from rice husk silica (R-MCM-41) were investigated for CO_2 adsorption.	2011	76
Production and characterization of water-steam activated carbons made from sugarcane bagasse and molasses pellets	Pellets made from sugarcane bagasse and molasses were water-steam activated at high temperature, by two processes, namely, (1) pyrolysis and activation in two different assays or (2) pyrolysis and sequenced activation in a single experiment. All carbons showed basic characteristic.	2012	77

I.9.2. TECHNOLOGY

The Previous works according to method and technology are summarized in table (6).

Table (6) Summary of the previous work according to methods.

Title	**Summary**	**Years**	**Reference**
The Preparation of 4A and 5A Carbon Molecular Sieves.	The polymer was carbonized in a stream of O_2 free nitrogen, during the carbonization step the rate of heating, temperature and the time was studied to determine its effect on the pore structure.	1990	78
Preparation of Carbon Molecular Sieve by Chemical Vapor Infiltration.	Preparation of CMSs from lignin-based chars by pyrolytic carbon deposition from benzene cracking seems to be possible by controlling the cracking temperature and time and the microporous structure of the substrate, the principal parameters governing the deposition process.	1999	79
Preparation of Carbon Molecular Sieves by Controlled Oxidation Treatments.	The carbon molecular sieves can be prepared by mild oxidation treatments of a char and subsequent removal of the surface complexes formed.	2000	80
Polyfurfuryl Alcohol Derived Carbon Molecular Sieves.	The deposition and carbonization of polyfurfuryl alcohol decreases the pore size. It (was) observed that when the polymer is deposited on small particles, the microporous volume is increased, due to more uniform polymer deposition on the surface.	2001	81

Modification of Pore Size in Activated Carbon by Polymer Deposition.	The Carbon molecular sieves were prepared by deposition and carbonization of polyfurfyl alcohol on activated carbon. These materials are characterized by a high selectivity towards O_2	2000	82
Molecular Sieve Properties Obtained by Cracking of Methane on Activated Carbon Fibers.	This cracking treatment was able to produce samples with molecular sieve properties	2002	83
Structural Ordering of Coal Char during Heat Treatment.	The crystallite size of carbon during heat treatment in the temperature range studied does not vary strongly with temperature and heating time. However, the crystallites are more ordered after heat treatment at high temperature and for longer time.	2002	84
Preparation of Carbon Molecular Sieves by Carbon Deposition from Methane.	The methane was pyrolyzed in an attempt to deposit fine carbon particles on the micropore mouths of the carbon substrates being heated	2007	85
Microwave Heating as a Novel Method for Introducing Molecular Sieve Properties.	The microwave heating could be a useful alternative to more commonly used methods for introducing molecular sieve properties into activated carbon adsorbents.	2004	86
Modification of Activated Carbon by Means of Microwave Heating.	The microwave heating was a very effective mean for modifying the properties of activated carbon to remove oxygen-containing surface groups, especially those of an acidic nature. The result is the pore volume and micropore volume slightly increased under microwave treatment.	2013	87

I.9.3.AIM OF THE WORK.

The scope of this work is to prepare Carbon Molecular Sieves (CMS) from bagasse and corncobs as a waste lignocellulosic biomass. The study includes; investigating the effect of the preparation parameters (time of carbonization and temperature) on the average pore size, pore volume and average pore density of products. Additionally, a trial will be carried out to precipitate carbon from hydrocarbon gas (LPG) on micropores of bagasse and corncobs samples to develop micropore porosity and control on; the average pore size, average pore density and total pore volume of samples to improve its adsorption selectivity for application in gas separation. Moreover, studying the yield from both wastes (bagasse and corncobs) and evaluating the economics from these yields produced form bagasse and corncobs.

CHAPTER II

II. MATERIALS AND METHODS

II.1. MATERIALS USED:

II.1.1. BAGASSE AND CORN-COBS

In this experiment, the used Bagasse and Corncobs had the following initial physical shape:

i. Bagasse: In form of powder particle sample (mesh no. 20)
ii. Corn-cobs: Irregular particles (mesh no. 1/4 in). See Figure 10.

a) Bagasse. b) Corn-cobs.

Figure 10: Photograph of used raw materials.

II.1.2. Liquefied Petroleum Gas

Liquefied Petroleum Gas (LPG) was used in the experiment. Table 7, shows the composition of LPG used, and table 8 shows the specification of LPG used.

Table 7: Composition of the LPG used.

Components	Mole%
Methane	0.0
Ethane	1.45
Propane	41.83
I-Butane	24.966
N-Butane	27.34
I-Pentane	4.26
N-Pentane	0.094
Neo-Pentane	0.001
C_6^+	0.059

Table 8: Specifications of LPG used.

Gas Specifications	**Value**
Vapor pressure @50 C^o Kg/Cm^2g	11.5
M.wt. average	57.73
Specific Gravity to air.60/60 ^oF (Kg/m^3)	0.5450

II.1.3. Nitrogen Gas

Nitrogen gas cylinders were used in the experiment as an inert gas. The purity of nitrogen is 99.5%≈ 99.8%.

II.2.CHARACTERIZATIONS OF BAGASSE AND CORNCOBS.

All samples are characterized in terms of surface area, micro-pore volume and pore size distribution by N_2 adsorption at 77 K in a BELSORP-mini II Gas Sorption System. Brunauer-Emmett-Teller (BET) equation was used to measure the apparent surface area. The surface characteristics of the activated carbon was analyzed using Scanning Electron Microscope (SEM) (88-92).

II.2.1. Brunauer-Emmett-Teller (BET) Surface Area Analysis.

The instrument used is BELSORP-mini II Gas Sorption System. The BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2g^{-1} thus yielding important information in studying the effects of surface porosity and particle size in many applications (88,90).

In physical adsorption, adsorption isotherms can be classified as one of six types, as shown in table 9. The size of pores is classified as in table10. This classification is based on the strength of the interaction between the sample surface and adsorptive, and the existence or absence of pores.

II.2.2. Scanning Electron Microscope (SEM).

The traditional Scanning Electron Microscope, model JEOL JSM 6360LV Scanning Electron Microscope was used (91, 92).

II.2.2.1. Apparatus Specifications.

Jeol-JSM-6360LV Scanning Electron Microscope. Magnification: 5 to 300000X. Resolution: 3.00 nm. Accelerating Voltage: 0 to 30 kilovolts (91, 92).

Table 9: Features of adsorption Isotherms (90).

Type	**Features**		Sample –Adsorptive example
	Interaction between sample surface and adsorbate	**porosity**	
I	Relatively strong	Micropores	Activated carbon-Nitrogen
II	Relatively strong	Nonporous	Nitrogen
III	Weak	Nonporous	Carbon-water vapor
IV	Relatively strong	Mesopore	Silica-Nitrogen
V	Weak	Mesopore / Micropore	Activated carbon-Water Vapor
VI	Relatively strong sample surface Has an even distribution of	Nonporous	Graphite-Krypton

Table 10: IUPAC classification of pores (90).

	Pore diameter/nm
Micropore	Up to 2
Mesopore	2 to 50
Macropore	50 or up

II.3. METHOD OF MEASUREMENTS AND EXPERIMENTAL SETUP

II.3.1. Gases' Flow Rate Measurements.

Two gas flow meters (Rota meter type) with different ranges were used as follows:

i) Flow meters for LPG cylinder (type 212-J-1-G4-C0 low range):

- Flow rate reading range: 0-10 L/min.
- Calibrated for LPG; specific gravity: 0.56 kg/m^3.
- Working temperature range: 20 - 80 ^{0}C.
- Maximum working pressure: 10 kg/cm^2

The supplier was Arabic group (Bb Officine Orobiche Manufacture).

ii) Flow meters for N_2 cylinder (type 102 high way 212 series RMA high range):

- Flow rate reading range: 0-25 L/min.
- Working temperature range: 20 -80 ^{0}C.
- Maximum working pressure: 10 kg/cm^2

The supplier was Dwyer Company. Figure 11, shows a photograph of the two types of flow meters.

II.3.2. Gases' Pressure Measurements.

- Pressure indicator Bourdon tube type range: 0-25 kg/cm^2.
- Regulator type Rich OR-03K regulator range from 0-250 kg/cm^2 to outlet pressure 0-25 Kg/cm^2.

II.3.3. Temperature Measurements and Temperature Controller.

- Temperature ceramic thermocouple type J (Model 86 Selectron), range 0 - 1500 ^{0}C accuracy ± 0.25% of full scale, resolution 1.0 ^{0}C.
- Temperature PID controller used to control temperature increasing rate by control of the heating rate from heater coil. Figure 12, shows a photograph of temperature element and controller.

High range flow meter for N_2 cylinder.

Low range flow meter for LPG cylinder.

Figure 11: High and low range flow meters.

a) Temperature controller

b) Temperature element

Figure 12: Temperature element & controller.

II.3.4. Experimental Setup

The following are the components of the experimental setup:

II.3.4.1. Parts of Furnace:

i) The Cylinder: is made from Stainless steel 316 Nickel chromium in the form of a cylinder with the following specifications:

Hollow volume:	28.8 cm^3.
Internal Diameter:	60 mm.
Outer Diameter:	71 mm.
Cylinder length:	240 mm.
Wall thickness:	5.5 mm.
Cylinder weight:	1.0 kg.
Maximum tested pressure:	8.0 kg/cm^2
No. of ports in heater cylinder:	4

ii) The Furnace heating coil: is a nickel chrome heater coil, bended around stainless steel cylinder to form a spiral shape and is fixed by stainless steel wire.

A heating coil was used to increase the temperature of the heater cylinder up to 1000 ^oC with the following specifications:

Length:	3 m.
Heating power:	3000 Watt.

Figure 13, shows the accessories of this heater cylinder.

The heating coil was fitted with a temperature limit switch to adjust the increasing of core temperature at the required rate.

iii) The Furnace Temperature Thermo-well: A stainless steel thermo-well was installed in the center of the heater cylinder to monitor temperature with the depth of the thermo-well inside the center of the heater cylinder: 250 mm. (see figure 14).

iv) Holding Sample crucible; a) half cylinder sample holder which is a stainless Steel half cylinder separated into two parts used to carry two samples in the same run. b) High Pressure holding sample; (see figure 15).

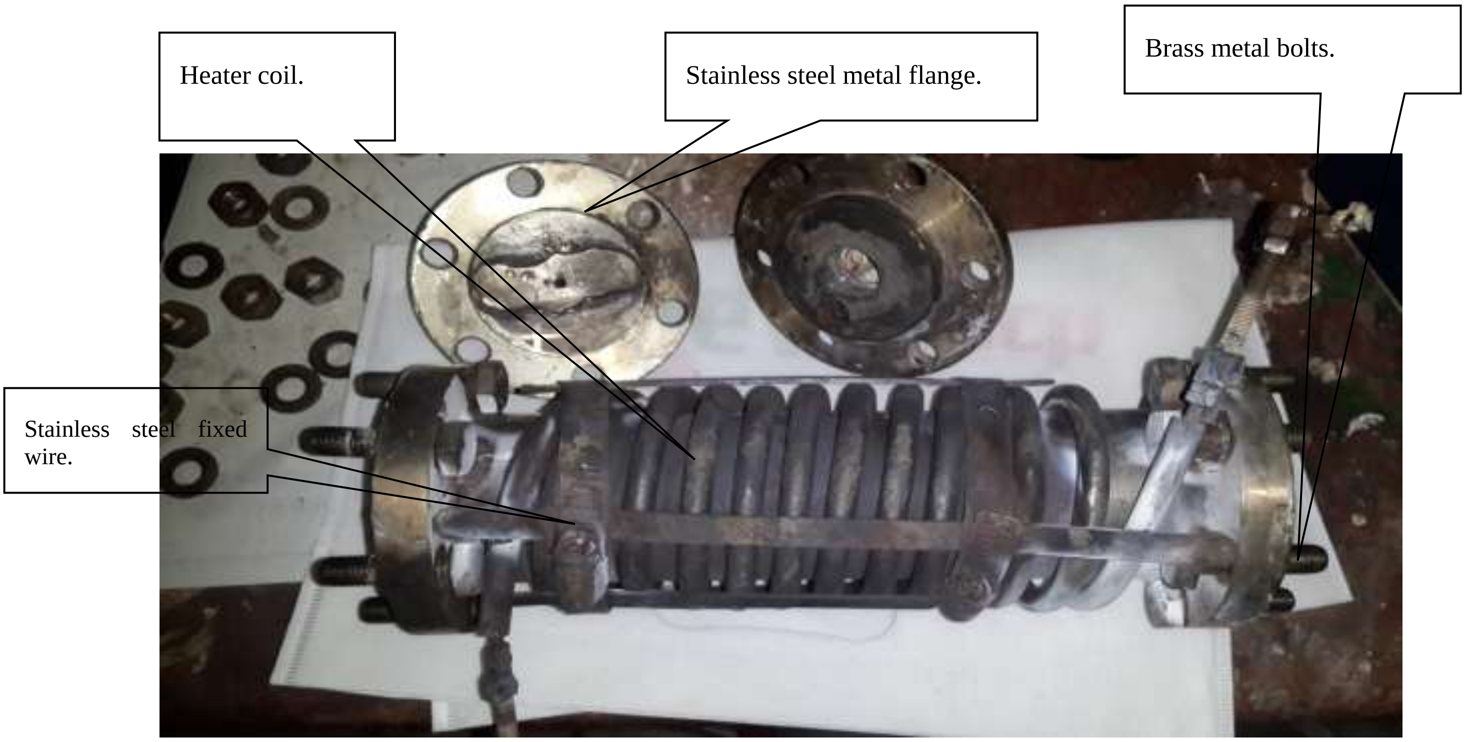


Figure 13: Stainless steel cylinder heater and its accessories.

Figure 14: thermo-well inside heater cylinder.

a) Half cylinder sample holder b) High pressure holding sample

Figure 15: Holding samples inside heater cylinder.

II.3.4.2. Insulation of Heater

- Refractory rock was used for insulating the heater coil to reduce heat losses from heater to the surroundings. The thickness of insulation layer is 5.0 cm. (see figure 16).

II.3.4.3. Gas Cylinders Used in Experiment:

Two capacities of gas cylinders were used:

i) LPG Cylinder:

- At Pressure 5.0 kg/cm^2, capacity 15 liter.

ii) Nitrogen gas cylinder:

- Nitrogen gas cylinders were used with the capacity of 47 liters at pressure 95 Kg/Cm^2

II.3.4.4. Cooling coil

The hot outlet gases pass through stainless (a) steel coil to cool down the temperature of exit gas. The length of this coil is 3.0 m and the internal diameter is 2.5 cm (see figure 17).

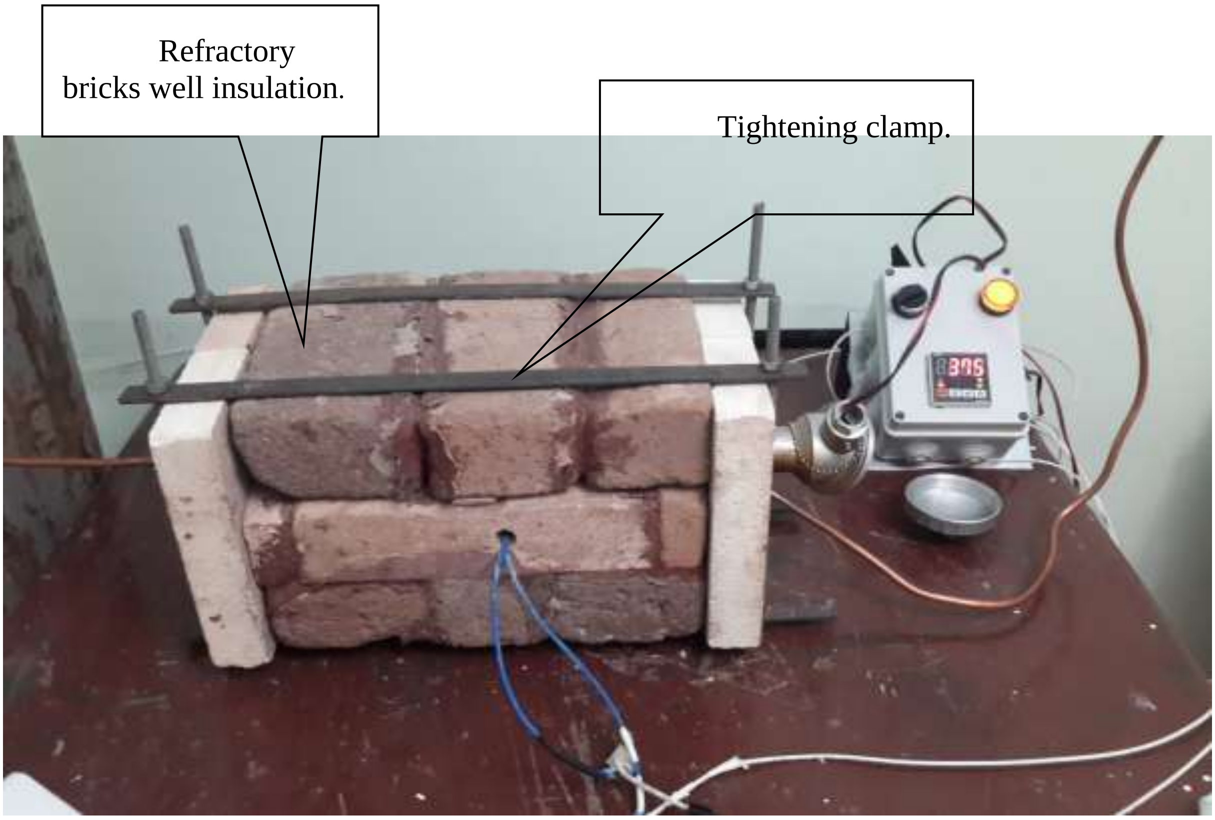


Figure 16: Heater insulation

Figure 17: Illustrate the cooling coil.

