

ORIGINAL ARTICLE

Yasumitsu Uraki · Akira Nakatani · Satoshi Kubo
Yoshihiro Sano

Preparation of activated carbon fibers with large specific surface area from softwood acetic acid lignin

Received: May 17, 2000 / Accepted: December 6, 2000

Abstract Softwood acetic acid lignin (SAL) free from a high-molecular-mass fraction could be spun at 220°C by a spinning machine equipped with an extruder. Although the resulting fibers required thermostabilization, this step could be conducted with a faster heating rate than that for fibers obtained from hardwood acetic acid lignin (HAL). The thermostabilized SAL fibers were converted to activated carbon fibers (ACF) by carbonization in a stream of nitrogen at 1000°C, followed by steam activation at 900°C. At an activation time of 40min, the SAL-ACF had a larger specific surface area than the corresponding HAL-ACF. When the activation time for SAL carbon fibers was prolonged to 80min, the adsorption capacities of resulting ACF against iodine and methylene blue were markedly increased, as was the surface area of the ACF. It was found that SAL-ACF had adsorption properties comparable to those of high-performance commercial ACF. Also, it had a tensile strength equal to that of a pitch-derived ACF.

Key words Activated carbon fibers · Softwood acetic acid lignin · Specific surface area · Steam activation

Introduction

Utilization of lignin is one of the most important objectives for achieving effective utilization of woody biomass components. From this viewpoint, atmospheric acetic acid pulping has been developed as an efficient method for separating

wood components. The resulting lignin, acetic acid lignin (AL), was then characterized in terms of chemical structure and thermal properties. In particular, hardwood acetic acid lignin (HAL) was found to have a unique thermal property: It is fusible.¹ HAL was also found to undergo readily transformation to fibers by fusion spinning, which were then converted to carbon fibers (CFs) after thermostabilization.² The CFs were subsequently activated with steam to produce activated carbon fibers (ACFs).³ The ACFs activated for 40min had an adsorption capacity comparable or superior to that of commercial AC powder. Thus, HAL seems to be a promising source for producing ACF, although it requires thermostabilization to preserve its fibrous shape during the carbonization process. In general, thermostabilization is a troublesome process.

In addition to HALs, softwood acetic acid lignin (SAL) was spun in our laboratory using the test-spinning apparatus at 350°C after removing the high-molecular-mass fraction with less thermal mobility by solvent fractionation.⁴ The resulting SAL fibers also could be converted to the corresponding CF by direct carbonization without thermostabilization, an advantage over the HAL fibers.⁵ Despite this advantage, the resulting SAL-CF has an inferior tensile strength compared to that of HAL-CF. This weak strength is attributed to the fact that the former has a more highly porous structure than the latter. However, when SAL-CF is converted to the corresponding ACF, the resulting SAL-ACF is expected to have better adsorption properties than HAL-ACF because SAL-CF has a more highly porous structure than HAL-CF.

The preparation and characterization of ACF from SAL were investigated here to clarify the potential of SAL as a source for manufacturing ACF. In particular, our effort was focused on the relation between adsorption properties and activation time for the resulting ACF. Because the characteristics of ACF were affected by the spinning conditions and the CF production process, we investigated these processes again here. We mainly examined the spinning conditions of SAL using the extruder to produce SAL fibers at an industrial scale, because technical melt spinning was performed on the extruder under high extrusion pressure.

Y. Uraki (✉) · A. Nakatani · S. Kubo · Y. Sano
Laboratory of Wood Chemistry, Graduate School of Agriculture,
Hokkaido University, Kita-9 Nishi-9, Kita-ku, Sapporo 060-8589,
Japan
Tel. +81-11-706-2817; Fax +81-11-716-0879
e-mail: uraki@for.agr.hokudai.ac.jp

Part of this work was presented at the 49th Annual Meeting of the Japan Wood Research Society, Tokyo, April 1999

Thermostabilization was also examined as the crucial process for converting the resulting SAL fibers to the corresponding ACF.

