Influence of Pyrolysis Conditions and Type of Resin on the Porosity of Activated Carbon Obtained From Phenolic Resins

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Abstract

In polymer precursor based activated carbon, the structure of starting material is likely to have profound effect on the surface properties of end product. To investigate this aspect phenolic resins of different types were prepared using phenol, m-cresol and formaldehyde as reactants and Et_3N and NH_4OH as catalyst. Out of these resins two resol resins PFR1 and CFR1 (prepared in excess of formaldehyde using Et_3N as catalyst in the basic pH range) were used as raw materials for the preparation of activated carbons by both chemical and physical activation methods. In chemical activation process both the resins gave activated carbons with high surface areas i.e. 2384 and 2895 m^2/g, but pore size distribution in PFR1 resin calculated from Horvath-Kawazoe method, contributes mainly in micropore range i.e. 84.1~88.7 volume percent of pores was covered by micropores. Whereas CFR1 resin when activated with KOH for 2h time, a considerable amount (32.8%) of mesopores was introduced in activated carbon prepared. Physical activation with CO_2 leads to the formation of activated carbon with a wide range of surface area (503~1119 m^2/g) with both of these resins. The maximum pore volume percentage was obtained in 3-20 Å region by physical activation method.

Keywords : *Activated Carbon, Resins, Thermosetting, Carbonization, Char, Porous Carbon, Surface Properties and Adsorption*

1. Introduction

This work is a continuation of our earlier activity on the development of microporous carbons using polymeric precursors in various forms [1-3]. The inherent nature of precursor and operating conditions strongly affect the porous behavior of activated carbon [4-8] hence in case of natural products as precursor, significant batch to batch variations are observed in properties. Among various types of active carbon precursors coal is most commonly used due to availability and low cost [9-11]. However, the use of polymeric precursors and pitch for preparation of active carbon is gaining a place of importance due to possibility of getting the activated carbon in various forms viz fibre, sphere and monolith and better control over the properties of precursor material which leads to possibility of tailoring the surface properties of end product. Some of notable examples include preparation of active carbons from synthetic resins as raw materials, i.e. phenol formaldehyde which showed molecular sieving behavior at low burn off [12, 13]. Ion exchange resins were used by Miura et al to study the pillar effect of multivalent cations to control the micropore formation [14]. Apart from the structure and the morphology of precursor, the type of activation process and processing parameters also determine the surface properties of end product. Another parameter which has shown significant

effect on the retention of structural integrity of starting material during carbonization, is the pretreatment given to starting material. Influence of oxidation on preparation of porous carbon from phenol formaldehyde has been studied by Teng *et al.* using KOH as activating agent [15]. The work reported in this paper aims to study the effect of polymeric structure of resin and the type of activation process on the pore development in carbonized resin and activated product, and to investigate the role of KOH and/or CO_2 activation in the development of micro and mesopores. For this purpose phenolic resins with different degree of curing were synthesized using phenol, m-cresol and formaldehyde as reactants, triethylamine and ammonia as catalysts and hexamethylenetetramine as curing agent. Resins prepared were carbonized in inert atmosphere. After carbonization the chemical activation by KOH and physical activation by CO_2 was performed in a wide range of temperature for different duration.

2. Experimental

2.1. Materials

In the present investigation, the phenolic resins used for carbonization and activation were synthesized in the lab. The materials used in the process were phenol LR Grade of Ranbaxy Laboratories Ltd., formaldehyde (37%) solution in

Table 1. Reaction conditions for resin preparation

Sample Code	P/F Ratio	C/F Ratio	Catalyst	pH of Reaction	Reaction Temp. ^{o}C	Reac. Time Hrs.	Curing Agent	Curing Temp. ^{o}C	Curing Time Hrs.
PFN$_1$	1:0.8	-	Et$_3$N	2-3	95-100	4	HMTA	150	1
PFN$_2$	1:0.6	-	NH$_4$OH	-do-	-do-	4	-do-	110	1
CFN$_1$	-	1:0.8	Et$_3$N	-do-	-do-	4	-do-	120	1
CFN$_2$	-	1:0.6	NH$_4$OH	-do-	-do-	4	-do-	100	1
PFR$_1$	1:1.5	-	Et$_3$N	8-9	98-100	5	Thermal	200	1
PFR$_2$	1:1.5	-	NH$_4$OH	-do-	95-100	4	-do-	170	1
CFR$_1$	-	1:1.5	Et$_3$N	-do-	98-100	4	-do-	160	1
CFR$_2$	-	1:1.5	NH$_4$OH	-do-	95-100	4	-do-	250	1

