Porosity Development on Activation of Char from Dry and Wet Babbool Wood

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Abstract

It is well known that the porosity and adsorption capacity in a carbon depends on the nature of precursor, pyrolysis and activation conditions and the ash content. The studies on carbon prepared from the dry and wet babbool wood were under taken to ascertain the effect of initial state of precursor on the development of porosity in the resulting activated carbon. The characterization and adsorption studies carried out shows the presence of mainly mesoporosity in the carbon prepared from dry wood while more of microporosity was observed in the activated carbon prepared from wet wood. The results on porosity in both the cases have been compared and correlated with their processing conditions.

Keywords : *Activated carbon, Pore structure, Adsorption, SEM*

1. Introduction

Activated carbons having high specific porosity, high surface area are extremely versatile adsorbents of major industrial significance. These are used in wide range of applications concerned principally with the removal of species by adsorption from the liquid or gas phase. Activated carbons can be produced from a number of precursor materials including wood, agricultural wastes, coal and synthetic resins. These precursors are normally exposed to a number of different activation method such as physical or chemical in an effort to achieve carbon with the high adsorption capacity for a particular application [1-6].

The adsorptive properties of activated carbons are derived from their extensive internal pore structure, which not only present a high surface area but also desired pore size distribution for the adsorption of molecular species. Although the selection of activation conditions can allow some degree of latitude in controlling the structure and properties of the final product, the properties of activated carbons are determined to a large extent by the nature of the precursor and pyrolyzing conditions [7, 8].

Present work was undertaken especially to study effect of char processing conditions on the surface characteristics of ultimate activated carbon. Activated carbons have been prepared from two types of chars from babbool wood (acacia arabico) i.e. lab made and commercial. The physical changes taking place during pyrolysis, activation of the char, the surface characteristics as well as adsorption properties of these carbons were studied and are reported in this paper.

2. Experimental

2.1. Raw materials

Babbool wood was used as precursor for preparation of activated carbon. The wood was cut in to small pieces of definite shape and dried in sun light for 30 days before pyrolysing in the laboratory.

2.2. Carbonization and activation

Carbonization of dried wood pieces was carried out in muffle furnace. Samples were place in stainlessteel reactor and carbonized @ 30ºC/hrs. to 650ºC for 2 hrs. under nitrogen atmosphere. This sample is designated as B. Another sample was the commercial charcoal made from pyrolysis of wet babbool wood, pyrolysed to about same temperature. This sample is designated as R. The proximate and ultimate physical as well as chemical analysis was performed on the two chars and is compiled in Table 1.

Activation of the two types of chars (B and R) was carried out at 750 and 800ºC using steam activation. The weighed amount of chars was taken in quartz tube having 40 mm diameter. The samples were heated in nitrogen atmosphere up to desired temperature at heating rate of 5ºC/min. On attainment of desired activation temperature, the mixture of steam and nitrogen was passed for different activation time from 45 min to 4 hrs. The samples were cooled in nitrogen atmosphere inside the furnace and stored in dessicator.

2.3. Nitrogen adsorption

Adsorption/desorption isotherms were plotted for the activated carbons using micromeritics Gemini 2375 instrument

Table 1. Proximate and ultimate analysis of chars

Samples	% Moisture	% Volatile	% Ash	% Fixed carbon	Bulk Density cc/gm	%C	%H	%N	Surface area m^2/gm
B char	3.0	14	4	79	0.42	79.26	2.22	1.15	201
R char	1.7	12.94	2.71	82.65	0.52	81.15	0.81	1.22	79

with nitrogen (N$_2$) as the adsorbate at liquid nitrogen temperature (77 K). Prior to adsorption, representative samples were degassed at 300ºC for 24 hrs. in argon atmosphere. Surface area, micropore volume, pore size distribution and total pore volume were measured using BET equation, t-plot method and BJH method respectively. Mesopore volume was calculated by subtracting the value of micropore from value of total pore volume [9].

2.4. Iodine number

The activated carbons were characterized by measuring iodine number (mg/gm iodine) using 0.1 N standardized iodine solution. The titrant used was 0.1 N sodium thiosulfate [10].

2.5. Methylene blue number

Adsorption test of methylene blue on activated carbons was studied by placing 1gm of carbon in 250 ml beaker. Methylene blue stock solution was added from a burette, with continuous stirring. The residual colour of the solution was observed. If any blue colour remains, the endpoint has been reached. Methylene blue number is thus calculated in mg/gm [11].

2.6. SEM

The surface morphologies of B and R chars as such as well as after activation viz BACs and RACs were observed with SEM (HITACHI S3000N)

3. Results and Discussion

3.1. Proximate and ultimate analysis

Results of the proximate and ultimate chemical analysis of various samples are shown in the Table 1. The char B showed higher value of moisture and ash content compared to char R. The bulk density as well as fixed carbon of char R are found to be higher than of B char. The C:H ratio is also higher for char R which shows that commercial charcoal R is more compact than char B.