Materials and methods

Softwood acetic acid lignin (SAL) was prepared by acetic acid pulping of todo fir (*Abies sachalinensis* Masters) under air atmosphere. The high-molecular-mass fraction in SAL was removed by solvent fractionation to give SAL.⁴ SAL fibers were prepared by fusion spinning on our laboratory spinning apparatus and a melt spinning test machine at Fuji Spinning Co. as described previously.² The spinning temperatures for the machines were 320°C and 220°C, respectively.

The SAL fibers were thermostabilized in air at 250°C for 1 h. The heating rate was 2°C/min from room temperature. The thermostabilized SAL fibers were subsequently carbonized at 1000°C for 1 h under a nitrogen stream. The heating rate was 180°C/min. The SAL-CFs were activated at 900°C for 40–80 min in an electric furnace by introducing steam mixed with nitrogen.³

Nitrogen adsorption isotherms were measured on a Belsorp 28 (Nippon Bell, Japan). The specific surface area of ACF was calculated from nitrogen adsorption by the BET equation. The micropore distribution was estimated by the micropore method of *t*-plot⁶ and the mesopore distribution by the Dollimore-Heal method.⁷ Adsorption capacities of ACFs against iodine and methylene blue were measured from the adsorption isotherm according to JIS K-1474. Tensile strength was measured according to JIS K-1477.

Results and discussion

Fusion spinning and thermostabilization

As previously reported, SALs were spun at a spinning temperature of 350–370°C on our laboratory apparatus, although SAL free from the high-molecular-mass fraction showed fusibility at 186°C.⁴ This temperature is denoted as the thermal flow-starting temperature (Tf). The spinning temperature of SAL is much higher than that of HAL despite a small difference in Tf between them. This could be the reason for the high melt viscosity of SAL. In the case of HAL, the melt viscosity decreased with increasing temperature; but after reaching the minimum it increased, probably because of condensation and charring.² SAL might behave in a manner similar to the thermal behavior of HAL. Therefore, only a fused part of SAL with low melt viscosity at an elevated spinning temperature, but without charring, could be likely spun by the apparatus that could be pressurized only up to 5 kgf/cm². Actually, most of SAL in a spinning tube remained as char with this spinning. SAL in fusion was assumed to be more easily extruded when spun at lower temperatures by employing higher extrusion pressures. This

would lead to an increase in the proportion of fibers to be spun without charring.

In the laboratory apparatus, the spinning temperature could be lowered to 320°C by slightly increasing the nitrogen pressure (to approximately 6 kgf/cm²). Therefore, much higher pressure might result in lowering the temperature. Hence, SALs were subjected to the fusion spinning on a machine equipped with an extruder that can be pressurized to 400 kgf/cm².² The SAL fibers were spun at a temperature of 220°C. The winding rate was 350 m/min. The spinning temperature was a little higher than the Tf and similar to that used for HAL fibers. By contrast, SAL could not be spun at the elevated temperature (320°C) because most of the SAL was charred. The achievement of low temperature spinning was attributable to the fact that a screw of the extruder could physically carry the SAL melt with relatively high viscosity to the nozzle. This resulted in high-pressure extrusion of fibers from the nozzle. Because spinning using the extruder is a typical method for industrial melt spinning, achievement of the spinning implies that the process for mass production of SAL fibers is a viable technology.

The SAL fibers spun at 350°C could be carbonized directly without thermostabilization. However, SAL fibers spun at 220°C and 320°C required such treatment, because the fibers adhered to each other, and their shape changed during the direct carbonization process. The thermostabilization involved oxidative reactions that resulted in cross-linking fusible SAL molecules with oxygen to give infusible materials with oxygen bridges. To keep the fibrous shape it was necessary to proceed with the reaction gradually. HAL fibers were thermostabilized at a heating rate of 0.5°C/min. In contrast, thermostabilization of the SAL fibers was performed at a heating rate of 2.0°C/min. The thermostabilization was accomplished even at a heating rate of 3.0°C/min, in which a significant number of the fibers adhered to the glass plate used as the support. However, this is not a major problem because the actual thermostabilization process is conducted in air, in which the treated fibers do not come into contact with any materials. These results suggested that thermostabilization of SAL fibers should be carried out only for a short time – approximately one-sixth of the time required for HAL fibers.

