

## A New Method for Stabilizing Softwood Kraft Lignin Fibers for Carbon Fiber Production

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**ABSTRACT:** Renewable resources, such as kraft lignin, have shown great potential as precursors for carbon fiber production. This manuscript reports an investigation into the stabilization of softwood kraft lignin (SKL) fibers and the determination of the difference in stabilization between hardwood- and softwood-based kraft lignin fibers. The stabilization was achieved either thermally by using only heat or oxidatively in the presence of air, at various heating rates. A heating rate of  $4^{\circ}\text{C min}^{-1}$  and a holding time of 30 min at  $250^{\circ}\text{C}$  were successfully used for the thermal stabilization experiments. Faster stabilization was achieved using oxidative conditions at a heating rate of  $15^{\circ}\text{C min}^{-1}$  and 30 min holding time at  $250^{\circ}\text{C}$ . Furthermore, stabilization and carbonization in a one-step process was performed on SKL fibers, which show great potential to reduce both production time and costs. The stabilized and carbonized fibers were evaluated using thermal, spectroscopic, and microscopic methods. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 3824–3830, 2013

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### INTRODUCTION

The development of environmentally friendly materials with high strength and low density is a worldwide endeavor that has led to the possibility of using lignin as a precursor for the manufacturing of carbon fiber (CF).<sup>1</sup> CF is a low-density, strong material that may be able to replace some of the steel in cars and thereby lowering weight, which would decrease fuel consumption. Other areas of application are in the aerospace industry and in many sport applications. The CF manufacturing process involves melt- or wet-spinning (the method is dependent on the raw material), oxidative stabilization at  $200\text{--}300^{\circ}\text{C}$  and carbonization under an inert atmosphere at  $1000\text{--}2000^{\circ}\text{C}$  (in some cases, graphitization at  $2000\text{--}3000^{\circ}\text{C}$ ), which is then followed by surface treatment and sizing.<sup>2</sup>

Today, the main raw material for manufacturing CF is polyacrylonitrile (PAN), which is a synthetic petroleum-based polymer. Other raw materials include coal- and petroleum-derived pitches and regenerated cellulose (Rayon).<sup>2</sup> The application areas of CFs are limited because of the high production cost; however, the demand would increase if the price decreased.<sup>3</sup> The production of PAN as a precursor accounts for approximately half of the total production cost.<sup>3,4</sup> The high costs have increased the interest in identifying alternative fiber precursors, for which lignin is a possible material.

Lignin is one of the most abundant biomacromolecules in the world and is made from three different phenylpropane units: coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol.<sup>5</sup> The chemical structure of softwood lignin is composed of guaiacylic units, which have a greater tendency to crosslink than the more linear hardwood lignins that also contain syringylic units. Several studies investigated the possibility of using various technical lignins as raw material for CF production, e.g., lignosulfonates,<sup>6</sup> organosolv lignins,<sup>7,8</sup> steam explosion lignins,<sup>9,10</sup> and kraft lignins.<sup>4,7,11</sup> Kraft pulping is the most common wood pulping process in the world for the production of paper; therefore, kraft lignin has potential to be readily available. Most of the previous studies on kraft lignins investigated hardwood lignins. The kraft lignin-based CF with the best mechanical properties was obtained from hardwood kraft lignin with 5% polyethylene terephthalate (PET) added.<sup>11</sup> However, the poor processability through spinning appears to be the reason why no neat softwood kraft lignin (SKL)-based CFs have been produced. Kubo et al. reported a discontinuous spinnable lignin prepared from softwood acetic acid lignin.<sup>12</sup> For hardwood kraft lignins, the spinnability is often satisfactory, but stabilization is a time-consuming step. Stabilization aims to transform a spun fiber from a thermoplastic to a thermoset character through methods including crosslinking, oxidation, and cyclization reactions, among others.<sup>2</sup> Oxidative stabilization in air is the most common method to

**Table I.** The Purity and Characteristics of the Lignin Samples Used in the Present Study

Lignin	Acid insolubles (%)	Carbohydrates (%)	Ash (%)	$T_g$ (°C)	$T_d$ (°C)	$M_w$	$M_n$	PD
SKL	96	2	0.93	150	273	6400	1300	5.0
SKLP	96	0.4	0.75	146	273	3300	1300	2.6
HKLP	86	0.4	0.93	114	274	1700	780	2.2

Acid insoluble is a measure of the lignin content.  $T_g$  = glass transition temperature,  $T_d$  = decomposition temperature,  $M_w$  = weight average molecular mass,  $M_n$  = number average molecular mass, PD = polydispersity ( $M_w/M_n$ ).

