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ENHANCEMENT OF MICROPOROSITY THROUGH PHYSICAL ACTIVATION

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ABSTRACT

Micro porous carbons are used for the sorption/separation of light gases, where as the carbon with broad pore size is applied for removal of large organic molecules. In this work activated carbon was prepared from natural material pine wood. Pine wood monoliths were carbonized in inert nitrogen atmosphere for different intervals of times. To enhance the surface area and to develop interconnecting porosity, the pyrolysed monoliths were activated with steam at different flow rates of steam under identical conditions. It was found that flow rate of steam has profound effect on both surface characteristic and surface morphology. Surface characteristic were determined by BET method and surface morphology was seen by using SEM (scanning electron microscope). Further the flow rate of steam was optimized to retain monolith structure as well as higher surface area.

Key words: *Wood, Pyrolysis, Physical Activation*

INTRODUCTION

Activated carbon adsorbs molecules from both liquid and gaseous phases depending upon the pore size and pore size distribution of the adsorbent. For adsorption from gas phase, mainly micro porous carbon is used whereas, meso porous carbon is applied in liquid phase process. In general both large surface area and wide pores are desirable. Large surface area allows large adsorption amounts and wide pores enhance diffusion, which influences the overall kinetics of adsorption. Two general methods are used for the preparation of activated carbon [1-3] One, the "physical activation", consists of heating at a high temperature with steam gasification reactant e.g. H_2O, CO_2, O_2. The other method, "chemical activation", consists of heating at a relatively lower temperature (e.g. 500^0C) with addition of dehydration agent. (e.g. H_3PO_4).

According to Jagtoyen M. and Derbyshire [4], and Benaddi H et al, [5] chemical activation of wood by phosphoric acid is an useful technique for obtaining activated carbon having low cost due to low heat treatment temperature but the main disadvantage of this process is the loss of some of the activating agent on the char which results in changes in surface chemistry. It has been noted that high specific surface area and favorable pore structure of activated carbon contribute to effective contaminant sequestration [6, 7] and on the other hand, surface chemistry of activated carbon also plays key roles in adsorption mechanisms and behaviors [8, 9]. All these attributes depend on the activation agent, activation temperature and activation time.

The production of activated carbon with desired pore size distribution and surface chemistry from low cost precursor and at low a temperature is an important challenge. However, the control of pore sizes in the synthesis of activated carbons is an important aspect but not much literature is available. For a good pore development, the reaction should occur inside the pores and it must have an appropriate rate compared to the diffusion of reactants and products. [10- 12] Therefore, in the present work rate of flow of steam during activation was controlled quantitatively to study variation of pore size, micro porosity, pore volume, surface area and also surface morphology. Also this study could helps in producing desired pore size and porosity for specific applications.

MATERIALS AND METHODS

Pine wood was shaped and dried for 2-4 days and subsequently, carbonized under inert nitrogen atmosphere at 750^oC for 6 hour in an electrically heated furnace with slow heating rate 10^oC/hr up to 350^oC, 15^oC/hr up to 550^oC and higher rate of 20^oC/hr up to peak temperature, resulting in a crack free bio carbon template (charcoal). After pyrolysis, percentage axial, radial and tangential shrinkages were 28.47, 20.93, and 11.9 respectively. Pine wood contains 24.2% carbon and 0.38% of ash. After pyrolysis, samples were activated at 750^oC in a steam atmosphere having controlled steam rate (Fig 1) to increase their surface area and micro porosity. Fig.1 is the schematic of physical activation process. The dried sample of pine wood was placed in the heating zone of electric furnace in nitrogen atmosphere. With the help of syringe pump the flow rate of steam was controlled. The smooth flow of steam and nitrogen mixture through the sample was observed by the out coming gases in to the bubbler. The thermal characterization (TGA) was carried out by using Mettler TG 50. The thermal analysis was carried out in nitrogen atmosphere at 950^0C. The surface area of samples was determined by using BET 2375 (Micromeritics-Gemini) apparatus. The structure of raw, carbonized and activated wood was observed using scanning electron microscope (SEM), Hitachi S-3000N.