3.2. Burn off and porosity development

Figure 1, shows the % burn off for B and R chars as a function of activation time at 750 and 800ºC respectively. Figure shows that burn off increases with activation time for both chars. At 800ºC the % burn off for B char is higher than R char. This indicates that the reactivity of steam for B char is higher at higher temperature than for R char. On
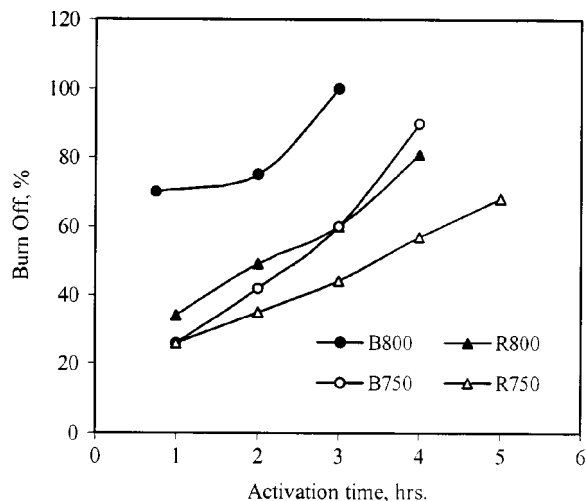
Fig. 1. Evolution of burn off as a function of activation time.

increasing the activation time for B chars to 3hrs. at 800ºC, the net-work collapsed resulting in formation of only ash. On activation at 750ºC/1 hr. same burn off i.e., 26% occured in both chars. However, on increasing the time of activation, the burn off of B char was found to be higher than for R char. These results indicate that the reactivity of steam is higher for B char at higher activation temperature and time than for R char.

Table 2 gives the burn off and porosity characteristics of two type of carbons. The comparison of BACs and RACs with similar burn off values i.e. 26%, produced at 750ºC for 1 hrs. shows that activated carbon produced from B char exhibits considerable higher total pore volume, i.e. 0.46 cc/gm as compared to that from char R, as 0.29 cc/gm. However, micro pore volume of latter samples is found to be higher than for former samples. (i.e. 0.16 for BACs and 0.19 for RACs). The surface area is also higher for BACs than RACs at same level of burn off (26%). This is because of the reactivity of steam with B char is higher and therefore gasification rate is also high. This rate restricts the development of microporosity.

Table 2 also shows that the total and micro pore volumes of the BACs increase with the % burn off up to 60% at 750ºC. Further increase in % burn off decreases total and micro pore volume of the BACs because of extensive gasification at longer activation time (4 hrs at 750ºC). The porosity also starts to collapse, for RACs as the % burn off is increased. The total and micro pore volume is found to

Table 2. Burn off and porosity characteristic of activated carbons

Sample	%Burn off	V_{Total} cc/gm	V_{Micro} cc/gm	V_{Meso} cc/gm	S_{BET} m^2/gm
B750/1	26	0.46	0.16	0.3	607
B750/2	42	0.69	0.22	0.47	844
B750/3	60	1.02	0.22	0.8	1025
B750/4	90	1.67	0.14	0.53	845
B800/0.45	70	0.5	0.20	0.3	987
B800/2	75	0.7	0.3	0.4	1226
B800/3			Ash		
R750/1	26	0.29	0.19	0.09	515
R750/2	35	0.38	0.20	0.18	595
R750/3	44	0.44	0.24	0.2	700
R750/4	57	0.46	0.26	0.21	831
R750/5	68	0.59	0.27	0.32	979
R800/1	34	0.33	0.22	0.11	610
R800/2	49	0.43	0.27	0.16	745
R800/3	60	0.59	0.30	0.30	876
R800/4	81	0.74	0.28	0.46	1020

increase. Longer activation times at 750°C considerably increase the total pore volume but the increase in the micropore volume slows down. For BACs both total and micro pore volume have been found to increase at 800°C activation temperature. However, in case of RACs at higher activation temperature (800°C) the total pore volume is found to increase with activation time where as micropore volume decreases for longer activation (4 hrs. or more). These results clearly show that the microporosity is very sensitive to changes in activation time at 750°C for BACs and at 800°C for RACs. In other words the gasification process at activation time higher than 3 hrs. resulting decrease in the microporosity

Differences were observed in the mesoporosity development in the two carbon samples as well. The change in the mesoporosity of the BACs follows the same trend as the total pore volume: it increases with increasing % burn off up to 60% at 750°C activation temperature and then begins to decrease with further activation. The development of mesoporosity in RACs shows a different behavior, the mesoporosity increase with total pore volume at 750 and 800°C. The initial small increase in mesoporosity with increase in % burn off up to 49% at 800°C was followed by rapid increase in mesoporosity. This may be because of extensive gasification at higher activation temperature and time and thereby causing widening of micropores. The overall results of both activation temperature and activation time can be used to control the porosity development in both carbons. In activated carbon, prepared from B char developed higher mesoporosity while activated carbon prepared from R char contains predominantly micropores at lower activation

temperature and time i.e. 750°C for 1hr. and increased mesoporosity at higher activation time and temperature.

3.3 Development of Surface area

The change in surface area with burn off for BACs and RACs is shown in Table 2 and Fig. 2. The highest surface areas were obtained for activated carbons produced from B char at 750 and 800°C activation temperature. BACs with highest surface areas (1226 and 1025 m^2/gm) were produced at 800°C for 2 hrs and 750°C for 3 hrs. respectively. Increasing the activation temperature to 800°C was found to be more effective to obtain high surface area for both carbons (i.e. 1226 m^2/gm for BACs and 1020 m^2/gm for RACs). As seen from Fig. 2 the surface area of the carbon from BACs decreases at burn off higher than 60% at 750°C. For RACs the surface area was found to contineously increase with increase in % burn off at 750 and 800°C activation temperature.