Abbreviations: P=Phenol, F=Formaldehyde, C=m-Cresol, N=Novolac, R=Resol, 1=Et$_3$N, 2=NH$_4$OH.

water provided by Sarabhai Chemicals, ammonia solution (30%) and hexamethylenetetramine (LR) of S.D. Fine Chemicals, and triethylamine (99%) of Lancaster and methanol AR grade of Qualigens Fine Chemicals.

2.2. Resin Preparation and curing

Phenolic resins of two types namely novolac and resol type were prepared using phenol, m-cresol and formaldehyde as reactants and triethylamine and ammonia as catalyst [16]. Novolacs were cured by hexamethylene tetramine as curing agent at temperatures 100~150°C whereas resols were thermally cured by raising the temperature to 200~250°C. The details of preparation procedure are given elsewhere [17].

All the eight resin samples synthesized by above said method were evaluated for the extent of polymerization by refluxing them in methanol for eight hours at the boiling point of methanol. Samples were filtered, cooled, dried and weighed again. Results are given in Table 2.

2.3. Char Preparation

Before carbonization the thermogravimetric analysis was performed in nitrogen as well as in oxygen atmosphere at the heating rate of 10°C/min and a gas flow of 60 ml/min upto 800°C. In nitrogen atmosphere almost all these resins are stable upto 400°C and maximum weight loss occurred between 400~600°C. Carbonization of these resins was

Table 2. Yield % of resin after reflux

Sample	Solvent	Curing
PFR$_2$	Methanol	98.67%
PFN$_2$	-do-	85.43%
PFR$_1$	-do-	84.45%
PFN$_1$	-do-	-
CFR$_1$	-do-	67.76%
CFR$_2$	-do-	65.09%
CFN$_2$	-do-	64.9%
CFN$_1$	-do-	64.25%

carried out in a tubular furnace by raising the temperature of the furnace from ambient to 700°C at the rate of 10°C/min in the N$_2$ atmosphere. The resins were kept at 700°C for 1/2h. The carbonized samples were cooled down to room temperature in inert atmosphere. The plot between the cross-linking percentage and char yield is given in Figure 1.

2.4. Activation

2.4.1. Chemical Activation

The conditions adopted for chemical activation were same as used by Teng *et al.* [15]. The chars prepared were mixed with KOH solution. Char to KOH ratio was maintained 1:4 approximately by weight. Mixing was performed at 85°C for 3h to make a slurry. Mixture was dried at 110°C for 10 hrs. Dried samples were subjected for chemical activation by raising the temperature at the rate of 25°C/min to 400°C. The mixture was kept at this temperature for 1/2h to avoid vigorous reaction with steam. Activation was done in the range 550~750°C in a tubular furnace (I.D. 2.2 cm and length 80 cm) in a silver boat. Time of activation was varied from 30 min to 120 min. After cooling in inert atmosphere the active carbon samples were treated with 0.5 N hydro-
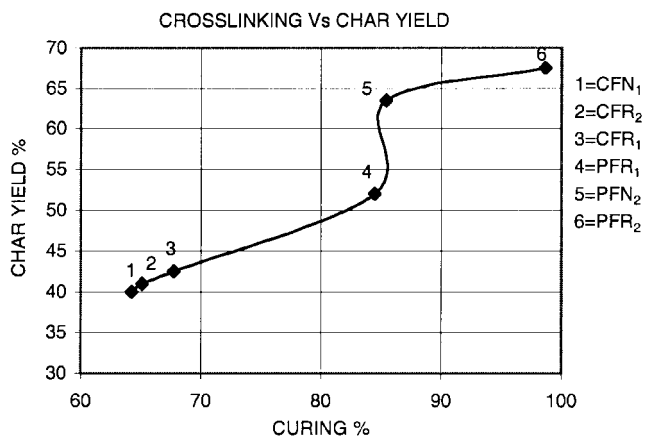
Fig. 1. Effect of extent of curing on char yield.

chloric acid at 100°C for 1h for removal of potassium ion. Afterward samples were washed with distilled water until the neutral pH and dried to get final product.

