

Superficial velocity of H₂O/N₂ mixed gas flow in the furnace for the simultaneous carbonization/activation of pretreated cellulose fibers

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Abstract - Superficial velocity of H₂O/N₂ mixed gas flow in the high temperature activation furnace was studied during the simultaneous carbonization/activation of phosphoric acid pretreated wood pulp based cellulose fibers. Phosphoric acid pretreatment of the cellulose fibers reduced the starting and finishing the stabilization temperature and resulted in 3.66 times higher yield of activated carbon fibers than that of non-pretreated as-received fibers. Simultaneous carbonization and activation in a high temperature furnace is preferable than continuous processes. The ratio of H₂O/N₂ mixed gas is regarded as one of important factors, but careful control of superficial velocity of this mixed gas flow in the furnace is necessary to increase yield and specific surface area of activated carbon fibers.

Key words - cellulose fibers, pretreatment, activation, superficial velocity, specific surface area

I. INTRODUCTION

The production of highly effective fibrous carbon adsorbents with smaller diameter, excluding of minimizing external and intra-diffusional resistance to mass transfer, and therefore, exhibiting high sorption rates, is a challenging task for investigators in the science and technology of carbon fibers. With low hydrodynamic resistance, to be used in thin layers for the treatment of high gas flows, these materials will increase efficiency and permit a far greater flexibility and simplification in the design of sorption process for environmental pollution control. The application of activated carbon fiber (ACF) is extended not only adsorbents but also catalyst supports, electrical and electronic materials for its unique pore structures and useful level of electrical conductivity. Thus efforts have been under way to prepare cheaper activated carbon fibers with controlled pore size distribution and high surface area [1]. ACFs have been obtained from an appropriate fibrous precursor by an adequate carbonization and activation process. ACFs are now manufactured from regenerated cellulose (viscose rayon), phenolic resin (Kynol), polyacrylonitrile (PAN), and pitch-based fibers.

The activation process of carbonized fibers is basically analogous to those for producing non-fibrous forms of activated carbon, and can be separated into three main groups : (i) vapor/gas activation [2,3]; (ii) chemical activation [4-6]; and (iii) a mixed approach including vapor/gas activation of chemically pre-activated samples [7-9]. The preferred activating gases are atmospheric oxygen, carbon dioxide, steam, and their combinations. Chemical activation is brought about by the action of various chemical agents producing a dehydration effect. Among the most commonly used chemical activations are orthophosphoric acid and zinc chloride, followed by activation in steam or carbon dioxide in the temperature range 600-900 oC. Use of zinc chloride resulted in larger mesopore volume than KOH or other chemicals, however, the use of zinc chloride has declined due to problems of environmental contamination with zinc compounds [4,7,8]. Recently, cheap natural cellulose fibers are being used as the precursor for the preparation of commercial ACF due to their low metal content, low density, and ease of production. However, in general, the yield of activated carbon fibers from cellulose fibers was very low compare to those of other organic fiber precursors. Therefore, many kinds of pretreatment to

cellulose based precursors were performed for increasing the activation yield. Among the pretreatments, phosphoric acid pretreatment was known as one of the most effective method [9]. There are many process conditions to obtain promising activated carbon fibers such as pretreatment of precursor, stabilization, carbonization and activation conditions. Up to now, the optimum activation conditions were studied by controlling the temperature, time, vapor/gas ratio, and so on, to increase the yield and specific surface area of the activated carbon fibers. Actually, there are so many reports to investigate the above conditions. However, only one report mentioned on ratio of steam/nitrogen mixing gas during the activation of precursor fibers using 3.8 cm inside diameter furnace [10], but which did not mention on superficial velocity of the mixed gases in the high temperature activation furnace. In fact, the superficial velocity is a very important factor in carbonization and activation process, especially for the scale-up furnace. Therefore, the purposes of this study are to investigate the effects of, i) phosphoric acid pretreatment to wood based cellulose fibers and ii) superficial velocity of mixing gas flow in the high temperature activation furnace.