On comparing the surface area development in the two samples, it has been found that for same activation time, i.e. 1 hr., but different activation temperature, i.e. 750 and 800°C, the surface area increase for BACs is 607 to 987 m^2/gm i.e. 380 m^2/gm increase, while for RACs at same condition the surface area increase from 515 to 610 m^2/gm i.e. 95 m^2/gm increase. This shows that temperature of activation has more effect on development of surface area in BACs. At constant activation temperature i.e. 800°C and different activation time 1 and 2 hrs. the surface area of BACs increase from 987 to 1226 m^2/gm while this increase in RACs is from 610 to 745 m^2/gm. The net increase in surface area was found to be 239 and 135 m^2/gm for BACs and RACs respectively. This result suggests that the time of activation also is quit effective in development of surface area for BACs. The overall results suggest that both temperature and time of activation create noticeable effect on
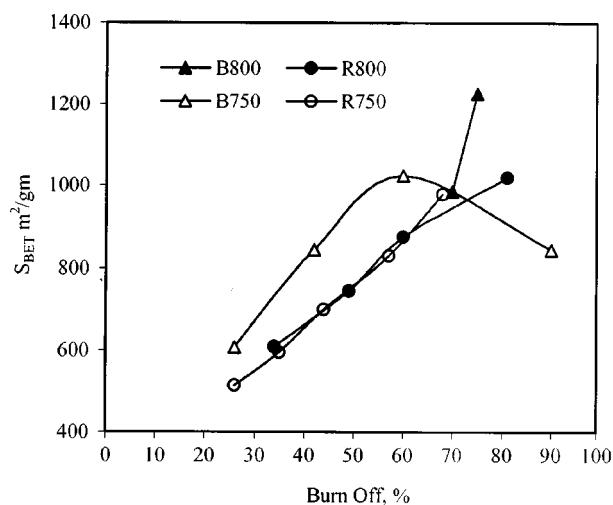
Fig. 2. Evaluation of surface area as a function of burn off.

surface area development. Both the parameters are more effective in surface area development for BACs than for RACs.
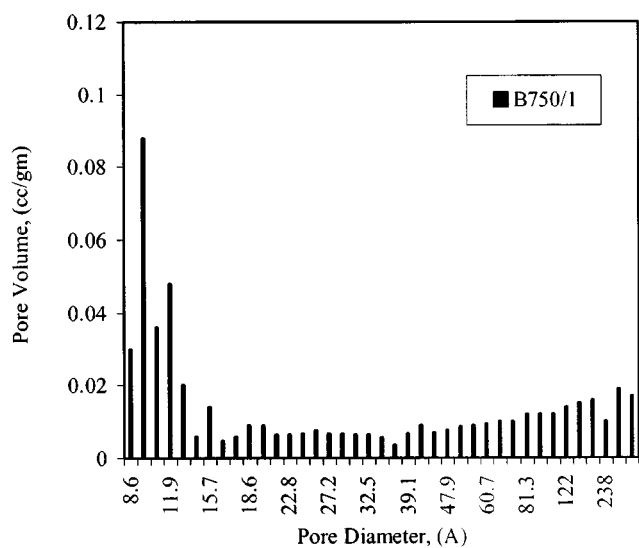
3.4. Pore size distribution

To compare porosity development of activated carbons prepared from B and R chars, pore size distribution is shown in Figures 3, 4, 5 and 6. As the activation time increases, the development of mesopores also increases. This may be an indication that, somewhat disorganized carbons are eliminated by opening of closed pores, however, above 1 hr. activation time the existing pores are widened to larger pores by the gasification of carbon in the pore walls.

Figure 3a & b shows the pore size distribution of BACs at

750°C activation temperature for 1 and 3 hrs. respectively. From the figure it is observed that as the activation time increased the development of mesopores was increased and the bigger size mesopores are developed in the sample. The micropore present in the sample are in the range of 7 to 15A diameter predominantly around 9A. In case of RACs (Fig. 4a & b) at similar condition the development of micropore was found to be higher than the mesopore. As the time of activation is increased, the development of mesopores increases. These increase are slower for RACs than the BACs.