stabilize fibers during the manufacture of CFs from PAN- and pitch-derived fibers, as well as lignin fibers. Other possible oxidative gases or liquids usable for stabilization include oxygen, nitrogen dioxide, sulfur dioxide, sulfur trioxide, nitric acid, sulfuric acid, potassium permanganate, and hydrogen peroxide.<sup>2</sup> During the manufacture of pitch-based CFs, the reactions that occur during the stabilization process are oxidation, dehydration, condensation, crosslinking, and elimination.<sup>13–15</sup> The extent of the chemical transformation depends on the starting pitch raw material.<sup>15</sup> During thermal treatment of lignins, the actual temperature was maintained lower than the glass-transition temperature ( $T_g$ ), model calculations performed by Braun et al. predicted that a temperature increase of less than  $0.06^\circ\text{C min}^{-1}$  is required to hinder the fusion of the fibers.<sup>16</sup> In an experimental study of hardwood kraft lignin, a heating rate of less than  $0.5^\circ\text{C min}^{-1}$  was required to obtain excellent fiber integrity, and a heating rate less than  $3^\circ\text{C min}^{-1}$  was necessary to obtain separable fibers that could be separated but stick together.<sup>11</sup> Furthermore, hardwood kraft lignins purified using organic solvents required an even lower heating rate, i.e., as low as  $0.05^\circ\text{C min}^{-1}$ , to maintain intact fibers after carbonization.<sup>2</sup>

Recently, we successfully demonstrated the continuous spinning of SKL with a lignin-based softening agent.<sup>17,18</sup> Pyrolysis-gas chromatography/mass spectroscopy (GC/MS) was used to demonstrate that oxidative stabilization in air atmosphere introduces oxygen and changes the lignin structure.<sup>19</sup> Thermal gravimetric analysis performed after further thermal treatment (i.e., carbonization) of oxidatively stabilized softwood and hardwood kraft lignins showed an increase in the final CF yield. This result indicates that oxidative stabilization prior to carbonization causes the lignin to have an increased resistance to further thermal treatment. The oxidative stabilization of hardwood lignin fibers can result in a so-called skin-core structure on the fiber that prevents further oxygen penetration into the fiber.<sup>20</sup> The skin-core structure prolongs the stabilization time or hinders the full stabilization of the fibers.

To the best of our knowledge, studies of stabilization conditions for softwood-based lignin fibers have not been reported. The lack of reports is probably caused by the poor spinnability of the material, which leads to difficulty in producing softwood lignin fibers. In an earlier study,  $T_g$  measurements of fractionated kraft lignin powders indicated that softwood is more easily oxidatively stabilized than hardwood. For softwood, a  $T_g$  was not observed after stabilization at a heating rate of  $0.2^\circ\text{C min}^{-1}$  to  $250^\circ\text{C}$  with a holding time of 60 min, which indicates that comprehensive crosslinking of the lignin occurred.<sup>20</sup>

In this report, pure fractionated SKL fibers and fibers containing SKL with various percentages of fractionated hardwood kraft lignin added were used for stabilization and carbonization experiments. The fractionation of black liquor using ultra filtration through a 15 kDa membrane prior to isolation results in a raw material with higher purity and lower polydispersity<sup>21</sup> that enabled continuous fiber spinning. The different lignin fibers were thermally stabilized in the absence and presence of oxygen and were further carbonized into CFs. The stabilization procedure was optimized by studying the influence of heating rate, final stabilization temperature, and holding time. After stabilization, the fibers were evaluated with respect to melt ability using ocular melting point analysis and were further characterized by thermal, spectroscopic, and microscopic analyses.

## EXPERIMENTAL

### Materials

Kraft lignins used for the extrusion of lignin fibers originated from the pulping of softwood (spruce/pine) and hardwood (birch/aspens). The lignin samples were isolated according to the LignoBoost-concept<sup>22</sup> and were termed SKL, softwood kraft lignin permeate (SKLP), and hardwood kraft lignin permeate (HKLP). For the permeate lignins, the black liquors were ultrafiltered through a 15 kDa ceramic membrane before isolation.<sup>21</sup> The characteristics of the lignin samples used in this study is shown in Table I. All of the methods used are thoroughly described in Brodin et al. 2009.<sup>21</sup>

### Extrusion

Approximately, 7 g of a lignin or lignin-blend sample (manually mixed) was recycled in the extruder for 10 min at a temperature of  $200^\circ\text{C}$  prior to extrusion. A Thermo Fisher MiniLab laboratory extruder (HAAKE Minilab II, Thermo Fischer, Germany) equipped with twin-screws, a 0.5 mm-diameter die, and a take-up system (TUS, Dynisco, United Kingdom) was used for extrusion and fiber spinning.

