

Studies on Development of Porosity in Carbon from Different Types of Bio-wastes

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Abstract

The regional bio-wastes available in abundance in India were converted into porous carbon by heat treatment at different temperatures from 650-950°C. The wood retain shapes after pyrolysis though shrinkage occurred both in axial and radial directions. The shrinkage in radial direction was found to be more than in axial direction in all woods. The density of woods and chars from these at a given temperature has been found to follow linear relationship. Chars were steam activated at temperature 700-800°C for different times between 45-240 min. Both the temperature and time of activation with steam has a profound effect on surface area. Chars from softwoods like bagasse and castor oil plant were activated at lower temperature, *i.e.* 700-750°C whereas hard wood chars have to be activated at higher temperature around 800°C. The morphology of wood as well as of chars has been studied by SEM. The comparison of the two showed that the nature of porosity in chars depends on precursor morphology, nature and physical state of wood and presence of inorganic compounds in the wood. Hard wood results in cross inter connected pores while softwood leads to fibrillar structure. The present studies show that activated carbon with reasonably good surface area (~1000 m²/gm) can be prepared from soft wood bio-wastes like bagasse and castor oil plant, while surface area ~1370 m²/gm was achieved from hard wood bio waste of pine wood

Keywords : Porous carbon, Pyrolysis, Porosity, BET surface area

1. Introduction

Activated carbon are one of the most important types of industrial carbons widely used in various sectors such as environment protection against both gaseous and liquid pollutants, pharmaceutical, energy production, domestic appliances as well as in a large variety of consumer based industries. Each application requires activated carbons of specific characteristics such as surface area, porosity and pore size distribution and adsorption characteristics. For adsorption from gas phase mainly microporous carbon is used whereas mesoporous carbon is used for liquid phase adsorption. These carbons are produced virtually from any carbonaceous solid precursor both naturally occurring such as coconut shell [1], almond shell, grape seed [2], walnut shell [3] and various fruit stones [4, 5] or synthetic precursor such as rayon, phenolic resins and PAN etc. [6, 7]. The nature of precursor and method of activation, both have strong influence on the porous structure and adsorption capacity of resulting activated carbon. Though new synthetic precursors such as polymeric fibers [8, 9] are being used to produce activated carbon with high surface area, feed stock of biological origin are still the major raw materials for commercial activated carbons. Wood is most abundantly available cellulosic material obtained from all types of plants. In some cases, it is hard while in other cases it is of soft texture

and highly porous. Whatever may be the type of wood, on pyrolysis, porous char is obtained. In general the chars is not reactive and reactivity is incorporated by activation and thus char is then converted into activated carbon.

Interest in wood of different texture is on regional basis and is primarily aimed at utilizing cheap and abundantly available vegetation and bio-wastes to produce low cost activated carbon. Present work has been undertaken in this institute to study the pyrolysis of wood from castor oil plant (*saccharum affcinarum*), sugarcane bagasse and babbool (*acacia arabico*) and their activation. Pinewood has also been included for comparison. The pyrolysis behaviour of wood from these plants, microstructure of the chars prepared from these woods, their surface characteristics and nitrogen adsorption characteristic have been correlated with the type, composition and texture of wood.

2. Experimental

2.1. Raw Materials and Treatment

Castor oil plant wood, babbool, sugarcane bagasse and pinewood were used for the present studies. These materials except bagasse were cut in to 2.5 cm. long specimen and dried in controlled way at 100°C. These dried pieces were then used as precursor for obtaining char and activated car-

bon.

Pyrolysis of the samples was carried out in muffle type furnace. In all series, the samples were heated at a rate of 30°C/hr. up to desired end temperature and held at maximum temperature for 2 hrs. Cooling was done at a rate of 60°C/hr. Shrinkage of the samples during pyrolysis was monitored by taking physical dimensions both before and after pyrolysis.

Char from castor oil plant wood, sugarcane bagasse, babbool and pinewood were activated at 700-800°C for 45-240 min. using steam as activating agent.