2.4.2. Physical Activation

For physical activation, constant mass of resin chars i.e. 5 gm was taken in the same tubular furnace as used in chemical activation for all the experiments. Resin chars were physically activated using CO_2 as activating agent at a constant flow of 50 ml/min and a heating rate of 25°C/min. The activation was performed at 750, 850, 950 and 1000°C for 2, 4, 6 and 8 h duration.

2.5. Characterization

The resins were characterized by elemental analysis. The pyrolysis behaviour of resin granules was determined by TGA and DSC techniques [1, 17]. The adsorption isotherms of porous carbons obtained from phenolic resin chars were determined using Sorptomatic 1990. The porous carbon samples weighing .1~.5 gm were degassed at 250°C under vacuum in degassing unit for 8h and characterized by measuring N_2 adsorption isotherms at 77°K. The adsorption isotherms were interpreted using BET [19] and DR [18] equations. DR method was used to calculate the micropore volume. Horvath-Kawazoe [20] method was used to calculate micropore size distribution.

3. Results and Discussion

The first step towards the characterization of precursor material was the determination of curing percentage. The uncured resins are soluble in methanol, therefore on refluxing, uncured part goes into methanol leaving behind the cured part. It has been observed that phenol-formaldehyde resin with ammonia catalyst (PFR_2) showed maximum resistance to solvent due to highly cross-linked polymer network showing 98.67% curing. On the other hand m-cresol-formaldehyde resin with triethylamine catalyst (CFN_1) showed maximum affinity towards solvent i.e. 35.75% of resin weight dissolved in solvent yielding 64.25% cured resin due to poor cross-linking. It appears from the data that m-cresol based resins show poor cross-linking than phenol based resins which is probably due to the steric hindrance of extra methyl group ($-CH_3$) present in the m-cresol. Methyl group present in the meta position of phenol will facilitate the ortho and para substitution in benzene ring hence formation of methylol phenols, but hinders the condensation reaction, therefore restricts the formation of compact polymer network.

The effect of curing on char yield is shown in Fig. 1. The char yield after carbonization varies from 39.2~67.5%. It is evident from the figure that char yield increases with increase in percentage of curing. It may be noted from the

Table 3. Elemental analysis data % before and after carbonization

S.No.	Sample	N	C	S	H	O
1	PFR_1	.77	72.9	0.00	6.25	20.08
2	PFR_2	.86	72.9	0.00	5.56	20.68
3	PFN_1	1.29	74.88	0.00	5.89	17.94
4	PFN_2	.50	74.87	0.00	5.72	18.91
5	CFR_1	.53	73.96	.16	7.05	18.3
6	CFR_2	3.69	73.21	0.00	7.18	15.92
7	CFN_1	2.74	74.8	.005	7.09	15.365
8	CFN_2	2.08	75.97	.71	7.15	14.09
9	PFR_1C	.14	87.4	0.00	2.4	10.06
10	PFR_2C	.27	85.0	0.00	2.34	12.39
11	PFN_1C	.14	85.20	0.00	2.6	12.06
12	PFN_2C	.45	89.35	.54	2.93	6.73
13	CFR_1C	.40	90.77	.467	2.99	5.373
14	CFR_2C	.35	86.25	.029	2.67	10.701
15	CFN_1C	.27	89.96	0.00	2.10	7.67
16	CFN_2C	.11	88.66	0.00	2.76	8.47

Fig. 1 that at same curing percentage of 85% phenol novolac type of resin gives better char yield than phenol resol resin, however, highest char yield ie. 67.5% was obtained with phenol resol resin showing 98% curing. This indicates that both physical and chemical structures of resin significantly affect the char yield and the resins prepared with ammonia as catalyst show better curing.