Figure 5 and 6 show the pore size distribution of BACs and RACs at 800°C activation temperature with increasing activation time. In case of BACs (Fig. 5a & b) mesopores
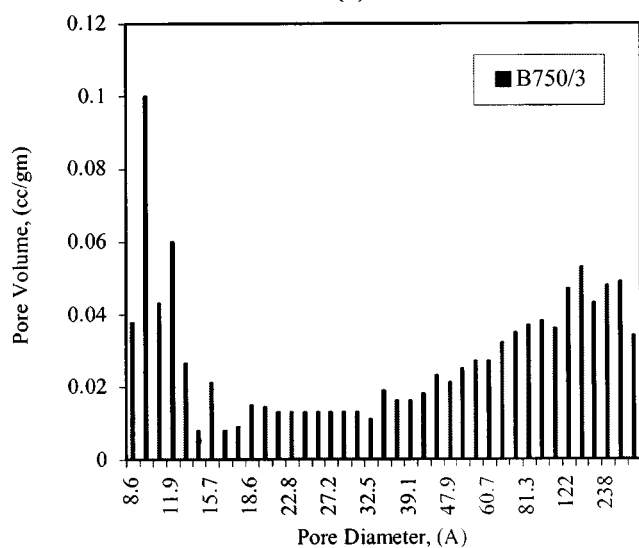
(a)
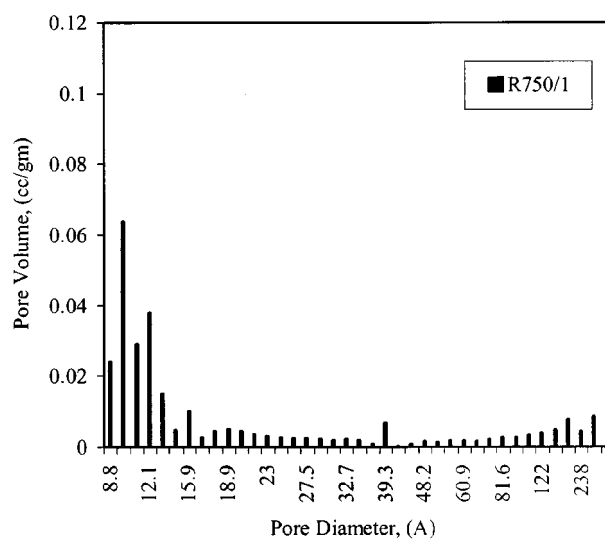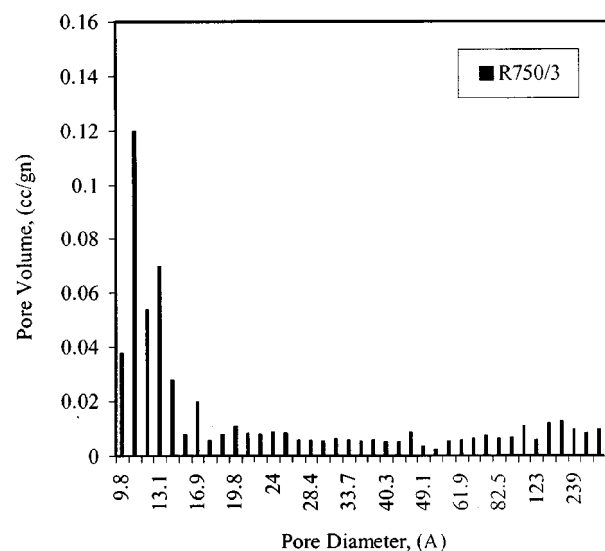
(b)

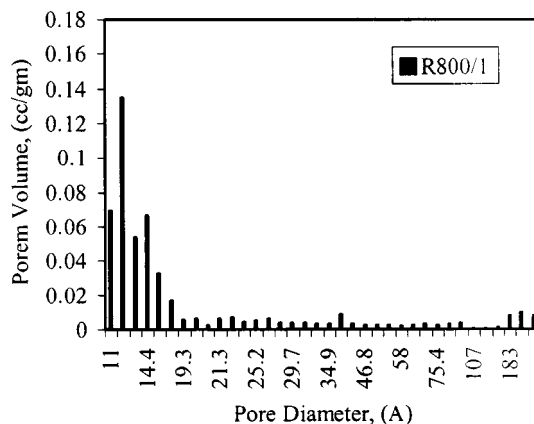**Fig. 3.** Pore size distribution of BACs at 750°C for 1 & 3 hrs.

(a)

(b)

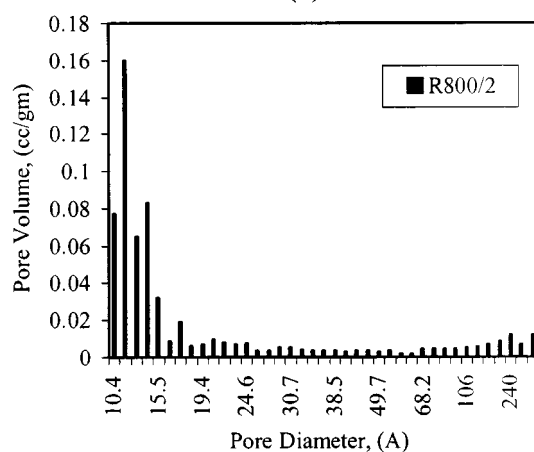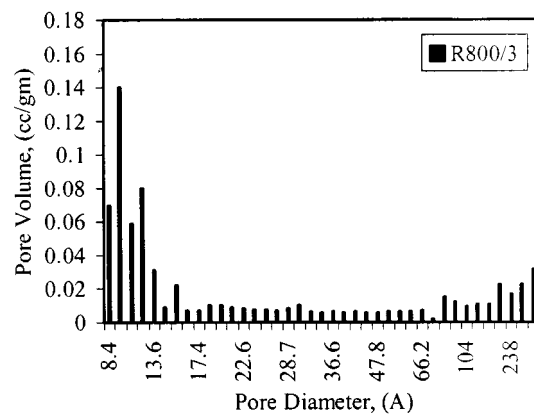**Fig. 4.** Pore size distribution of RACs at 750°C for 1 & 3 hrs.

(a)