### Stabilization

The lignin fibers were placed vertically in a conventional GC oven (HP 5890, Hewlett Packard, Switzerland). Stabilization was performed at various heating rates under an air or nitrogen atmosphere. For stabilization in nitrogen atmosphere, the fibers were placed in a closed vial containing nitrogen ( $\geq 99.999\%$  purity).

### Carbonization

The stabilized lignin fibers were placed in a ceramic ship in a tube furnace (VTF 50/15 -L, Entech, Sweden). Carbonization was performed under a nitrogen flow of  $15\text{--}20\text{ mLmin}^{-1}$  at a

heating rate of  $1^{\circ}\text{C min}^{-1}$  to  $600^{\circ}\text{C}$  followed by a heating rate of  $3^{\circ}\text{C min}^{-1}$  to  $1000^{\circ}\text{C}$ .

For stabilization and carbonization conducted as a one-step process, the following temperature program was used:  $10^{\circ}\text{C min}^{-1}$  to  $250^{\circ}\text{C}$ , held for 10 min, and then heat at a rate of  $3^{\circ}\text{C min}^{-1}$  to  $1000^{\circ}\text{C}$ .

### Thermal Analyses

After the stabilization of the lignin fibers, analyses using an Ernst Leitz melting point microscope (Ernst Leitz GMBH Wetzlar, Germany) were performed. Two crossed fibers were placed on the heating zone, and the temperature was increased to  $350^{\circ}\text{C}$  at the maximum heating rate (approximately  $30^{\circ}\text{C min}^{-1}$ ) during ocular observation. Fibers that did not stick together were manifested as stabilized fibers.

The differential scanning calorimetry (DSC) experiments were performed by placing a sample with a mass of approximately 2 mg in aluminum pans. A Waters DSC Q1000 V9.4 Build 287 instrument with a heating rate of  $1^{\circ}\text{C min}^{-1}$  was used to reach a temperature of  $105^{\circ}\text{C}$  to dry the samples. After cooling, the sample was heated to  $330^{\circ}\text{C}$  with a heating rate of  $3^{\circ}\text{C min}^{-1}$ . The  $T_g$  was measured as the inflection point of the transition.

### Spectroscopic Analyses

Cross polarized/magic angle spinning  $^{13}\text{C}$  nuclear magnetic resonance (CP/MAS  $^{13}\text{C}$ -NMR) spectra were recorded at  $290 \pm 1$  K using a Bruker Avance AQS 300 WB instrument at 7.04 T. The MAS rate was 5 kHz. The samples were carefully mortared and packed in a zirconium oxide rotor. A 7-mm double air-bearing probe was used. Acquisition was performed with a CP pulse sequence, using a  $4.3 \mu\text{s}$  proton  $90^{\circ}$  pulse, an  $800 \mu\text{s}$  ramped (100–50%) falling contact pulse and a 2.5 s delay between repetitions. A two-pulse phase modulation (TPPM15) pulse sequence was used for  $^1\text{H}$  decoupling. Glycine and an external standard were used for the Hartmann–Hahn matching procedure.

Fourier transform infrared (FTIR) spectroscopy was performed using a Varian 680-IR, FTIR spectrometer on a tablet containing mortared lignin and KBr (ratio  $\approx 1 : 100$ ). The measurements were made in the transmission mode with a mercury-cadmium-telluride (MCT) detector in air.

### Microscopic Analysis

Environmental scanning electron microscopy (ESEM) was performed using a Philips XL30 ESEM-field emission gun equipped with a backscattered electron detector in the low-vacuum mode. The operating conditions were as follows: the acceleration voltage was 10–12 kV, the pressure in the sample chamber was approximately 0.8 mbar, and the working distance was 8–10 mm. No conductive coating was used for the analyzed samples. Energy dispersive spectroscopy (EDS) with an Inca X-ray analysis system simultaneously detected the X-ray signals from all elements present in the analyzed material and provided semi-quantitative results.

## RESULTS AND DISCUSSION

In contrast to hardwood lignins, softwood lignins were previously reported to be unsuitable for fiber spinning because of a branched and crosslinked structure that prohibited melting.<sup>7,12</sup> However, at our laboratory the continuous spinning of SKL

fibers was shown to be viable.<sup>17,18</sup> In this work, we investigated the stabilization of the SKLP and SKL+10% HKLP fibers in the presence or absence of oxygen and with respect to the total stabilization time.

