

## Extrusion of Softwood Kraft Lignins as Precursors for Carbon Fibres

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There is much interest in using less expensive raw materials as precursors for carbon fibre manufacture to increase the utilisation of strong, light-weight composite materials in the transportation sector. One such potential raw material is lignin. Most studies exploring melt spinning of lignin have used lignins from organosolv or hardwood kraft delignification processes. There has been little success reported in utilisation of the more commercially available softwood kraft lignins. In this study, lignins from different softwood kraft cooking processes were investigated with respect to their melt spinning performance and conversion to carbon fibres. The isolated lignins differed mainly in molecular weight, glass transition temperature, and softening temperature. All of the lignins produced from the laboratory cooks could be extruded without any plasticizer addition. However, the lignins contained volatiles that resulted in bubbles being formed along the length of the fibres. After vacuum drying, at elevated temperatures to remove volatiles, only the lignin originating from conventional kraft cooking was able to be melt extruded without plasticiser addition; this lignin had the lowest molecular weight amongst the samples. The stabilisation and carbonisation of these fibres gave carbon fibres with strengths comparable to those produced from lignins of other origins.

*Keywords:* Carbon fiber; Kraft lignins; Kraft pulping; Softwood; Strength properties

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### INTRODUCTION

There are strong driving forces for the transportation sector to reduce vehicle weights. Decreases in fuel consumption, pollution, and raw material costs are major benefits that lighter composite parts bring to the automotive industry. One option is to increase the use of carbon fibres in several new and existing structural applications. Carbon fibres (CF) are highly interesting in terms of the production of stiff and strong light-weight composite materials. However, there is a shortage in production capacity, and the cost of carbon fibre is too high for many potential automotive applications. Renewable wood-derived lignins are a potential source of interest for the development of carbon fibre. Such lignins have an advantage in that they are readily available as a co-product from pulping processes. In calculations based on world pulp production in 2009, it was found that the lignin available for carbon fibre production is far beyond future needs (Baker and Rials 2013).

Most studies exploring the melt spinning of lignin have dealt with lignins from organosolv and hardwood kraft processes (Kadla *et al.* 2002), while there has been little

success regarding the use of softwood kraft lignins. So far only fractionated softwood lignins, chemically modified softwood lignin, and those used with the addition of plasticisers have been successful (Baker and Rials 2013; Nordström *et al.* 2013; Chatterjee *et al.* 2014). Softwood kraft lignin is today the most available commercial lignin. Kraft pulping of softwood is also dominant in Europe, and North America possessing a large potential for increased utilisation of the lignin in the black liquor, now used as an energy resource. In this study the possibility of using softwood kraft lignins without further treatment has been explored. By employing differing kraft cooking processes together with LignoBoost technology, the properties of the lignins produced and their ability to be melt spun and converted to carbon fibres has been evaluated. To increase the applicability of the LignoBoost recovery process, a conventional kraft delignification (cook) was compared with two other processes: one, a dissolving type of treatment, where hemicelluloses were removed by pre-hydrolysis of the wood chips before kraft cooking; and the other where hemicelluloses, in particular glucomannan, were retained to a higher degree in a polysulphide cook. The lignins from these laboratory cooks were isolated from the black liquors using the LignoBoost process (Öhman *et al.* 2006), characterised, and evaluated for melt spinning and conversion performance.

## EXPERIMENTAL

Softwood lignins were produced using three different kraft cooking processes. The wood chips used for the experiments were a mixture of 50 wt% Norway spruce, *Picea abies* (L.) Karst., and 50 wt% Scots pine, *Pinus sylvestris* L. The chips were made from logs using a pilot scale chipper at Innventia and were screened using a Rader thickness screen; the 2 to 8 mm fraction was used for cooking. Bark and knots were removed by hand sorting and the chips were dried and stored under dry conditions.