II. EXPERIMENTAL

2.1 Pretreatment of cellulose fibers

As-received wood pulp based cellulose fibers (5 μ m fiber dia., 900 fiber filaments, 1,650 denier, 7.0 g/d strength, 7.1% elongation) was supplied from Kolon Industries Co., Korea. Firstly, 1, 2, 3, and 5 ml phosphoric acid (Aldrich Co. USA, 85%) were added to the 200 ml distilled water contained in an Erlenmeyer flask, and noted as 0.5, 1.0, 1.5, and 2.5% phosphoric acid solutions for the convenience sake. And 0.35 g cellulose fibers were immersed in these different concentration phosphoric acids, respectively and gently stirred in a shaking incubator at room temperature. Immersed times were 5, 10, 15, and 20 min. After pretreatment, fibers were filtered with glass filter (2G-1) and dried in an oven maintained at 60 $^{\circ}$ C, for 2 hrs. After cooling to room temperature, weights of fibers were measured to study the weight change during the pretreatment. The moisture content of the as-received cellulose fibers was 5.77%.

2.2 Stabilization, simultaneous carbonization/activation

Pretreated cellulose fibers were air stabilized in a horizontal tubular furnace with three temperature control zones. The stabilized fibers were simultaneously carbonized/activated in steam/nitrogen mixed gas flow using the same horizontal tubular furnace at various process conditions such as activation temperature, steam/nitrogen ratio, and superficial velocity of flow gas. The diameter and length of the tubular furnace are 5 and 60 cm, respectively. Therefore, the cross-sectional area and volume of the furnace are 19.625 cm² and 1177.5 cm³. If the volumetric velocity of nitrogen is 2000 ml/min at room temperature (20 $^{\circ}$ C), the superficial velocity of nitrogen through the furnace will be 1.70 cm/sec. This superficial velocity increased as increasing the furnace temperature following the Boyle-Charles' law, and the superficial velocity of 1.70 cm/sec became approximately 2.16 cm/sec at 100 $^{\circ}$ C (2546 ml/min) and 5.06 cm/sec at 600 $^{\circ}$ C (5959 ml/min). Steam was mixed to nitrogen in a container maintained at 100 $^{\circ}$ C, then transferred to next container which was preheated to 400 $^{\circ}$ C, then inlet to the furnace. If the outlet velocity of steam/nitrogen mixed flow is 3974 ml/min (1428 ml H₂O/2546 ml N₂) at 100 $^{\circ}$ C from the mixing container (H₂O/N₂ ratio = 0.56), the superficial velocity is estimated to 3.375 cm/sec, which became 7.54 cm/sec at 600 $^{\circ}$ C and 9.27 cm/sec at 800 $^{\circ}$ C in the furnace. Even the mixing ratio (v/v) is the same (=0.56), the superficial velocity can be changed by the cross-sectional area of furnace, amount of flow, and furnace temperature.

2.3 Characterization

FT-IR (Bruker optics IFS 66/S Reflectance_ATR mode, Scans: 64 scans) curves of the as-received and phosphoric acid treated cellulose fibers were measured. TGA (TGA/DSC1/1600 LF, Mettler-Toledo) was used to measure the as-received and phosphoric acid treated cellulose fibers. BET specific surface area and pore size distribution of the activated carbon fibers were analyzed by nitrogen adsorption isotherms at 77 K (Micromeritics ASAP 2020, USA). The yield of activated cellulose fibers was calculated by following equation,

$$\text{Yield (wt\%)} = \frac{W_a}{W_o} \times \frac{W_{(c/a)}}{W_a} \quad (1)$$

where, W_o : weight of as-received or pretreated cellulose fibers, W_a : weight of stabilized fibers, and $W_{(c/a)}$: weight of carbonized/activated fibers.

III. RESULTS AND DISCUSSION

Fig.1 shows weight increases of the pretreated cellulose fibers in comparison with the as-received fibers (a) after pretreatment in different concentration phosphoric acids, and (b) for different immersion time. Obviously, the weight of pretreated cellulose fibers linearly increased with the increase of phosphoric acid concentration. An important function of the phosphoric acid is to promote bond cleavage in the biopolymers at low temperature, which are followed by extensive crosslinking that can account for the high carbon yields [9,11]. Freeman et al. [12] also reported the weight increase of rayon fibers by pretreatment with zinc chloride solution, and the optimal pretreatment concentration of solution was 3 wt%. However, Lee et al. [13] reported that rayon fibers pretreated in a 3 wt% zinc chloride solution resulted in some amount of zinc chloride powder after high temperature (> 800 oC) carbonization. Fig.1 also shows the weight changes of cellulose fibers pretreated in phosphoric acid by varying the immersion time. Molina-Sabio et al. [14] reported that immersion time also affects on the yield of stabilized cellulose fibers. However, in this experiment, as increasing the immersion time up to 20 min. in 1.0% phosphoric acid, the weight change of cellulose fibers was almost constant to 5 min. immersion time. This means increasing the immersion time is no more important, and the most weight change was carried out in the beginning of immersion.