Relation between activation time and adsorption property

All infusible SAL fibers could be converted to ACFs by carbonization followed by steam activation. In this study the performance of ACFs prepared from SAL fibers spun at 320°C was evaluated with an activation time of 40–80 min. Figures 1 and 2 show the yield and specific surface area versus the activation time for ACFs, respectively. The results of HAL-ACF are included as a reference. In general, the yield is decreased as the activation time is prolonged.⁸ With an activation time of 40 min, SAL-ACF had a larger specific surface area than did HAL-ACF, although the yield of the former was higher. An area of this magnitude might result from the highly porous structure of the original SAL fibers. By prolonging the activation time, the surface area

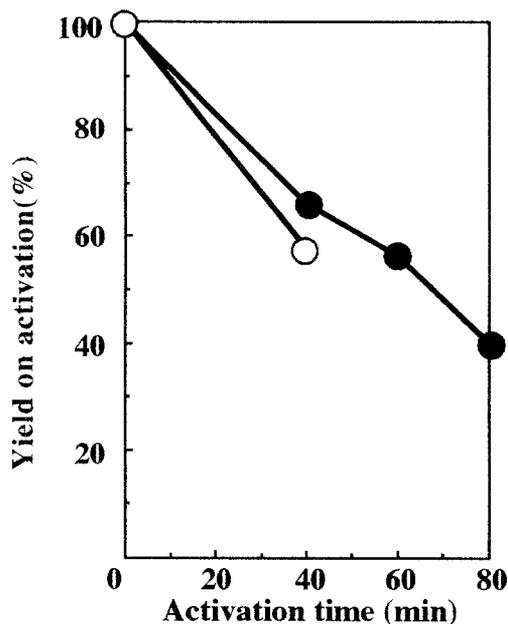


Fig. 1. Relation between yield and the activation time. *Closed circles*, softwood acetic acid lignin-activated carbon fibers (SAL-ACF); *open circles*, hardwood acetic acid lignin-activated carbon fibers (HAL-ACF)

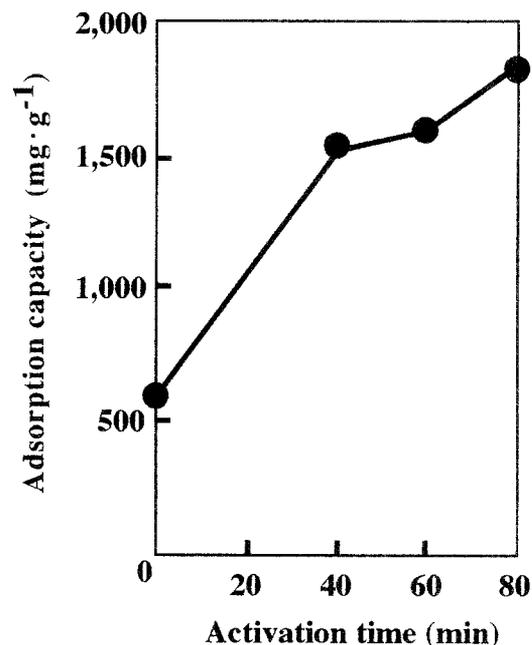


Fig. 3. Iodine adsorption capacity of SAL-ACF

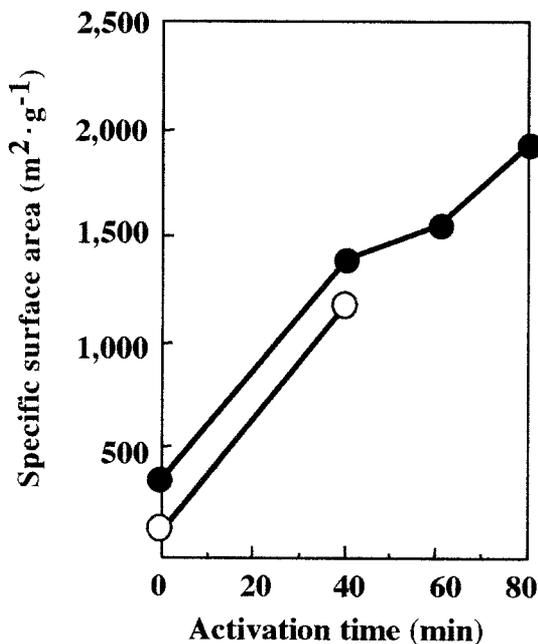


Fig. 2. Relation between specific surface area and activation time. *Closed circles*, SAL-ACF; *open circles*, HAL-ACF

was markedly increased. The surface area of SAL-ACF was approximately $2000\text{m}^2\cdot\text{g}^{-1}$, when activated for 80 min. This value was comparable to that of high-grade commercial ACF.⁹