As catalyst and cross-linking agent both have amine group, we performed elemental analysis to know whether nitrogen was present in polymer network or not. Elemental analysis of resins and resin chars was done by Elementar Analyser Vario-EL Fabri-NR 11961010 and results are given in Table 3. Percentage of nitrogen is negligible in all the samples revealing that nitrogen does not participate in polymer network bonding. Oxygen is present from 14.09-20.68% as a result of formation of bridge in polymer network. The carbon content in precursor resin is around 73-75% which increases to 87-90% after carbonization. The decrease in oxygen and hydrogen content on carbonization is due to the cleavage of network and evaporation of volatile matter.

3.1. Surface Properties

N_2 adsorption isotherms at -196°C of chemically and physically activated samples are presented as Fig. 4 & 5 respectively. All the samples show type I isotherm according to BDDT classification as there is a steep rise in volume adsorbed at low pressure region which is followed by a plateau at higher relative pressure. However, in case of CFR1-1000 sample there is large hysteresis indicating the presence of transitional pores. The volume adsorbed is very high in chemically activated samples in comparison to
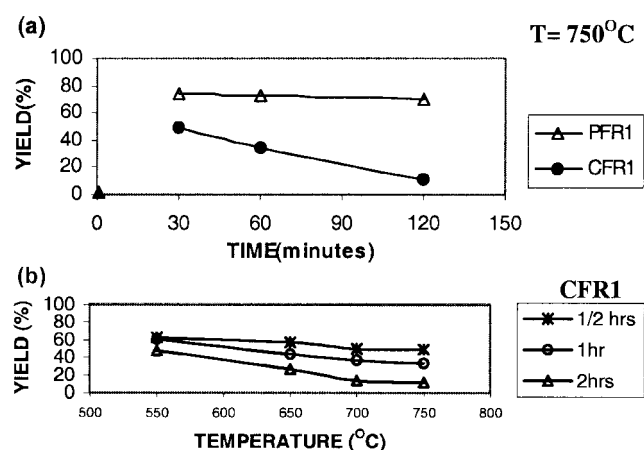
Fig. 2. Effect of activation time and temperature on the yield of porous carbon during chemical activation.

physically activated samples. CFR1 when chemically activated at 750°C for 2h shows a significant rise in volume adsorbed with increasing pressure indicating that there are some transitional pores in these samples along with micropores.

3.2. Chemical Activation: (Effect of time and temperature)

The reaction conditions and nomenclature of various types of phenolic resins prepared are given in Table 1. Out of these resins, CFR1 and PFR1 were selected for further activation studies as representative for two classes of resins prepared. The activation behaviour and surface properties of two resins PFR1 and CFR1 are reported in this section. PFR1 is a resol type resin prepared using phenol, formaldehyde and triethylamine and CFR1 was prepared using m-Cresol, formaldehyde and triethylamine.

Fig. 2(a) gives a plot between time of activation and yield. It may be seen that even after 2h activation the weight loss in case of PFR1 resin is insignificant while in case of CFR1 resin it is quite large. Due to compact matrix available in PFR1 resin; as evident from crosslinking pattern, activation is not that facile. This is interesting to note that in case of PFR1 resin the samples which gave 80% and 69% yields had surface area 2382 and 2020 m²/g. This indicates that highly microporous material was prepared within short duration of activation i.e. 30 min. However, no further increase in surface area was observed, but on the contrary it declines marginally from 2384 to 2017 m²/g. It seems that decrease in yield from 30 to 120 min is mainly due to widening of pores in transitional and mesopore regions which does not effect surface area significantly. The rate of chemical activation is faster in case of activation of chars of CFR1 resins shown in Fig. 2(b). The yield of porous carbon varies from 45 to 10% within surface area range 1745 to 2505 m²/g as given in Table 4. The maximum surface area obtained, 2895 m²/g drops to 2505 m²/g perhaps due to widening of pores beyond 60 min activation time. The effect of activation temperature on yield was studied for different duration i.e. 30, 60 and 120 min for CFR1 resin only. The weight loss pattern is shown in Figure 2(b). The rate of burn off is almost steady from 550 to 750°C but at 2 h residence time there is a sudden increase in rate of activation when we move from 650 to 700°C, that is probably due to the formation of considerable amount of metallic potassium [20, 21] at and above 700°C. This will also contribute to activation.