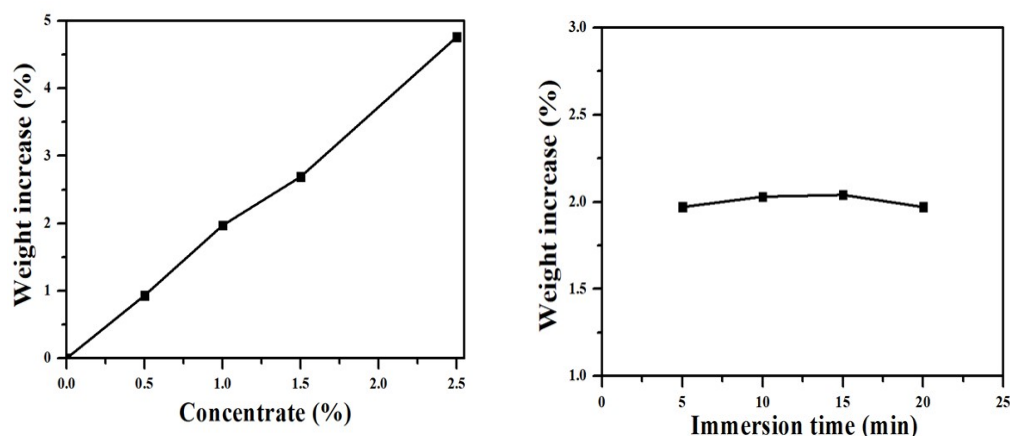


Figure 1. Weight increase of cellulose fibers pretreated in phosphoric acid (a) different concentration at room temperature for 5 min. immersion time, (b) different immersion time at room temperature with 1.0% concentration.

Fig.2 shows FT-IR curves of the as-received and phosphoric acid treated cellulose fibers. From the curves, significant intensity reductions in the C-O-C and C-OH groups that adsorb at around $\lambda = 1069$, 1118 and 1273 were shown due to the loss of aliphaticity and resulted in the increase of aromaticity [15]. On the other hand, intensities in C=O peak at around $\lambda = 1750$, CH₂ peak at around $\lambda = 2880$, and OH peak at around $\lambda = 3130$ -3460 were strengthened by pretreatment. This is due to the C=O stretch in esters and carboxylic acids, and these were also lowered the degradation starting temperature of precursor fibers to 150 oC [16].

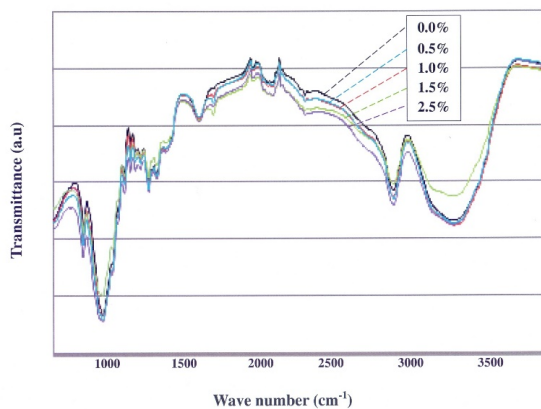


Figure 2. FT-IR curves of cellulose fibers (0.0% : as received, and 0.5, 1.0, 1.5, 2.5% : pretreated in phosphoric acid for 5 min. at room temperature.