(b)
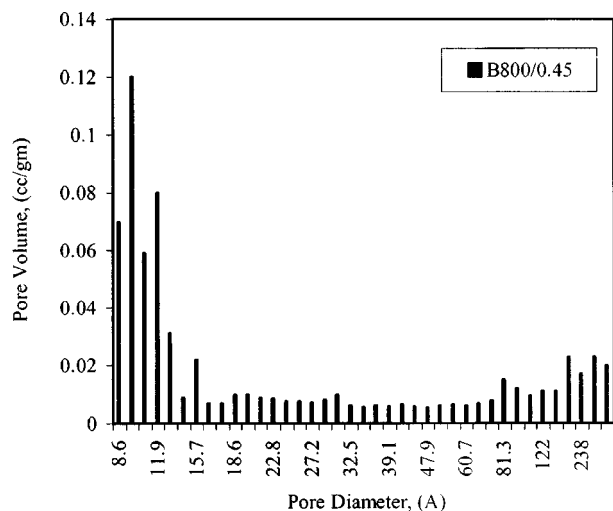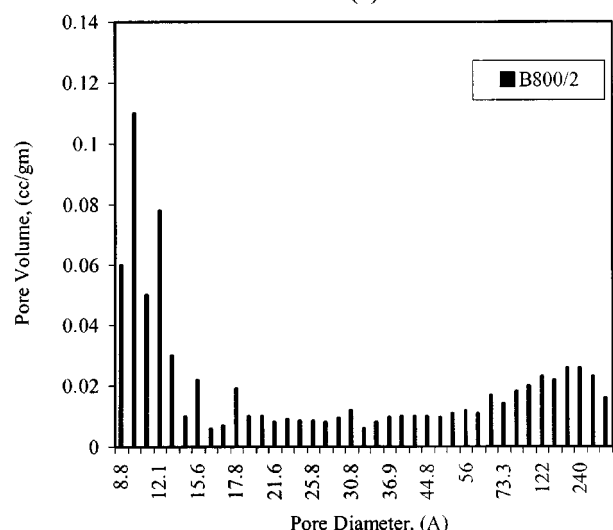
Fig. 5. Pore size distribution of BACs at 800°C for 0.45 & 2 hrs.

are increased with activation but this development of mesopores was slower than BACs at 750°C for 3 hrs. and in case of RACs (Fig. 6a, b and c) the development of mesopore increased after 2 hrs.

It seems that for BACs and RACs, micropores are created on activation both by increasing the temperature and time to an extent followed by decrease in micropores owing to coalescence and transition to larger pores on further activation. This processes was faster in BACs than RACs. The overall result shows that the volume of mesopores having diameter above 50A was higher and these development was higher in BACs than RACs.

3.5. N_2 gas adsorption

The adsorptiondesorption isotherms for BACs and RACs samples are shown in Fig. 7a and 7b. As seen from Fig. 7a

(a)

(b)

(c)

Fig. 6. Pore size distribution of RACs at 800°C for 1, 2 & 3 hrs.

the nature of the isotherms change from type I with a characteristic H4 hysteresis loop for sample B750/1 to a type IV isotherm exhibiting a broader line type H3/H4 hysteresis loop for sample B750/3 and has the highest pore volume of all the samples. The extent of the hysteresis loops suggests that latter samples posses a greater mesopore volume than
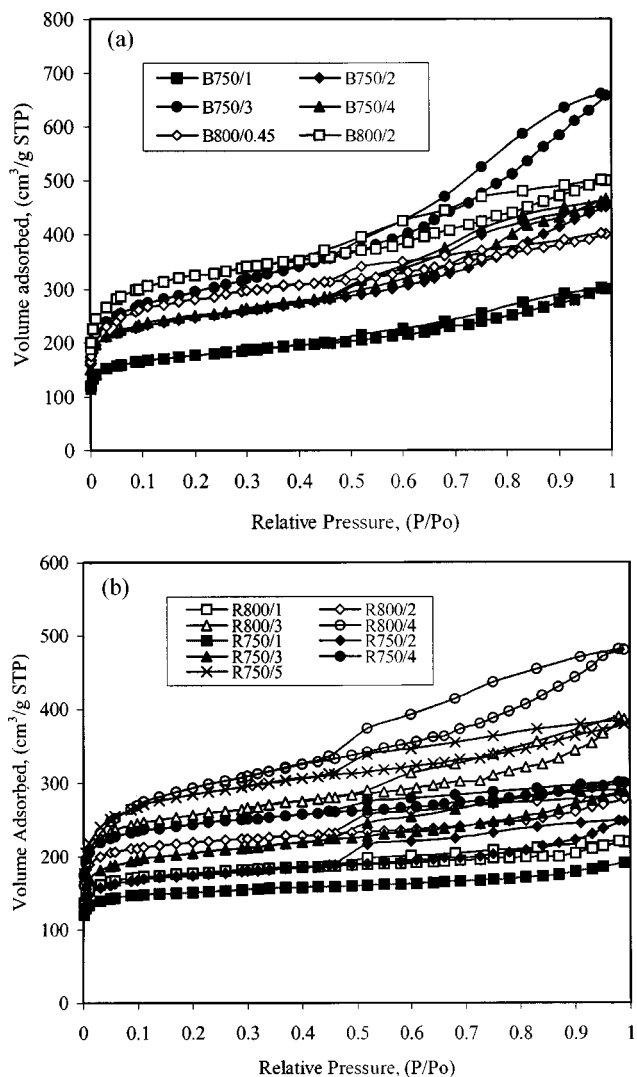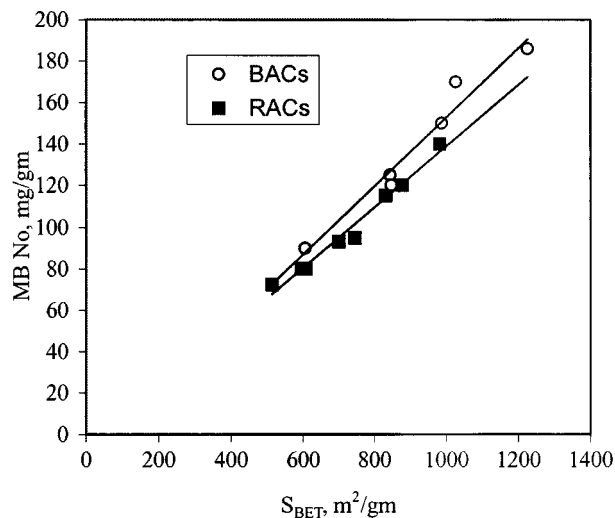
Fig. 8. Methylene blue adsorption capacity of BACs and RACs.

samples and the shape of the isotherm changes to type IV having H4 hysteresis loop.