Figures 3 and 4 show the adsorption capacities of SAL-ACF against iodine and methylene blue, respectively. Evidently, the activation time had a considerable effect on the

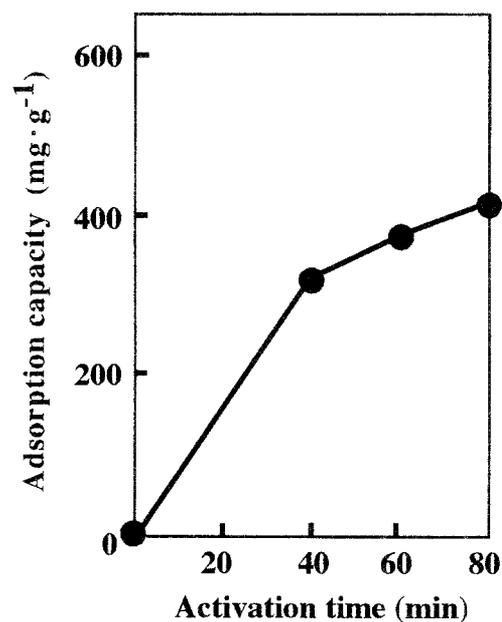


Fig. 4. Methylene blue adsorption capacity of SAL-ACF

adsorption capacities of SAL-ACF against adsorbates in addition to the specific surface area. The capacities of SAL-ACF to adsorb iodine and methylene blue with an 80-min activation were 1930 and $1830\text{mg}\cdot\text{g}^{-1}$, respectively. For the SAL-ACF obtained, the adsorbed amounts of methylene blue and iodine were superior and almost equal to a high grade pitch-derived ACF, respectively.⁹

The adsorption characteristics of ACF are closely related to the internal surface area and the development of micro- and mesopores, which act as adsorption sites. Although the iodine capacities of the 40- and 60-min activated

Table 1. Internal and external surface areas for various activated carbons

Sample	Activation time (min)	Surface area ($\text{m}^2\cdot\text{g}^{-1}$)			Ratio ^c
		Total ^a	Internal ^b	External ^b	
SAL-CF	0	370	355	15	24
SAL-ACF	40	1400	1360	40	34
	60	1550	1500	50	30
	80	1930	1790	140	13
HAL-ACF	40	1180	1130	50	23
AC powder ^d		1180	810	370	2.2
AC granule ^d		960	930	30	31

SAL, softwood acetic acid lignin; CF, carbon fibers; ACF, activated carbon fibers; HAL, hardwood acetic acid lignin; AC, activated carbon