### Cooking

Three different cooking processes were selected, *i.e.*, “conventional” kraft cooking, pre-hydrolysis kraft cooking, and polysulphide cooking. All cooking was performed in a laboratory circulation digester using 2 kg (o.d.) wood chip blend for each cook at a liquor-to-wood ratio of 6:1 with a carbonate charge of 0.1 mol/L.

Conventional kraft cooking was performed using white liquor. The temperature was increased from 20 °C to 120 °C at a rate of 10 °C/min and held for 30 min for chip impregnation. Thereafter, the temperature was increased at 5 °C/min to the cooking temperature, *i.e.*, 165 °C, where it was held isothermally until the targeted H-factor was reached.

Pre-hydrolysis kraft cooking was performed by first adding deionized water to the chips in the digester and then raising the temperature to 165 °C at 5 °C/min, which was then held for 60 min. The hydrolysate was withdrawn, and white liquor was pumped into the digester. The temperature was ~100 °C after charging and was increased at 5 °C/min to the impregnation temperature of 120 °C, where it was held for 30 min. Thereafter, the temperature was increased at 5 °C/min to the cooking temperature, *i.e.*, 165 °C, where it was held isothermally to reach the target H-factor.

Polysulphide cooking was performed at a charge of 3% polysulphide. The temperature was increased from 20 °C to 120 °C at 10 °C/min, and held for 30 min for impregnation. Thereafter the temperature was increased at 5 °C/min to the cooking temperature, *i.e.*, 165 °C, where it was held to reach the target H-factor.

The resulting unbleached pulps were washed with de-ionized water for 10 h. The pulps were then screened in a water jet defibrator (2 mm holes) followed by a Wennberg screen (0.2 mm slits) before determination of their kappa number. The unbleached screened pulp yield was determined gravimetrically. Experimental data for the different pulps are shown in Table 1.

**Table 1.** Kraft Cooking Conditions and Pulp Data \*

	Conv. Kraft	Pre-hydrolysis	Polysulphide
Kappa number	22.7	15.4	25.0
H-factor	1350	1500	1250
Effective alkali as NaOH %	26	26	27.5
Sulphidity %	35	35	20
Polysulphide %	0	0	3
Residual alkali g/l	12.5	12.6	9.8
HS <sup>-</sup> mol/L	0.17	0.18	0.21
Total yield % on wood	46.2	37.8	49.7

\* The conditions used for cooking were selected to be representative of the different processes and to give a degree of delignification that was not too dissimilar.

### Lignin Isolation

Lignin was separated from each of the three resulting black liquors using the LignoBoost process at the laboratory scale with a 25 cm<sup>2</sup> (3.9 in<sup>2</sup>) filtration area. Carbon dioxide was bubbled through the black liquor until the target pH of 10 was reached. The slurry was then allowed to mature for 30 min, after which it was filtered at constant pressure. The resulting filter cake was re-suspended in sulphuric acid (to pH 2 to 3) and filtered again. The second filter cake was displacement-washed to purify the lignin.

### Analysis

Lignin and carbohydrate contents were determined according to SCAN-CM 71:09. Solubilized monosaccharides were quantified using an ion chromatograph coupled to a pulsed amperometric detector (IC-PAD). Acid-insoluble lignin residue was determined gravimetrically according to TAPPI T222 om-11. The acid-soluble lignin residue was measured by UV spectrophotometry at 205 nm.

Ash contents were determined according to SS-EN 14775:2009.

Lignin molar mass distributions (MMD) were determined on the acetylated lignins (acetic anhydride), using size exclusion chromatography (SEC) with tetrahydrofuran (THF) as the mobile phase and a refractive index detector. The SEC system was calibrated using polystyrene standards. From the MMD, the weight average molecular weight ( $M_w$ ), number average molecular weight ( $M_n$ ), and the polydispersity (PD) index ( $M_w/M_n$ ) were determined.

Lignin structures were analysed in detail using phosphorus  $^{31}\text{P}$  nuclear magnetic resonance (NMR) according to a method devised by Garanta and Argyropoulos (1995). The lignins were first dissolved in a mixture of dimethylformamide and pyridine. The lignin was then derivatised, *i.e.*, phosphitylised, using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in deuterated chloroform. The quantification was made by integrating the signals in the spectra.