The activated carbon obtained from phenolic resins by chemical activation have poor mechanical strength. Therefore it was thought worthwhile to study the activation of these resins by CO_2 as activating agent. Change in yield

Table 4. Chemical activation change in surface properties with increasing time (T=750°C)

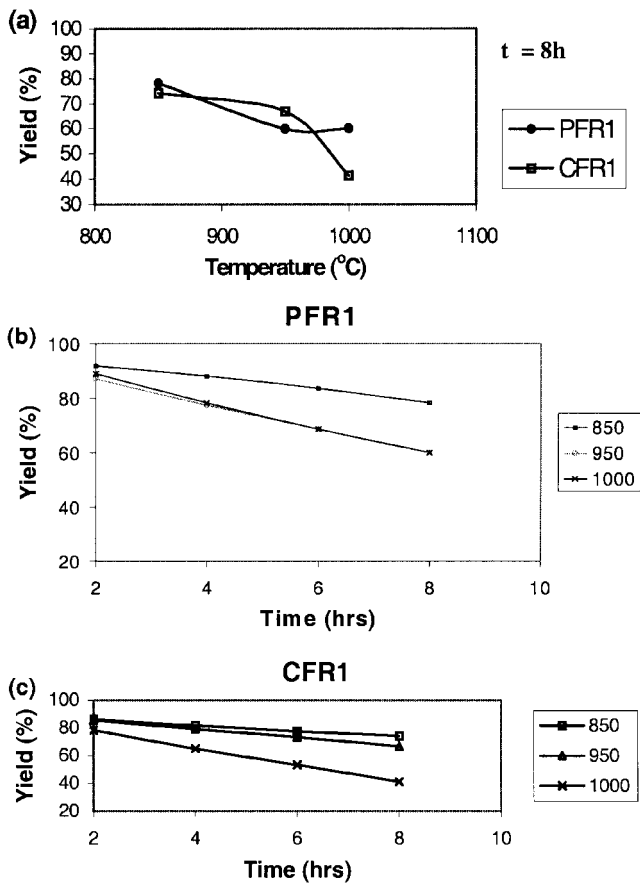| Property	PFR1						CFR1					
	1/2hr		1hr		2hrs		1/2hr		1hr		2hrs	
Surface area (m²/g)	2384		2006		2017		1745		2895		2505	
Pore vol. (cm³/g)	1.23		1.09		.99		.94		1.63		2.16	
Micropore vol. (cm³/g)	.99		.89		.78		.70		1.23		.67	
Micropore vol. (%)	80.5		81.7		78.8		74.5		75.5		31	
PSD (Diameter in A⁰)	Relative Vol. (%)	Pore Vol. (cm³/g)	Relative Vol. (%)	Pore Vol. (cm³/g)	Relative Vol. (%)	Pore Vol. (cm³/g)	Relative Vol. (%)	Pore Vol. (cm³/g)	Relative Vol. (%)	Pore Vol. (cm³/g)	Relative Vol. (%)	Pore Vol. (cm³/g)
3-7	33.5	.64	51.2	.55	30.7	.59	40.7	.52	28	.68	12.7	.35
7-20	50.6	.43	37.5	.40	55.1	.28	40.2	.24	49.6	.65	20.7	.43
20-500	14.3	.16	10.9	.14	14.1	.12	17.6	.19	20.8	.29	32.8	.99
500-5000	1.6	.02	.41	0	0.0	0.0	1.6		1.6		33.8	

Fig. 3. Effect of activation time and temperature on the yield of porous carbon during physical activation.

during physical activation process with temperature and time in respect of two resins are shown in Fig. 3(a)~(c)