### Oxidative and Thermal Stabilization

During stabilization, heat and oxygen are usually used to turn thermoplastic lignin into a material with thermoset characteristics that prevents the fusion of the fibers during further thermal treatment.<sup>2</sup> In the following experiments, the stabilization in both heat and air are denoted as oxidative stabilization, and stabilization in heat in the absence of oxygen is termed thermal stabilization. To optimize the stabilization step, i.e. to achieve stabilization in shortest time, the influence of factors such as temperature, heating rate, holding time, and the presence of oxygen were investigated. The stabilization was optimized with respect to the total stabilization time to produce infusible fibers that do not stick together while keeping the fiber form, according to the behavior of crossed fibers during heating in a melting point microscope. Oxidative stabilization was compared with thermal stabilization. In Table II, the optimized stabilization conditions are shown for the SKLP and SKL+10% HKLP fibers. The SKL fibers were stabilized more quickly (Table II) than the hardwood lignins, which were previously shown to require a long oxidative stabilization time.<sup>4,16,20</sup> The most remarkable discovery was the successful thermal stabilization of the softwood-based lignin fibers, based on either fractionated lignin or unfractionated lignin with addition of a small amount of purified hardwood kraft lignin. In contrast, hardwood kraft lignin fibers could not be thermally stabilized with these conditions, and the fibers melted when using a heating rate of  $0.2^{\circ}\text{C min}^{-1}$  or greater. Thus, the presence of oxygen may be vital for complete stabilization of hardwood kraft lignin fibers.

### Thermal Evaluation After Stabilization

The successfully stabilized fibers were further evaluated by analyzing the  $T_g$ . The appearance of a  $T_g$  indicates an incompletely stabilized lignin. The softwood-based lignin fibers shown in Table II (SKLP and SKL+10% HKLP) were placed in a crossed configuration during the stabilization procedure. Subsequently, the fibers could be separated and remained intact, i.e. a stabilizing effect was observed. To obtain an oxidatively stabilized SKLP fiber, a heating rate of  $15^{\circ}\text{C min}^{-1}$  was used (Table II). For neat hardwood kraft lignin fibers, Kadla et al. reported a heating rate of  $2^{\circ}\text{C min}^{-1}$  to maintain the fiber form.<sup>7</sup> However, the same group later reported that a heating rate of  $0.2^{\circ}\text{C min}^{-1}$  is required to hinder the inter-fusion of fibers after oxidative stabilization.<sup>7,16</sup> In the present work, the thermal stabilization of SKLP was accomplished using a heating rate of  $4^{\circ}\text{C min}^{-1}$ , which was faster than the rate reported for hardwood kraft lignin-based fibers, but slower than the heating rate for the oxidative stabilization of SKLP (Table II). No  $T_g$  was detected using DSC for the SKLP fibers (Table II), which indicates that the fibers were fully stabilized (i.e., the fusible thermoplastic lignin fiber transformed into an infusible thermoset structure).<sup>23</sup> Figure 1 shows thermograms after DSC analysis of SKLP fiber before and after oxidative and thermal stabilization, respectively.

**Table II.** The Conditions Used for the Optimized Stabilization of Softwood Kraft Lignin Permeate (SKLP) and Softwood Kraft Lignin (SKL) with Addition of Hardwood Kraft Lignin Permeate (HKLP), Respectively

Type of fiber	Atmosphere	Heating rate ( $^{\circ}\text{C min}^{-1}$ )	Holding time at $250^{\circ}\text{C}$ (min)	Total time (min)	$T_g$ ( $^{\circ}\text{C}$ )
SKLP lignin fiber	-	-	-	-	140
SKL+10%HKLP lignin fiber	-	-	-	-	138
SKLP	Air	0.2	60	1185	n.d. <sup>a</sup>
SKLP	Air	15	30	45	n.d. <sup>a</sup>
SKLP	Nitrogen	4	30	86	n.d. <sup>a</sup>
SKL+5%HKLP	Air	0.2	60	1185	n.d. <sup>a</sup>
SKL+10%HKLP	Air	0.2	60	1185	182
SKL+10%HKLP	Air	3	30	105	n.d. <sup>a</sup>
SKL+10%HKLP	Nitrogen	1	30	255	195

<sup>a</sup>n.d. = not detected. The final temperature was  $250^{\circ}\text{C}$  for all stabilization experiments. The glass-transition temperature ( $T_g$ ) for untreated lignin fibers and stabilized lignin fibers is also shown.