Glass transition temperatures,  $T_g$ s, were determined using modulated differential scanning calorimetry (DSC) on a DSC Q 1000 (TA Instruments). 1 to 5 mg of dry sample was pre-dried in the DSC for 20 min at 105 °C. A sinusoidal modulation of the temperature of  $\pm 3$  °C/60 s was superimposed on a temperature ramp of 3 °C/min to enhance sensitivity. The  $T_g$  was determined from the inflection point of the reversible heat flow decrease.  $T_g$ s were calculated as an average of two or three measurements.

Lignin softening points,  $T_s$ s, were determined using a Fisher-Johns melting point apparatus (Fisher Scientific) and by mounting between two microscope cover slips.

Viscosities of the lignins were measured as a function of temperature at a heating rate of 3 °C/min. from 100 to 200 °C on a Discovery HR-1 rheometer (TA Instruments). The lignin powders were compressed to a tablet, and mounted on a parallel plate geometry device. Measurements were made using a constant oscillating displacement of  $1.0 \times 10^{-4}$  rad, a frequency of 1 Hz, and with a constant axial force of 10 N. The onset of the  $\tan \delta$  peak was used to rank the lignins.

The thermal degradation behaviour of the lignins was measured using a thermogravimetric analyser (TGA) (TGA7 Perkin Elmer). The sample was first dried at 105 °C for 20 min before the weight was measured. Around 2 to 4 mg of lignin was tested. Samples were then heated at a rate of 15 °C/min up to 350 °C under nitrogen purge gas with a flow rate of 20 to 35 mL/min. The weight % remaining at 220 °C was used to compare the lignins and their volatile material content.

The melt spinning performance of each lignin was assessed using a twin screw micro compounding extruder (DSM Xplore MC 15) at a temperature of 220 to 230 °C. Prior to extrusion the lignin was dried in vacuum (12 mbar) at 80 °C for 24 h. Fifteen grams of lignin was fed to the compounder over a period of 5 min and was blended during 5 additional min using a screw speed of 25 rpm. The lignin was then extruded through a die using a screw speed ranging from 150 to 200 rpm. The reference lignin originating from the standard kraft cook was extruded through a die with a 150  $\mu\text{m}$  diameter hole, while the other two lignin samples were extruded through a die with a 250  $\mu\text{m}$  diameter hole.

Lignin fibre samples were oxidatively thermostabilised as bundles between two fixed clamps. The thermal treatment was done using a conventional gas chromatography (GC) oven (HP 5890) under air atmosphere. A heating rate of 0.2 °C/min from room temperature to 250 °C was applied, followed by an isothermal treatment for 60 min.

Carbonisation of the oxidatively thermostabilized fibres was done under nitrogen purge (15 to 20 mL/min) in a tube furnace (VTF 50/15-L, Entech, Sweden). Each sample was treated using a heating rate of 1 °C/min to 600 °C and 3 °C/min to 1200 °C.

The tensile strengths of the resulting carbon fibres were tested using a dynamic mechanical analyser (DMA 7; Perkin Elmer). Single carbon fibres were glued to a metal plate with cyanoacrylate adhesive. The assembly was mounted in the DMA and the fibre glued to the lower plate of the instrument. A load was applied using a rate of 100 mN/min until fibre failure. The fibre diameter was measured using optical microscopy.

SEM (Scanning Electron Microscopy) images were obtained using a Hitachi SU3500 microscope with backscatter electron detector; acceleration voltage 4 to 6 kV.

## RESULTS AND DISCUSSION

The compositions of the lignins isolated using the LignoBoost process from each of the three different cooking conditions (conventional kraft cooking, pre-hydrolysis kraft cooking, and polysulphide kraft cooking) are shown in Table 2. The lignin isolated from the pre-hydrolysis cook had a much higher purity, *i.e.*, lower ash and carbohydrate content, in comparison to the other two lignins. This increase in purity is most likely because a significant proportion of the free carbohydrates and ash had been removed from the wood chips prior to delignification.