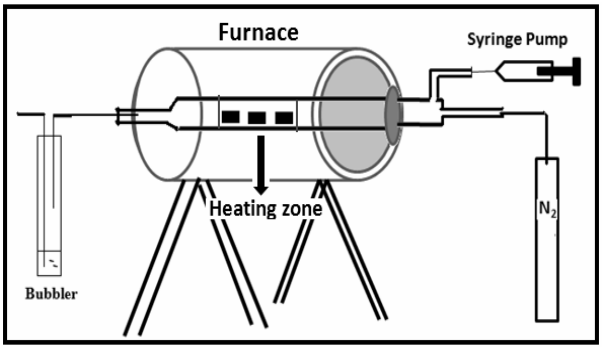

Fig. 1 Schematic representation of physical activation process

RESULTS AND DISCUSSION

CARBONIZATION OF PINE WOOD

In the conversion of wood into carbon, the following stages are included: (a) desorption of adsorbed water up to 150^0C, (b) splitting off of cellulose structure water between 150 and 240^0C [13], (c) formation of hydrocarbon structure formed through the chain scissions, or depolymerization, and breakdown of C– O and C– C bonds within ring units evolving water, CO and CO_2 between 240 and 400^0C, (d) formation of

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aromatic polynuclear structures at 400^0C and gradual development continued above 500^0C [14], (e) occurrence of aromatic reactions yield network shrinkage to accommodate the excessive volume left by the evolving gases between 400 and 800^0C, (f) formation of thermal induced decomposition and rearrangement reactions leaving a carbon structure above 800^0C. Detailed pyrolysis behavior of pine wood was explained in an earlier paper. [15]

SURFACE AREA ANALYSIS BY BET METHOD

Macro pore enable the molecule of the adsorbate to pass rapidly to smaller pore situated deeper within the particles. The adsorption in macro pore is insignificant, while the micro pore have large internal surface area and contributes significantly to adsorption. Since the average micro pore area increase due to activation process, adsorption capacity of carbon also gets increased. The pyrolysed samples were activated with steam at 750^0C for one hour with different flow rate of steam varying between 0.1-0.7 ml/min. Above 0.7ml/min steam rate causes breaking of the surface material (fig.5c). The activated samples were characterized for surface area, microporosity and average pore diameters. The results are shown in Table 1.

Table - 1 Physical properties of activated carbon derived from pine wood under different steam rate.

Sr. No	Input steam rate (ml/min)	Activation temperature (°C)	Activation time (min)	% micro pore area (m^2/gm)	Average Pore diameter (nm)	Surface area (m^2/g)
1	0.1	750	60	90.56	1.65	497.697
2	0.3	750	60	87.17	1.76	654.73
3	0.5	750	60	86.50	1.78	710.45
4	0.7	750	60	79.87	1.92	721.28

Fig.2 shows nitrogen adsorption isotherms if activated carbons with different flow rate of steam. All samples show type I adsorption isotherms, i.e. micro porous carbon. The volume of nitrogen adsorbed is seen to be increasing with increase in steam flow rate, being highest for sample activated by 0.7ml/min and minimum for sample activated by steam at flow rate of 0.1 ml/min. With increase in flow rate of steam, micro pore area and average pore diameter show interesting results. The percentage micro pore area decrease due to widening of pore as a result the pore diameter increase from 1.65nm to 1.92nm or increasing the flow rate from 0.1ml/min to 0.7ml/min.

The comparison of surface characteristic of activated carbons complied in table 1 further show an increase in surface area with increasing flow rate of steam, while percentage micro porosity decreases with increasing flow rate of steam during activation process. Also surface area of activated carbon increase with increasing flow rate of steam. Steam rate having 0.3ml/min gives 654.73 m^2/g as surface area and 0.5ml/min gives 710.45 m^2/g as surface area.

