

A New Modification Method of Exploded Lignin for the Preparation of a Carbon Fiber Precursor

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SYNOPSIS

A lignin-pitch for carbon fiber was prepared in a high yield from exploded lignin on phenolysis followed by heat treatment under a vacuum. The lignin-pitch had an excellent spinnability in the melt state to form a fine filament. The green fibers were easily made infusible when heated in air at a relatively high heating rate (15–60°C/h). The lignin-based carbon fiber was produced in 43.7% of yield based on a starting material. The tensile strength was more than 400 MPa, indicating that the lignin-based carbon fiber is classified into a general purpose grade. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

A lot of comprehensive work has been made on the development of a fractionation method for wood components, aimed at utilizing such materials as fuel, fine chemicals, feedstock, etc.

We have studied the total utilization of wood components by steam explosion pretreatment.¹ The three main components, hemicellulose, lignin, and cellulose could be fractionated from the steam-exploded hardwoods such as aspen, birch, acacia, etc. by successive extraction with water and dilute alkali. The hemicellulose is recovered as xylose and xylo-oligosaccharides that can be used as food additives, sweeteners, and so on. The cellulose is hydrolyzed with cellulose and fermented to alcohol or single-cell protein. However, the success of the steam-explosion process depends on the accomplishment of an effective utilization method of lignin.

We reported the conversion process of the steam-exploded lignin into a carbon fibers of the general purpose grade in our previous paper.² This process involves solving serious problems of the practical application. One of them is that the yield of carbon fiber was quite low. It was 15.7–17.4% based on the starting material, compared with that produced commercially from tar-pitch with a yield of 33%. In

the process, the lignin is modified to melt thermally on hydrogenolysis. The yield of hydrogenolated lignin is about 50%. Another disadvantage is that the production cost is high because of high energy consumption and high initial capital cost in the hydrogenolysis process. Therefore, an alternative method of modification of lignin into a fusible polymer must be developed instead of hydrogenolysis.

It is common knowledge that introduction of certain kinds of substituents in polymers results in changes of the thermal behaviors. For example, cellulose derivatives such as cellulose acetate and cellulose nitrate have softening and melting properties. Even wood is converted into thermoplastic and fusible material by esterification and etherification.³ Hatakeyama has reported that softening of lignin was caused by the motion of aromatic nuclei brought about by heating.⁴ It is expected that an addition of phenolic compounds to lignin would give it melting properties.

This article deals with the method of preparation of a molten viscous material as a precursor for carbon fiber with phenolysis of the steam-exploded lignin.

EXPERIMENTAL

Lignin Preparation

Two kinds of steam-exploded lignin from white birch were used as samples. One (EXL-1) is the same one

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used in the previous work.² Another (EXL-2) was from Mitsubishi Heavy Industry Co. Ltd. EXL-2 was extracted with 1% NaOH from birch wood, steam-exploded at 1.96 MPa (20 kgf/cm², ca. 215°C) for 6 min by using a continuous steam explosion pilot plant (4 ton/day). The alkaline extracts were acidified to pH 4. The precipitated lignin was collected by a filter press and dried at 50°C in an oven. The yield of EXL-2 was 33.3% based on Klason lignin in birchwood. Klason lignin and water contents in EXL-2 were 82.4% and 4.8%, respectively. The carbohydrate content was quite low, 2.81% as glucose.

Modification of Lignin

EXL-1 was subjected to phenolysis at 180–300°C for 2–5 h with an equal amount of phenol in weight. The phenolysis at 180°C was carried out in the presence of *p*-toluenesulfonic acid (2% based on the lignin) as a catalyst. The reaction mixture in a round flask equipped with a cooler was immersed in a preheated oil bath and mixed by a magnetic stirrer. After the reaction the mixture was heated at 130°C under reduced pressure to remove the unreacted phenol. An autoclave with an agitator was used for the phenolysis at the temperatures beyond 180°C. At these temperatures, catalyst was not added. After cooling, the reaction mixture was taken out of the vessel with acetone. After the evaporation of acetone, the reaction mixture was heated to remove the unreacted phenol in the same way as described above.