3.6. Adsorption properties

The adsorption of methylene blue has been used for a long time as a tool for the evaluation of the adsorption properties of activated carbons, particularly liquid phase carbons. Methylene blue adsorption capacity of activated carbons was measured and is shown in Fig. 8. As seen from the fig. 8, good correlations exist between methylene blue adsorption and BET surface area. Activated carbons from char B exhibit higher methylene blue adsorption than R Char. This is again attributed to higher mesopore volume in B samples than in R samples. This fact confirms that the average pore size of BACs is larger than RACs and BACs can adsorb larger adsorbate more easily.
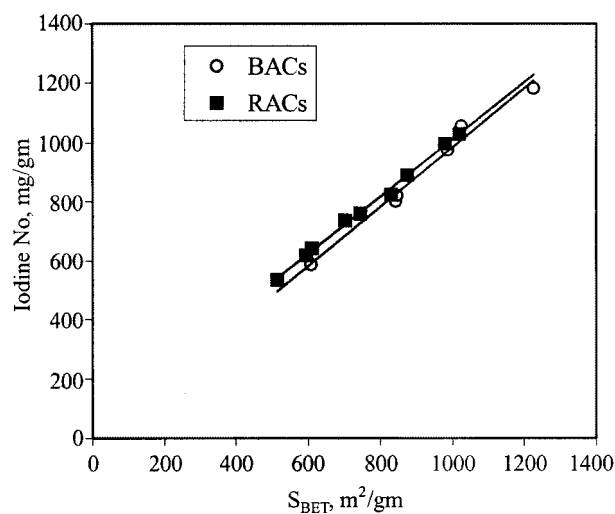

Fig. 7. Nitrogen adsorption isotherms of BACs at 77 K.

other samples. The broadning of "knee" of the isotherm imply a reduction in the micropore in the samples with activation. Fig. 7b shows adsorptiondesorption isotherms for RACs. From the figure, according to the classification of Physorption isotherm recommended by the International Union of Pure and Applied Chemistry (12) the shape of the isotherms for nitrogen at 77 K for R750/1 carbons may be considered as of type I, which is characteristic of microporous solid. As the activation temperature and time is increased or in other words % burn is increased, the shape of the isotherms change from a type I to a type I with H4 hysteresis loop. This type of isotherms suggests the presence of micropores with increasing development of mesoporosity. Adsorption characteristics of R800/3 and R800/4 carbon show that the adsorption of nitrogen increase after P/Po equal to 0.75. This indicates that the volume of bigger size mesopores has increased in these samples than in other

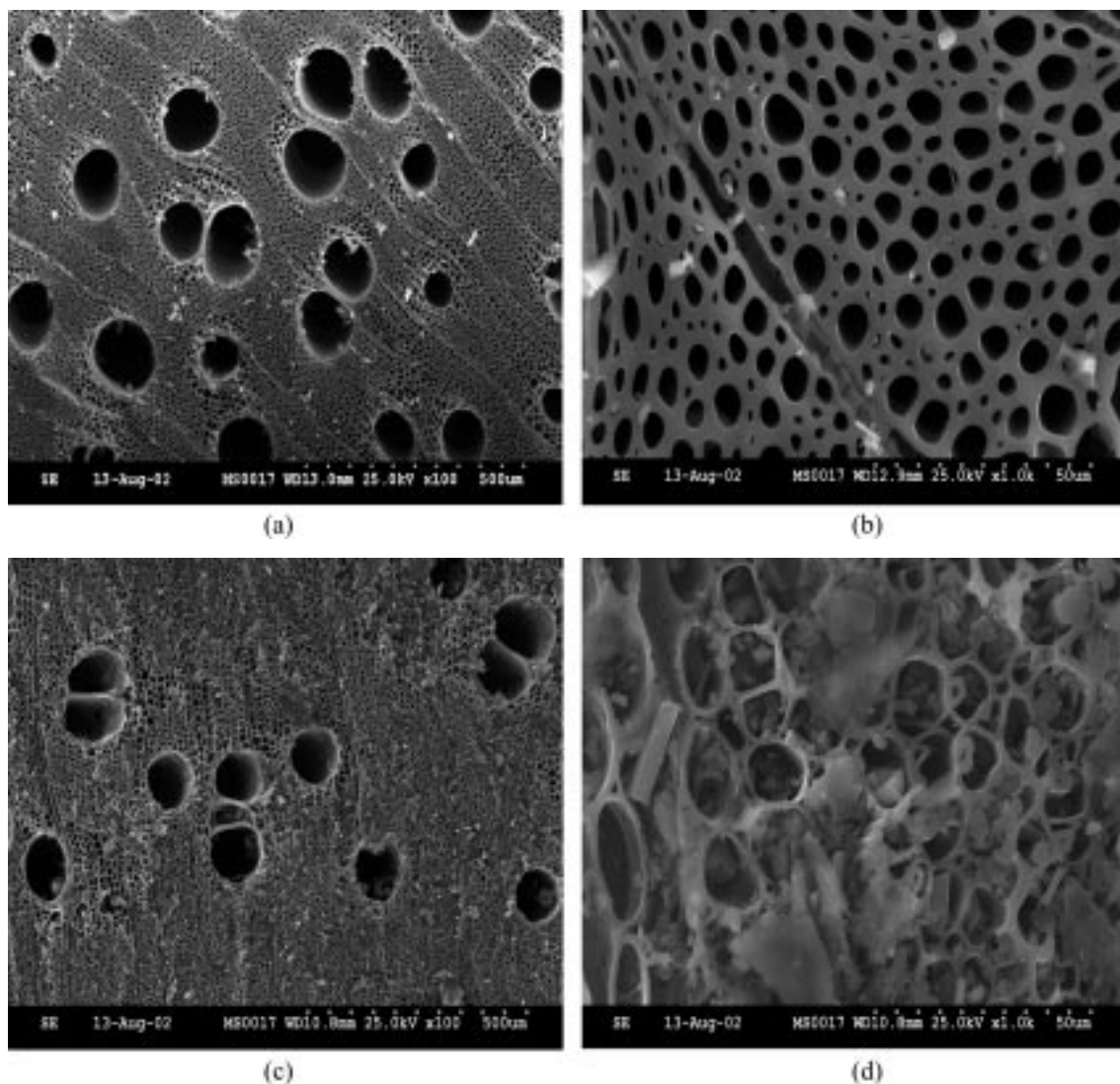**Fig. 9.** Iodine adsorption capacity of BACs and RACs.