II.3.4.5. Pipes Network and Valves

i) The Pipes Network

The pipe network consisted of two types as the following:

a) A 1/4 inch rubber high pressure, and high pressure joints were used to connect the tube. This pipe was used to achieve the following targets:

- Purging of the whole system.
- Delivering gases to the heater cylinder.

b) A 1/4 inch brass tube used to discharge outlet hot gases.

ii) The Valves:

Two types of valves were used:

- A regulator valve was used to reduce the gas pressure, and control the pressure at the experiments' inlet point.
- 316 Stainless steel 1/4 inch ball valves were used to direct the gas flow and to control the quantity of gas flow at the outlet of the experiments. (See figure 18).

Figure 18: Experimental pipes network and valves used.

II.4. PLAN OF WORK

The following are the steps of the work plan:

II.4.1. Preparation of carbonization samples from Bagasse and Corncobs

The carbonization process was performed under a N_2 flow of 5.0 mL min^{-1}. The temperature of the reactor was increased at average rate of 15 min^{-1} until the carbonization temperature of 850 °C was reached. The samples were pyrolyzed at various times (4 to 12 hours).

II.4.2. Developing of Porous Structure in Carbon Samples Using Chemical Treatment

The carbonized samples were impregnated in KOH (2 M) solution for 3.5 hrs at 350 °C. KOH was used as a chemical agent that causes the swelling of the carbonized shells. It also creates some porosity inside the chars and inhibits particle narrowing during the next heat treatment process. The chemically activated shells were rinsed with distilled water until a neutral pH in the filtrate was achieved. Then, the samples were oven dried at 110 °C for 3 hrs.

II.4.3. Physical Activation of Carbonized Samples

This process was conducted while the chemically activated chars were reloaded in the reactor under a N_2 flow of 5.0 mL min^{-1} until the temperature reached up to 850 °C.

II.4.4. Developing of Micropore Structure Using Chemical Vapor Deposition Technique

Deposition process carried out by loading 15 g of the activated carbon in activation column. Prior to deposition step, a N_2 flow of 5.0 mL min^{-1} passed through the column to swipe out O_2 until deposition temperature of 850 ºC was achieved. The deposition experiments were conducted at 850 ºC under a diluted stream of LPG. After deposition process, N_2 was introduced into the column to flush out residual LPG and cool the sample to room temperature.

II.5. EXPERIMENTAL PROCEDURE

II.5.1. Preparing The Raw Materials

In these experiments two samples were used and treated as the following procedure:

a) Bagasse: 15.0 grams of Sugarcane bagasse were dried and grinded to powder form. Then the sample was washed and dried in an oven at 110 °C for 4 hrs.
b) Corn-cobs: 15.0 grams of corncobs were dried, crushed and sieved to particles. Then the sample was washed and dried in an oven at 110 °C for 4 hrs.

II.5.2. Purging the Pipes Network and Gas-Test

i) Two samples (known weight) were inserted in half a cylinder sample then insert it into a stainless steel heater cylinder after that tighten the flange and put the insulation bricks as mentioned before (part II.3.4.2). (see figure 19).
ii) The inventory of the experiment was purged with inert gas (Nitrogen) to sweep out any dust, oxygen, water vapor from the pipes network and stainless steel heater cylinder.
iii) The experimental setup was checked for any gas leakage (gas-test) in the connections and fitting (soap gas test was used). The gas-test was conducted at 15 kg/cm^2 for 30 min. by nitrogen gas.

II.5.3. Preparing Carbonization Samples From Bagasse And Corn-Cobs

The following are the steps of carbonization of raw samples:

i) Drying out; by increasing the temperature of the heater until 110~150 C^o with a continuous flow of pure nitrogen (5 mL min^{-1}) for one hour.

ii) After drying out is completed, the pressure was set inside the heater cylinder at 1 kg/cm^2 gauge. The carbonization process was performed under a N_2 flow of 5 mL min^{-1}. The temperature of the heater was increased at a rate of 15 °C min^{-1} until the carbonization temperature of 850 °C was reached.

iii) At 850 °C the samples were pyrolyzed for 4 to 12 hrs.

iv) Cooling down; is done by switching off the heater and leaving the apparatus to cool under ambient conditions with a continuous flow of (Nitrogen) at rate of 5 mL min^{-1}.

v) Recording weight of samples to determine the losses.

vi) Determining the surface characteristic of the resulting carbonized samples using scanning electron microscope (SEM).

Vii) Running BET analysis to determine the specific surface area by measuring the external surface area and open pores of macroporous and mesoporous materials.

II.5.4.Development of Porous Structure in Samples Using Chemical Treatment

KOH was used as the chemical agent that causes the swelling of the carbonized shells. It also creates some porosity inside the chars and inhibits particle narrowing during the next heat treatment process (18). The following are the steps of chemical treatment of samples:

i) The samples (known weight) were inserted in a high pressure holding sample where the carbonized samples were impregnated in KOH (2 M) solution.

ii) A high pressure sample was put in a stainless steel heater cylinder and step no. II.5.3.ii was repeated.

iii) The heater cylinder temperature was increased with a rate of 15 °C min^{-1} up to 350 ^{0}C, then that temperature was held for one hr.

iv) The heater was Switched off then the sample was left to cool down.

v) The chemically activated samples were rinsed with distilled water until a neutral pH in the filtrate was achieved.

vi) The samples were oven dried at 110 °C for 3 hrs.

vii) The weight of samples was recorded to determine the losses.

viii) The surface characteristic of activated carbon were determined using scanning electron microscope (SEM).

Viiii) BET analysis was run to determine the specific surface area by measuring the external surface area and open pores of macroporous and mesoporous materials.

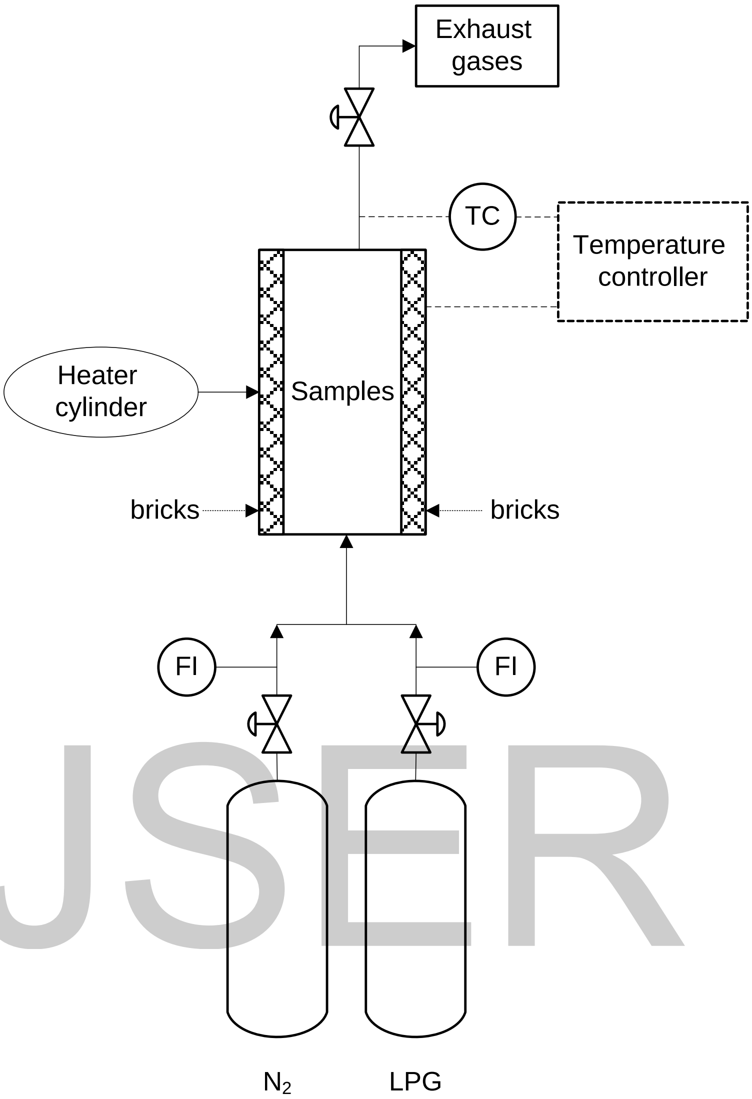


Figure 19: The experimental setup.

II.5.5. Physical Activation of Carbonized Samples

Physical activation was carried out to develop the microporosity of the lignocellulosic char. This process was conducted while the chemically activated chars were reloaded in the heating cylinder under a N_2 flow similar to all the steps mentioned in II.5.3.

II.5.6. Developing Micropore Using Chemical Vapor Deposition Technique

The deposition process was carried out by loading samples of the carbonaceous materials in the pre-described heater cylinder as shown in figure 19, according to the following steps:

i) Two samples (known weight) were inserted in a half cylinder sample inside the stainless steel heater cylinder then the flanges were tightened and the insulation bricks were put. The same steps were repeated as mentioned in II.5.3 until temperature up to 850 ^{o}C.

ii) Prior to deposition step, N_2 flow of 5.0 mL min^{-1} was passed through the pipe to the heating cylinder. Then mixed N_2 stream with a stream of LPG (0.5 mL min^{-1} LPG mixed with 5 mL min^{-1} N_2) were passed for 30 to 60 min^{-1}.

iii) The heater was switched off then the sample was left to cool down while passing inert gas (Nitrogen) at a rate of 5.0 mL min-1.

iv) The weight of the samples was recorded to determine the losses.

v) The change that took place in the surface characteristic of Carbon Molecular Sieves was determined using scanning electron microscope (SEM).

II.6.VARIABLES STUDIED

The effect of the following treatment parameters on the average pore size and surface was studied:

a. Carbonization temperature (350ºC, 750ºC – 850ºC) over the properties (Pore Size and Holes Density) of bagasse and corncobs samples, during activated carbon preparation step.

b. Chemical treatments by KOH on properties (Pore Size and Holes Density) of bagasse and corncobs samples, during chemical treatments step.

c. Carbon Deposition on properties (Pore Size and Holes Density) of bagasse and corncobs samples, during Carbon Deposition step.

d. Carbonization time (4 and 12 hours) on micro-porosity development and total pore volume.

e. Carbonization, chemical treatments and Carbon Deposition on the total yield.

CHAPTER III

III. Results and Discussion

III.1. CHARACTERIZATION OF RAW MATERIALS

Table 11 shows the characterization of raw materials (Corn-cobs and Bagasse). The average pore diameter of corn-cobs is (7.93 μm x 10^{-2}) is approximately the same as bagasse which is (8.40 μm x 10^{-2}). In contrast, the total pore volume for bagasse is 0.9 cm^3 g^{-1} which shows a better capacity than for corncobs that is 0.78 cm^3 g^{-1}.

Table 11: properties of raw materials

Raw Material	**Av. Pore diameter µm x 10^{-2}**	**V_P Total pore volume (cm^3 g^{-1})x10^{-2}**
Corn-cobs	**7.93**	**0.78**
Bagasse	**8.40**	**0.90**

III.2. PORE SIZE AND HOLE DENSITIES VARIATION DURING CARBONIZATION STEP

III.2.1. Pore Size Variation during Carbonization step

Figure 20, shows the effect of Carbonization Temperature on pore size of Corncobs. It is clear that at the highest temperature of carbonization process, the average pore diameter of corncobs has decreased sharply. It can be concluded that, not only the extent of gasification but also the pore development are both strongly dependent on the carbonization temperature. It was hypothesized that the decomposition of hemicellulose over this low carbonization temperature (≤ 350 °C) range could be a responsible factor for this decrease in pore size. (54)

In addition to this, it has been reported that, at high carbonization temperatures (≥ 750 °C), a more ordered structure is more likely to be developed in the corn-cobs, which leads to a low marked decrease in the average pore diameter during the activation step. (54)

In fact, the decomposition of hemicellulose and cellulose started over the range from 200-380 °C and 250-400 °C, respectively, while the decomposition of lignin occurred over a wider range of temperature of 160-900 °C. (58)

Furthermore, in addition to the higher percentage of lignin, the bagasse contains lower percentage of hemicellulose compared to corncobs. Therefore, figure 21, shows the effect of carbonization temperature on bagasse, where the decrease in diameter is slightly low at low temperature 350°C compared with corncobs. Then, there is a decrease in the average pore diameter at higher temperature 750-850°C compared to corncobs.

The same results were obtained by Arvind Kumar and Hara Mohan Jena, when they prepared activated carbon from nutshells where the carbonization temperature accelerated thermal degradation and the volatilization process of the sample. That high temperature leads to increases in the surface area and pore development hence the average pore diameter decrease. They have also reported that the rise in carbonization temperature from 700 °C to 800 °C may have induced shrinkage in the carbon structure, resulting in a reduction in the surface area and the total pore volume (100).

A similar trend is also reported by various researchers while showing the influence of activation temperature on the BET surface area and total pore volume of activated carbon obtained through H_3PO_4activation of other lignocellulosic precursors (101).

The same results were obtained by by Ya LIU, Zi-Feng YAN, when they prepared carbon molecular sieves from petroleum cokes. They concluded that both micropore diameter and micropore volume increased initially and then decreased as temperature rose. This means that higher activation temperature accelerated the process of nanopore or micropore generation, but excessively high temperature resulted in the shrinkage of the micropore.(102)

In contrast, as reported by Hsisheng Teng and Jui-AnHo, when they tried to prepare activated carbons from Bituminous Coals with CO_2 , where for the same coal precursor, the average pore diameter of the activated carbon increases as the temperature for activation is increased in the range of 800−900 °C (91). This different result may be the result of the use of different raw materials because corn-cobs and bagasse contain lignin and hemicelluloses.