**Table 2.** Composition of the Softwood Lignins Obtained from Three Different Variants of Laboratory Kraft Cooks of Softwood

<b>Black liquor from kraft cooks</b>	<b>Ash %-w</b>	<b>Klason lignin %-w</b>	<b>Acid soluble lignin %-w</b>	<b>Carbohydrates %-w</b>
Conventional	0.04	93.3	6.5	1.7
Pre-hydrolysis	0.02	92.7	7.1	0.2
Polysulphide	0.04	89.8	6.4	1.9

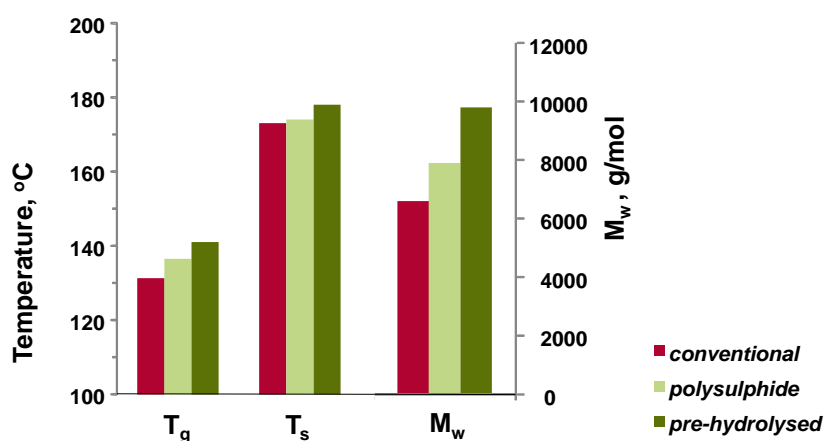
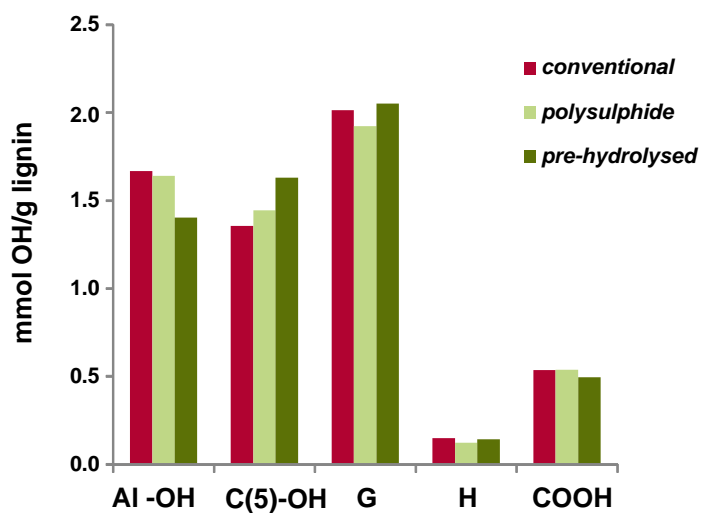
The isolated softwood lignins differed in their molecular weights (Table 3), so that the lignin from conventional kraft cooking had the lowest, followed by that obtained from the polysulphide cooking, and the lignin from the pre-hydrolysed cooking having the highest (lignin yields were rather similar). The polydispersity of the lignins increased in a similar way. This difference was also reflected in differences in  $T_g$  and  $T_s$  (Fig. 1), with the lignin from the conventional kraft cooking having the lowest and the pre-hydrolysed cook lignin having the highest. This dependence of lignin  $T_g$  on molecular weight is similar to what has earlier been reported (Tanahashi *et al.* 1982; Dodd *et al.* 2015). Structural analysis using NMR (Fig. 2) indicated that these differences could be explained by a higher content of C(5)-substituted aromatic structures coupled with a lower content of aliphatic hydroxyls, which was observed in the pre-hydrolysed lignin, as compared to the polysulphide lignin and the lignin from the conventional cook. These structural differences are comparable to structural changes that occur during heat treatments, giving rise to increased molecular weights (Rönnöls *et al.* 2015). However, the present data is in contrast to other investigations that used fractionated lignins, where a decreased aliphatic hydroxyl content in relation to the aromatic hydroxyl was found to be accompanied by decreased molecular weight (Li *et al.* 2014; Sevastyanova *et al.* 2014).