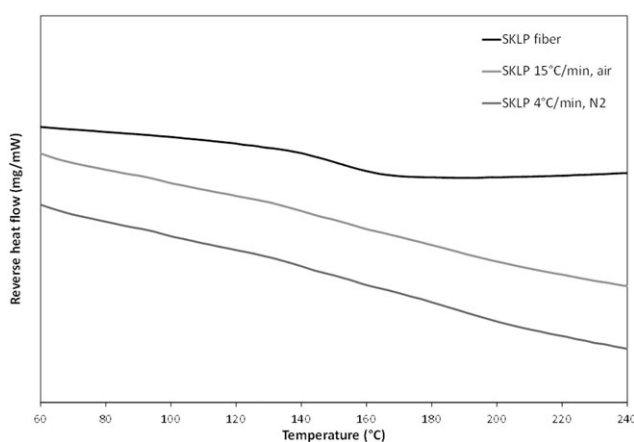
The SKL with addition of HKLP resulted in faster oxidative stabilization compared with hardwood kraft lignin fibers with 5% Poly(ethylene oxide) (PEO) added,<sup>7</sup> probably due to much higher reactivity of SKLs on thermal treatment. The highest heating rate during oxidative stabilization of SKL+10% HKLP fibers, was  $3^{\circ}\text{C min}^{-1}$ , which was lower than the heating rate used for pure SKLP. The HKLP acts as a softening agent when added to the SKL,<sup>17</sup> but the influence of the amount of HKLP on the optimal stabilization conditions was not investigated in this study. However, previous studies on hardwood kraft lignins indicate that higher amounts of softening agent (e.g., PEO) in the lignin requires a slower stabilization procedure and results in a lower  $T_g$  of the lignin blends.<sup>7,24</sup> Thermal stabilization of SKL+HKLP fibers was successfully performed using a heating rate of  $1^{\circ}\text{C min}^{-1}$ . As was the case with oxidative stabilization of SKLP and SKL+10% HKLP, a lower heating rate was

required for the SKL+10% HKLP fibers. For the SKL+10% HKLP fibers listed in Table II, a  $T_g$  was observed for the thermally stabilized fibers, which indicates incomplete stabilization. After oxidative stabilization, a  $T_g$  was not observed, even when using the highest possible heating rate that allowed intact fiber formation ( $3^{\circ}\text{C min}^{-1}$ ).

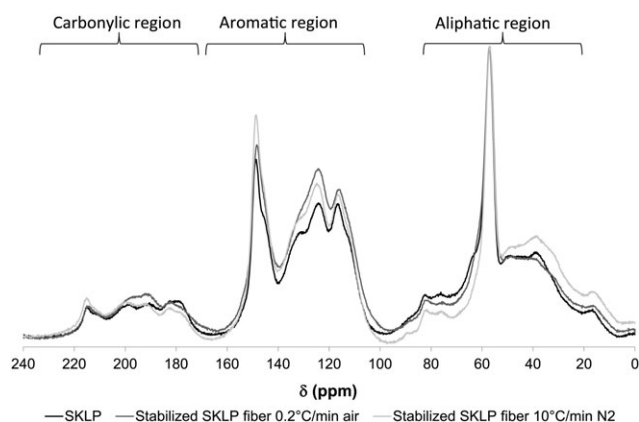
#### Chemical Characterization of Lignin Fibers and Stabilized Lignin Fibers

Few analytical methods are available for the analysis of the structural changes of the lignin structure after thermal treatment. In this study, the commonly used methods CP/MAS  $^{13}\text{C}$ -NMR and FTIR spectroscopy were applied.<sup>16,25–27</sup> To further investigate the structural changes that occurred during stabilization, powdered SKLP was compared with fibrous SKLP, a thermally stabilized SKLP fiber ( $10^{\circ}\text{C min}^{-1}$ ,  $250^{\circ}\text{C}$  for 60 min) and an oxidatively stabilized SKLP fiber ( $0.2^{\circ}\text{C min}^{-1}$ ,  $250^{\circ}\text{C}$  for 60 min).