Fig.3 shows TGA curves of (a) as-received and phosphoric acid treated (0.0, 0.5, 1.0, 1.5, 2.5%) cellulose fibers in the air surrounding. Thermal degradation of the as-received cellulose fibers was started from 200 oC and the residual yield was about 15% at 400oC, and less than 3% at 600oC. While the residual yields of pretreated cellulose fibers were much increased at 400 oC and 600 oC, which means pretreatment of cellulose fibers is necessary for the increase yield of activated cellulose fibers. The degradation starting temperature of cellulose fibers was reduced to 190 oC by pretreatment with 0.5% phosphoric acid. While residual yield was about 33.7% at 400 oC, but the residual yield at 600 oC was 3.3%, which is similar to the as-received fibers. However, as increasing the concentration of phosphoric acid to 1.0% and 2.5%, the degradation starting temperature of cellulose fibers reduced to 180 oC and 170 oC, respectively. On the other hand, the residual yield was about 41% at 400 oC, and 5.7% at 600 oC for the pretreated with 2.5% phosphoric acid, which is larger than that of 0.5% phosphoric acid treated fibers, and increased as increasing the acid concentration. Teng et al. [7] and Jagtoyen et al. [17,18] reported that phosphoric acid accelerates the bond cleavage reactions by expansion of the wood cellulose structure, leading to the early evolution of volatiles. A further effect of the phosphoric acid was to increase the carbon yield. Bai et al. [19] also reported the decrease of degradation starting temperature of the same cellulose fibers, which was pretreated with di-ammonium hydrogen phosphate (DAHP). This is due to the thermal degradation of DAHP and volatiles. After degradation, cellulose fibers released water by the phosphorylation reaction [20].

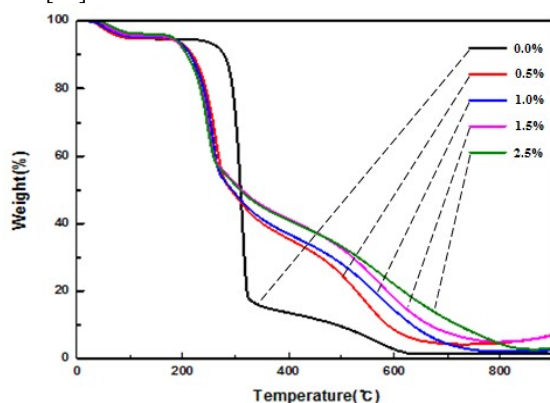


Figure 3. TGA curves of cellulose fibers in air (0.0% : as received, and 0.5, 1.0, 1.5, 2.5% : pretreated in phosphoric acid for 5 min. at room temperature.

Fig.4 shows yields of cellulose fibers stabilized in air for 20 min. As studied from TGA curves, the weight change was not so much happened with the as-received fibers. On the other hand, the yield of stabilized cellulose fibers linearly decreased as increasing the stabilization temperature. In general, the carbonization process of the organic polymers is itself accompanied by the formation of porous fiber structure. At the same time, an increase in the specific surface area, due to the development of pores, occurs only during low temperature stages (400-600 oC) of carbonization when the strength of the material is low, which is due to the deposition of some tarry substance in the entrances of sorbing pores which prevent adsorption at these sites [7]. Therefore, activation is necessary to discard deposited tarry substance to open the entrances of sorbing pores.

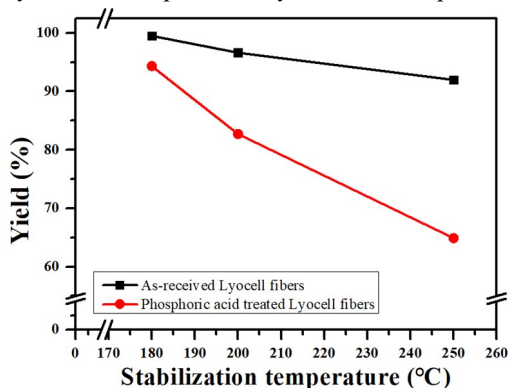


Figure 4. Yields of of cellulose fibers stabilized in air at 250 °C for 20 min., ■: as-received, and●: pretreated with 2.5% phosphoric acid at room temperature for 5 min.

Fig.5 shows yields of only carbonized cellulose fibers. The air stabilized (250 oC, 20 min.) fibers was carbonized at 600 oC, 7.54 cm/sec in nitrogen flow. For these experiments, the stabilized cellulose fibers was suddenly put to the center of furnace from the output side of furnace. In the beginning, large amount of smoke were gushed out from both the as-received and pretreated cellulose fibers, and the yields were rapidly decreased within 5 min. However, the yield of the as-received cellulose fibers continuously decreased and become less than 10 % during 20 min., while that of phosphoric acid pretreated fibers slowly decreased after 5 min. carbonization time, and about 23.08% yield can be obtained. Therefore, proper pretreatment of the as-received cellulose fibers was recommended to increase the carbonization yield. Bohra et al. [21] also reported that further increase of the carbonization temperature, as a rule, does not remove the tar from the pores but rather results in its carbonization, which finally seals the pores against any external sorbate. Therefore, effective carbonization temperatures were recommended 450 oC for the preparation of carbons from biomass [15] and lignite [22], and 550 oC from bituminous [17]. Previous study shows that the yields of carbonization, followed activation were very similar to those of one-step carbonization/activation at same process conditions. Therefore, to reduce processes, the air stabilized cellulose fibers was simultaneously carbonized and activated with various process conditions, such as activation temperature, steam/nitrogen ratio, and superficial velocity of flow gas.