EXL-2 was reacted in a mixture of phenol and water (3/2, 2/3, w/w) with (10% based on lignin) and without acetic acid at 240°C and 260°C for 3 h and 6 h, respectively. The phenolyzed lignin was taken out of the vessel in the same manner as described above. The phenolyzed lignins were subjected to a heat treatment at 180–280°C for 10–300 min under a vacuum (1 mmHg) giving pitch-like materials.

Production Procedure of Carbon Fiber

Spinning of the modified lignin, thermostabilization, and carbonization of green fiber were carried out in the same ways as reported previously.²

Physical and Thermochemical Properties of the Modified Lignin

The modified lignins were characterized by fluidity measurement, thermogravimetry, and gel permeation chromatography in the same manner described previously.² Mechanical properties of the carbon fibers were also measured.²

RESULTS AND DISCUSSION

EXL-1 was modified by phenolysis and successive heat treatment under a vacuum, forming a pitch-like material (lignin-pitch). The reaction conditions and yield of lignin-pitch are listed in Table I. The yields were more than 90% based on starting ma-

Table I Effects of Preparation Conditions on Production of Lignin-Pitch From EXL-1

Exp. No.	Phenolysis Conditions			Heat Treatment		Yield (%)	Spinnability	Thermostabilization
	Temperature (°C)	Time (h)	Catalyst (%) ^a	Temperature (°C)	Time			
1	180	2	2	220	30 min	90.1	—	
2	180	3	2	180	3 h	96.0	+++	—
3	180	3	2	180	5 h	93.6	± ^b	± ^c
4	180	5	2	180	3 h	100.3	+++ ^d	±
5	180	5	2	180	4 h	96.8	+++	±
6	180	5	0	180	5 h	90.2	±	
7	250	3	0	280	40 min	80.2	+++	+++ ^e
8 ^f	180	5	2	200	15 min	96.5	±	
9 ^f	300	1	0	250	60 min	85.5	+++	+++

^a *p*-toluenesulfonic acid.

^b Sometimes not spun continuously on the spinning at a speed of 100 m/min.

^c Spun continuously at a speed of more than 300 m/min.

^d Part of fiber fused on heating at the rate of 15°C/h from 60°C to 250°C.

^e Thermosetted on heating at the rate of 60°C/h.

^f Creosote was used instead of phenol.

terial. These are more than two times higher than those prepared by the hydrogenolysis method reported previously.² At first, EXL-1 was subjected to phenolysis at 180°C for 2–5 h in the presence of catalyst and successive heat treatment at 180°C for 3–5 h. To get the lignin-pitch to have enough spinnability, the phenolated lignin was heated at 180°C for 3–4 h (Exp. No. 2, 4, and 5 in Table I). The lignin-pitch prepared by heating at 180°C for 3 h showed an excellent spinnability. It was spun into fine filaments at a speed of more than 300 m/min by the method of fusion spinning. With prolonged heating, the spinnability decreased (Exp. No. 3 in Table I).

However, the fine filaments (green fibers) could not be thermosetted on heating in air from 60°C to 250°C at a heating rate of 15°C/h. During the thermoset stabilization process, the green fibers melted partially and adhered to each other. This may be caused by the presence of the materials with low melting point. Therefore, to remove these substances the phenolyzed lignin was treated at 220°C for 30 min under reduced pressure (Exp. No. 1, Table I). However, the spinnability of the lignin-pitch decreased because of high viscosity in the melt-state, suggesting the insufficient phenol substitution and the presence of functional groups still remained in the lignin molecule to form cross-linkages by absorbing heat energy even after phenolysis.

Second, EXL-1 was phenolyzed at a higher temperature, 250°C (Exp. No. 7, Table I). No catalyst was added. The yield of phenolyzed lignin was 119.1%. Though all of the unreacted phenol could not be removed by a vacuum distillation, as shown in the gel permeation chromatogram (Fig. 1), the

phenolyzed lignin seemed to contain about 20% of condensed phenol by weight considering the yield (119.1%) and the decomposition of lignin during phenolysis. Comparing the GPC curve of the phenolyzed lignin with that of the original steam-exploded lignin (see Fig. 3 in Ref. 2) it is clear that the phenolysis results in the depolymerization of lignin. If the molecular weight of the phenylpropane unit in the steam-exploded lignin is assumed to be 200, the amount of phenol bonded is about one per 2.5 units. About 70% of unreacted phenol was recovered. A part of phenol was lost because of inhalation by the vacuum pump.