2.2. Characterization of samples

Thermogravimetric analysis of the samples was carried out using Mettler TA 4000 thermal analysis system at heating rate of 10°C/min. Elemental analyses was carried out on Perkin-Elmer 2400 CHN analyzer with acetanilide as standard. Chars were characterized for bulk density, ash content and dimensional shrinkage.

BET surface area of the samples was measured on Micromeritics Gemini 2375 Surface area analyzer. The samples were cleaned prior to measurement by heating the samples at 300°C for 24 hrs. under continuous flow of argon. The morphology of the chars as such as well as after activation was studied using HITACHI S3000N SEM.

3. Results and Discussion

3.1. Pyrolysis behaviour of different precursors

3.1.1. TGA studies

Pyrolysis behaviour of dried precursors was studied using thermogravimetric analysis. Fig. 1 shows TGA plot of these samples in nitrogen. All samples show broadly four domains of weight loss in almost similar temperature ranges but differing in peak temperature and amount of weight loss. The

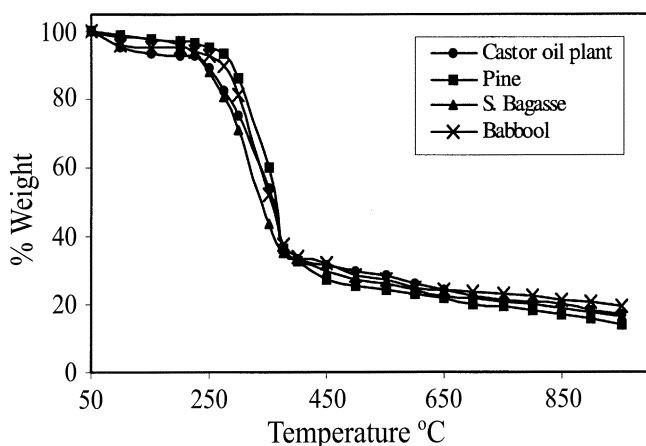


Fig. 1. Thermogravimetric analysis (TGA) of different precursor in N₂.

Table 1. Percentage yield, ash and carbon content of chars prepared at 950°C

Sample	% Yield	% Ash	% Carbon
Pine	24.59	0.38	24.20
Castor oil plant	26.90	1.58	25.32
Sugar can bagasse	26.90	1.72	25.18
Babbool	27.26	1.26	26.00

first weight loss occurs around 100-150°C due to desorption and evolution of water molecule. It is more pronounced in castor oil plant wood. In pine and babbool wood the weight loss starts at higher temperature. Next steep weight loss in all samples is observed between 250-370°C. This, as proposed by Tang and Bacon [10], is due to splitting of cellulosic structure, chain scission and breaking of some carboxyl, carbonyl bonds etc. in the ring structure evolving water, CO and CO₂. Weight loss in higher temperature region (500-900°C) is due to polycondensation, molecular rearrangement and formation of carbon structure.

3.1.2. Yield and ash content

The yield of carbon at 950°C and ash content for different precursors is given in Table 1. The %yield is minimum for pinewood while all other precursors on pyrolysis yield almost same amount of carbon at 950°C. The ash content in babbool, castor oil plant and bagasse is around 1%, while in pine the ash content is lower than 1%. It contains less inorganic compounds as compared to other wood.

3.1.3. Physical changes during pyrolysis

Fig. 2 shows shrinkage in axial as well as in radial direction of castor oil plant, babbool and pinewood. As seen from Fig. 2, though in all chars the shrinkage increases with increase in pyrolysis temperature, these show different pattern. Babbool wood shows lower shrinkage than castor oil plant and pinewood in all temperature regions. Castor oil plant wood exhibit higher shrinkage both in axial and radial direction in the temperature range 650-750°C. This is due to molecular rearrangement and structural transformation taking place in this temperature range. Babbool wood with hard and dense morphology result in overall lower pyrolysis shrinkage than other woods. The radial shrinkage in all three samples is found to be higher than axial shrinkage. The dimensional changes taking place during carbonization relates to the original cellular structure of wood. The wood is comprised of elongated tubular cell referred as longitudinal cell or fiber grown in axial direction. The low molecular weight organic polymers like cellulose and hemicellulose are present within the boundary of cell walls. On carbonization, depending upon the temperature of heat treatment, the cellulose and hemicellulose gradually loose tarry products making the boundary walls shrink and finally get converted into