Fig. 10. SEM micrographs of B chars (a and b) and R char (c and d).

Iodine adsorption capacity of BACs and RACs is shown in Fig. 9. The iodine adsorption capacity is also found to increase linearly with increase of BET surface area. The iodine adsorption capacity of RACs is found to be slightly higher than that of BACs. This result indicates that the volumes of smaller pores (corresponding to iodine molecule) are higher in RACs than in BACs.

3.7. SEM studies on chars and activated carbons

Fig. 10(a, b, c, & d) shows SEM micrographs of two types of chars. As seen from the Fig. 10, a char from completely dried wood (B) shows clean pores where as that from moist wood (R) shows partially filled pores. On activation, the B char (Fig. 11) exhibits thinning of the pore walls and at place creation of pores within the walls. In case of R char, activation first clears the pores and then the walls of the

pores start getting reacted. This results in creation of more pores within the pore walls (Fig. 12) At places, cell structures in both the chars are found to be quite different than usual one. The unique features are some solid mass within the pores. These may be the places the wood is branching. However, this solid mass also reacts during activation and acts center for creation of pores with them (Fig. 13). These are found in both types of chars. These also contribute to the mesoporosity generation in the chars during activation.
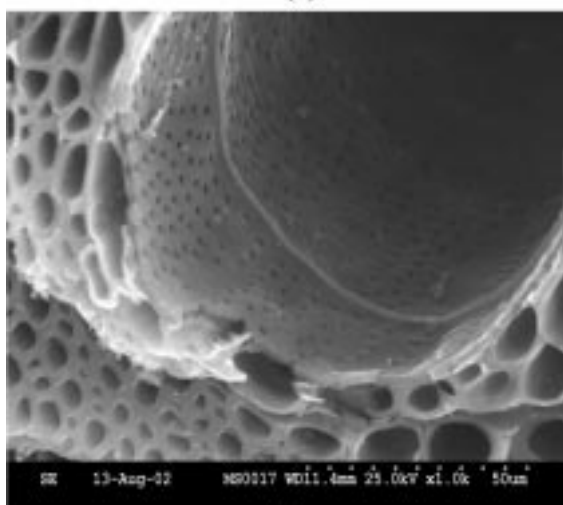
4. Conclusion