The phenolyzed lignin was converted to a lignin-pitch having an excellent spinnability when heated at 280°C for 40 min under reduced pressure. The increase of average molecular weight of lignin-pitch to phenolyzed lignin may be one of the reasons for its spinnability, as shown in Figure 1. The loss of weight in the heat treatment was 32.7%. Consequently, the yield of the lignin-pitch was 80.2% based on steam-exploded lignin (Table I, Exp. No. 7). The green fibers could be converted successfully to infusible fibers on heating from 60°C to 300°C at a heating rate of 60°C/h in air.

The thermosetted fibers were carbonized on heating at two different heating profiles from a room temperature to 1,000°C in a stream of nitrogen (Fig. 2). One (CF-1) was prepared on carbonizing at the constant heating rate (5°C/min) as described previously.² Another (CF-2) was carbonized according to the heating profile with different heating stages from a room temperature to 1,000°C, namely, from a room temperature to 300°C at the rate of 10°C/min, isothermally held at 300°C for 10 min, to 450°C

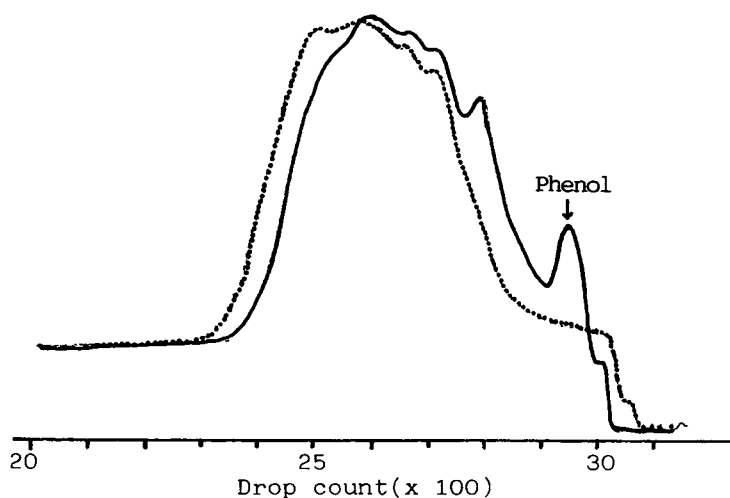


Figure 1 GPC curves of EXL-1 phenolyzed at 250°C for 3 h and the lignin-pitch prepared by heating at 280°C for 40 min. (—) EXL-1 phenolyzed; (· · · ·) lignin-pitch.

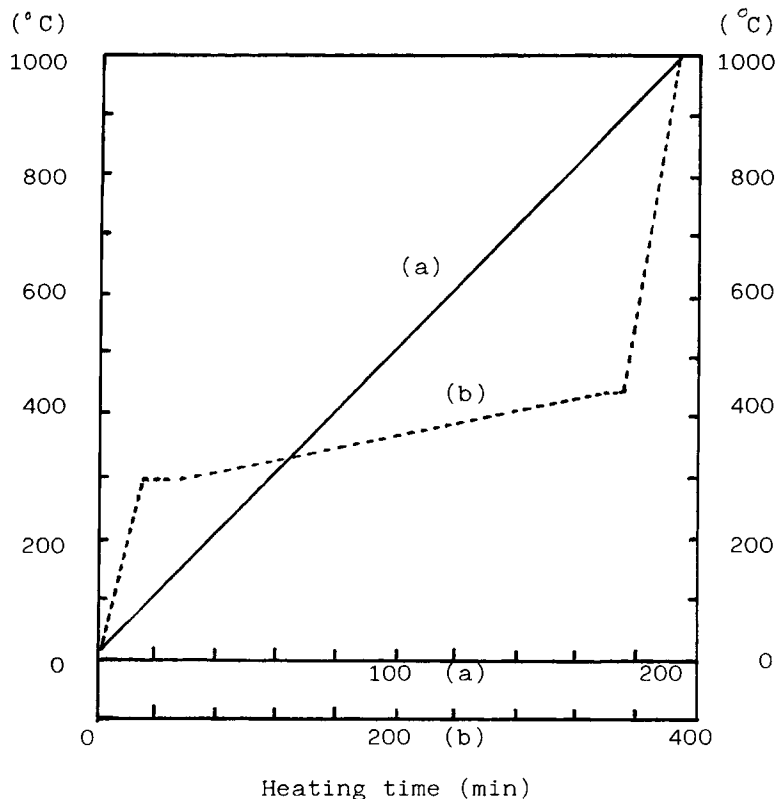


Figure 2 Carbonization profiles of the thermosetted lignin-based green fibers. (a) Constant heating rate at 5°C/min; (b) heating profile with various heating stages.