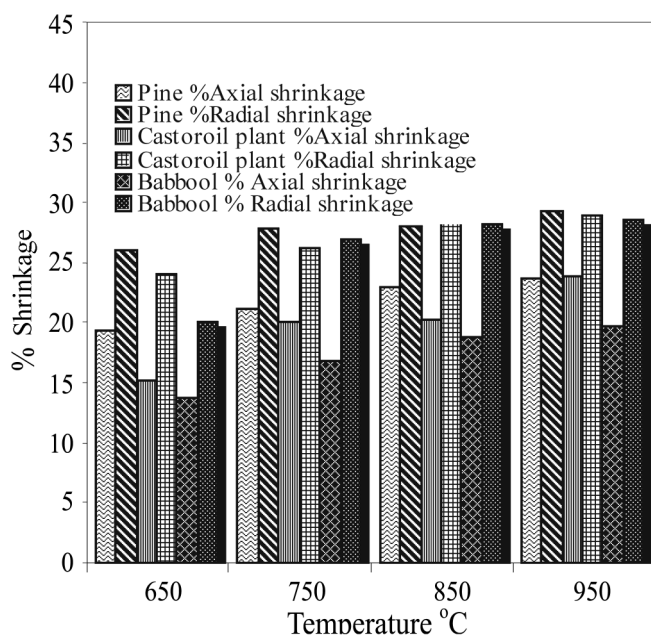


Fig. 2. Shrinkage in principal directions for pine, castor oil plant and babbool wood at different HTT.

carbon. The walls shrink more in transverse direction than longitudinal direction thus radial shrinkage on carbonization is comparatively higher than axial shrinkage. The shrinkage behaviour of bagasse was difficult to study because of its fibrous nature.

Density of chars obtained from different precursors is plotted against density of original wood precursors and is shown in Fig. 3. It shows that a definite linear relation exists between the wood density and density of its char obtained at particular temperature under similar pyrolysis conditions.

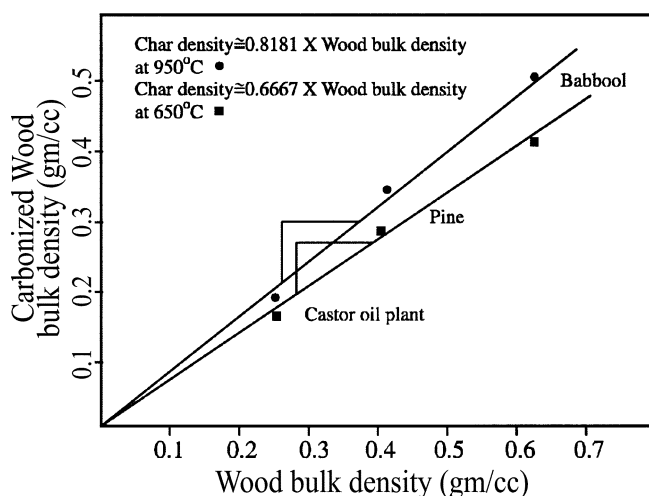


Fig. 3. Bulk density of chars from pine, castor oil plant and babbool wood at 650°C ◆ and 950°C ●.