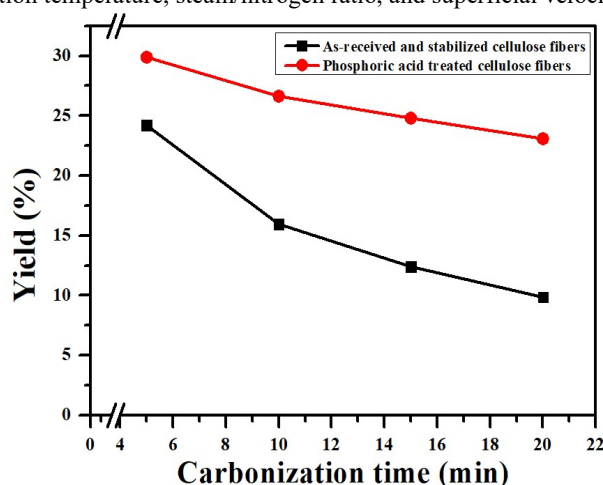


Fig.5. Yields of cellulose fibers carbonized at 600 °C, 7.54 cm/sec nitrogen flow,

■: as-received, and ●: pretreated with 2.5% phosphoric acid at room temperature for 5 min.

Fig.6 shows the yields of cellulose fibers which was stabilized for 20 min., at 250 oC in air, and followed simultaneous carbonization/activation at 600 oC, 7.54 cm/sec of superficial velocity of steam/nitrogen mixed gas flow ($H_2O/N_2=0.56$). The simultaneous carbonization and activation of both the as-received and pretreated cellulose fibers at 600 oC were rapidly performed with gushed out of gases in the beginning of the reaction. And then, the amount of gushed gases quickly reduced. However, the yield of activated as-received cellulose fibers decreased as increasing the activation time, remaining only 4.03 % for 20 min. This means only 3.7% activated cellulose fibers can be obtained from the as-received fibers through air stabilization at 250 oC for 20 min., and simultaneous carbonization and activation at 600 oC for 20 min. On the other hand, the yield of activated cellulose fibers was 23.08%, which can be converted to 13.55% with same stabilization and activation conditions by phosphoric acid pretreatment. So to speak, the yield of activated cellulose fibers increased to 3.36 times higher by pretreatment. Also, this yield can be increased by careful controlling the pretreatment conditions. Fig.7 also shows yields of activated cellulose fibers linearly decreased as increasing the activation time. While, only increasing the temperature to 800 oC in maintaining the same flow rate ($H_2O/N_2=0.56$), the superficial velocity increased to 9.27 cm/sec due to the expansion of gas. Yields decreased compare to those of obtained from 600 oC. The yield linearly decreased as increasing the activation time, and the decreasing rate is larger than that of obtained from 600 oC. About 6.6% final yield was obtained from 20 min. activation at 800 oC. Increasing temperature effects stronger than increasing flow rate of mixed gas in this condition.