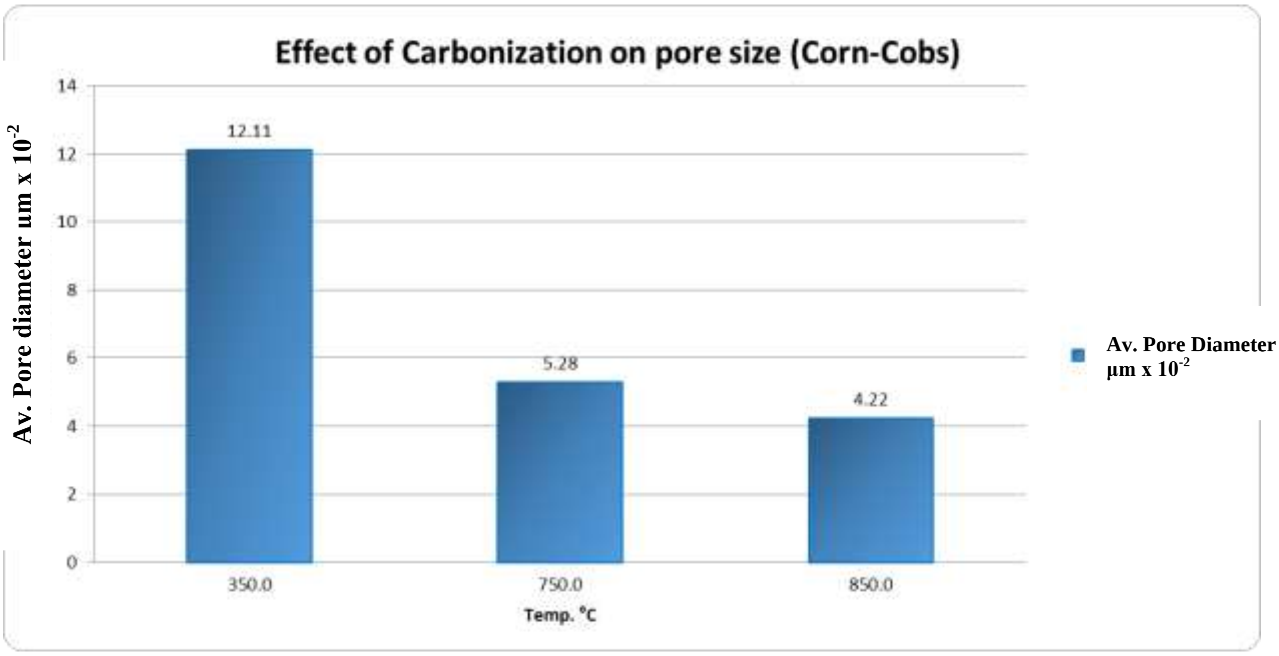


Figure 20: Variations of pore diameters with temperature during carbonization "Corn-Cobs".

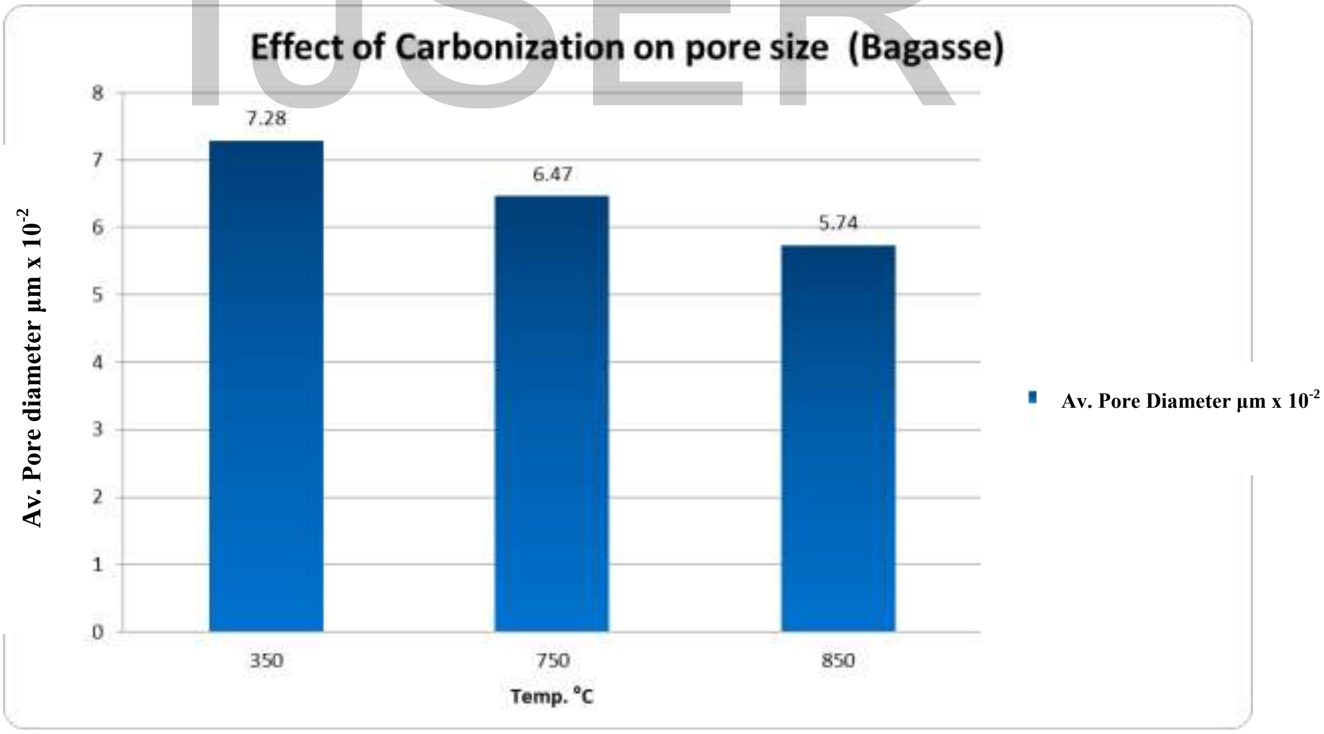


Figure 21: Variations of pore diameters with temperature during carbonization "Bagasse".

III.2.2. The Effect of Carbonization Temperature on Holes Density

Figure 22 illustrates the variation of holes density during carbonization of corncobs. Figure 22 shows clearly that at low temperature range (350-750 ^{o}C) there is a very slight change in holes' density. The increase in holes' density at higher temperature ≥ 750 ^{o}C can be attributed to the rupture of the biomass structure resulting from the release of more volatile species as the heat treatment temperature is increased. (100)

Figure 23 shows the variations of holes' density during carbonization of Bagasse. It is also clear from figure 23 that at lower temperature range (350-750 ^{o}C) the change in hole density is less sensitive to temperature change than at high temperature range (750-850 ^{o}C).

These results suggest that the carbonization temperature has an effect not only on char reactivity, which results in different values of porous properties, but also on the physical structure of char upon heat treatment during the carbonization step, leading to activated carbons with different distribution of pore sizes. It is probable that the char prepared at a high carbonization temperature, due to a greater loss of volatiles, possesses a more densely packed structure, from which it is difficult to enlarge the small pores to larger pores by gasification with the activating gas. (54)

J. Mater. Chem. A, reported that the heating of a high carbon-containing metal salt under nitrogen generates microporous carbons. He noted as the carbonisation temperature increases, there is a widening of the ‘knee’ of the isotherm, which indicates a slight broadening of the micropore size range with incrasing the average holes density. (99)

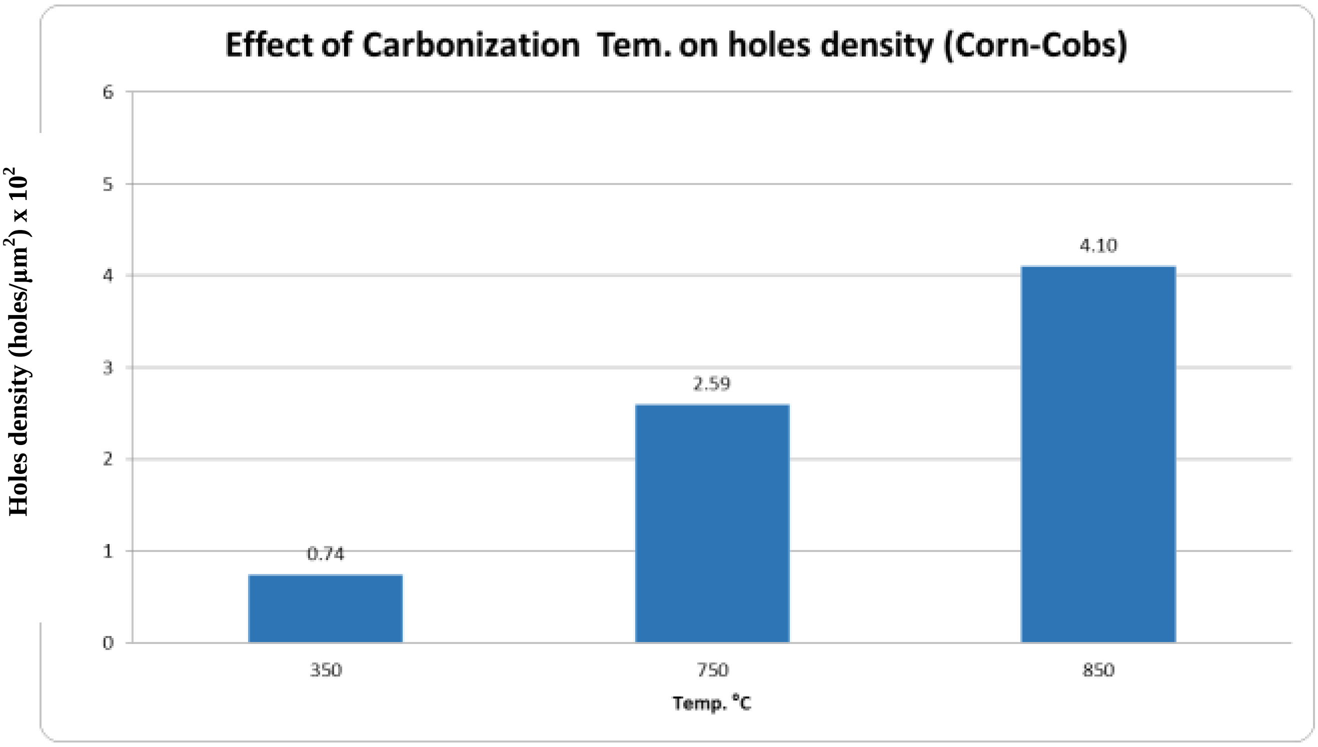


Figure 22: Effect of carbonization temperature on holes' density of corn-cobs.

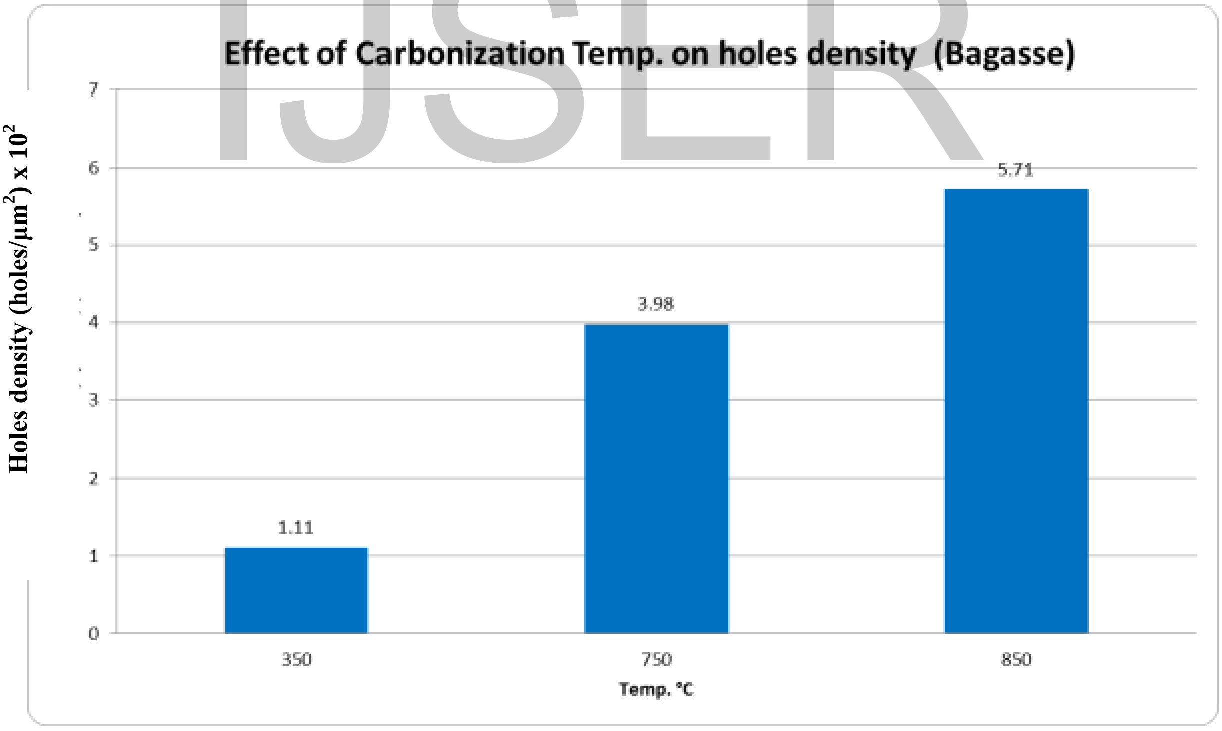


Figure 23: Effect of carbonization temperature on holes' density of Bagasse.

III.3. PORE SIZE AND HOLE DENSITIES VARIATIONS DURING CHEMICAL TREATMENTS STEP

III.3.1. The Effect of Chemical Treatments on Average Pore Diameter

It is clear from both figures (24 & 25) that chemical treatment has a much stronger effect on pore diameter and the following was recorded:

Figure 24 shows the variation of the average pore diameter after alkaline chemical treatment for corncobs. It is clear, that the average diameter of pore size increased by approximately 300% after being chemically treated. (55)

The variation of pore diameter after chemical treatment of bagasse is shown in figure 25. The average pore diameter has increased remarkably after chemical treatment. This can be attributed to the effect of alkaline treatment by KOH, which has a strong effect on the bagasse average pore diameter that increased the average pore diameter by approximately 250%. (55)

These results suggest that the effect of alkaline treatment at high temperature (350 C°) has a strong impact on the bagasse which led to the physical merge of some holes in bagasse because of the weakness of the structure of Lignin. On the contrary, the effect of alkaline on corncobs is lower than on bagasse due to the strong structure of hemicellulose in corncobs. (55)

Similar results were obtained by Arvind Kumar and Hara Mohan Jena. They prepared activated carbon from nutshells and noted that the alkaline treatment by NaOH (instead of KOH) soaking is an important step during the preparation of high surface area activated carbon. When the biomass is was treated with a low concentration of NaOH, the ester bonds between lignin and carbohydrate are were broken due to saponification, causing the destruction of lignin structure and increasing the porosity of material. This can help the activating agent to enter the interior of the raw material and increase the contact area between the activating agent and the carbon precursor (89).

Furthermore, the hemicellulose can partially be dissolved in alkali solution and washed away in the base-leaching process, which may also result in a more porous structure of the raw material, helping the activating agent to enter the interior of the raw material (89).

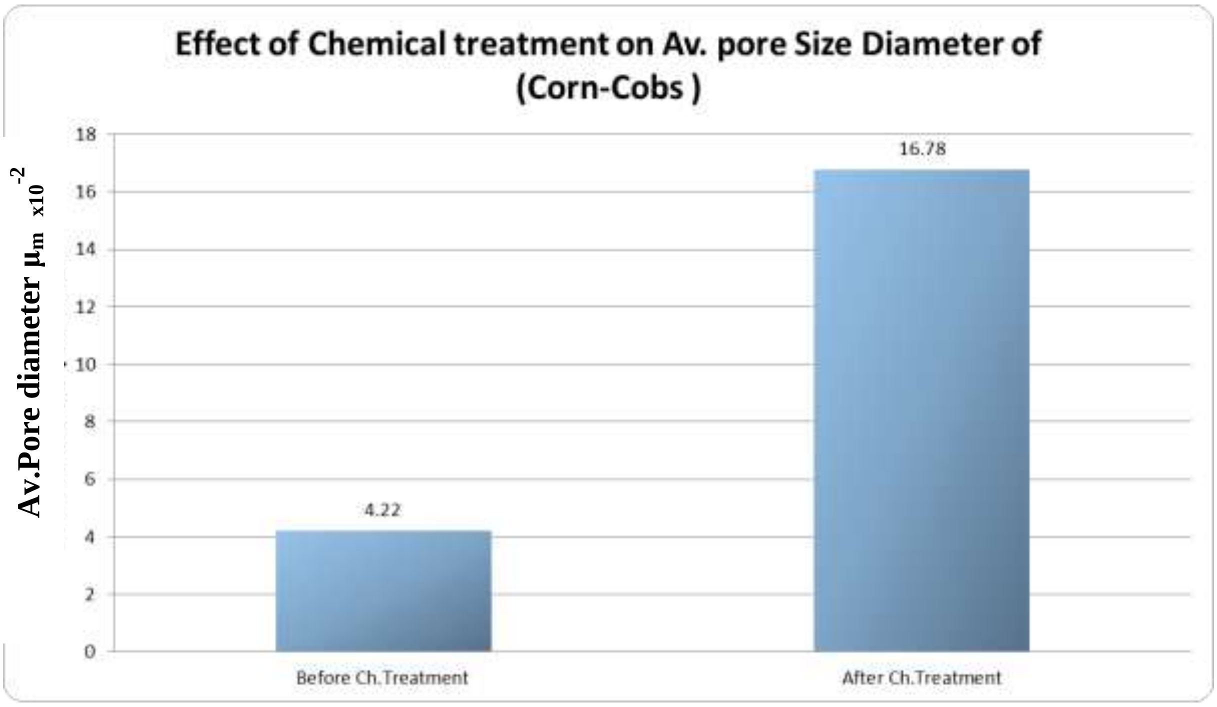


Figure 24: The effect of chemical treatment on Av. pore diameter of corncobs.