The CP/MAS  $^{13}\text{C}$ -NMR spectra shown in Figure 2 are normalized to the methoxyl groups (55 ppm). After the oxidative treatment of the SKLP powder, the lignin was shown to be stable up to  $250^{\circ}\text{C}$  according to thermal gravimetric analysis.<sup>19</sup> A previous report regarding the pyrolysis of lignin model compounds indicated that in addition to the rapid homolytic cleavage of the  $\beta$ -O-4-linkage, the methoxyl group on the C3-position of the aromatic ring was also cleaved but at a much slower rate.<sup>28</sup> Based on these results, the methoxyl group was assumed to be stable. The spectra did not show any differences between the SKLP powder and the SKLP fiber (not shown), which indicates that few lignin structural changes occur during the melt spinning process. Furthermore, the  $T_g$  remained the same before and after extrusion. The reactions that occur during the oxidative stabilization of lignin were previously investigated.<sup>4,16,20</sup> The chemical reactions that occur during the oxidative stabilization of the SKLP fibers ( $0.2^{\circ}\text{C min}^{-1}$ ,  $280^{\circ}\text{C}$ , 2 h) were thoroughly discussed by Brodin et al., who used X-ray photoelectron spectroscopy as an analytical tool.<sup>20</sup> On the fiber surface, the formation of oxygen-containing functional groups, such as carboxyl groups, in the side-chain was observed. In  $\beta$ -O-4' structures,



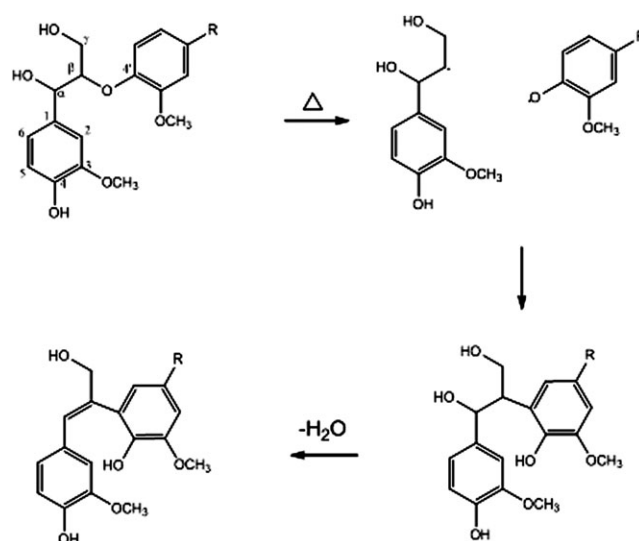
**Figure 1.** DSC thermograms of fractionated softwood kraft lignin (SKLP) fibers before stabilization and after oxidative stabilization at a heating rate of  $15^{\circ}\text{C min}^{-1}$  and thermal stabilization at a heating rate of  $4^{\circ}\text{C min}^{-1}$ , respectively. The absence of a thermal transition of the stabilized fibers indicates complete stabilization. The final stabilization temperature was  $250^{\circ}\text{C}$  for 30 min.



**Figure 2.** CP/MAS  $^{13}\text{C}$ -NMR spectra for SKLP and corresponding stabilized lignin fiber in air and nitrogen atmosphere. The spectra are normalized according to the methoxyl peak at 55 ppm.

the well-known homolytic cleavage of the alkyl-aryl ether linkage seems to occur with the formation of a new linkage between the aromatic C5-carbon and the  $\beta$ -carbon in the side-chain, the latter in accordance with literature.<sup>29</sup> It was also shown that a lower heating rate during oxidative stabilization results in a higher oxygen content in the fiber and greater changes in the chemical structure.<sup>16</sup>

Successful thermal stabilization of SKLP fiber was performed using a heating rate of  $4^\circ\text{C min}^{-1}$  (Table II). The stabilized ( $10^\circ\text{C min}^{-1}$ ,  $250^\circ\text{C}$ , 1 h) SKLP fiber used for the NMR and FTIR analysis underwent inter-fusion of the fibers during stabilization. However, the evaluation of the melting properties after



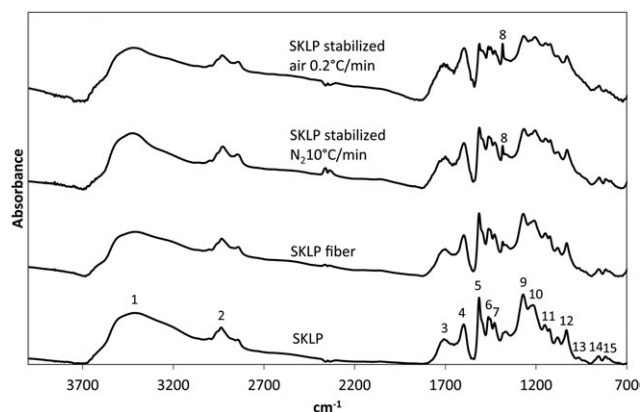
**Figure 3.** One possible reaction of SKLPs during heat treatment starting with the homolytic cleavage of the  $\beta$ -O-4' linkage, followed by a rearrangement reaction and formation of a stilbene structure by loss of water.<sup>27</sup> The nomenclature of the lignin is also shown.