SEM

The micrograph of as such pine wood is shown in fig 3a. It shows a porous network. But the pores are not clear. These contain certain cellulosic products. On pyrolysis, the wood gets decomposed into smaller molecules, while the walls of the struts retain their morphology. The filled mass gets highly decomposed resulting in clear pore structure (Fig 3b). The fig 4 (a) shows well distributed pores in activated carbon with flow rate of 0.1ml/min. With increasing flow rate, not only the original voids get enhanced but the carbon constituting the walls of the pores get removed resulting in formation of new pores.

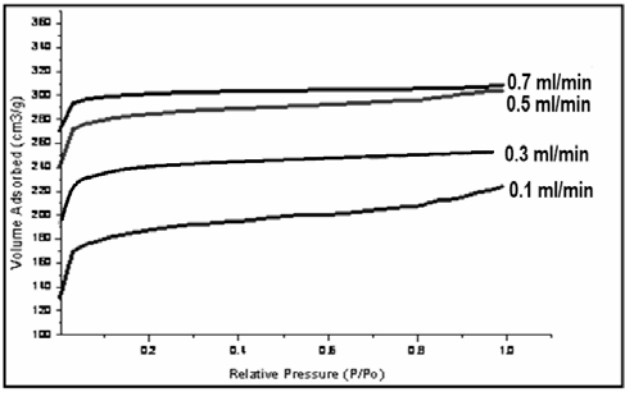
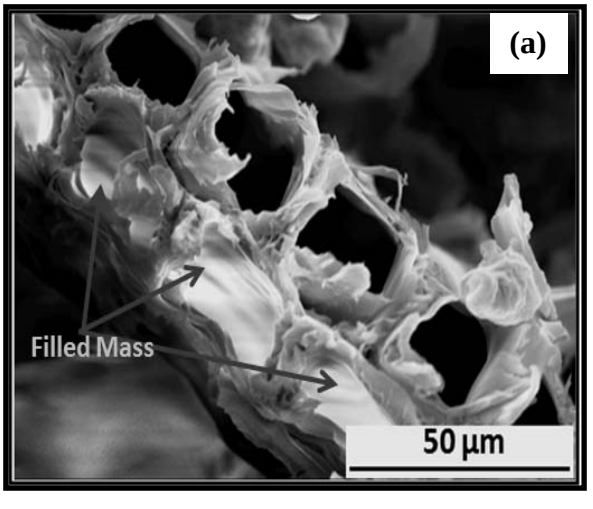


Fig. 2 Nitrogen adsorption isotherms of activated carbons with different flow rate of steam.

Though the surface area of all samples increases on increasing the flow rate of steam, but due to higher flow rate, diffusion is faster resulting in collapsing of pore walls, hence the micro pores get widened and average pore diameter increase from 1.65nm to 1.92 nm, also percentage micro porosity also falls from 90 % to 79%. On further increasing steam rate gets broken the cell wall as shown in fig 4b.

Fig.5 shows the variation of pore diameter with changing the flow rate of steam. Due to high rate of oxidation beyond 0.7ml/min leads to fracture of the materials and entire structure collapse including the pore walls (fig.4b). The surface area of material was higher but it led to the formation of meso porous structure. The average pore diameters in all samples were less than two nano meter showing microporous nature of samples. The sample activated with steam at flow rate 0.1ml/min has smaller pore volume than sample activated with steam flow rate 0.7ml/min.