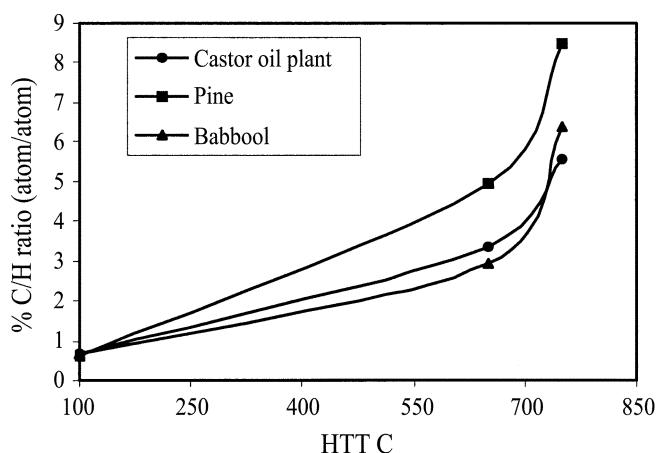


Fig. 4. C/H ratio of castor oil plant, pine and babbool wood as a function of HTT.

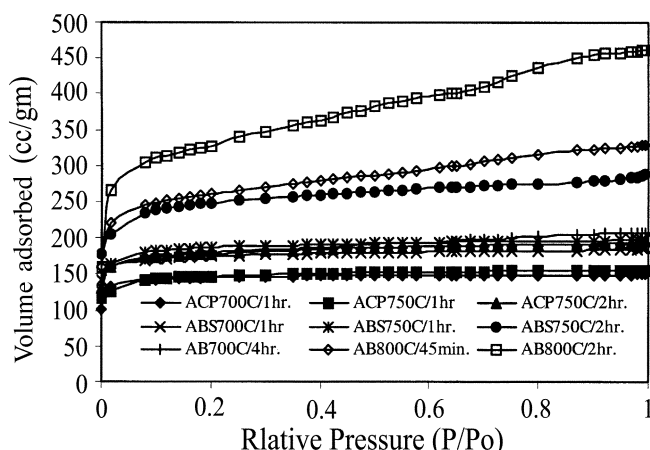
With rise in pyrolysis temperature, the slope of this linear relation increases. Generally, char yield and pyrolysis shrinkage are function of pyrolysis temperature, pressure, time and atmosphere. Alteration of one or more of these parameters can affect the slope and resulting carbonized wood bulk density. It agrees with the results reported by Nagle and Byrne [11] for other types of wood.

3.1.4. Elemental analysis

Fig. 4 shows C/H ratio of dry wood as well as of chars obtained from castor oil plant, babbool and pinewood. As the pyrolysis temperature increases, C/H ratio also shows an increase. This increase is more for samples heated to temperature higher than 600°C. Corresponding to the removal of hydrogen containing volatiles and condensation reactions leading to long C-chain molecules. As seen from Fig. 4, though C/H ratio of pinewood is same as that of castor oil plant and babbool wood but these are different for the pyrolysed mass. C/H ratio of pyrolysed pine is higher than for those from babbool and castor oil plant pyrolysed to the same temperature. It means that latter still contain hydrogen. In castor oil plant and babbool wood the evolution of hydrogen and hydrogen containing volatiles continue till higher temperature. It suggests that castor oil plant and babbool wood undergo slow pyrolysis as compared to hard pinewood.

3.2. Surface area analysis

Surface area of all the samples was measured by nitrogen adsorption at liquid nitrogen temperature. The nitrogen adsorption isotherms for castor oil plant, bagasse and babbool wood are given in Fig. 5. All isotherms are of type I showing microporous nature of the solids. However, the shape of the isotherm is found to change with steam activation. As the activation temperature and time are raised there is an opening of the knee of the isotherms with more gradual



ACP: Activated castor oil plant wood AB: Activated babbool wood ABS: Activated bagasse

Fig. 5. Adsorption isotherm of N_2 at 77 K on activated carbon.

approximation to the plateau. This change is usually associated with widening of microporosity.