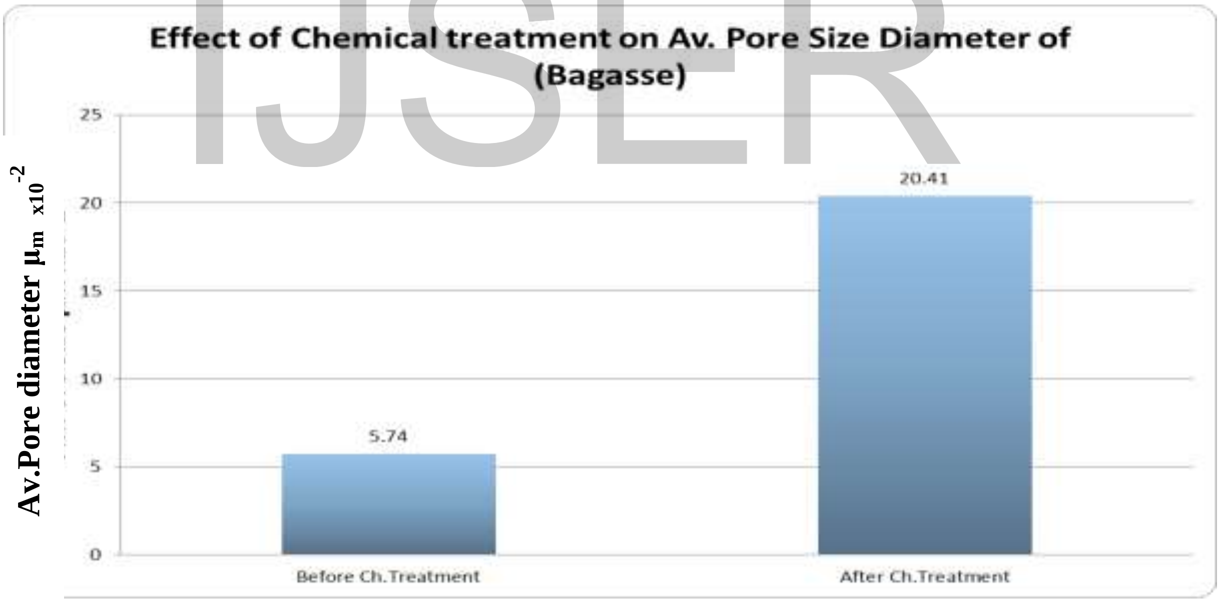


Figure 25: The effect of chemical treatment on Av. pore diameter of bagasse.

III.3.2. The Effect of Chemical treatment on holes' Density of Surface

Figure 26, shows the variation of holes' density after the chemical treatment of corncobs. It is clear from figure 26 that the average holes' density increased sharply (390%) after being chemically treated.

Percentage of increase in holes density:

$$\text{Corncobs} = \frac{(4.1- 20.18) *100}{4.1} = 390\%$$

This can be associated with the effect of alkaline treatment, which increases the diameter by the incorporation of simple holes, so the density increased.

Figure 27 shows the variation of pore diameter after the chemical treatment of bagasse. It is clear from figure 27 that the average holes' density increased sharply (550%) after the chemical treatment.

Percentage of increase in holes density:

$$\text{Bagasse} = \frac{(5.71- 32.37) * 100}{5.71} = 550\%$$

This can be attributed to the effect of alkaline treatment by KOH that has a strong effect on bagasse pore size, which ruptures the biomass structure of the surface. Therefore, the holes' density has increased.(55)

In addition to this/ Additionally, these results show that the strong effect of KOH on bagasse compared to its effect on corncobs is the result of the strong structure of hemicellulose in corncobs compared to the weakness of the structure of Lignin in bagasse. (55)

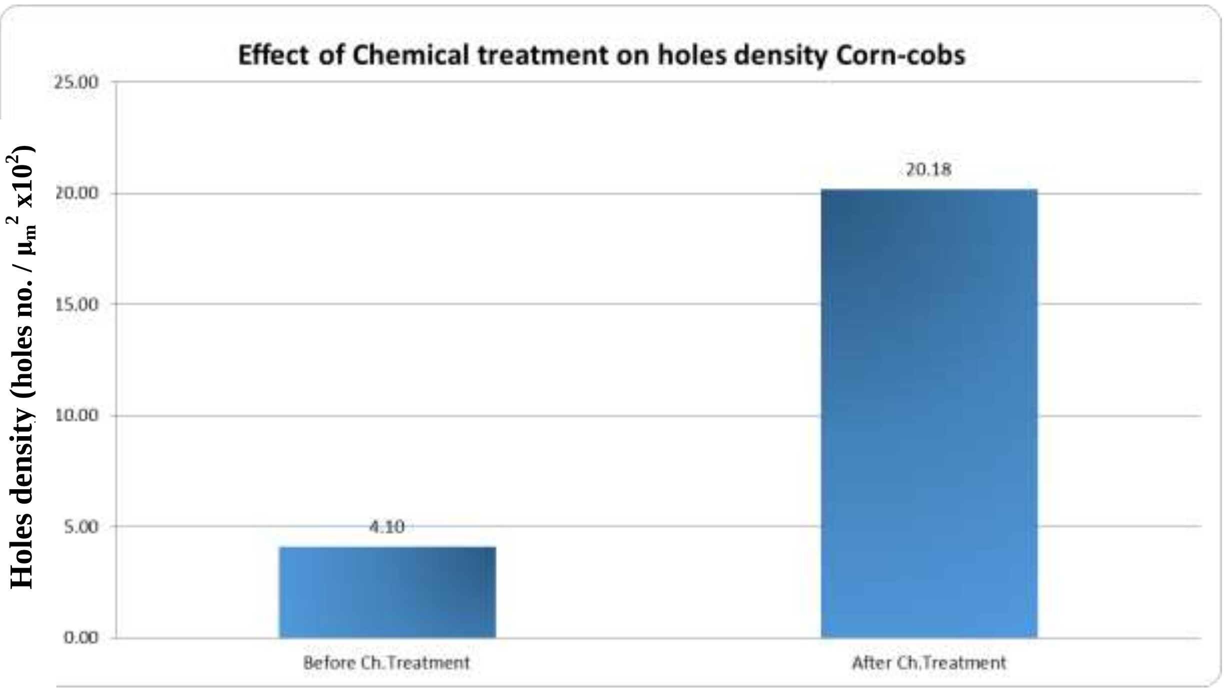


Figure 26: Effect of chemical treatment on (the) pore density (of) corncobs.

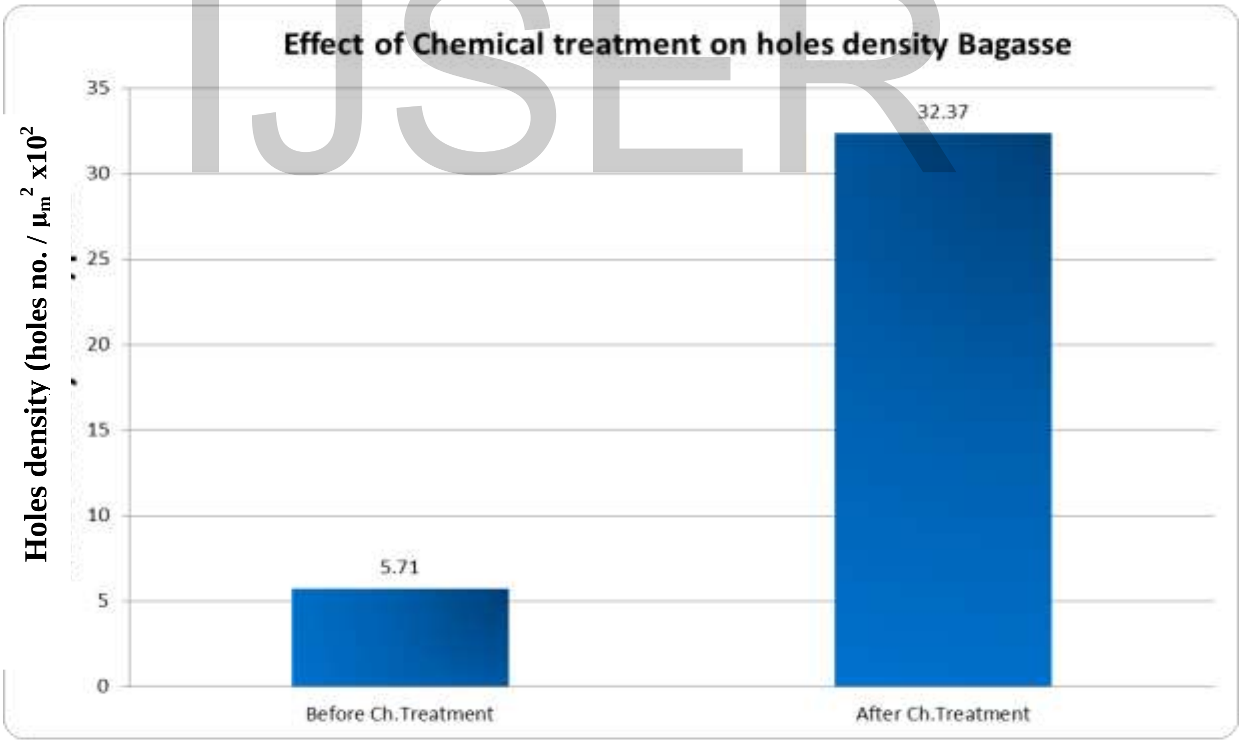


Figure 27: Effect of chemical treatment on (the) pore density of bagasse.

IV.4. PORE SIZE AND HOLE DENSITIES VARIATIONS DURING VAPOR CARBON DEPOSITION STEP

III.4.1. The Effect of Carbon Deposition on the Pore diameter

This step deals with carbon deposition at the pore mouth that narrows the pore entrance to match the molecular size of the analytic. Therefore, figure 28 shows the variations of pore size after carbon deposition of corncobs. It is clear from figure 28 that the average pore diameter decreases by almost 97.5% after carbon deposition. This can be attributed to the effect of carbon (LPG gas) treatment which decreases the diameter by the precipitation of carbon on sample holes.(54)

$$\% \text{ decrease} = \frac{(0.1678-0.0041)}{0.1678} *100 = 97.5\%$$

Figure 29 shows the variations of pore diameter after carbon deposition for bagasse. It is clear from figure 29 that the average pore diameter decreased sharply (by 97.1%) after carbon deposition.

$$\% \text{ decrease} = \frac{(0.2041-0.0058)}{0.2041} *100 = 97.1\%$$

This can be linked to the effect of carbon (LPG gas) treatment that decreases the diameter by the precipitation of carbon in sample holes.

The same results were obtained by MOREIRA and A. E. Rodrigues when they prepared carbon molecular sieves by depositing polyfurfuryl alcohol. They proved that the deposition and carbonization of polyfurfuryl alcohol decreases the pore size. Furthermore, it was observed that when the polymer is deposited on small particles, the microporous volume is increased, due to more uniform polymer deposition on the surface.(23)

In addition to this, results by M.A. de la Casa-Lillo and Brian C. Moore when they prepared Carbon Molecular sieve properties by the cracking of methane on activated carbon fibers. The major results indicated that CVD treatment at 1173 K deposited carbon inside the porosity of activated carbon fibers, which reduced the overall pore volume and led to the improved kinetics of gas separation. (100)

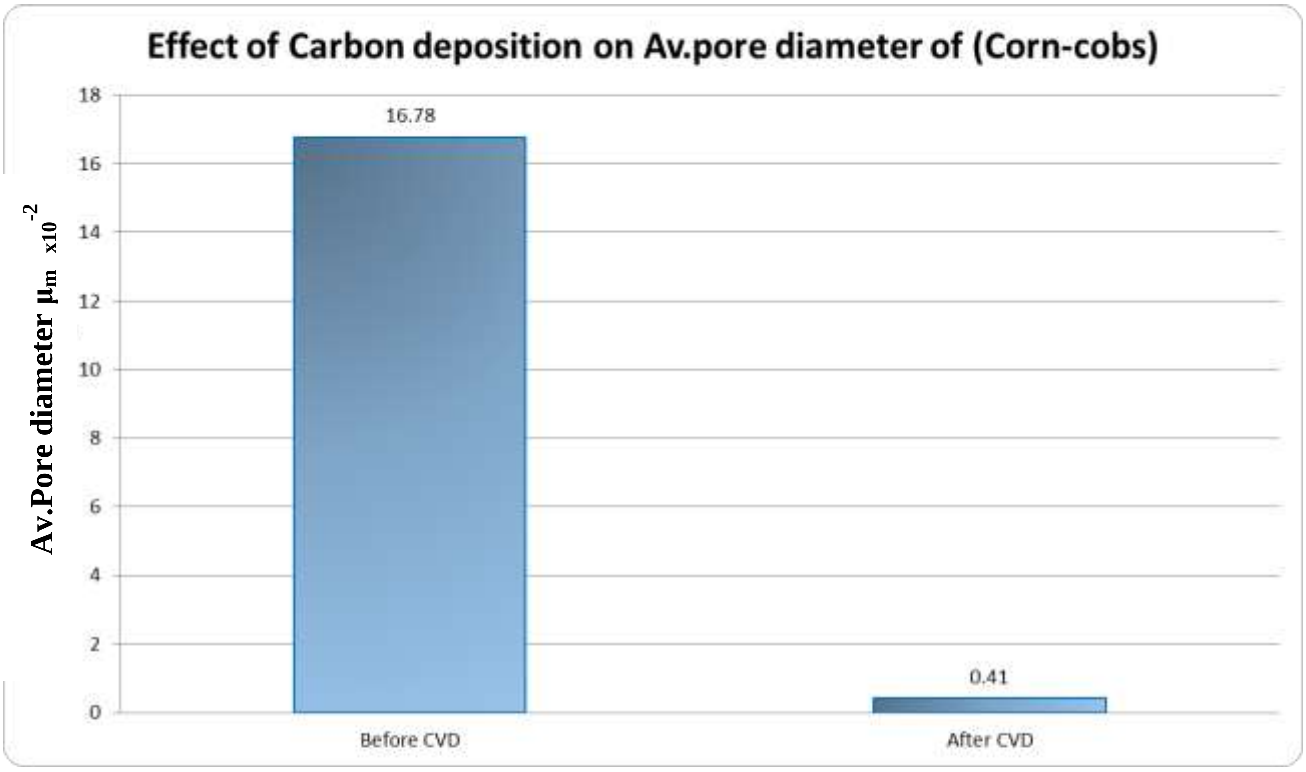


Figure 28: the Effect of carbon deposition on the average pore diameter of corncobs.