respectively. Both of these resins were initially activated at 750°C using CO_2 as activating agent but there was no activation at this temperature so we performed activation of these resins at a higher temperature i.e. 850~1000°C. In general PFR1 resin has shown better stability than CFR1 on physical activation in different conditions of activation. When we look at the yield patterns of samples within the temperature range 850~1000°C for 8h. It has been observed that yield of PFR1 drops from 78.1 to 59.9% (approx. 18% wt. loss) on increasing activation temperature from 850 to 950°C. However, no further decrease in yield was observed at 1000°C. It clearly indicates that rate of activation becomes constant beyond 950°C. This is again confirmed by BET surface area which changes from 701 to 1000 m^2/g when temperature was raised from 850 to 950°C and no further enhancement in surface area was observed when temperature was raised to 1000°C. The reason behind the slower rate of oxidation in PFR1 resin may be the compact structure which could have arose due to better packing of graphitic planes. In case of CFR1 resin the remarkable increase in rate of activation was observed when temperature changes from 850 to 1000°C which resulted into improvement in BET surface area from 503 to 1119 m^2/g. The effect of activation time on surface properties and yield of these resins was studied at 1000°C for 4 to 8 h duration. It was seen that in this duration yield of PFR1 comes down from 78.3 to 60.1%. The surface area of these samples was found to vary from 583 to 1050 m^2/g. The yield pattern suggests that in case of CFR1 the rate of activation is faster and sharp decrease in yield i.e. 65.2 to 41.3% is observed in this interval.

3.3. Pore size distribution

Horvath-Kawazoe method was used to evaluate the pore

Table 5. Physical activation change in surface properties with increasing temperature (t=8 hrs)

Property	PFR1						CFR1					
	850°C		950°C		1000°C		850°C		950°C		1000°C	
Surface area (m^2/g)	701		1084		1050		503		685		1119	
Pore vol. (cm^3/g)	.37		.58		.65		.51		.39		.62	
Micropore vol. (cm^3/g)	.32		.47		.44		.25		.31		.38	
Micropore vol. (%)	86.5		81.0		73.8		80.0		82.0		77.4	
PSD (Diameter in A⁰)	Relative Vol. (%)	Pore Vol. (cm^3/g)	Relative Vol. (%)	Pore Vol. (cm^3/g)	Relative Vol. (%)	Pore Vol. (cm^3/g)	Relative Vol. (%)	Pore Vol. (cm^3/g)	Relative Vol. (%)	Pore Vol. (cm^3/g)	Relative Vol. (%)	Pore Vol. (cm^3/g)
3-7	67.8	.26	57.2	.33	54.6	.31	46.1	.16	62.1	.24	26.2	.16
7-20	22.1	.07	32.9	.18	35.0	.17	28.0	.08	24.1	.09	52.1	.33
20-500	10.1	.04	9.5	.07	10.1	.08	23.2	.07	13.2	.05	20.5	.12
500-5000	0.0	0.0	.37		0.3		2.8		0.6		1.2	

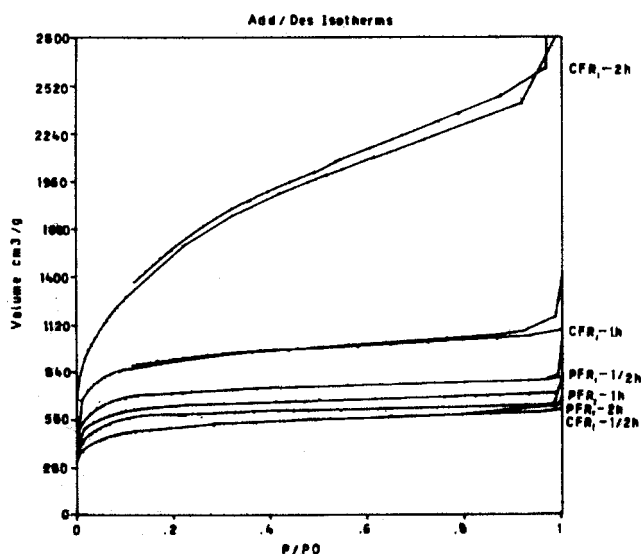**Fig. 4.** Chemical activation.

Fig. 5. Physical activation.

size distribution. The relationship between the potential energy of adsorbate inside a pore and the change of free energy upon adsorption as suggested by Horvath and Kawazoe [22] is as follows :

$$RT \ln (P/P_0) = U_0 + U_a$$

Where P_0 is saturated vapour pressure of adsorbate, T is the temperature and R is gas constant. U_0 & U_a are the adsorbate-adsorbent and adsorbate-adsorbate interaction energy, respectively, averaged over the pore volume.