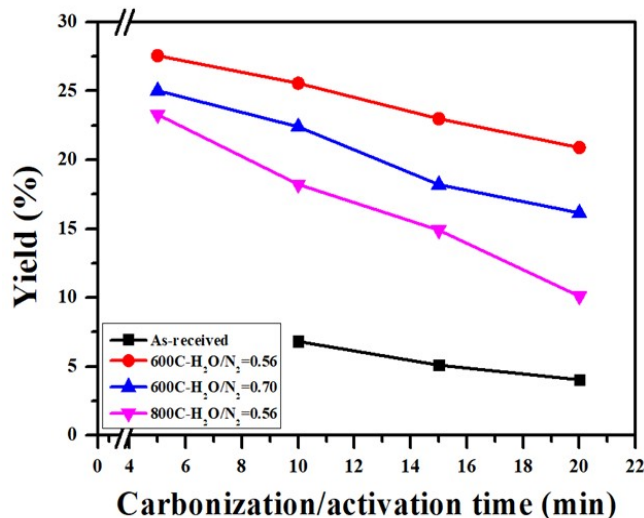


Figure 6. Yields of activated cellulose fibers prepared by stabilized at 250 °C, for 20 min. in air, and simultaneous carbonization/activation
 ■:as-received, activated at 600 °C, 7.54 cm/sec H₂O/N₂(=0.56) flow, ●:pretreated, activated at 600 °C, 7.54 cm/sec H₂O/N₂(=0.56) flow, ▲: pretreated, activated at 600 °C, 8.69 cm/sec H₂O/N₂(=0.70) flow, ▼: pretreated, activated at 800 °C, 9.27 cm/sec H₂O/N₂(=0.56) flow.

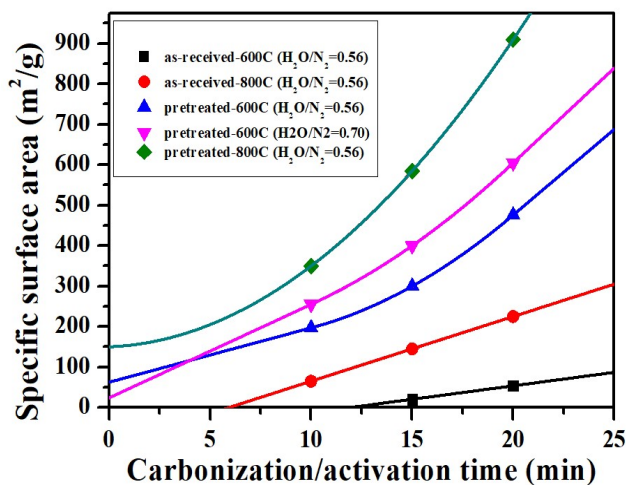


Figure 7. Specific surface areas of activated cellulose fibers prepared by stabilized at 250 °C, for 20 min. in air, and simultaneous carbonization/activation for 20 min. ■: as-received, activated at 600 °C, 7.54 cm/sec H₂O/N₂(=0.56) flow, ●: as-received, activated at 800 °C, 9.27 cm/sec H₂O/N₂(=0.56) flow, ▲: pretreated, activated at 600 °C, 7.54 cm/sec H₂O/N₂(=0.56) flow, ▼: pretreated, activated at 600 °C, 8.69 cm/sec H₂O/N₂(=0.70) flow, ◆: pretreated, activated at 800 °C, 9.27 cm/sec H₂O/N₂(=0.56) flow.

Table 1 and Table 2 show the characteristics of activated as-received and pretreated cellulose fibers, and Fig. 7 shows specific surface areas of activated cellulose fibers prepared with various carbonization/activation

conditions. All the surface areas exponentially increased as increasing the activation temperature. In comparison ■, ● with ▲, ▼, ◆, specific surface areas of phosphoric acid treated cellulose fibers were far larger than those of the as-received cellulose fibers. For the as-received cellulose fibers, the results show not only low yield but also low specific surface area. As increasing the superficial velocity of H₂O/N₂ mixed gas from ▲ 7.54 to ▼ 8.69 cm/sec at 600°C, the specific surface area prepared at 8.69 cm/sec increased 1.27~1.33 times larger than those of prepared at 7.54 cm/sec depending on the increase of activation time. These results were a little smaller than that of ACF prepared by dual-simultaneous pretreated (di-ammonium hydrogen phosphate and urea solution) and activated cellulose fibers at 600°C for 1 h, because of shorter (20 min.) activation time [19]. As increasing the carbonization/activation temperature from 600 to 800°C, even though same flow rate of H₂O/N₂ mixed gas, the superficial velocity increased from ▲ 7.54 to ◆ 9.27 cm/sec due to the expansion of gas, and the specific surface area prepared at 9.27 cm/sec was about 910 m²/g, which increased 4.04 times larger than that of prepared from as-received cellulose fibers and 1.91 times larger than that of prepared at 600 °C, 7.54 cm/sec. These results including average pore size were similar to those results of Teng et al. [7]. Even though Toles et al. [22, 15, 17] mentioned that the effective carbonization temperature was about 450 °C, activation should be performed at higher temperature than carbonization. In general, activation at high temperature affect stronger than activation at increased superficial velocity by increase in the steam ratio. From the Tables, total pore volume of the activated cellulose fibers increased with the increase of specific surface area. This is due to the different amount of surface functional groups obtained from phosphoric acid pretreatment.