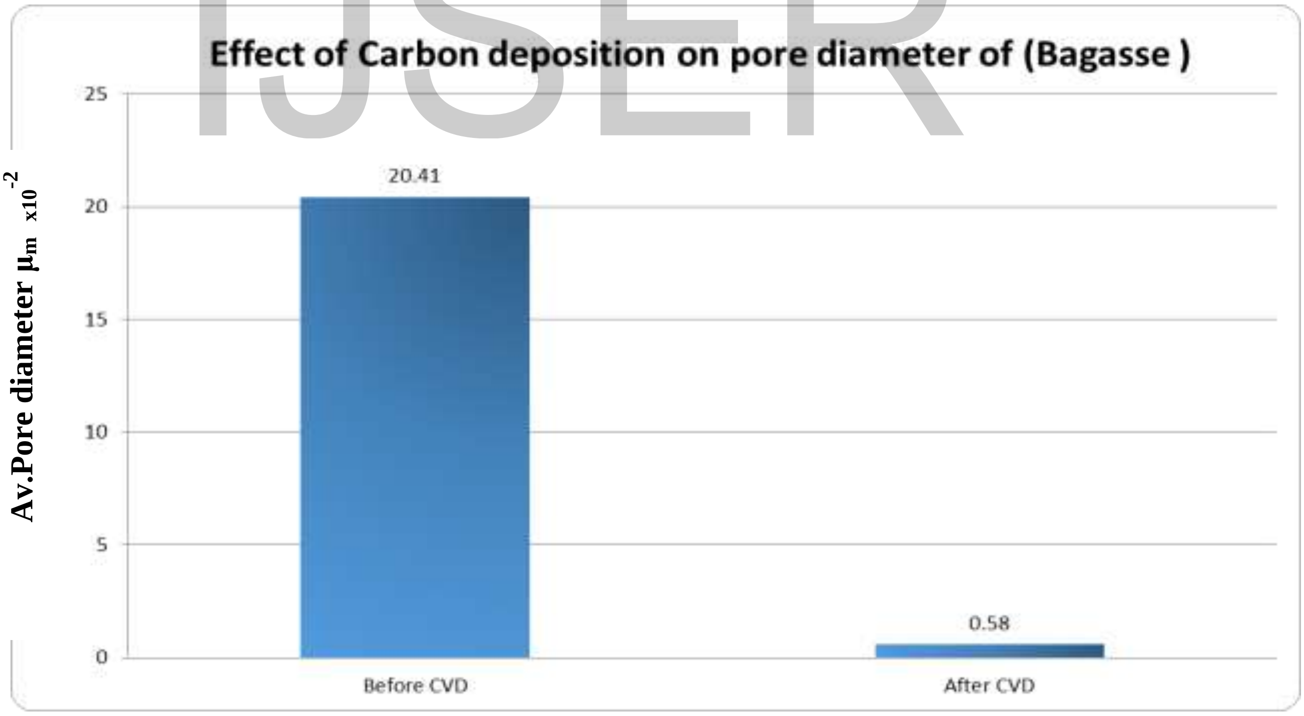


Figure 29: the Effect of carbon deposition on the average pore diameter of Bagasse.

III.4.2. The Effect of Carbon Deposition on the Average holes' density of the Surface

Figure 30 shows the variations of holes' density after carbon deposition of corncobs. It is clear from figure 30 that the average holes' density decreases by 20% after carbon deposition. This can be attributed to the effect of carbon (LPG gas) treatment that decreases the diameter by the precipitation of carbon on sample holes.

$$\% \text{ of increase} = \frac{(20.18-9.68)\ 100}{20.18} = 52.0\%$$

Figure 31 shows the variation of holes' density after carbon deposition of bagasse. It is clear from figure 31 that the average holes' density has decreased by 75.90% after carbon deposition and it appears that the decreases are higher than that of corncobs. It is understood that this could reflect the effect of larger surface area of bagasse powder compared to the granules of corncobs. (60) The decline in holes density can also be attributed to the effect of carbon (LPG gas) treatment that decreases the diameter by the precipitation of carbon on sample holes.

$$\% \text{ of decrease} = \frac{(32.37-7.8)*100}{32.37} = 75.90\%$$

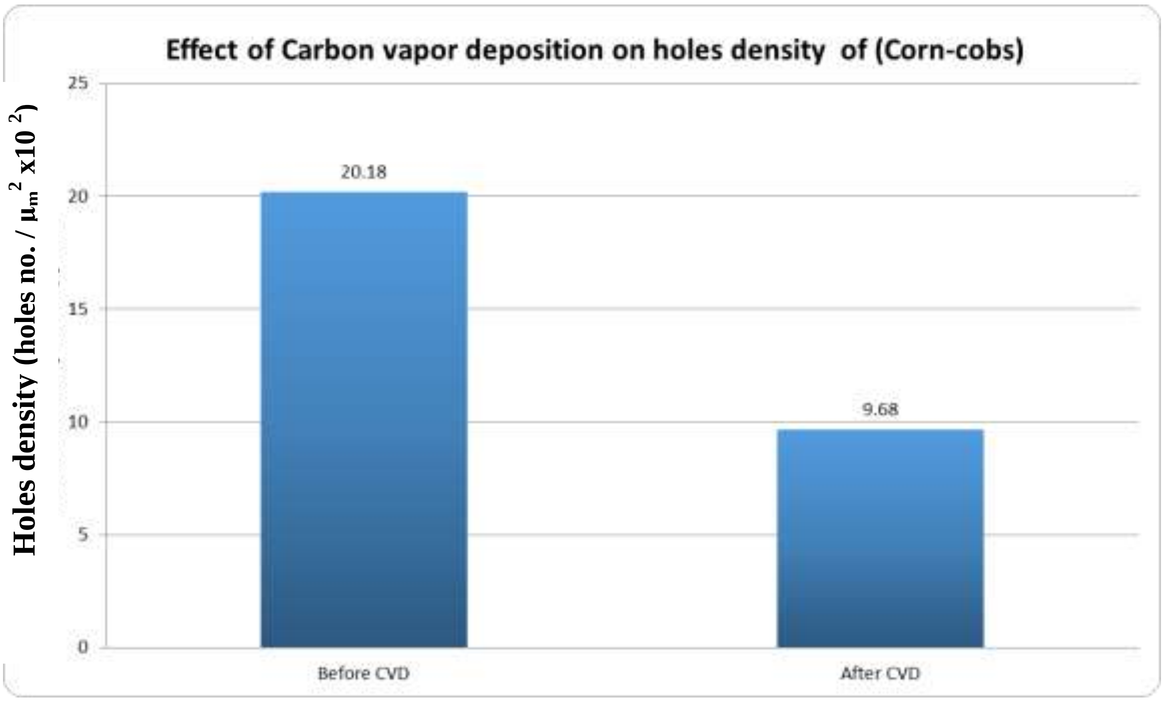


Figure 30: the Effect of carbon deposition on holes' density of corncobs.

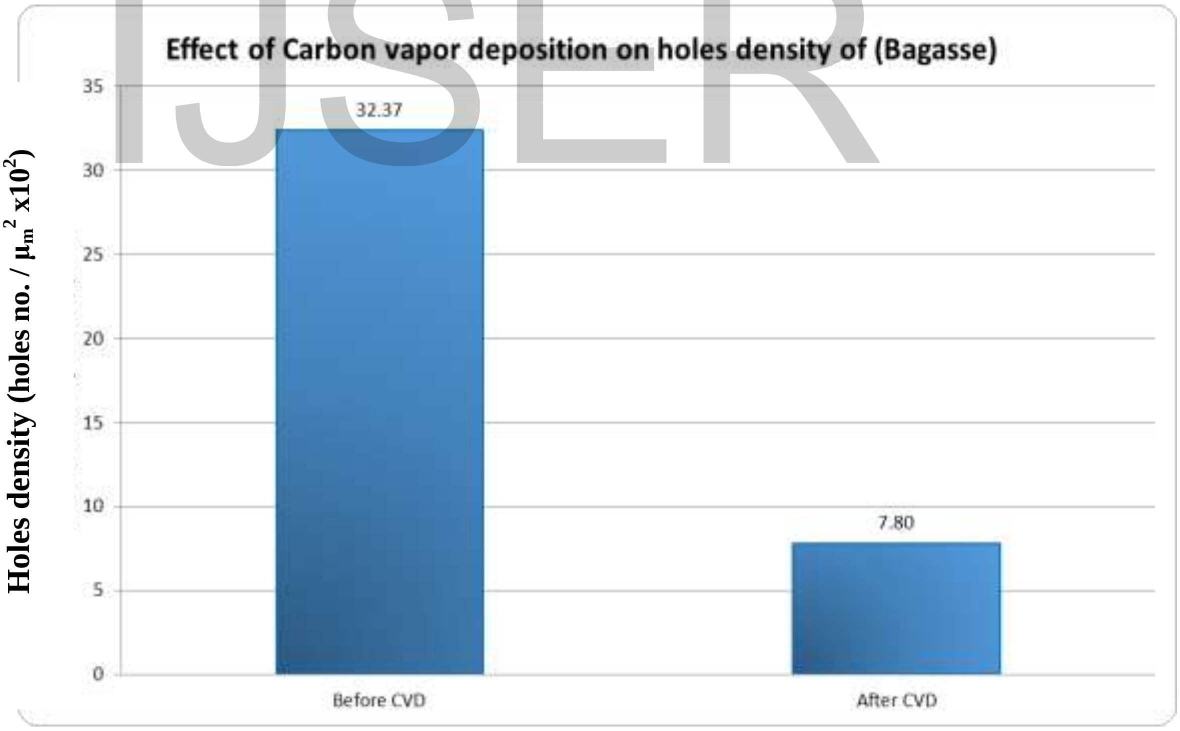


Figure 31: the Effect of carbon vapor deposition on holes' density of bagasse.

III.5. THE EFFECT OF CARBONIZATION TIME ON PORE DIAMETER AND TOTAL PORE VOLUME

III.5.1. The Effect of Carbonization Time on The Average Pore Diameter

Table 12 shows the variations of average pore diameter in each stage during the treatment of Corncobs. It shows the effect of decreasing the carbonization time (from 12 hrs. to 4 hrs) on the average pore diameter. It clarifies that the average pore diameter of corncobs has increased by 53% in the carbonization stage.

This can be attributed to the effect of rapid pyrolysis, with high heating rates that increases the yield of volatiles. Furthermore, slow pyrolysis increases the yield of char. (9) Therefore, when char products increased, the average pore diameter decreased.

Additionally, table 12 shows the variations of the average pore diameter in each stage during the treatment of bagasse, which shows the impact of the decreasing time of carbonization stage (from 12 hrs to 4 hrs) on the average pore diameter. It is clear that the average pore size of bagasse has increased by 41% in the carbonization stage.

This can be attributed to the effect of rapid pyrolysis, with high heating rates that increases the yield of volatiles. Furthermore, slow pyrolysis increases the yield of char. Therefore, when char products increased, the average pore size decreased.

The same results were obtained by C. Pedrero, T. Cordero, J. Rodríguez-Mirasol and J.J. Rodrígue, when they successfully prepared carbon molecular sieves by pyrolytic carbon deposition of benzene over lignin-based chars. They concluded that it is important to control the cracking temperature and time to obtain a carbon molecular sieve with properties suitable for efficient separation of gases such as O_2 from N_2 and CO_2 from CH_4. (31).

In contrary to another research for activated carbon hollow fiber when carbonization time increased, pores began to increase on the surface and had uniform size, 2005 (32).

Table 12: The percentage of change in the average pore diameter resulting from the decreasing treatment time from 12 to 4 hrs.' in corncobs and bagasse during different stages.

Samples	Carbonization Time (hours)	Stages	Av. Pore diameter µm x 10^{-2}	% Change
Corn-cobs	12	Carbonization	4.22	-53%
Corn-cobs	4	Carbonization	9.13	
Bagasse	12	Carbonization	5.74	-41.%
Bagasse	4	Carbonization	9.74	

III.5.2. The Effect of Carbonization Time on Total Pore Volume

Table 13 shows the BET surface area, monolayer volume (V_m) and total pore volume (V_p) of four activated samples after the carbonization step. Comparing the characteristics of the four samples revealed that increasing the carbonization time from 4 to 12 hrs, improved the BET surface area from 36.509 to 66.09 cm^2 g^{-1} (for corncobs) and from 6.24 to 13.94 cm^2 g^{-1} (for bagasse).

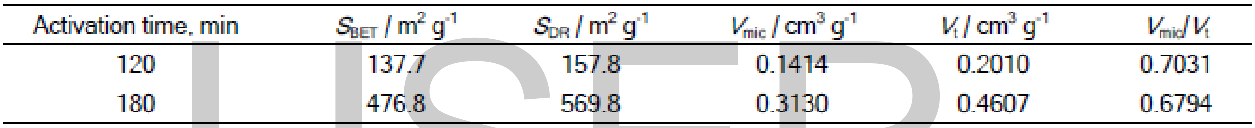
Such improvement in pore diameter structure can be attributed to the opening of previously unreachable pores, formation of new pores and widening of the existing pores in the structure during the carbonization of samples (33). As a result, the micropore and total pore volume of the activated samples increased as the activation time was increased from 4 hours to 12 hours. The porosity of the activated carbon samples was investigated in terms of BET surface area and total volume to decide on the suitable sample for the consequent vapor deposition step after carbonization.

The same effect of time was obtained by Maedeh Mohammadi, Ghasem D. Najafpour and Abdul Rahman Mohamed, when they prepared carbon molecular sieves from palm shells through carbon deposition from methane. Table 14 shows the BET surface area, micropore surface area, micropore volume, total pore volume and microporous fraction of the two activated carbon samples. (5)

Table 13. Characteristics of activated samples during the carbonization steps.

Sample	**Activation Time (hr.)**	**a_{sBET} (m^2 g^{-1})**	**V_m (cm^3(STP) g^{-1})**	**V_P Total pore volume (cm^3 g^{-1})**
Corncobs	4	36.509	0.0167760	0.01844
Bagasse	4	6.2446	0.0143470	0.02004
Corncobs	12	66.09	0.0251830	0.07269
Bagasse	12	13.94	0.0220330	0.02972

Table 14. Textural characteristics of activated carbons. (5)

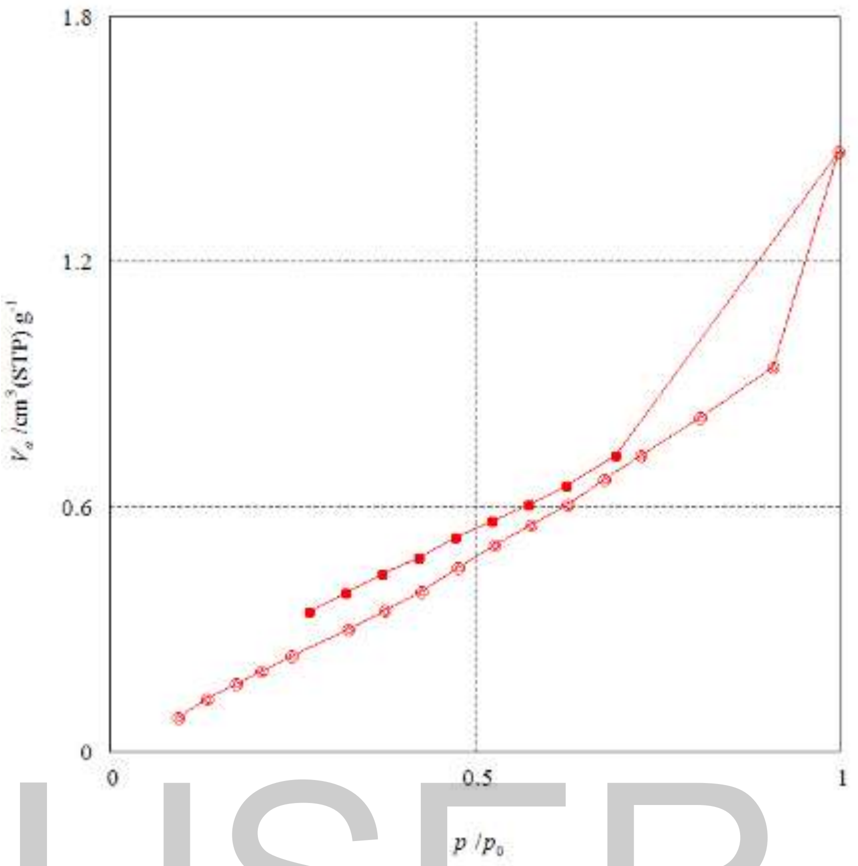


Activation time, min	S_{BET} / m^2 g^{-1}	S_{DR} / m^2 g^{-1}	V_{mic} / cm^3 g^{-1}	V_t / cm^3 g^{-1}	V_{mic}/V_t
120	137.7	157.8	0.1414	0.2010	0.7031
180	476.8	569.8	0.3130	0.4607	0.6794

III.6.CHARACTERIZATION OF CARBONACEOUS SAMPLES AND PRODUCTS

III.6.1.N_2 Adsorption / Desorption on Samples After Carbonization Step

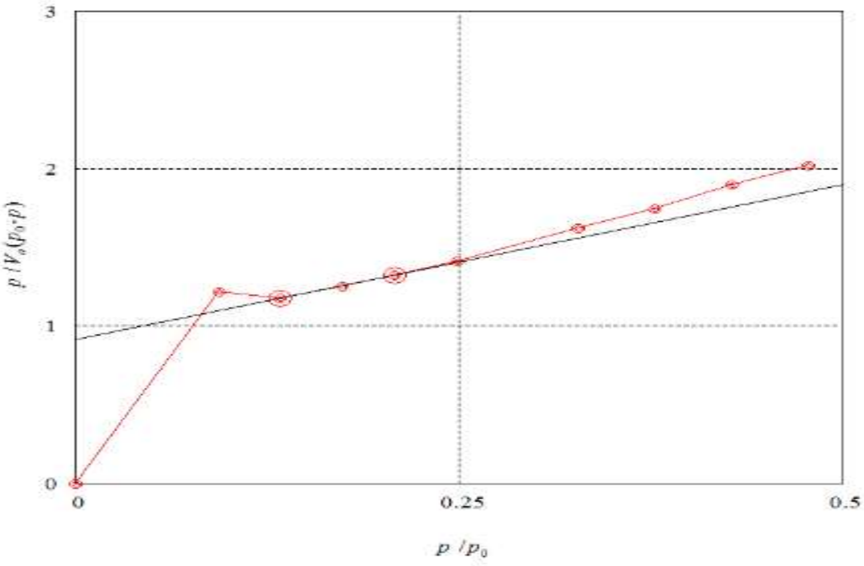
Figures 32 & 33 show Nitrogen adsorption / desorption isotherms and BET plot for two carbonaceous samples Bagasse and corncobs respectively, after the carbonization stage. These adsorption isotherms have low adsorption volume at a relatively low-pressure range, and show a type I adsorption isotherm. From these conditions, it could be concluded that these samples have micropores.