^aValue was obtained by the BET equation

^bThese values were calculated from the t -plot on the basis of BET surface area

^cRatio is internal surface/external surface

^dAC samples were purchased from Wako Pure Chemicals, Co., Japan

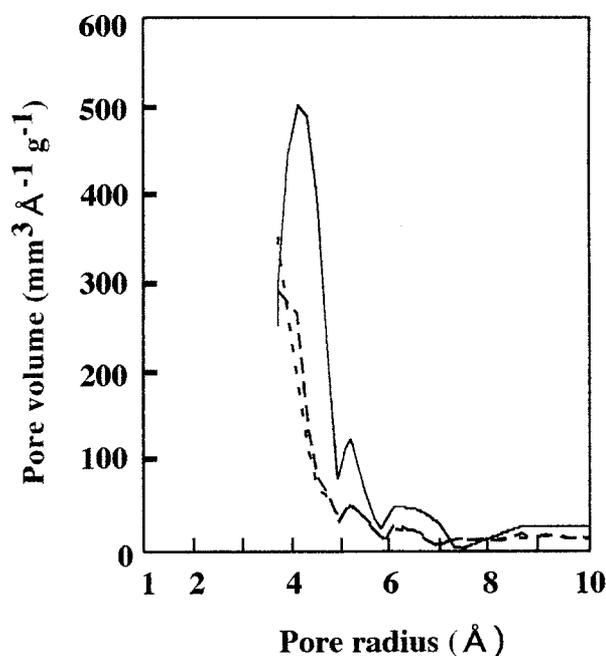


Fig. 5. Micropore distribution of SAL-ACF. Dotted line, 40-min activation; broken line, 60-min activation; solid line, 80-min activation

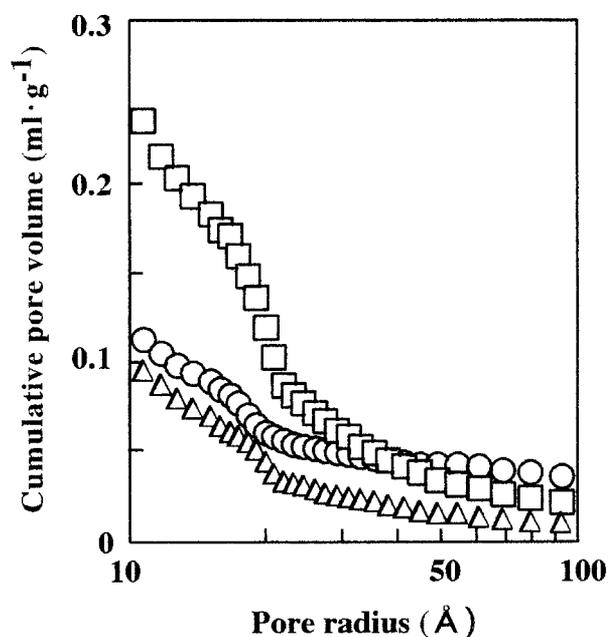


Fig. 6. Cumulative pore volume of SAL-ACF in mesopore region. Circles, 40-min activation; triangles, 60-min activation; squares, 80-min activation

ACFs were almost the same, the methylene blue capacities were considerably different. It is generally accepted that the amount of adsorbed methylene blue is highly correlated with the specific surface area of an adsorbent.¹⁰ As shown in Table 1, the internal area of the resulting ACF was preferentially increased as the activation time was prolonged. The results were in good agreement with previous observations.

Figure 5 shows micropore distribution, and Fig. 6 depicts the cumulative pore volume plot for the mesopore. The developments of the pores for the ACF activated for 40 and 60 min were apparently almost the same, whereas the development of the mesopore was slightly different. The mesopores in the 40 min-activated ACF were probably developed from pores with a large radius, which SAL fibers originally have before activation. In contrast, the development of mesopores in the 60 min-activated ACF took place

mostly in the region of 10–20 Å. In the 80 min-activated ACF, the mesopores of less than 50 Å were gradually developed with a large increase of pores having radii of less than 20 Å. In addition, micropores developed noticeably, as shown in Fig. 5. Thus, the mesopores and micropores developed in the 80 min-activated ACF brought about the large adsorption capacities for the resulting ACFs.

Tensile strength of SAL-ACF

The mechanical strength of SAL-ACF is one of the most important factors with respect to durability and handling for the subsequent processes. Figure 7 shows the tensile strength and diameter of SAL-ACF versus the activation time. The tensile strength of SAL-CF was approximately