Table-1 Characterization of activated as-received cellulose fibers

	H ₂ O/N ₂ : 0.56 Superficial velocity at 600 °C : 7.54 cm/sec			H ₂ O/N ₂ : 0.56 Superficial velocity : at 800 °C : 9.27 cm/sec		
	10	15	20	10	15	20
Carbonization/ activation time (min.)	10	15	20	10	15	20
Specific surface area (m ² /g)	-	20.4	53.7	65	145	225
Total pore volume (cc/g)	-	0.014	0.033	0.022	0.046	0.077
Average pore size (nm)	-	2.8	2.9	3.0	3.2	3.2

Table-2 Characterization of activated cellulose fibers pretreated in phosphoric acid (2.5%, 5 min.)

	H ₂ O/N ₂ : 0.56 Superficial velocity at 600 °C : 7.54 cm/sec			H ₂ O/N ₂ : 0.70 Superficial velocity at 600 °C : 8.69 cm/sec			H ₂ O/N ₂ : 0.56 Superficial velocity : at 800 °C : 9.27 cm/sec		
	10	15	20	10	15	20	10	15	20
Carbonization/ activation time (min.)	10	15	20	10	15	20	10	15	20
Specific surface area (m ² /g)	197	300	476	255	400	605	350	585	910
Total pore volume (cc/g)	0.11	0.17	0.26	0.14	0.22	0.33	0.193	0.32	0.50
Average pore size (nm)	1.6	1.8	1.8	1.8	1.8	1.9	1.8	1.9	1.9

In consideration of experimental conditions: phosphoric acid treatment (2.5%) of cellulose fibers, stabilization (at 250°C, 20 min.), and simultaneous carbonization/activation (at 600 °C, 20 min., $H_2O/N_2= 0.56$, and 7.54 cm/sec superficial velocity of mixed gas), the final yields of activated cellulose fibers was 13.55% ($Y=Y_s \cdot Y_a$), which was 3.66 times higher than that (3.7%) of the as-received activated cellulose fibers, and the specific surface area was about 476 m²/g. Increase the superficial velocity from 7.54 to 8.69 cm/sec by increasing the ratio of H_2O/N_2 to 0.70 at 600 °C, 20 min., the specific surface area increased to about 605 m²/g, and increase the superficial velocity from 7.54 to 9.27 cm/sec by increasing the activation temperature to 800 °C, 20 min., at $H_2O/N_2= 0.56$ the specific surface area increased to about 910 m²/g. On the other hand, increasing the activation temperature from 600 to 800 °C resulted in decrease the yield.

IV. CONCLUSIONS

Phosphoric acid pretreatment of wood pulp based cellulose fibers can be reduced the starting and finishing the stabilization temperature and resulted in high yield of activated carbon fibers. Simultaneous carbonization and activation in a high temperature furnace is preferable than continuous processes. The ratio of vapor/nitrogen mixed gas is one of important factors, but careful control of superficial velocity of this mixed gas flow in the furnace is also necessary to increase yield and specific surface area of activated carbon fibers. This superficial velocity is rapidly changed not only the ratio of mixed gas but also the amount of mixed gas in a high activation temperature furnace.