at the rate of 0.5°C/min, isothermally held at 450°C for 10 min, and then to 1,000°C at the rate of 10°C/min. As shown in Figure 3, weight loss of the thermosetted green fibers (CF-1) began at 240°C and the rate of weight loss rapidly increased, reaching a maximum at 384°C where the DTA curve showed the endothermic nadir. The deep endotherm and rapid weight loss continued until about 450°C. Beyond 450°C, the weight loss slowed down leaving about 50% residue (carbon fiber) at 800°C. In the case of CF-2, the endothermic nadir shifted to a lower temperature by 22°C and the residue increased by about 10% until 800°C. However, the significant difference in the yields between CF-1 and CF-2 was not observed (54.8% and 54.8% based on the thermosetted fibers, respectively) when they were heated up to 1,000°C under different heating profiles [(a) and (b) in Fig. 2].

The tensile strength and elongation of CF-1 and CF-2 are 394 MPa and 1.22%, and 311 MPa and 1.00%, respectively, indicating no significant differences of physical properties between them.

Third, instead of phenol as the phenolysis reagent, creosote was used because it is cheaper than

phenol (Table I, Exp. No. 8 and 9). The lignin-pitch prepared by phenolysis at a low temperature (180°C) followed by heat treatment did not have spinnability (Table I, Exp. No. 8). To improve the reactivity, an equal amount of EXL-1 and creosote by weight was reacted at 300°C for 1 h. The residue after vacuum distillation of creosote was 96.7% based on starting material. Creosote contains about 80% mono-phenolic compounds such as cresole, guaiacole, xylenole, and so on. Among these substituted phenols, phenols with alkyl groups seem to react more readily with the lignin molecule than phenol itself. On the contrary, phenols with alkoxy groups react unsatisfactorily with lignin molecules. Therefore, it is expected that phenols with alkyl groups like cresole and xylenole would react mainly with lignin. The carbon fibers (CF-3) could be successfully produced from the lignin phenolyzed with creosote according to the same manner as described previously.² The phenolyzed lignin could be converted to lignin-pitch on heating at 250°C for 60 min under a vacuum. The yield was 85.5% based on EXL-1. After spinning at a speed of 300 m/min, the green fibers were thermosetted from 60°C to 300°C