stabilization showed intact and separable fibers. In Figure 2, small differences in the NMR spectra of thermally and oxidative stabilized SKLP can be observed. In the aliphatic region in Figure 2, the intensity of the signal for the carbon linked to oxygen (65–90 ppm) decreased, and the signal for the carbon linked to carbon (25–50 ppm) increased, which indicates that  $\beta$ -O-4-linkages were cleaved, and a rearrangement reaction that formed, e.g., phenylcoumaran was possible (Figure 3). In the

**Table III.** FTIR Band Assignments for Softwood Kraft Lignin Permeate Lignins (SKLP)

Id.	Band assignment	Peak wavenumber ( $\text{cm}^{-1}$ )
1	O—H stretch	3412–3460
2	C—H stretch in methyl and methylene groups	2842–3000
3	C=O stretch in unconjugated ketones, carbonyls and ester groups	1695–1720
<b>4</b>	Aromatic skeletal vibrations plus C=O stretch	1600
5	Aromatic skeletal vibrations	1505–1515
6	C—H def.; asym. in $-\text{CH}_3$ and $-\text{CH}_2-$	1450–1465
7	Aromatic skeletal vibrations combined with C—H in-plane def.	1430
8	Aliphatic C—H stretch in $\text{CH}_3$ , not in OMe, phen.OH	1384
9	G ring plus C=O stretch	1270
10	C—C, C—O, C=O stretch	1210–1220
11	C—O deformation in sec. alcohols and aliphatic ethers	1080
12	Aromatic C—H in-plane def. + C—O stretch in prim. alcohols + unconj. C=O stretch	1030–1035
13	$\text{HC}=\text{CH}-$ out-of-plane def.	966
<b>14</b>	C—H out-of-plane in position 5 and 6 of G-units	822
<b>15</b>	C—H out-of-plane in position 2 of G-units	855

Bold numbers refers to the most important peaks during stabilization.<sup>26</sup>



**Figure 4.** FTIR of SKLP, SKLP fibers, and stabilized fibers in air and nitrogen atmosphere. The spectra are normalized relative to the aromatic peak at 1505–1515  $\text{cm}^{-1}$ .

aromatic region, an increase in the intensity can be observed in the region of approximately 110–130 ppm after stabilization. This increase in intensity might be caused by an increase in the number of aliphatic carbon signals in the region of 110–130 ppm by formation of a stilbene structure and elimination of water (Figure 2). Presence of liquid crystallinity, i.e., molecular orientation of the material may also have an impact on the thermal behavior of fibers. By using lignin model compounds, it has been shown that liquid crystal (LC) formation during heating in inert atmosphere is less pronounced for models having ether linkages while carbon–carbon linkages promote LC formation.<sup>30</sup> This is in line with the suggested reaction showed in Figure 3. The three-dimensional molecular diversity and partly crosslinked structure was, by the same authors, suggested to be the reason for the lack of anisotropy of un-fractionated lignin. It was however suggested that a decrease in the molecular mass distribution of lignin would probably have a positive influence on the formation of a LC structure. Although this has not been studied in the present article, the studied permeate lignins indeed have a lower polydispersity (see Table I), which may contribute to the faster stabilization observed for, e.g., the SKLP fibers as compared to the SKL+HKLP fibers.

FTIR analysis of native and technical lignins has been thoroughly discussed in the literature.<sup>16,31</sup> Sharma et al. studied the