As may be seen from Table 4, when these resins were activated with KOH as activating agent the total pore volume decreases with activation time for PFR1 resin compared to regular increase in total pore volume in case of CFR1 resin during chemical activation. However rate of activation is faster in case of CFR1 resin which results into faster burn off as shown in Fig. 2(a). It seems that the enhancement in the activation in case of PFR1 resin results into the creation of new pores in the ultra micropore region upto 1 h activation time and the relative volume of micropores in 3~7 Å region increases from 33.5 to 51.2%. This gives high micropore volume that is 81.70%. Further activation upto 2 h time causes the slight increase in pore diameter i.e. micropore percentage increases in 7 to 20 Å region. In CFR1 resin the total pore volume regularly increases after 2 h activation. However, there is marginal decrease in surface area from 2895 to 2505 m²/g, that may be due to the pore widening in mesopore region as evident from the mesopore volume increase from 0.40 to 1.49 cm³/g. In CFR1 resin after 2 h activation with KOH a large amount of nitrogen accumulated in the outer surface indicating that there is pore widening leading to formation of macropore, giving a very high total pore volume i.e 4.2 cm³/g.

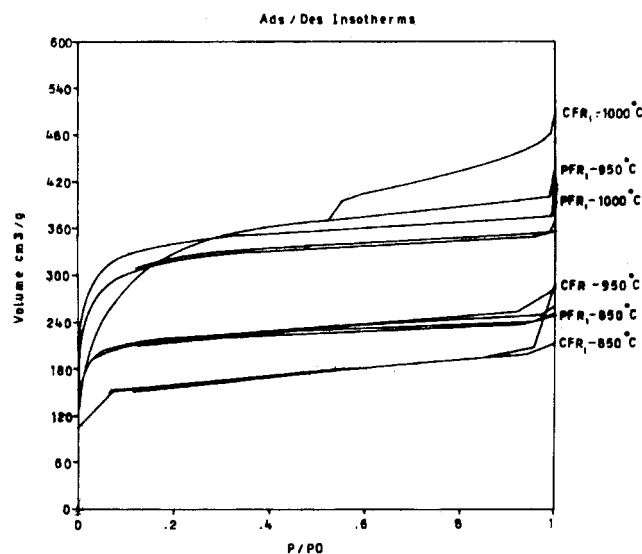In case of physical activation of PFR1 resin, when

temperature changes from 850 to 950°C the micro as well as total pore volume increases as expected. At 850°C the maximum pores were found in ultra micropore region i.e. 67.8% of total pore volume while 22.1% pore volume ties in 7~20 Å region. There are hardly any pores in mesopore region. When we go to 950°C temperature, the pore size increases within micropore region and the micropore volume percentage decreases in ultra micropore region from 67.8 to 57% and increases in 7-20 Å region from 22.1~32.9%. Beyond 950°C the enhancement in the surface properties i.e pore volume and surface area is not significant. It can be concluded from the activation results of PFR1 resin that the best combination of surface properties is obtained at activation temperature of 950°C. In the activation of CFR1 resin surface properties i.e micro pore volume, total pore volume and surface area regularly increases with temperature. At 1000°C CFR1 resin gives same order of surface area as shown by PFR1 resin at 950°C. The burn off of CFR1 resin is very high compared to PFR1 resin giving the poor yield for comparable surface properties. In CFR1 resin on going from 850 to 950°C, the new pores are created in ultra micropore region showing an increase in relative volume percentage from 46.1~62.1%. On further increase in temperature to 1000°C causes an increase in pore diameter resulting the enhancement in pore volume percentage in 7~20 Å region from 24.1 to 52.1%. A small volume of mesopores (20.5% of total volume) was also introduced at 1000°C. This is also evident from nitrogen adsorption isotherm as there is large hysteresis in this particular sample.

4. Conclusion

It may be concluded from the above studies that there is a

profound effect of structure of precursor material on the carbonization and activation pattern obtainable in different set of conditions, which in turn determine the surface properties of end product. These studies also show that process of chemical activation leads to very high surface area in short duration of time at lower temperature. It is a general belief that polymeric precursors lead to highly microporous products but it becomes evident from these studies that if precursor is chosen carefully (such as CFR1 resin in present study), mesoporous carbon can also be prepared from polymeric precursors.