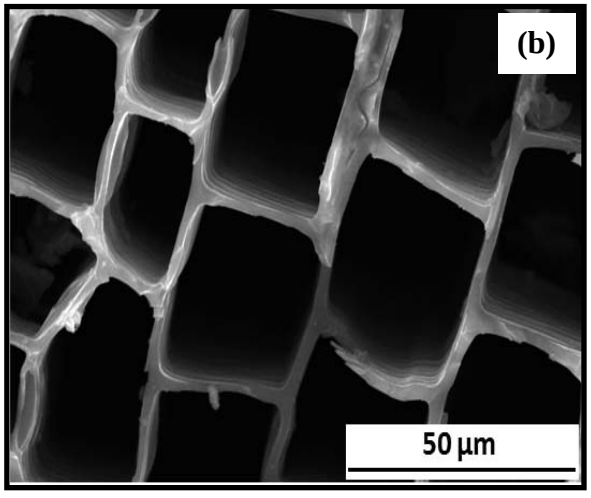
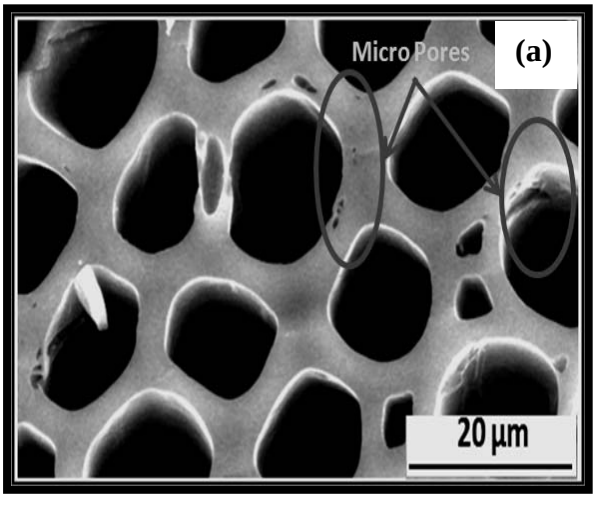


Fig. 3 scanning electron micrograph of (a) as such pine wood (b) pyrolysed pine wood [Both micrographs are in axial direction]



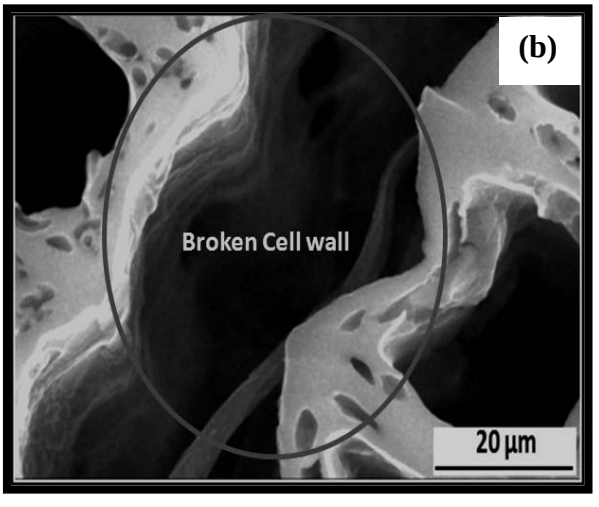


Fig. 4 scanning electron micrograph of steam activated carbonized pine wood with steam flow rate (a) 0.1ml/min (b) 0.7ml/min

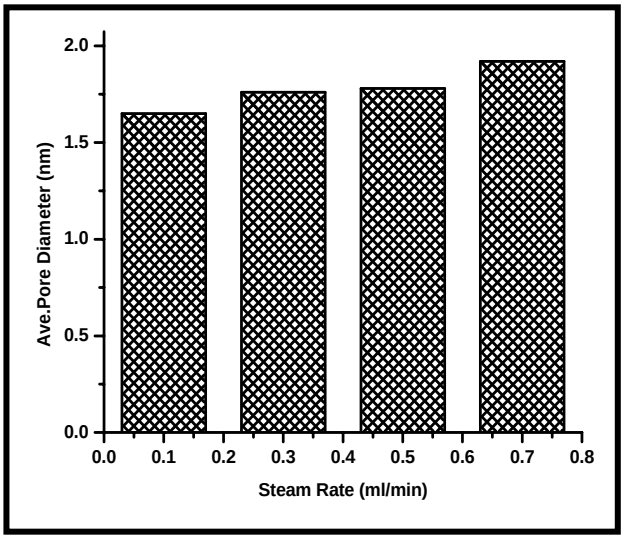


Fig. 5 Relation of effect of steam rate verses average pore diameter

CONCLUSION

Activated carbon with high percentage of micro pores and surface area can be developed by controlling the flow rate of steam during activation process. By controlling the parameters of activation process tailor made porous material can be developed from cellulosic materials. Controlling of processing parameters is very important for the production of desired porosities that could be used in specific applications e.g. for separation of light gases micro pores are used, while broad pore size pores could be used in removal of organic molecules.

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