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REFERENCES

- [1] J.B. Donnet, Wang T.K. Wang, S. Rebouillat, and C.M. Peng, "Carbon Fibers", 3rd ed., Marcel Dekker, New York, pp. 524-525, 1998.
- [2] D.L. Biederman, A.J. Miles, F.J. Vastola, and Jr. Walker, "Carbon-carbon dioxide reaction: Kinetics at low pressures and hydrogen inhibition", Carbon, Vol. 14, No. 6, pp.351-356, 1976.
- [3] D.R. Olander, and M.J. Balooch, "Platinum-catalyzed gasification of graphite by hydrogen", J Catal., Vol. 60, No. 1, pp.41-56, 1979.
- [4] A. Amadpour, and D.D. Do, "Preparation of active carbons from coal by chemical and physical activation", Carbon, Vol. 34, No. 4, pp.471-479, 1996.
- [5] H. Yuan, L.Y. Meng, and S.J. Park, "KOH-activated graphite nanofibers as CO₂ adsorbents", Carbon Letters, Vol. 19, pp.99-103, 2016.
- [6] S.M. Lee, S.C. Lee, W.G. Hong, and H.J. Kim, "N₂ and H₂ adsorption behavior of KOH-activated ordered mesoporous carbon", Chem Phys Lett, 554, pp.133-136, 2012.
- [7] H. Teng, T.S. Yeh, and L.Y. Hsu, "Preparation of activated carbon from bituminous coal with phosphoric acid activation", Carbon, Vol. 36, No. 9, pp.1387-1395, 1998.
- [8] M.A. Lillo-Rodenas, D. Cazorla-Amoros, and A. Linares-Solano, "Understanding chemical reactions between carbons and NaOH and KOH: an insight into the chemical activation mechanism", Carbon, Vol. 41, No. 2, pp.267-275, 2003.
- [9] M.S. Solum, R.J. Pugmire, M. Jagtoyen, and F. Derbyshire, "Evolution of carbon structure in chemically activated wood", Carbon, Vol. 33, No. 9, pp.1247-1254, 1995.
- [10] J.J. Freeman, and F.G.R. Gimblett, "Studies of activated charcoal cloth. II. Influence of boron-containing impregnants on the rate of activation in carbon dioxide gas", Carbon, Vol. 25, No. 4, pp.565-568, 1987.
- [11] F. Shafizadeh, and P.P.S. Chin, " In Wood Technology: Chemical Aspect" (Edited by Goldstein IS), Am. Chem. Soc., Washington, 1977, Vol. 5, pp.57-81.
- [12] J.J. Freeman, K.S.W. Sing, and J.B. Tomlinson, "A comparison of carbon dioxide and steam as activating gases for viscose rayon chars", Proceedings, Carbon '90, Paris, p.164, 1990.
- [13] Y.C. Lee, "Adsorption characteristics of activated rayon fibers with ZnCl₂", Master Thesis, Chungnam National University, Daejeon, Korea, 1993.
- [14] M. Molina-Sabio, F. Rodriguez-Reinosa, F. Caturla, and M.I. Selles, "Porosity in granular carbons activated with phosphoric acid", Carbon, Vol. 33, No. 8, pp.1105-1113, 1995.
- [15] P.C. Painter, R.W. Snyder, M. Starsinic, M. Coleman, D.W. Kuehn, and A. Davis, "Concerning the application of FT-IR to the study of coal: A critical assessment of band assignment and the application of spectral analysis programs", Appl. Spectrosc. Vol. 35, No. 5, pp.475-485, 1981.
- [16] J.L. Lambert, H.F. Shovel, L. Verbit, R.G. Cooks, and G.H. Stout, "In organic Structure Analysis", Macmillan Publishing Co., New York, 1976, pp.258.
- [17] M. Jaytoyen, M. Thweites, J. Stencel, B. McCaney, and F. Derbyshire, "Adsorbent carbon synthesis from coals by phosphoric acid activation", Carbon, Vol. 30, No. 7, pp.1089-1096, 1992.
- [18] M. Jaytoyen, and F. Derbyshire, "Some considerations of the origins of porosity in carbons from chemically activated wood", Carbon, Vol. 31, No. 7, pp.1185-1192, 1993.
- [19] B.C. Bai, J.S. Im, and Y.S. Lee, "Lyocell-based activated carbon fibers improved the adsorption of harmful gas properties when produced via dual-simultaneous treatments", Carbon Letters, 23, pp.69-73, 2017.
- [20] M. Statheropoulos, and S.A. Kyriakou, "Quantitative thermogravimetric mass spectrometric analysis for monitoring the effects of fire

- retardants on cellulose pyrolysis", *Anal ChimActa*, Vol. 409, No. 1-2, pp.203-214, 2000.
- [21] J.N. Bohra, B.R. Awasthy, and S.S. Chari, "Adsorption characteristics of carbonised rayon yarn", *Fiber Sci. Technol.* Vol. 14, No. 3, pp.221-227, 1981.
- [22] C. Toles, S. Rimmer, and J.C. Hower, "Production of activated carbons from Washington lignite using phosphoric acid activation", *Carbon*, Vol. 34, No. 11, pp.1419-1426, 1996.