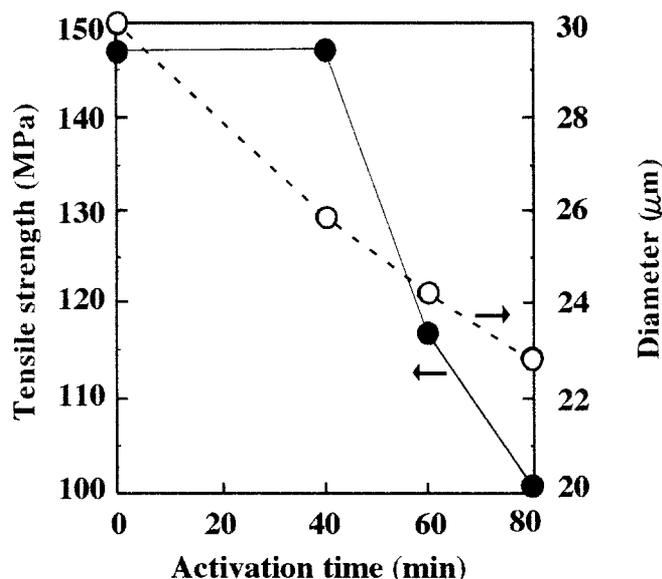


Fig. 7. Tensile strength and diameter of SAL-ACF

150 MPa, which was weak compared with commercial CFs. The strength did not change after a 40-min activation. By prolonging the activation time the strength became slightly less. However, the 80-min-activated SAL-ACF had a tensile strength of 100 MPa, which was comparable to that of commercial pitch-derived ACF, even though weaker than that of polyacrylonitrile (PAN)-derived ACF.⁹ Thus, SAL-ACF has practically sufficient strength despite the weak strength property of the original SAL-CF.

The SAL-ACF was found to shrink by the activation, giving thinner fibers. However, even after 80 min of activation the diameter of the SAL-ACF was 20 μm , which is much thicker than those of commercial ACFs. The mechanical strength of AL-based CF depends mostly on their diameter.⁵ Preparation of thin SAL fibers is being developed by improving the nozzle and the winding rate. Therefore, much stronger SAL-ACF, comparable to PAN-derived ACF, is expected to be prepared using thin SAL fibers as precursory fibers, although even the thick ACF prepared in this study has sufficient strength for commercial use.

Conclusions

Softwood acetic acid lignin fibers could be prepared at 220°C, a temperature slightly higher than the thermal flow-starting temperature. Although the fibers required thermostabilization to preserve their fibrous shape during the carbonization process, the thermostabilization of SAL fibers could be conducted at a faster heating rate than that used for the corresponding treatment of HAL fibers. SAL-ACF activated for 80 min had a large specific surface area and adsorption capacity comparable to those of commercial ACF with the highest performance. Furthermore, the SAL-ACF had sufficient strength for commercial use. Therefore, SAL is a promising source for production of ACF.

Acknowledgment The authors are thankful to Mr. M. Yamamoto at Hokkaido National Industrial Research Institute for helping with measuring nitrogen adsorption.

References

1. Kubo S, Uraki Y, Sano Y (1996) Thermomechanical analysis of isolated lignins. *Holzforschung* 50:144–150
2. Uraki Y, Kubo S, Nigo N, Sano Y, Sasaya T (1995) Preparation of carbon fibers from organosolv lignin obtained by aqueous acetic acid pulping. *Holzforschung* 49:343–350
3. Uraki Y, Kubo S, Kurakami H, Sano Y (1997) Activated carbon fibers from acetic acid lignin. *Holzforschung* 51:188–192
4. Kubo S, Ishikawa M, Uraki Y, Sano Y (1997) Preparation of lignin fibers from softwood acetic acid lignin: relationship between fusibility and the chemical structure of lignin. *Mokuzai Gakkaishi* 43:655–662
5. Kubo S, Uraki Y, Sano Y (1998) Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping. *Carbon* 36:1119–1124
6. De Boer JH, Lippens BC, Linsen BG, Broekhoff JCP, van den Heuvel A, Osinga TJ (1966) The t-curve of multimolecular N_2 -adsorption. *J Colloid Interface Sci* 21:405–414
7. Dollimore D, Heal GR (1970) Pore-size distribution in typical adsorbent system. *J Colloid Interface Sci* 33:508–519
8. Uraki Y, Taniwatashi R, Kubo S, Sano Y (2000) Activated carbon sheet prepared from softwood acetic acid lignin. *J Wood Sci* 46:52–58
9. Tai K, Shindo N (1993) Activated carbon fiber (in Japanese). *Sen I Gakkaishi* 49(5):177–182
10. Shimazaki K, Ono T (2000) Application of activated carbon fiber (ACF) for environmental clean-up (in Japanese). *Kobunshi* 49(3):125–128