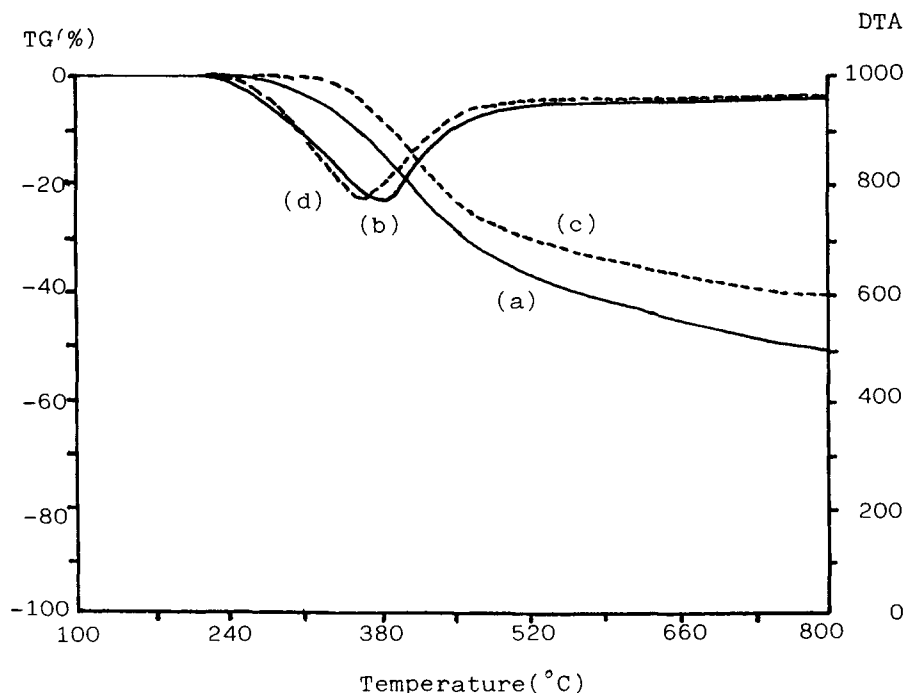


Figure 3 Thermograms of thermosetted green fibers. (—) Heated at constant heating rate at 5°C/min; (---) heated at the carbonization profile (b) shown in Figure 2. (a) and (c): TG curve; (b) and (d): DTA curve.

at the rate of 60°C/h in air. The thermosetted fibers were carbonized on heating at the rate of 5°C/min up to 1,000°C in a nitrogen stream. The yield of carbon fiber was 53.7% based on the starting material. The tensile strength and elongation were 455 MPa and 1.4%, respectively, indicating similar properties to those of the carbon fibers produced by the methods of hydrogenolysis² and phenolysis described above. These facts indicate that creosote can be used as a phenolysis reagent instead of expensive phenol.

EXL-2 did not make a homogeneous mixture with phenol by phenolysis with phenol alone when heated at 250°C for 3 h. This may be caused by the low substitution degree by phenol because of insufficient reaction sites in EXL-2. In order to promote the phenol substitution, the reaction sites of EXL-2 must be increased. From this viewpoint, the effect of the addition of water on the reaction was investigated. Water was expected to contribute to the increase of the reaction sites by promoting the cleavage of alkyl-aryl ether linkages in EXL-2. The conditions are listed in Table II. As expected, no solid was found in the reaction mixture in eight batches of experiment (Exp. No. 10–17 in Table II).

Among several factors, the ratio of reaction reagent to lignin seems to be the most important as

far as the softening temperature of phenolated lignin is concerned. The phenolated lignins obtained by Exp. No. 15–17 showed the softening temperature to be under 130°C. In these cases, the ratio of reaction reagent to lignin was 4; whereas in the case of phenolic reagent the ratio to lignin was 2, the softening temperatures of the phenolated lignins obtained were higher than 140°C (Exp. No. 10–13).

Softening temperature seems to have a correlation with the substitution degree of phenol. Yield of phenolated lignin was also related closely to substitution degree of phenol. However, there was no significant relationship between softening temperature and yield (Table II). This was probably caused by the difference in the extent of depolymerization of lignin itself during the reaction in addition to the different substitution degree of phenol.

In order to promote the depolymerization reaction, acetic acid (10% based on lignin) was added to the phenolysis reagent as a catalyst. However, there were no significant changes in the yield and softening temperature of the phenolated lignins (Table II).

It was found that all of the phenolated lignins shown in Table III had relatively low softening temperatures and could be converted easily to the lignin-pitch with good spinnability by heating at 220°C for

Table II Yield and Softening Temperature of the Lignin (EXL-2) Phenolyzed Under Various Different Conditions

Exp. No.	Ph/H ₂ O (w/w)	Ratio ^a	Acetic Acid (%) ^b	Phenolysis Conditions		Yield (%)	TST ^c (°C)
				Temperature (°C)	Time (h)		
10	2/3	2	0	240	3	101.9	148.3
11	3/2	2	0	240	6	106.8	143.6
12	2/3	2	10	260	3	97.0	161.2
13	3/2	2	10	240	3	100.4	147.5
14	2/3	4	0	240	6	101.1	130.2
15	2/3	4	0	260	3	91.1	127.0
16	3/2	4	10	240	6	105.6	127.5
17	3/2	4	10	260	3	—	123.0

^a Ratio of solvent to lignin in weight.

^b Based on lignin.

^c Softening temperature.

20 min. However, the lignin-pitches obtained by heating at 240°C for 20 min from the phenolated lignins in Exp. No. 10–13 did not have a comparable spinnability to those prepared from the lignin-pitches in Exp. No. 14–17 when heated under the same conditions. This difference suggests that the lignin-pitches in Exp. No. 10–13 are relatively unstable thermally.