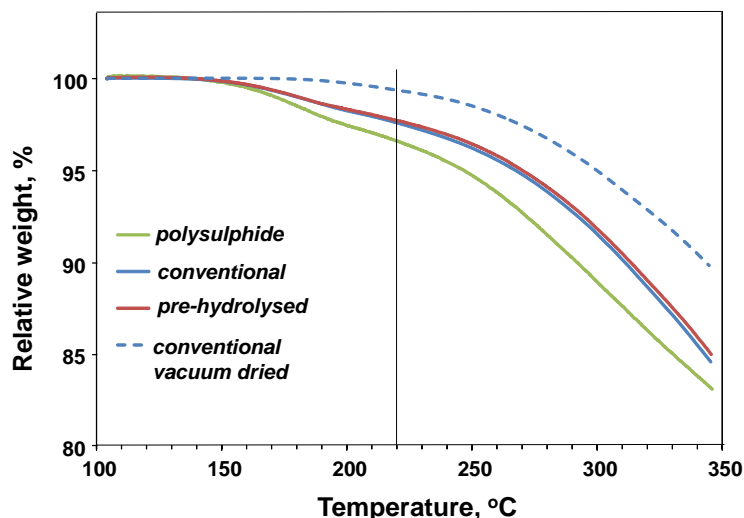
Thermogravimetric analysis of the lignins revealed that significant volatile materials could be found in each and that the weight remaining at 220 °C was lowest for the polysulphide lignin (Fig. 3). These volatile materials could cause problems during melt spinning due to the evolution of gases which become bubbles or flaws within the fibres. However, as can be seen from the SEM images (Fig. 4), the major part of the fibres produced were flaw-free, only showing a somewhat porous surface structure.

**Table 3.** Calculated Molecular Weights for Softwood Lignins from Different Kraft Cooking Processes \*

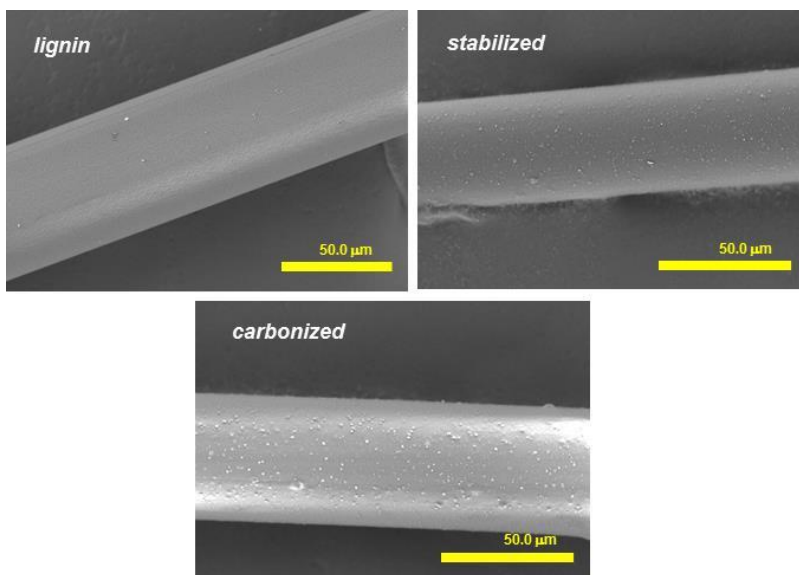
<i>Pulp</i>	$M_n$ , g/mol	$M_w$ , g/mol	<i>PD</i>
Conventional	1100	6600	6.2
Pre-hydrolysis	1200	9800	8.0
Polysulphide	1100	7900	7.2

\* The weight average molecular weight ( $M_w$ ), the number average molecular weight ( $M_n$ ) and the polydispersity (*PD*) index ( $M_w/M_n$ ) are shown.