Adsorption / desorption isotherm

Adsorptive N2

Adsorption temperature77.000[K]

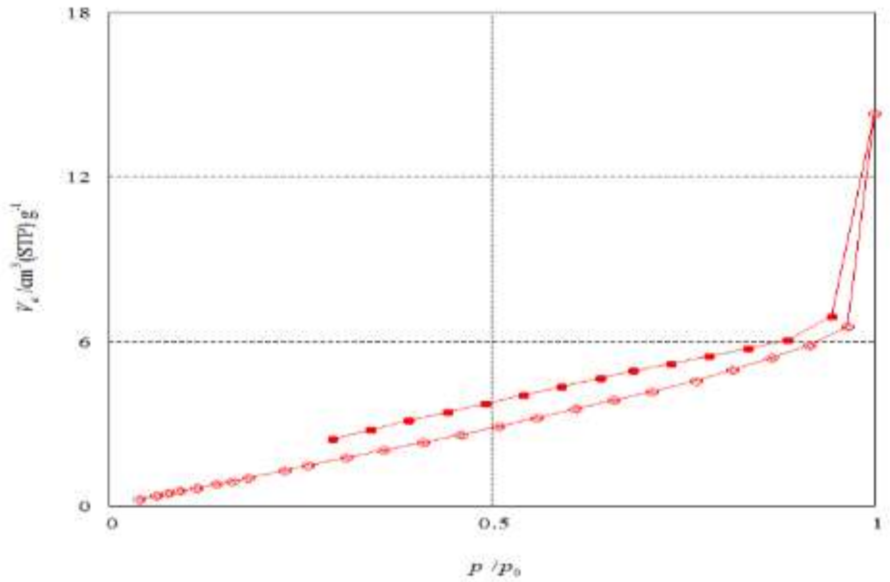


BET-Plot

Adsorptive N2

Adsorption temperature77.000[K]

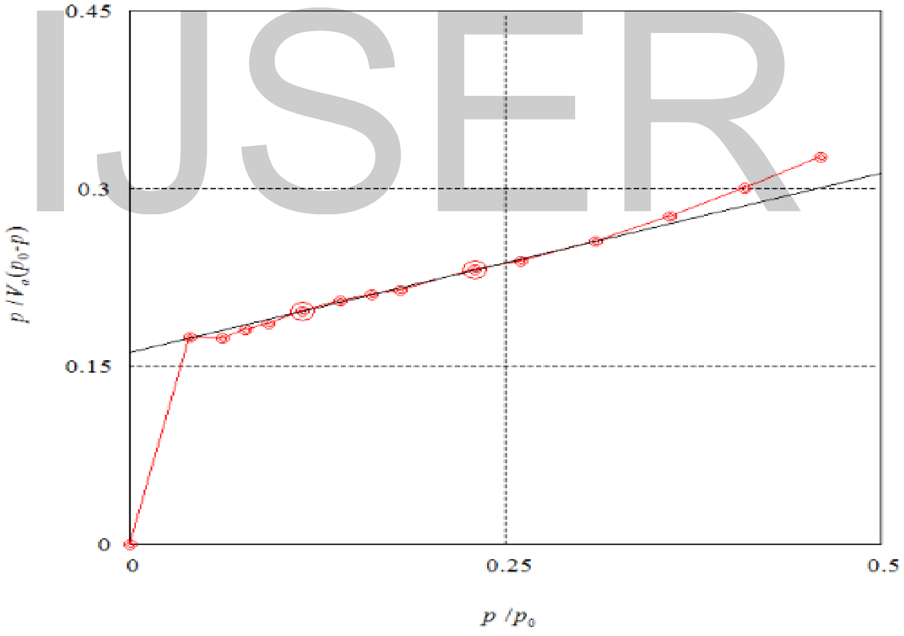
Figure 32. N_2 adsorption/desorption isotherms and BET-Plot of carbonaceous samples for (Bagasse).



Adsorption / desorption isotherm

Adsorptive N2

Adsorption temperature77.000[K]



BET-Plot

Adsorptive N2

Adsorption temperature77.000[K]

Figure 33. N_2 adsorption/desorption isotherms and BET-Plot of carbonaceous samples for (Corncobs).

III.5.2.N_2 Adsorption / Desorption For Bagasse and Corn-Cobs Carbon Molecular Sieves

The pore characteristics of the products were evaluated by N_2 adsorption–desorption and Figures 34 & 35 show the N_2 adsorption/desorption isotherm of the bagasse and corncobs samples after carbon depositions step at 77.00 K. The shape of the isotherm was similar to the International Union of Pure and Applied Chemistry (IUPAC) Type I. Meanwhile, the flat-plateau isotherms reveals the highly microporous structure of the samples. Moreover, as observed, the amount of adsorbed N_2 gradually increased with increasing P/P_0 (<0.95) (20).

It is also observed in figures 34 & 35, that the adsorption and desorption branches of the isotherm form a wide hysteresis loop (open loop) which is associated with the mesopores.

This phenomenon is called “capillary condensation” which is a function of the size and shape of the pores as well as the strength of the interaction between the pore walls and adsorbate (1, 33).

The two branches of the isotherm may be nearly vertical (H1) or parallel (H4) (see figure 7) or an intermediate between the two extremes may occur which represents types H2 and H3. The H1 hysteresis loop is usually formed with spherical agglomerates or particles that show a narrow distribution of uniform cylindrical pores. Some materials with complex pore structure produce H2 type loop in which network and pore blocking effects are important (1,20).

These two types of hysteresis loops are not closed until the equilibrium pressure is close to equal the saturation pressure. The open curves in the hysteresis loops shown in Figures 38 & 39 reflect low-pressure hysteresis, which may be observable down to (the) very low relative pressure. Low-pressure hysteresis may be associated with the change in (the) volume of the adsorbent, such as; the swelling of non-rigid pores or with the irreversible uptake of molecules in pores of about the same width as that of the adsorptive molecule. Additionally, chemisorption will also lead to such "open" hystereis loops (20).

In the case of H4 hysteresis loop, the pore size distribution is mostly in the micropore range. The hysteresis loops generated by the samples are very similar to H4 type, indicating that micropores are dominant in the structure of adsorbents (20).

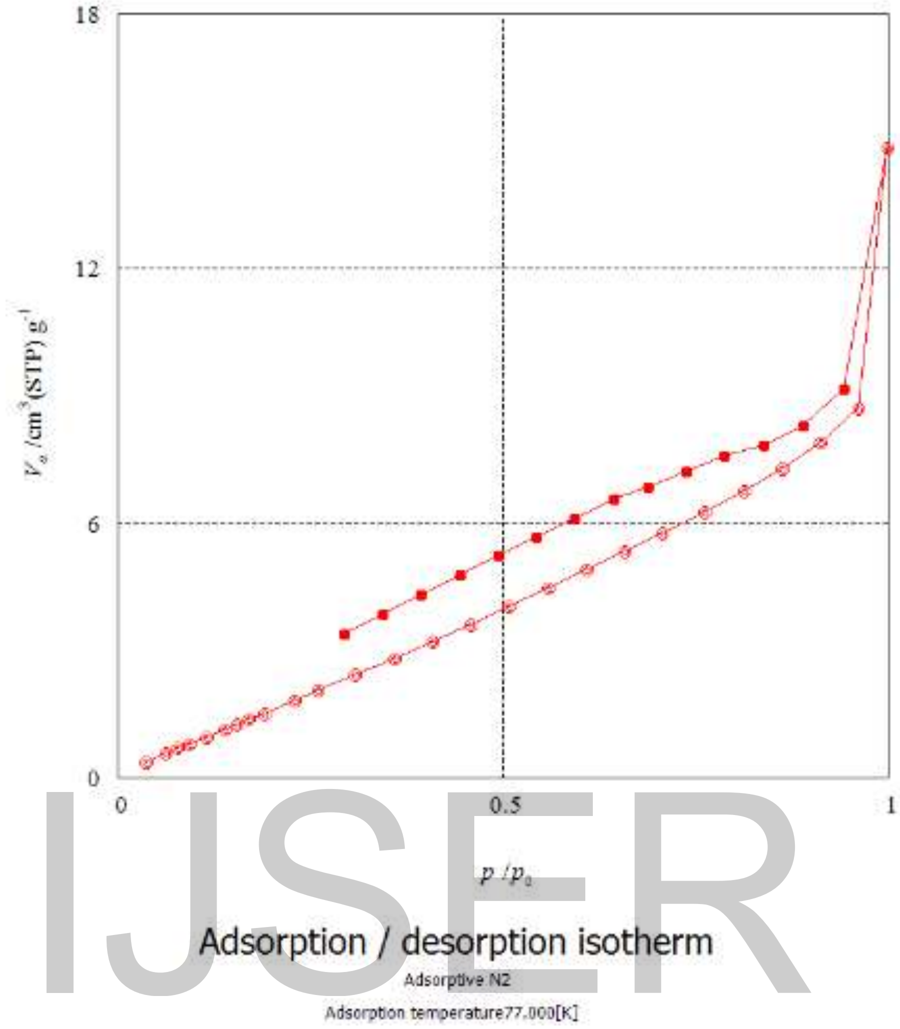


Figure 34. N_2 adsorption/desorption isotherms of carbon molecular sieves samples (Bagasse).

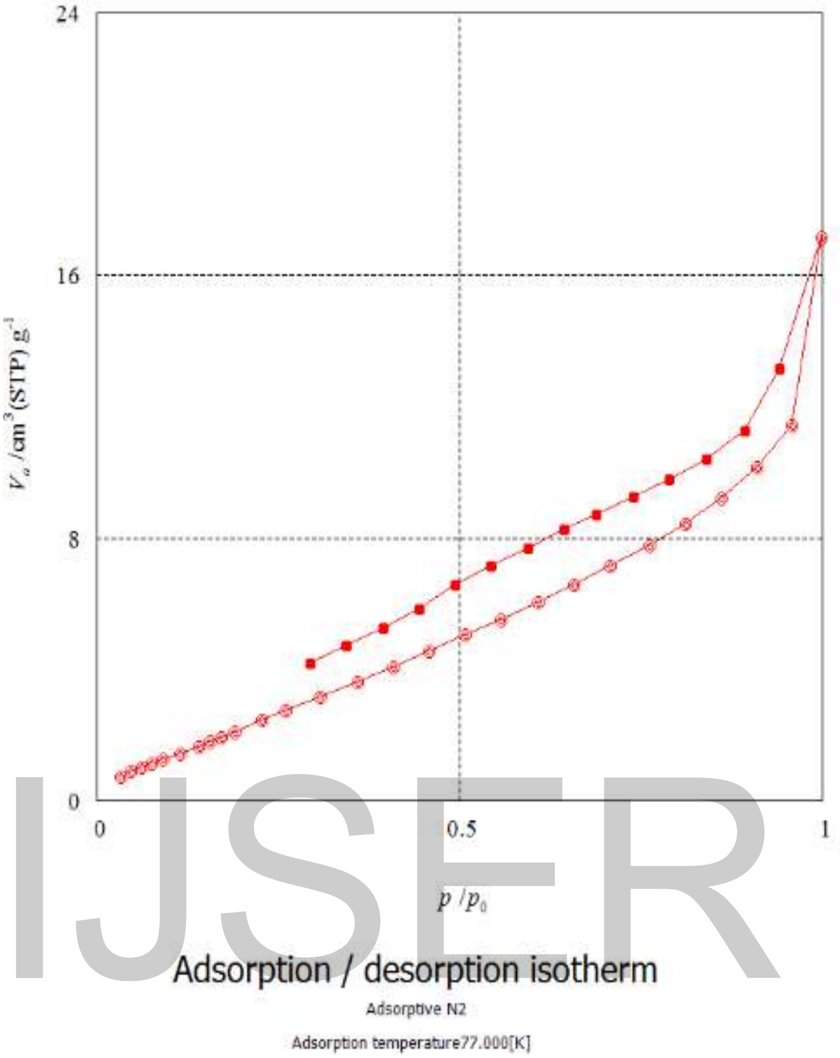


Figure 35. N_2 adsorption/desorption isotherms of carbon molecular sieves samples (Corncobs).

III.5.3.Characterization of Corncobs And Bagasse Carbon Molecular Sieves

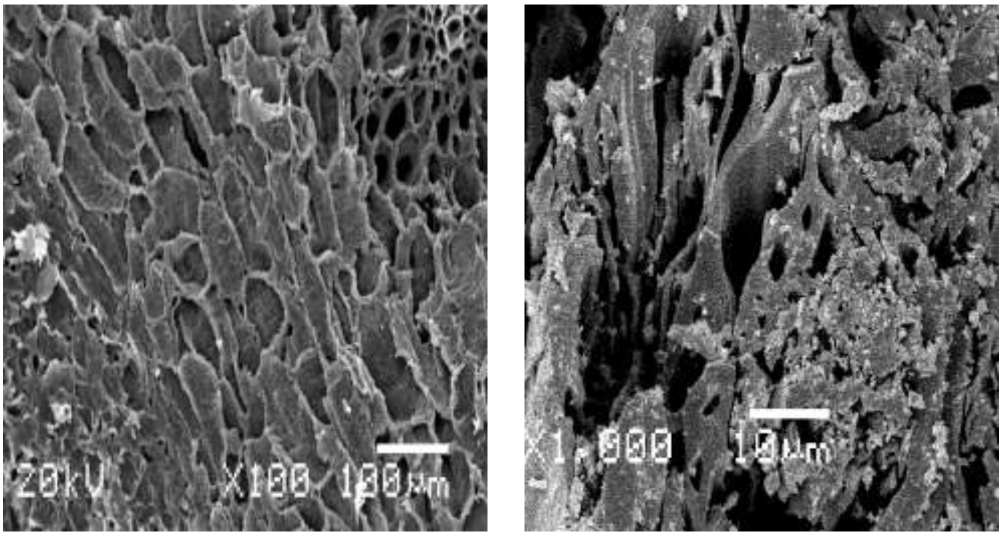
Table 15 shows the characterization of Corncobs and Bagasse carbon molecular sieves. The average pore diameter of corncobs (0.41 µm x 10^{-2}) approximately the same as bagasse (0.58 µm x 10^{-2}). In contrast, the total pore volume for corncobs (6.76 cm^3 g^{-1}) which shows a better capacity than that of bagasse (2.76 cm^3 g^{-1}). Furthermore, the holes' density of corncobs is (9.68 holes/$µm^2$ x10^2) which is better than that of bagasse (7.80 holes/$µm^2$ x10^2).

Table 15: shows the characterization of carbon molecular sieves (Corncobs and Bagasse).