Surface area of chars and steam activated carbons is given in Table 2. On activation, the surface area of all samples increases irrespective of nature of wood. The increase is observed to be nearly two folds for castor oil plant activated at 700°C for 60 minutes, while for bagasse this increase is small, nearly one and half fold. In castor oil plant and bagasse if the temperature of activation is increased from 700 to 750°C keeping the time of activation constant at 60 min., the increase in surface area is very small *i.e.* 20-40 m^2/gm . However, at activation temperature of 750°C, if the time of activation is increased from 60 to 120 min., the surface area increases by about 250 m^2/gm for castor oil plant and

110 m^2/gm for bagasse. In castor oil plant and bagasse the time of activation is found to have pronounced effect on surface area. In case of pinewood the results are very interesting. The pyrolysed pinewood at 650°C does not show measurable adsorption of nitrogen. Though on carbonization, pinewood also shows weight loss amounting to formation of porous structure, but the pores formed do not seem to be accessible for adsorption. May be volatiles formed on heat treatment clogg the pores making these unaccessible to adsorption. On activation this char at 800°C for 45 minutes, activated carbon having high surface area of 1370 m^2/gm was obtained. The total pore volume in pinewood is found to be 1.14 cc/gm while for the other two, the value is much lower. In case of babbool the increase in surface area is observed to be nearly three fold on activation under optimized condition. By increasing the temperature of activation from 700 to 750°C at constant time of activation (240 minute) the surface area is found to increase from 687 to 842 m^2/gm . By increasing the temperature of activation to 800°C and time of activation from 45 to 120 minute, the surface area is found to increase from 987 to 1226 m^2/gm . Further, by comparing the values in Table 2, one finds that the temperature of activation has more pronounced effect on the development of surface area. Surface area of babbool carbon activated at 800°C for lower time is much higher than of those produced at 700 to 750°C for longer time. Thus on activation with steam, the increase in surface area depends on temperature and time of activation but more on the nature and physical state of wood. The harder the wood, more is the increase in surface area on activation with steam.

3.3. SEM studies

Fig. 6(a, b, c and d) show SEM micrographs of the chars at 650°C obtained from different precursors. As seen from

Table 2. Surface properties of pyrolysed and activated chars from different precursor

Sample	HTT °C	Pyrolysis Yield %	Surface area m^2/gm	Activation temperature °C	Activation time min.	Burn off %	Surface area m^2/gm	Avg. pore diameter nm	Total pore volume cc/gm
Castor oil plant	650	29.58	323	Steam 700	60	32	590	1.9	0.289
				Steam 750	60	35	631	1.93	0.305
				Steam 750	120	62.5	863	2.10	0.445
Bagasse	650	28.90	314	Steam 700	60	16	480	1.9	0.234
				Steam 750	60	20	511	1.88	0.24
				Steam 750	120	30	620	2.0	0.30
Pine	650	26.32	–	Steam 800	45	85	1370	3.3	1.14
Babbool	650	34.20	201	Steam 700	240	33.68	687	1.6	0.31
				Steam 750	240	90	842	3.1	0.66
				Steam 800	45	70	987	2.02	0.51
				Steam 800	120	75	1226	2.2	0.70
				Steam 800	180	98.5	–	–	–
				Steam 800	240	ash	–	–	–

these figures, all these chars have different pore morphologies. Chars from castor oil plant, babbool and bagasse show big size pores surrounded by small pores of varying cross sections. These pores are of equisize in castor oil plant and babbool char and of varying size in bagasse char. Moreover, these pores are seen to be partially blocked at places. It is more in babbool char than for others. Accordingly, babbool char exhibit lower surface area than castor oil plant and bagasse chars.

Fig. 7(a, b, c and d) shows SEM micrographs of the activated chars. As seen from this figure activation with steam results in widening up of the pores. Cross-interconnected pores are also seen in activated castor oil plant wood, babbool and bagasse chars (Fig. 7a, 7b and 7c). These cross-interconnected pores might be present in pyrolysed chars as well but in blocked form and get cleared during steam activation. Contrary to these, pine chars shows macropores of uniform morphology. Fig. 6d and 7d show pore structure of pine wood chars. This structure is retained even after activation.

4. Conclusion

Pyrolysis behaviour and ultimate pore structure of chars depend on the morphology and physical state of the precursor, hard or softwood.

Bio-waste such as castor oil plant, babbool and bagasse are potential precursors for activated carbon. Steam activation of their chars under suitable conditions produce activated carbon of high surface area and highly developed porous structure with very small average pore diameter.

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