**Fig. 1.** Characteristics of softwood lignins isolated from different laboratory cooking procedures; softening temperature  $T_g$ , softening temperature  $T_s$ , and molecular weight  $M_w$ **Fig. 2.** Structural characteristics of the softwood lignins determined by NMR. The lignin groups are divided into; aliphatic hydroxyls, Al-OH; C(5) hydroxyls, C(5)-OH; Guaiacyl groups, G; Hydroxypropyl groups, H; Carboxylic groups, COOH.



**Fig. 3.** Thermal degradation of softwood lignins under nitrogen atmosphere showing remaining weight relative to initial dry weight, as a function of temperature. Solid lines represent samples dried at 80 °C and the dashed represent a heat treated sample. The vertical line at 220 °C indicates the temperature at which the amount of volatiles was quantified. Above 250 °C thermal decomposition of lignin occurs.



**Fig. 4.** SEM images representative of fibres from conventional lignin, dried at 80 °C for 24 h; extruded lignin fibres, after stabilization and after carbonisation.

Therefore, to minimize the presence of these volatile substances prior to melt spinning, the lignins were vacuum treated at 140 °C (12 mbar). However, while a considerable decrease in volatiles was observed (Fig. 3) the set target value (< 0.5 % volatiles) was not met and problems would still be expected during extrusion. In this case, and in general, the use of high temperature treatments of lignin tends to induce crosslinking, so that it resulted in noticeable increases in essential characteristics with regard to melt spinning properties; *i.e.*, increases in  $T_g$ ,  $T_s$ , and the onset of the viscosity drop (Table 4).

**Table 4.** Characteristics of the Softwood Lignins as Affected by Thermal Treatment

<i>Lignin/Treatment</i>	<i>T<sub>g</sub>, °C</i>	<i>T<sub>s</sub>, °C</i>	<i>Weight remaining at 220 °C, %</i>	<i>Onset viscosity drop, °C</i>
Conventional/ 80 °C 24h	131	173	97.6	162
Conventional/ 140 °C vacuum 8h	145	177	99.4	175
Polysulphide/ 80 °C 24h	137	174	96.6	164
Polysulphide/ 140 °C vacuum 8h	148	182	98.5	182
Pre-hydrolysed/ 80 °C 24h	141	178	97.7	168
Pre-hydrolysed/ 140 °C vacuum 8h	153	179	98.9	187

Each of the softwood lignins produced from the laboratory cooks were extruded after drying at 80 °C. The lignin from conventional cooking produced relatively fine fibres, in the range of 40 µm, but contained some bubbles, while the lignins obtained from the polysulphide cook and the pre-hydrolysed cook gave fibres with larger diameters in the range of 125 to 150 µm and which contained large quantities of bubbles. Of the thermally treated lignins, only the lignin from the conventional kraft cook was possible to melt extrude; however, the diameters of these fibres were much larger than those obtained for the original lignin.