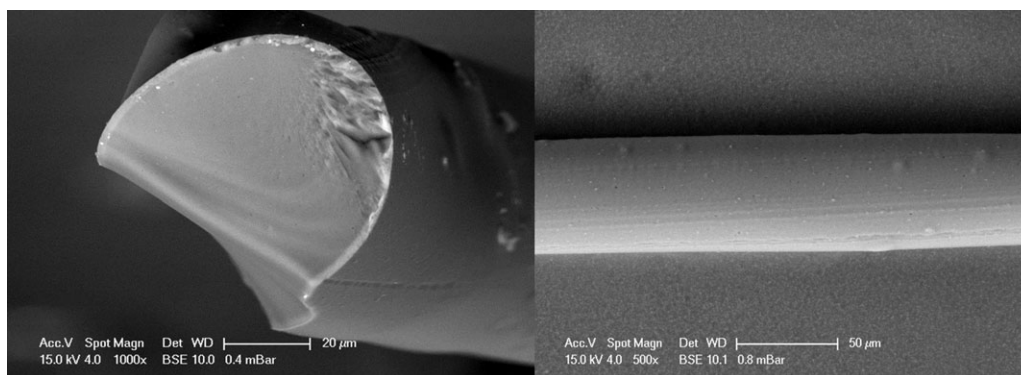
pyrolysis of lignin (i.e., thermal stabilization) at various temperatures and showed that minor changes in the lignin occurs at temperatures between 250 and 300°C.<sup>32</sup> Above 350°C, the methyl and methoxyl groups were removed from the aromatic rings. The FTIR band assignments obtained from the SKLP spectra are shown in Table III. In Figure 4, the FTIR spectra for the SKLP, SKLP fiber, oxidatively stabilized SKLP fiber, and thermal stabilized SKLP fiber are shown. As was observed for the NMR spectra, the FTIR spectra of the SKLP lignin fiber were the same before and after extrusion. After thermal and oxidative stabilization, a new peak at 1384  $\text{cm}^{-1}$  (peak 8) was observed, which could be attributed to the formation of a new phenolic hydroxyl group. This peak has not been reported for hardwood kraft lignins.<sup>16</sup> The peaks attributed to aromatic C–H stretching in the region of 780–860  $\text{cm}^{-1}$  (peaks 14 and 15) changed after stabilization, which is an indication of crosslinking reactions in the C5-position of the guaiacyl units during the stabilization process. Compared with SKLP powder, the increased intensity of the C=O stretch at 1715  $\text{cm}^{-1}$  (peak 3) was higher after oxidative stabilization than after thermal stabilization. This difference may be attributed to rearrangement and radical reactions that introduced oxidized structures. The presence of minor amounts of carbonyl groups in all spectra might be explained by autoxidation reactions. Carbonyl groups have previously been reported to be present in hardwood and SKLs.<sup>25,27</sup>

### Carbonization

A solid, homogenous cross-section of the oxidatively stabilized SKLP fiber after carbonization to 1000°C is shown in Figure 5. The outer surface was smooth and homogenous. The carbon content was approximately 96 atomic percent in the cross-section of the oxidatively and the thermally stabilized SKLP and SKL+10% HKLP fibers, which is satisfactory. In this study, all the stabilization experiments were performed on thick fibers (the diameters were approximately 100  $\mu\text{m}$ ). As previously shown for pitch fibers,<sup>33</sup> fibers with thicker diameters have a greater difficulty in achieving full stabilization during the oxidative stabilization conditions.

### Stabilization and Carbonization in a One-Step Operation

Successful thermal stabilization enables stabilization and carbonization to be performed in one step (i.e., a separate stabilization step can be omitted). This approach was applied to SKLP and



**Figure 5.** ESEM pictures of a carbonized fractionated softwood kraft lignin (SKLP) fiber that was stabilized at a heating rate of 15°C  $\text{min}^{-1}$  to 250°C for 30 min in air. Both the cross-section (left) and the fiber outer surface (right) is shown.

SKL+10% HKLP fibers. Both types of fibers were intact and did not stick together after the one-step process. The ESEM evaluation showed smooth fibers with a carbon content greater than 90%. A one-step process would result in a faster and probably less expensive process to form CFs.

## CONCLUSIONS

For the first time, thermal stabilization has been achieved for SKL fibers in the absence of oxygen. The conditions for successful thermal stabilization of lignin fibers, i.e., to obtain thermoset properties, were optimized with respect to stabilization time.

Two types of SKL fibers were used differing in raw material composition; one from a fractionated lignin (SKLP) and the other made by blending unfractionated SKL and 5–10% fractionated hardwood kraft lignin (HKLP), the latter acting as softening agent.

SKLP fibers could be thermally stabilized in 85 min and the fibers could be carbonized into CFs of smooth appearance. The corresponding stabilization time for the SKL-HKLP fiber was 255 min, reflecting the difference in reactivity between softwood lignin and hardwood lignin.

Stabilization in the presence of air was achieved even faster; after 45 min for the SKLP fiber and 105 min for the SKL-HKLP fiber, respectively. Thus, neat SKL fibers such as SKLP can be oxidatively stabilized about 26 times faster than that commonly reported for hardwood kraft lignin-softening agent blends.

It was shown that the stabilization and carbonization can be performed as a one-step process, differing merely in temperature and treatment time. These findings have a great potential to reduce the processing costs for a future commercialization of lignin as raw material for CFs.

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