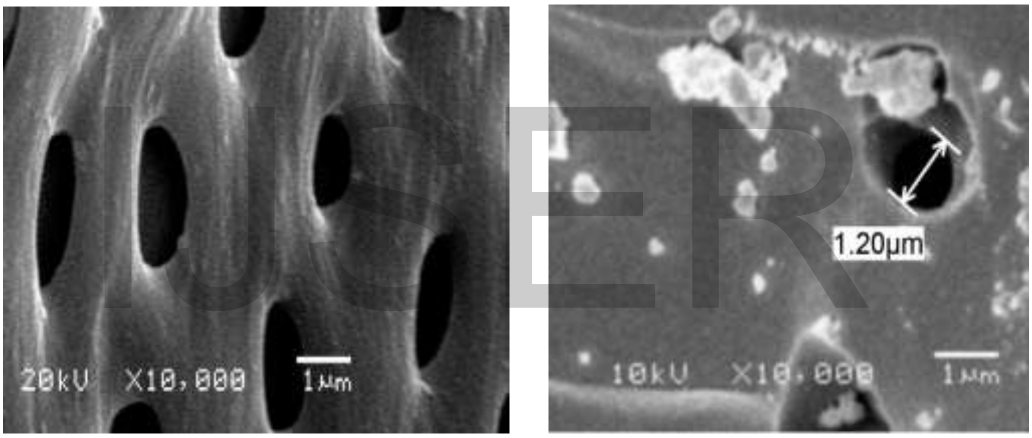
Samples After Treatment	**Av. Pore diameter µm x 10^{-2}**	**V_P Total pore volume (cm^3 g^{-1})x10^{-2}**	**Av. holes density (no. holes/$µm^2$ x10^2)**
Corncobs	0.41	6.76	9.68
Bagasse	0.58	2.76	7.80

III.6.2. SEM IMAGES.

Figure 36 shows representative SEM images of the Bagasse and corncobs products after LPG treatment (Carbon deposition). As observed in figure 36(a), the products featured large particles with a wide size distribution in the range of ∼5–20 μm, with non-spherical, randomly truncated shapes. Observation of the product surface at a higher magnification revealed that small carbon amorphous nanoparticles are organized accordingly to form an aggregated structure figure. 36(b). Randomly dispersed voids with sizes of less than 2 μm were additionally observed.



a) i) Bagasse ii) Corncobs



b) i) Bagasse ii) Corncobs

Figure 36 SEM images of Bagasse and corncobs after carbon deposition at (a) low and (b) high magnifications.

III.7. CALCULATION OF YIELD

Table 16 shows the yield in each stage to produce carbon molecular sieves from corncobs. Moreover, this table shows that the net yield is 5.89%. The carbonization stage led to the highest losses, which have reached 87.82% because at the initial time of carbonization, the corncobs loses its volatile components and water vapor in this stage. After that, the chemical stage has high yield of 90.76% by alkaline attack. Finally, the carbon deposition stage yields 53.33%, because of the losses of the water in pores after the washing step in chemical treatment. Hence, it was assumed to exclude this stage from the total yield because the deposition process by LPG adds carbon molecules to pore, so the weight should increase. Therefore, if we exclude losses in the carbon deposition stage from the total calculation, the total yield recalculated will be 11.05 %.

Table (16): Shows the losses and yield from corncobs

CornCobs			
Steps	**Stages**	**Losses %**	**Yield % of the stage**
1	**Carbonization**	87.83	12.17
2	**Chemical treatment**	9.23	90.77
3	**Carbon Deposition**	46.67	53.33
	Net Yield	3.78	5.89
	Cumulative Yield without step 3		**11.05 %**

Table 17 shows the yield in each stage to produce carbon molecular sieves from bagasse. In addition to this, this table shows that the net yield is 4.13% (less than that of corncobs, whose percentage was 5.89%).

The carbonization stage led to the highest losses, which reached 76.96% because at the initial time of carbonization, the bagasse loses its volatile components and water vapor in this stage. At the same time, if the result of corncobs is compared to that of the bagasse in this stage, the losses in bagasse are lower by 12.36%. This can be attributed to the amount of volatile components in bagasse that is lower than that of corncobs, which is the result of the composition of the bagasse. It contains a higher percentage of Lignin and lower percentage of hemicelluloses when compared to corncobs. Hemicellulose gives rise to more volatiles components. (30)

After that, the chemical stage gave a yield of 50.47% by alkaline attack. The losses are greater than the losses in the same stage in the case of corncobs, whose percentage is 9.23%. This may be attributed to the fracture of the fragile structure of bagasse into loose fine particles during the alkaline treatment.

Finally, the carbon deposition stage gave a loss of 64.39% because of the losses of water in the pores after the washing step in the chemical treatment. Hence, it was assumed to exclude this stage from the total yield (because the deposition process by LPG adds carbon molecules to pores, so the weight should increase). Therefore, if the assumption of excluding losses in the carbon deposition stage from the total calculation is considered, the net yield will be 11.62 %, which is approximately equal to the yield resulting from corncobs (11.05%).

Table (17): Shows the losses and yield from bagasse.

Bagasse			
Steps	**Stages**	**Losses%**	**Yield% of the stage**
1	**Carbonization**	76.97	23.03
2	**Chemical treatment**	49.52	50.48
3	**Carbon Deposition**	64.4	35.60
	Net Yield	24.55	4.14
	Net Yield without step 3		**11.62 %**

III.8. THE COMPARISON OF AVERAGE PORE DIAMETER AND HOLES' DENSITY RESULTS FROM DIFFERENT SOURCES

III.8.1. The Comparison of Average Pore Diameter

Figure 37 shows the variations of average pore size of the final product of both samples (Corncobs and Bagasse) compared to the activated carbon obtained from traditional market. The average pore diameter obtained from corncobs and bagasse is lower by 92.6% and 89.6% respectively, compared to the activated carbon from traditional market. This confirms the increase of the selectivity of the new products (Corncobs and Bagasse) as compared to the existing activated carbon obtained from traditional market. In addition to that, the average pore diameter in new products is controlled by carbon deposition to produce smaller pore size.

III.8.2. The Comparison of Average Holes' Density.

Figure 38 shows the variation of holes' density of the Corncobs and Bagasse compared to the activated carbon obtained from traditional market. It is clear from this figure that the average holes' density of samples Corncobs and Bagasse are lower by 25.6% and 40.0% respectively, when compared to the activated carbon from traditional market. This could decrease the capacity of the Corncobs and Bagasse as compared to the existing activated carbon from traditional market.

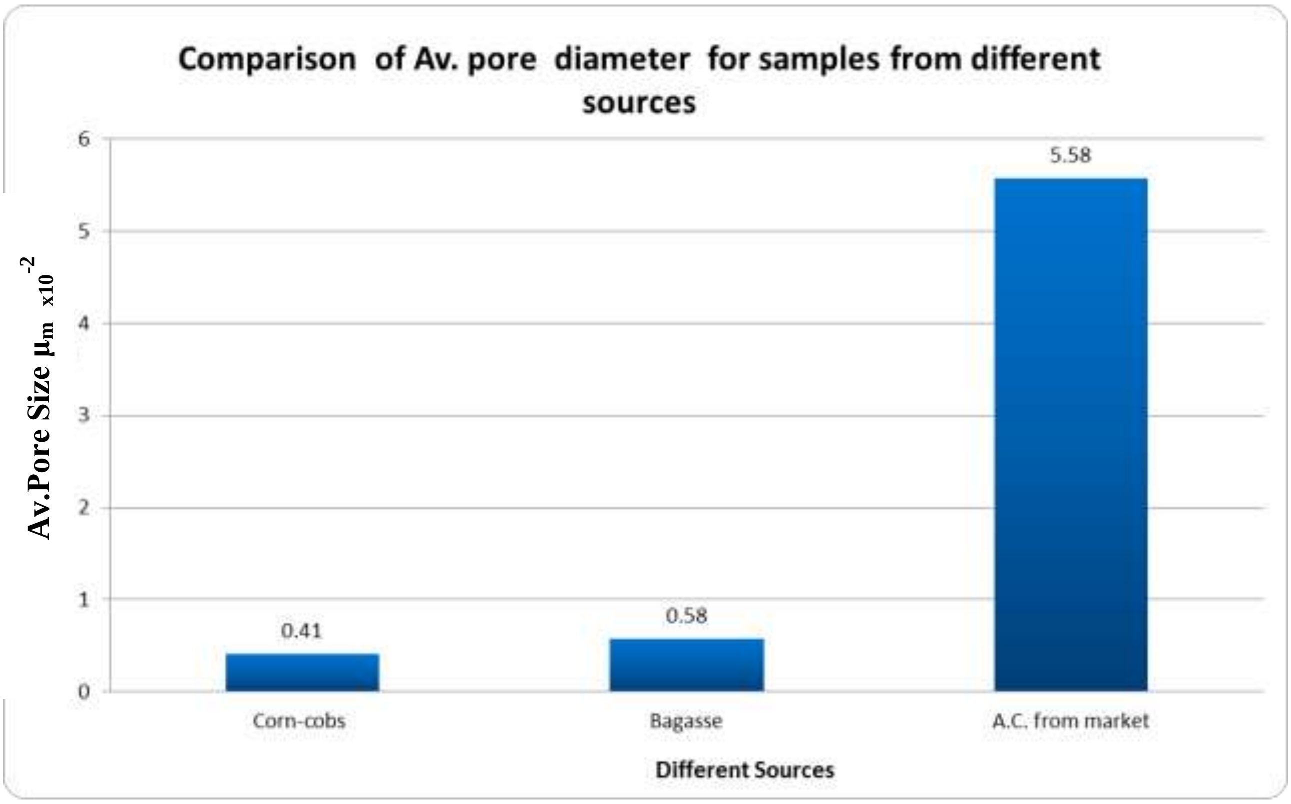


Figure 37: Comparison of the average pore diameters for samples obtained from traditional market.

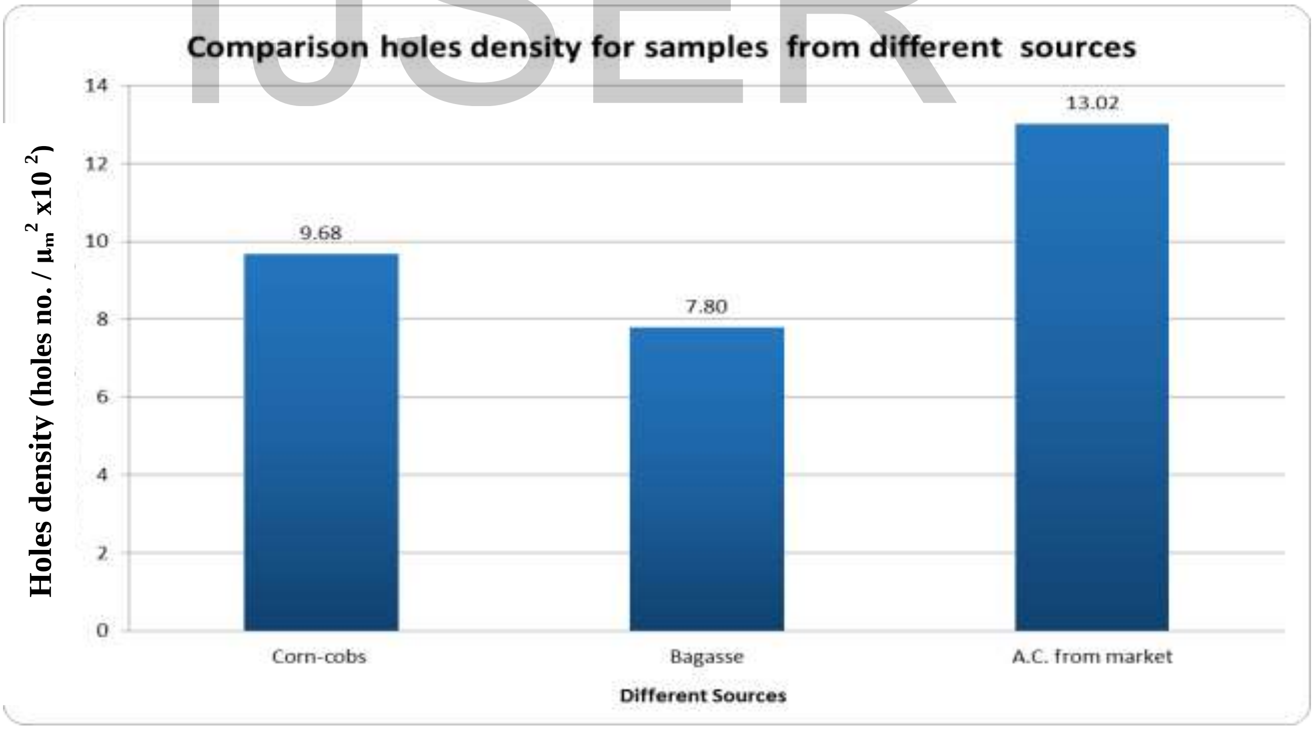


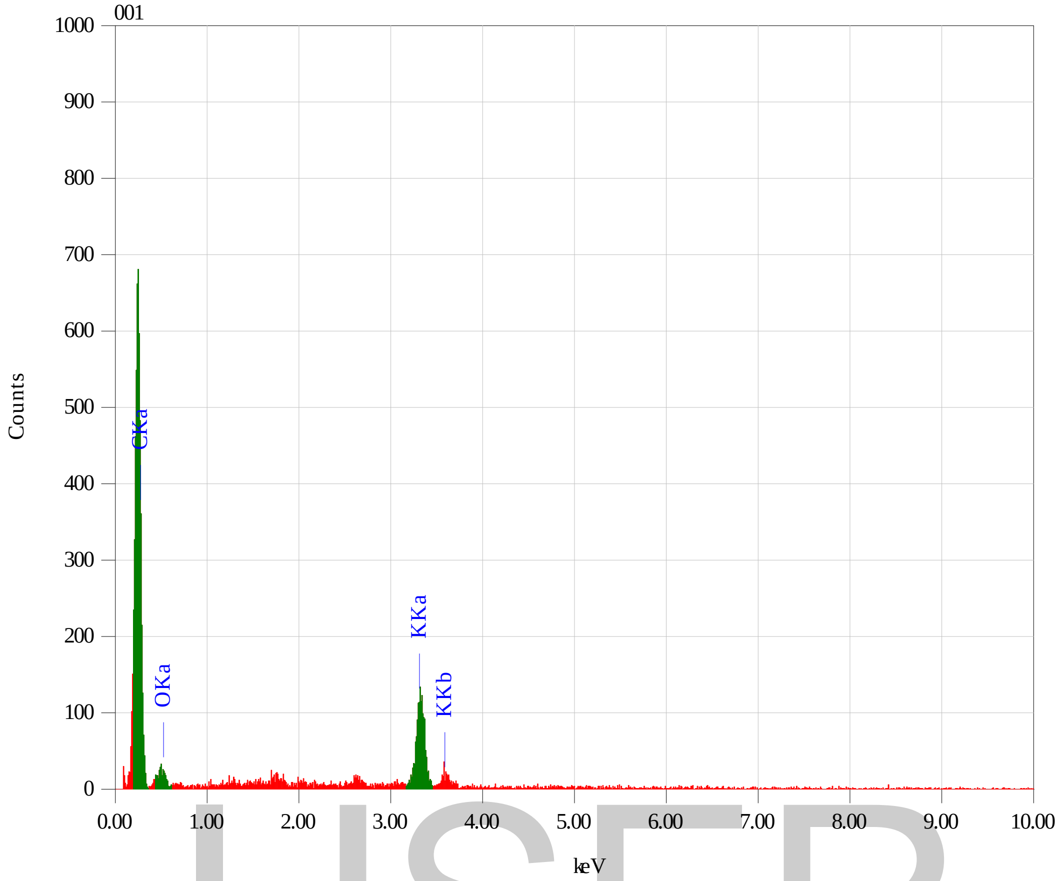
Figure 38: Comparison of holes' density obtained from samples from traditional market.

III.9. THE COMPARISON OF FINAL CARBON CONTENT OF CORN-COBS AND BAGASSE

Figure 39 shows the Edex analysis for products from Corncobs. It is clear from the analysis that the mass percentage in corncobs is carbon 67.90%, Oxygen 17.56% and Potassium 14.55%. The Potassium element could be adsorbed during the chemical treatment stage (Chemisorption reaction), therefore it was difficult to desorb it during the washing and the neutralization stages.