Activated carbons prepared by steam activation by using dry and wet babbool wood differ in porosity and pore size distribution. The % burn off of char from dry wood on
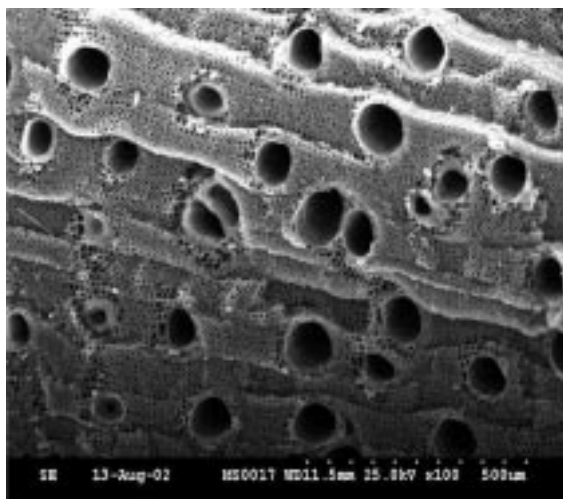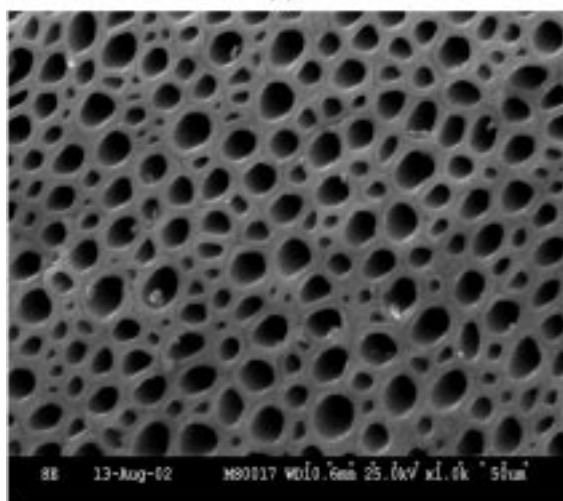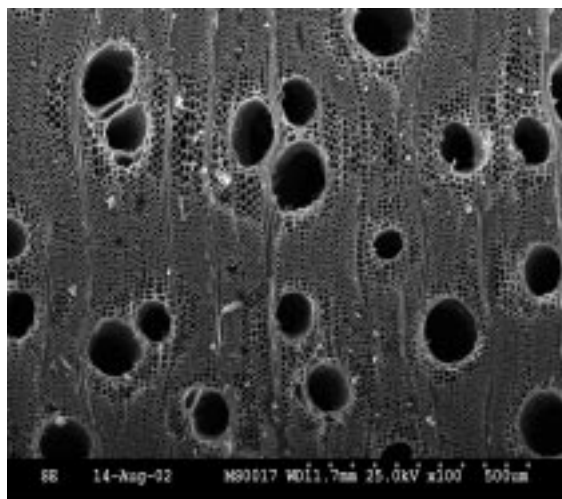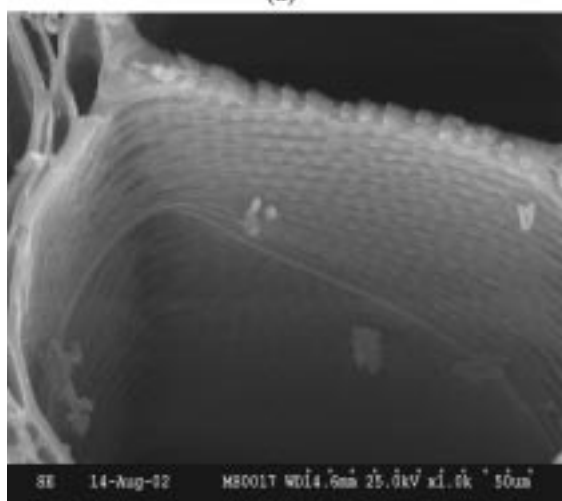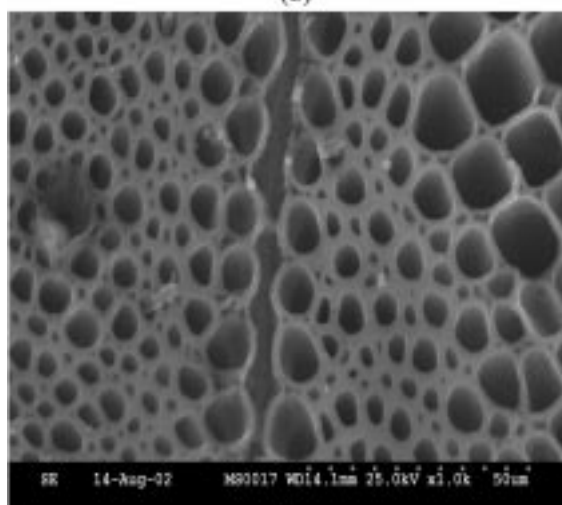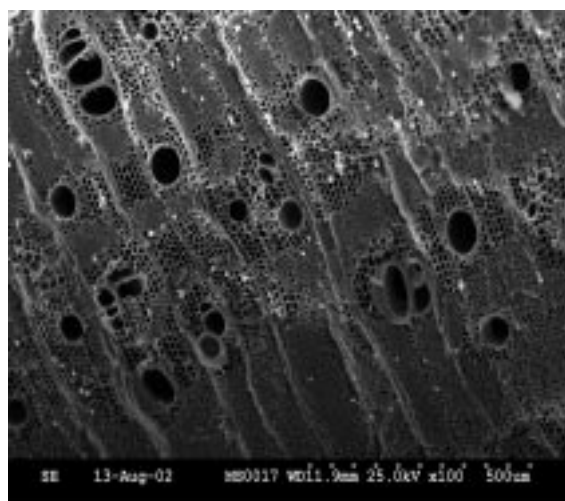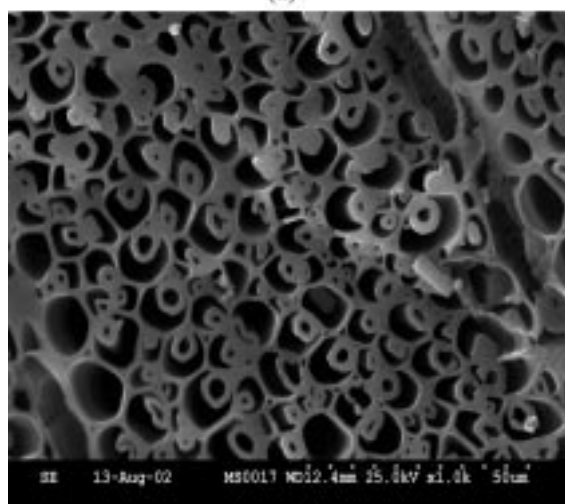
Fig. 11. SEM micrographs of BACs at 750°C for 3 hrs.

Fig. 12. SEM micrographs of RACs at 800°C for 4 hrs.

(a)

(b)

Fig. 13. SEM micrographs of RACs at 750°C for 5 hrs.

activation with steam was found to be higher than of char from wet wood showing higher reactivity or steam for dry woods chars. The mesoporosity was more in activated carbon prepared from dry wood while more of microporosity developed on steam activation of carbon prepared from wet wood. This has been attributed to clearing of the pores during activation, resulting in development of microporosity. The adsorption of iodine also supports these results. These results show that in addition to the nature of precursor and processing conditions, the initial state of precursor also play a vital role in developing a specific porosity.

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