Finally, the green fibers were converted to carbon fiber by heat treatment in air followed by carbonization as described above. The average tensile strength and elongation of the carbon fibers (Exp. No. 10–17) were 450 MPa and 1.2%, respectively,

indicating that their physical properties are very similar to those obtained so far.

As far as the yield of carbon fibers is concerned, the phenolysis method is superior to the hydrogenolysis method. The yield in each process of carbon fibers production by phenolysis is summarized in Table IV, including the case by hydrogenolysis for comparison. The table also contains the case of commercial production of carbon fiber from petroleum tar-pitch, data derived in industrial production in Nippon Carbon Co. Ltd.

The lignin-pitch and tar-pitch could be converted to the green fibers in the 95% yield by the method

Table III Softening Temperature and Spinnability of Lignin-Pitch Prepared by Phenolysis and Successive Heat Treatment

Exp. No.	Heat Treatment, 220°C, 20 min				Heat Treatment, 240°C, 20 min			
	Yield (%) ^a	ST (°C) ^b	Spin Time (s) ^c	Spin Speed (m/min) ^d	Yield (%)	TST (°C)	Spin Time (s)	Spin Speed (m/min)
10	86.7	188.8	73	500	79.3	229.6	No spinnability	
11	86.1	184.7	20	500	77.2	241.4	n.s.	n.s.
12	90.9	181.5	22	1,000	80.2	242.6	n.s.	n.s.
13	88.9	181.4	22	1,000	81.8	213.0	1	100
14	87.3	171.0	25	1,000	83.1	190.1	51	100
15	90.9	152.5	36	1,000	78.1	199.6	74	100
16	93.4	152.1	35	500	84.4	190.8	48	100
17	87.6	157.7	54	1,000	73.7	187.1	575 (40)	100 (1,000)

Exp. No. as in Table II.

^a Based on phenolyzed lignin.

^b Softening temperature.

^c Time spun continuously.

^d Spinning speed.

Table IV Yield in Each Process of Carbon Fiber Production From Steam-Exploded Lignin

Exp. No.	Phenolysis	Heat Treatment	Spinning	Thermostabilization	Carbonization	Final Product
10	101.9	86.7	95	88.2	49.3	36.5
11	106.8	86.1	95	90.7	54.1	42.9
12	97.0	90.9	95	95.7	56.7	45.5
13	100.4	88.9	95	94.7	54.7	43.9
14	101.1	87.3	95	95.1	57.0	45.5
15	91.4	90.9	95	91.5	58.3	42.1
16	105.6	93.4	95	92.1	56.6	48.8
17	—	87.6	95	94.3	56.8	—
Av. ^a	100.6	89.0	95	92.8	55.4	43.7
H ₂ -Method ^b	50.9	77.5	95	100.0	52.5	20.7
Tar pitch ^c		40.0	95	110.0	80.0	33.4

Experimental number is the same as those in Tables II and III. Each figure is a weight percent.

^a Average of exp. no. 10–17.

^b Yield in each process of carbon fiber production by hydrogenolysis method.

^c Yield in the commercial production process from tar pitch (Nippon Carbon Co. Ltd.).

of fusion spinning in pilot scale. The green fibers from the phenolated lignin were thermosetted on heating from 60°C to 210°C at the rate of 15°C/h in air. In the thermosetting process, the weight loss was about 7%. Since the thermosetting process is oxidative, weight of thermosetted fibers increases generally as in the case of tar-pitch (Table IV). However, in the case of phenolated and hydrogenolated lignins, an increase in weight was not observed possibly because of the degradation of the lignin molecule.

The yield of lignin based carbon fiber by phenolysis was 43.7% on average, 23% higher than that by hydrogenolysis and about 10% higher than that from the tar-pitch.

The relationship between thermal properties of phenolated lignin and degree of phenol substitution will be reported at a later date.

CONCLUSION

It was found that the steam-exploded lignin was converted to the melting material by phenolysis followed by heat treatment under a vacuum, the precursor for carbon fibers. Creosote was found to be effective as a phenolysis reagent. It is likely that the

addition of water in phenolysis promotes the degree of phenol substitution on lignin molecules.

The carbon fibers from the steam-exploded lignin by the phenolysis method could be produced in a high yield (more than 40%) based on starting material. Therefore, it is concluded that the phenolysis method is a promising procedure in carbon fiber production from the steam-exploded lignin.

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