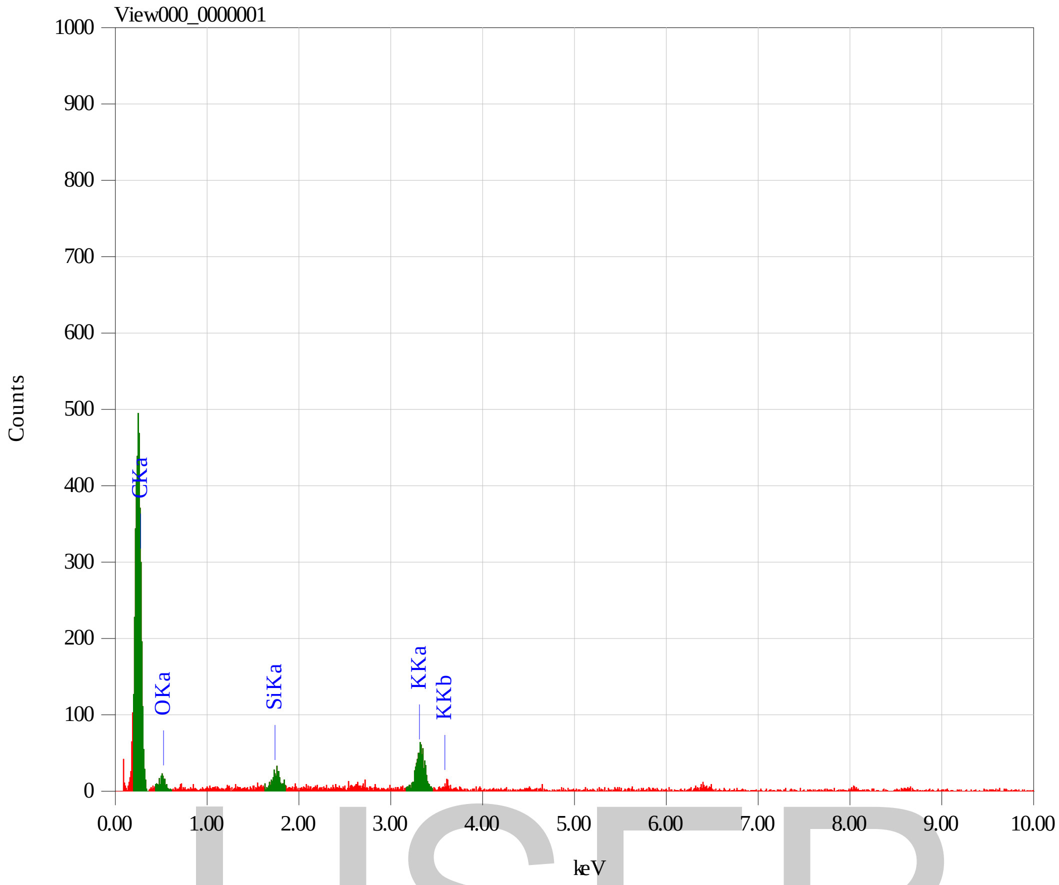
Figure 40 shows the Edex analysis for products from bsgasse. It is clear from the analysis that the mass percentage in corncobs is carbon 74.54%, Oxygen is 17.05% and Potassium 6.82%, Silicon 1.60%. The Potassium element could be adsorbed during the chemical treatment stage (Chemisorption reaction) but in a lower percentage than that of corncobs, therefore it was difficult to completely desorb during the washing stage.

Also, figures 39 and 40 show that the carbon percentages in bagasse increased by 8.9% than the percentage in Corncobs during the Carbon deposition stages.



Element	Mass%
C K	67.90
O K	17.56
K K	14.55
Total	100.00

Figure 39: The Edex analysis of the carbon molecular sieves from CornCobs.



Element	Mass%
C K	74.54
O K	17.05
Si K	1.60
K K	6.82

Figure 40: The Edex analysis of the carbon molecular sieves from Bagasse.

III.9. ECONOMIC EVALUATION

It was found that the total cost, including fixed (experiment setup cost such as heater cylinder) and operating cost (such as electric and gas used), of CMS production from waste agriculture (Bagasse or Corncobs) is $7330/ton, according to the laboratory scale data. In addition to this, it was found that the production on industrial scales is less than the production on laboratory scale by 40%. Therefore, the expected cost on the industrial scale will be:

0.6 * $7330 = $4398/ton.

In fact, the average price of CMS in the market is $7200/ton. As a result, the profit based on one-year deprecation to produce 365 tons/year is equal to:

$7200-$4398 = $2800/tons.

And from the definition of the return on investment (ROI);

ROI **= (**Net Profit **/ Cost of** Investment**)** x **100**

ROI = $2800 ÷ $4398 = 63% (±15% error) when using bagasse or corncobs for production CMS which is shown below in table 18

Table 18: Economic Evaluation

Laboratory Scale cost (pilot Scale)	**Industrial Scale**	**Avg. Market Price of CMS**	**Benefit (Gains) based on one year deprecation period to produce 365 tons/year**	ROI ±15% error
7330 $/ton	4398 $/ton	7200 $/ton	2800 $/ton	63%

CHAPTER IV

IV. CONCLUSIONS AND RECOMMENDATIONS

IV.1.CONCLUSIONS

- Preparation of CMS from bagasse and corncobs was investigated through some consequent heat treatment processes including carbonization, physical activation and CVD from LPG. The average pore diameter of CMS obtained from corncobs is (0.41 μm x 10^{-2}) while that obtained bagasse was (0.58 μm x 10^{-2}). In contrast, the total pore volume for corncobs is (6.76 $cm^3\ g^{-1}$) which means higher capacity than for bagasse (2.76 $cm^3\ g^{-1}$). Furthermore, the holes' density of corncobs was (9.68 holes/μm^2 x10^2) which i) better than for bagasse (7.80 holes/μm^2 x10^2).
- The effect of carbonization temperature and carbonization time, as two important process parameters on microporosity development of CMS, is determined at (350, 750, 850 °C) and carbonization time of 4~12 hours.
- The Scanning analysis of the CMS samples explored the successful deposition from LPG on pores of corncobs and bagasse-derived activated carbon and was found to yield a microporous CMS with a narrow pore size distribution.
- **The experiments showed the following results:**

  a) For average pore diameter of bagasse and corncobs:

    i) It decreased at low temperature during carbonization step.

    ii) It increased after Chemical Treatments.

    iii) It decreased after carbon vapor deposition technology (CVD) using LPG

  b) For holes density of bagasse and corn-cobs:

    i) It Increased at higher temperature (≥ 350 °C) during Carbonization Step.

    ii) It increased after being chemically treated

    iii) It decreased after carbon vapor deposition (CVD) technology using LPG

c) The effect of the carbonization time:

i) Increasing the carbonization time decreased the average pore diameter of corncobs and bagasse.

ii) Increasing the carbonization time there is improved in the BET surface area.

iii) The total pore volume of the activated samples increased when the carbonization time was increased from 4 hours to 12 hours.

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d) The shape of the isotherm obtained from corn-cobs and bagasse was similar to the International Union of Pure and Applied Chemistry (IUPAC) Type I.

- The net yield results from bagasse is 11.62 % and the net yield from corncobs (11.05%). Finally, the production of CMS from agriculture waste (bagasse and corncobs) has shown that the average return on investment (ROI) is around 63% (±15%) at a production rate of 365 tons/year.

V.2.RECOMMENDATIONS.

- Further study to investigate the effect of various concentrations of chemical vapor deposition (CVD) to control pore size and increase microspores volumes.
- Further study to investigate the effect of various heating rate and another method of activation such as microwave to improve the selectivity of CMS
- Further study to improve physical properties such as strength and hardness by controlling the carbonization time

CHAPTER V

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ملخص

يعتبرمصاصه قصب السكر منتج ثانوي من صناعات استخلاص السكر. وتنتج مصر حوالي 600 ألف طن مصاصة سنويا (التي تشارك بنحو 4.6٪ من إجمالي النفايات الزراعية السنوية في مصر) و 3450 ألف طن سنويا من قوالح الذرة. وتستخدم هذه النفايات فى الوقت الحالى كوقود للغلايات او يتم استخدامها كمواد خام لتصنيع الورق او كمواد تغذيه للحيوانات ويعتبر ثلث الناتج من هذه النفايات عبئ علي البيئة المحيطة. ويعتبر المكون الرئيسي لمصاصه القصب و قوالح الذرة هو السليلوز، هيميسيلولوز، واللجنين .

ان الغرض الرئيسي من هذا العمل هو انتاج المناخل الجزيئيه الكربونيه من المخلفات الزراعيه ذات القيمه الاقتصاديه المنخفضه وذلك من خلال عمليه سحق وطحن هذه المواد ثم اتباع عمليه الانحلال الحرارى (الكربنه) عند درجات حراره مختلفه فى وجود غاز خامل ثم تتبع هذه العمليه عمليه تنشيط كميائى وفيزيائى باستخدام هيدروكسيد البوتاسيوم.

وتم اجراء عمليه ترسيب ذرات الكربون الناتج من الغاز البترولي المسال على الاجزاء المساميه لمصاصه القصب و قوالح الذره وقد تم ايضا عمليه دراسه التاثير الزمنى للكربنة (4 ساعات و12 ساعه) وكذلك تاثير درجات الحراره المختلفه للكربنة (وهى 350 -750-850 درجه سيليزية) على متوسط قطر المسامى وحجم المسام ومتوسط كثافه المسام للعينات وبالاضافه الى ذلك ثم استخدام تكنولوجيا ترسيب بخار الكربون الناتج من تحلل الحرارى للغاز البترولي المسال (والتى لم تستخدم من قبل) لتطوير المساميه والسيطره على متوسط حجم المسام والكثافه العدديه للمسام. ويقاس التغير الذي حدث في الخصائص السطحية بواسطة المجهر الإلكتروني ونظام امتصاص الغاز باستخدام طريقة برونور-إيميت-تيلر.

وتتكون التجربة من العينات من مصاصه القصب و قوالح الذرة المعالجه مبدئيا من قبل حيث يتم ادخالها فى سخان اسطوانى من الفولاذ المقاوم للصدأ ثم يتم عمليه امرار غاز خامل (نيتروجين) مسخن لبعض الوقت ويلى هذه العمليه معالجة كميائية وفيزيائية وتستخدم اجهزه للتحكم فى ضغط السخان ومعدل التدقيق ودرجه حراره ومعدل رفع درجة حرارة العينات حيث تصل درجه حراره العينات فى نهايه التجربه الى 850 درجه سيليزية .

وأظهرت التجارب النتائج التالية:

أ) بالنسبة **لمتوسط قطر المسام** عينات كلا من مصاصة قصب السكر و وقوالح الذره:

1.بزيادة درجة الحرارة يقل قطر المسام وذلك خلال خطوة الكربنة.

2. متوسط قطر المسام يزداد بعد المعالجة الكيميائية.

3.متوسط قطر المسام يقل بعد استخدام تكنولوجيا ترسيب بخار الكربون باستخدام غاز البترول المسال

ب) بالنسبة **للكثافة العددية للمسام** في عينات كلا قصب الذرة وقوالح الذره:

1. تزداد في درجة حرارة أعلى (≤ 350 درجة مئوية) خلال خطوة الكربنة.

2. تزداد بعد المعالجة الكيميائية لعينات كلا قصب الذرة وقوالح الذره

3. تقل بعد ترسيب بخار الكربون باستخدام غاز البترول المسال

ج) **تأثير زمن الكربنة** في عينات كلا قصب الذرة وقوالح الذره:

1. أدت زيادة زمن الكربنة إلى انخفاض متوسط قطر المسام مع كلا من مصاصة القصب وقوالح الذره.

2.انه بزيادة زمن الكربنة يحدث تحسن في المساحة السطحية.

3. ازداد حجم الكلي للمسام للعينات عند زيادة زمن الكربنة من 4 ساعات إلى 12 ساعة.

.هذا وقد نتج عن التجارب المعملية تحسن ملموس للعملية الانتقائيه الامتزازيه لعينات مصاصه القصب و قوالح الذرة.

- وبلغت نسبة المناخل الجزيئة الكربونية الناتجة بعد تلك المعالجات حوالي 11.62٪ من اصل مصاصة القصب وحوالي 11.05٪ من اصل قوالح الذره وأخيرا، تم إجراء دراسة إقتصادية مبدئية لتلك العملية لانتاج المناخل الجزيئة الكربونية واتضح منها ارتفاع نسبة العائد علي الاستثمار في تلك الصناعة. سنويا .

مستخلص مختصر

المناخل الجزيئيه الكربونيه هى مواد مازه كربونية، حيث يبلغ القطر المتوسط للمسام 10 أنجستروم أو أقل. ويعتبر من اكثر التطبيقات شيوعا لهذا النوع من المناخل الجزيئة الكربونية هو استخدامه كمواد مازه فى تكنولوجيا فصل الغازات.

وقد تم بنجاح إنتاج هذه المناخل الجزيئيه الكربونيه عاليه القيمه الاقتصاديه من المخلفات الزراعيه مثل مصاصة القصب وقوالح الذره (للمرة الأولى)، وذلك من خلال عمليات المعالجه الحراريه باستخدام فرن تقايدى وعمليات تنشيط الفيزوكميائى ويتبعها عمليات ترسيب الابخره الكميائيه باستخدام غاز البترول المسال (للمره الاولى)

وعلاوة على ذلك، لقد اجريت تجارب لترسب الكربون (الناتج من التحلل الحراري لغاز البترول المسال) على العينات الكربونية المنتجه من مصاصه القصب وقوالح الذرة بحيث نجحت عمليه تقليل قطر المسام للعينات الكربونية المنتجة.

وقد أظهرت الدراسات التجريبية تأثير العوامل المختلفة (درجة حرارة الكربنة وزمن مرحلة الكربنة) على متوسط قطر المسام، وعلى الحجم الكلى للمسام ، ومتوسط كثافه المسام للعينات (مصاصه القصب و وقوالح الذرة) .

ويقاس التغير الذي حدث في الخصائص السطحية بواسطة المجهر الإلكتروني ونظام امتصاص الغاز باستخدام طريقة برونور-إيميت-تيلر.

وقد تم دراسه تأثير درجة حرارة الكربنة وزمن الكربنه ، كعمليتين رئيسيتين لعملية الحصول و تطوير التركيب الميكروبوروسيتي للمناخل الجزيئيه الكربونيه وذلك فى درجات حراره متغيره وهى (350، 750، 850 أوك) وزمن الكربنة فى خلال 4ساعات و 12 ساعة.

وقد اظهرت عمليات المسح المجهرى الضوئى للعينات نجاح عمليه ترسب ذرات الكربون على العينات (مصاصه القصب و وقوالح الذرة) وتبين انه ينتج مواد ذات مسام دقيقه جيدة الخواص.

وكانت النواتج النهائية المنتجه من المخلفات الزراعيه ذات خواص مساميه جيده حيث ان متوسط قطر المسام الناتجة من قوالح الذرة (0.41 ميكرون × 10^{-2}) ومن مصاصة القصب هو (0.58 ميكرون × 10^{-2}). وبالإضافة إلى ذلك، فإن الحجم الكلي للمسام في لقوالح الذرة (6.76 سم ^{3} /جرام) أفضل من مصاصة القصب (2.76 سم ^{3} /جرام). وقد أثبتت النتائج التي تم الحصول عليها في هذه الدراسة أن اختيار مصاصه القصب و وقوالح الذرة هواختيار مناسب لإنتاج المناخل الجزئيه الكربونيه ذات القيمة الاقتصادية العالية.

وبلغت نسبة المناخل الجزيئة الكربونية الناتجة بعد تلك المعالجات حوالي 11.62٪ من اصل مصاصة القصب وحوالي 11.05٪ من اصل قوالح الذره وأخيرا، تم إجراء دراسة إقتصادية مبدئية لتلك العملية لانتاج المناخل الجزيئة الكربونية واتضح منها ارتفاع نسبة العائد علي الاستثمار في تلك الصناعة.

جامعة الاسكندرية
ALEXANDRIA
UNIVERSITY

دراسة في انتاج المناخل الجزيئة الكربونية واستخداماتها"

رسالة علمية

مقدمة الى قسم الهندسة الكيميائة بكلية الهندسة – جامعه الاسكندرية

استيفاء للدراسات المقررة للحصول على درجة

دكتوراه الفلسفة

فى

الهندسة الكيميائة

مقدمة من

الطالب/ مصطفي محمد عزت محمود المنسي

يوليو 2017