References

[1] Agarwal, Damyanti; Lal, D.; Tripathi, V. S.; Mathur, G. N. Studies on chemical activation of phenolic resin chars. Proceedings of National Conference on carbon, 'Indo Carbon-2001' 2001 p. 73-81.

[2] Singh, G. S.; Lal, Darshan; Tripathi, V. S. Preparation of carbon molecular sieves using cation exchanged resin as precursor, Proceedings of Indo Carbon 2001, 2001 p 81-87.

[3] Gurudatt, K.; Tripathi, V. S. Studies on changes in morphology during carbonization and activation of pretreated viscose rayon fabrics. *Carbon* **1998**, *36*(9), 1371-1377.

[4] Byren, J. F.; Marsh, H. Introductory overview. In porosity in carbons, Patrick, J.W., Ed.; John Wiley and Sons Inc. London, GB, 1995.

[5] Solumn, M. S.; Pugmire, R. J.; Jagtoyen, M.; Derbyshire, F. Evolution of carbon structure in chemically activated wood. *Carbon* **1995**, *33*, 1247.

[6] Shopova, N.; Minkova, V.; Markova, K. Evaluation of the thermochemical changes in agricultural by products and in the carbon adsorbents obtained from them. *J. Thermal Anal.* **1997**, *48*, 309.

[7] Bota, A.; Laszlo, K.; Nagy, L. G.; Copitzky, T. Comparative study of active carbons from different precursors. *Langmuir* **1997**, *13*, 6502.

[8] Bahrton, A.; Horowitz, G.; Cerrella, G.; Bonelli, P.; Casanello, M.; Cukierman, A. L. Preparation of activated carbons using poplar wood and bark as precursors. In Biomass. A grow Opportunity in green energy and value-added products; Overend, R.P. Chornet, E., Eds.; Pergamon-Elsevier Science Ltd.; The Netherlands, 1999; Vol. 1, p 549.

[9] Munoz-Guillena, M. J.; Illan-Gomony, M. J.; Martin-Martinez, J. M.; Linares-Solano, A.; Salinas-Martinez Deleca, C. Activated carbon from Spanish coal. I. Two stage CO_2 activation. *Energy Fuels* **1992**, *6*, 9.

[10] Greenbank, M.; Spotts, S. Six Criteria for coal based carbons. *Water Technol.* **1993**, *16*, 56.

[11] Ahmdadpour, A.; Do, D. D. The preparation of active carbons from coal by chemical and physical activation. *Carbon* **1996**, *34*, 471.

[12] Falchuk, V. M.; Plachenov, T. G. *Zh. Prikl. Khim.* **1969**, *17*, 376.

[13] Plachenov, T. G.; Musakina, V. P.; Sevryugov, L. B. et al., *ibid* **1969**, *17*, 2020.

[14] Nakagawa, H.; Watanabe, K.; Horada, Y.; Miura, K. *Carbon* **1999**, *87*, 1455-1461.

[15] Hsisheng, Tang; Shong-Chi, Wang. *Industrial Eng. Chem. & Res.* **2000**, *39*, 673-678.

[16] Martin Robert, W. The chemistry of phenolic resins. Shell Development Co. Emeryville pp 87, 99 year 1956 by John Willey and Sons.

[17] Agarwal, Damyanti; Tripathi, V. S.; Mathur, G. N. proceeding of symposium on polymers and composites, 2000, p. 715-719.

[18] Dubinin, M. M.; Radushkevich, L. V.; Zhur. *Fis. Khim.* **1949**, *23*, 69.

[19] Brunauer, S.; Deming, L. S.; Deming, W. S.; Teller, J. *Amer. Chem. Soc.* **1940**, *62*, 1723.

[20] Otawa, T.; Tanibata, R.; Itoh, M. Gas separation and purification. **1993**, *7*, 241.

[21] Otawa, T.; Nojima, Y.; Itoh, M. Proceed. of 5th international conference on fundamentals of adsorption. Pacific Grove, May 13-18.

[22] Valladares, D. L.; Rodriguez Reinoso, F.; Zgrablich, G. *Carbon* **1998**, *36*(10), p. 1491-1499.