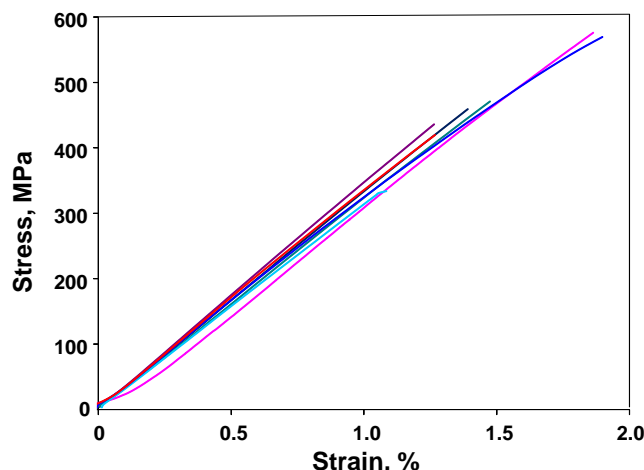
The other two heat-treated lignins could not be extruded due to increases in softening temperature and melt viscosity. Presumably the relatively low molecular weights of these laboratory produced lignins together with the fact that oxidative reactions at higher temperatures were as much as possible avoided made extrusion possible.

The lignin fibres obtained from both lignins (*i.e.*, dried and thermally treated) originating from the conventional kraft cook were converted to carbon fibre by oxidative thermostabilisation and carbonisation to 1200 °C. The strength properties of the two softwood kraft lignin fibre samples (Table 5) were found to be in the same range that had been reported earlier for carbon fibres produced from other lignins (Norberg 2012; Lin *et al.* 2014). However, the carbon fibres produced from the thermally treated lignin had increased tensile strength and modulus compared to those obtained from the untreated lignin, even though the fibre diameters were significantly increased.

**Table 5.** Strength Properties of Carbon Fibres from Softwood Lignin from a Conventional, Laboratory Kraft Cooking. Lignin was dried at 80 °C or thermally treated at 140 °C.

<i>Lignin/Treatment</i>	<i>Tensile strength, MPa</i>	<i>E-modulus, GPa</i>	<i>Fibre diameter, µm</i>
Conventional/ 80 °C 24h	380 +/-70	25.7 +/-3.5	39 +/-5
Conventional/vacuum 140 °C 8h	465 +/-85	32.3 +/-1.5	65 +/-7





**Fig. 5.** Stress-strain curves for carbon fibres produced from softwood lignin originating from conventional kraft cooking subjected to a vacuum treatment at 140 °C for 8 h.

The stress-strain curves for the carbon fibres produced from the heat treated lignin are shown in Fig. 5. While the standard deviation in moduli reveal consistency, their tensile strengths show some variability, and this may be attributed to difficulties in mounting of these thin carbon fibres in the DMA assembly which often led to a premature breakage due to stress concentrations in the glued mounting area.

## CONCLUSIONS

1. This study of the influence of pulping conditions on the properties of softwood kraft lignins showed that lignins produced from both pre-hydrolysed kraft cooking and polysulfide cooking have a higher molecular weight than lignins from conventional kraft cooking.
2. The higher  $M_w$  lignins reflected an increased content of condensed structures and therefore resulted in higher  $T_g$ ,  $T_s$ , and melt viscosity.
3. Each of the lignins produced from the laboratory cooks were able to be directly extruded as made (dried at 80 °C). However, a large amount of bubbles were observed in the extruded fibres caused by volatile components.
4. After thermal treatment under vacuum, only the lignin from the conventional kraft cook, having the lowest  $T_s$  among the samples, was possible to melt spin.
5. The study has demonstrated that it is possible to melt spin softwood kraft lignins, without the addition of plasticisers, into lignin fibres comparable in properties to carbon fibres produced from lignins of other origins.

## ACKNOWLEDGEMENTS

This work was performed as part of the Biorefinery Processes and Products research program 2012 to 2014 at Innventia AB. The financing companies; BillerudKorsnäs, Holmen, Mercer, SCA, Stora Enso, Södra, and UPM as well as the Swedish Energy Agency are gratefully acknowledged for their support. Lars Norberg and Jasna S. Stevanic are gratefully acknowledged for the preparation of the precipitated lignin and the NMR measurements, respectively. The linguistic revision by Darren Baker is highly appreciated.

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Article submitted: March 20, 2015; Peer review completed: June 30, 2015; Revised version received: August 12, 2015; Accepted: August 13, 2015; Published: September 22, 2015.

DOI: 10.15376/biores.10.4.7544-7554