

KRAFT LIGNIN RECOVERY AND ITS USE IN THE PREPARATION OF  
LIGNIN-BASED PHENOL FORMALDEHYDE RESINS  
FOR PLYWOOD

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Lignin was precipitated from kraft black liquor using carbon dioxide. To remove the residual black liquor and to purify the lignin, a pilot press filter or a pilot belt filter was used, and their performance was compared. The purity, molecular weight distribution, morphology, chemical and thermal properties of the final lignin product were characterized. The results showed that the lignin recovered from both the filter press and the belt filter was sufficiently pure to be used as a fuel in the lime kiln (or in most other combustion processes), or in any of the several possible high-value applications. No major difference was observed in the physico-chemical properties of lignins produced using a belt filter vs. a filter press. However, the solids content of the lignin filtered through the press filter was about 2 times higher than the one obtained using the belt filter, and the filtration rate obtained with the filter press was 5 to 6 times higher than that obtained with the belt filter. The purified lignin product recovered from the filter press was used to substitute 30, 40 and 50% of the phenol present in the formulation of the lignin-phenol-formaldehyde (LPF) resins used as an adhesive for the preparation of plywood samples. The results showed that up to 30% of phenol could be replaced by kraft lignin, without any major change in plywood shear strength.

**Keywords:** lignin, precipitation, black liquor, phenol-formaldehyde, resin, plywood, belt filter, filter press

## INTRODUCTION

During kraft pulping, lignin is removed from the wood chips and, following brownstock washing, it ends up in the spent pulping liquor (weak black liquor). This liquor is typically concentrated from about 15-20% to 70-80% solids, with an evaporator train, and then fired into a recovery boiler for the production of steam, electricity and inorganic chemicals (in the form of a smelt) for internal mill use. Over the last few years, North American pulp mills have been gradually increasing pulp production up to the point that the calorific load to their recovery boiler has, in most cases, reached or exceeded the design limits. Expanding the recovery boiler capacity is a very expensive proposition. A convenient way to expand pulp production without having to invest millions of dollars in extra recovery boiler

capacity is to offload the recovery boiler with respect to calorific load. This can be done easily by adding an acid (*e.g.* carbon dioxide, sulphuric acid, acetic acid) to a portion of the black liquor flow, thus precipitating out the lignin. Several processes for the recovery of lignin from the black liquor are available, among them a process developed by FPInnovations and currently commercialized by NORAM, and another one, developed by STFI (now called Innventia) and licensed to Metso.

The recovered lignin could be used as a fuel in the lime kiln (or in many other combustion processes) or in any of the numerous possible high-value applications. For example, in the past thirty years, much research effort has focused on using kraft and other types of lignin as phenol

substitutes in phenol-formaldehyde (PF) resins, for reaching a high level of phenol substitution with lignin, while maintaining and/or exceeding the physical/mechanical properties of the final product. Some of these efforts successfully replaced phenol with lignin at low substitution levels (up to 20%), without compromising the physical and mechanical properties of the wood product in question (*e.g.*, plywood or oriented strand board (OSB)).<sup>1-4</sup> Some researchers asserted that it was not technically possible to go beyond a phenol substitution rate of 20%, since, beyond this level, lignin would act more as a filler rather than as an adhesive.<sup>1-3</sup> To achieve higher substitution levels, other researchers used different forms of kraft lignin or tried to fractionate, activate or modify the lignin before its addition to the existing PF resin-making ingredients (phenol and formaldehyde).<sup>2-24</sup> Using phenolation or methylation as a lignin pretreatment, relatively high levels of phenol replacement (30 to 50%) were attained in PF resins, from which wood products of acceptable physical and mechanical properties were subsequently obtained. However, the bond strength values obtained at higher lignin concentrations were not as good as those obtained from the commercial PF resin control. In addition, a longer pressing time was needed during wood product manufacture for attaining acceptable physical and mechanical properties in these adhesives.

Thus, the main goals have been to: a) compare the performance of a filter press and a belt filter in the lignin filtration step during the recovery of lignin from kraft black liquor, and b) use the recovered lignin, without any modification, to replace phenol in PF resins, while preserving the final wood product properties.

## EXPERIMENTAL

Lignin precipitation from the black liquor, received from AbitibiBowater, Thunder Bay mill, Ontario, Canada, was accomplished by sparging CO<sub>2</sub> into the black liquor solution. The precipitation temperature was kept between 70 and 75 °C. Precipitation was stopped at a pH around 9.5, after which the lignin slurry suspension was filtered using a commercial filter press from LAROX (Model PF 0.1 H2), or a commercial belt filter from BHS-filtration (Model LBF-1.0/1.0). In both cases, the filter area was of 0.1 m<sup>2</sup>. A standard filter cloth from Tamfelt (S-2108-L1) and a belt filter (PP 1001-K 079) were used, respectively, for the filter press

and the belt filter. The filtration cycle included the following steps: formation of the lignin cake, washing with 0.4 N sulfuric acid followed by 0.01 N sulfuric acid and water, then pressing and, finally, air drying. The filtration rate in kg/m<sup>2</sup>.h (kilograms of recovered lignin filtered per unit surface area per hour) was evaluated, and the results obtained from the two filters were compared. The chemical requirements of the two lignin recovery processes were also evaluated by measuring the consumption of carbon dioxide, sulfuric acid and wash water required.

The recovered lignin samples were analyzed for dry solids, calorific value, carbohydrates, UV-lignin, sodium, sulfur and ash content. The morphology of the lignin samples was examined on a Scanning Electron Microscope (SEM). The molecular weight (Mw) and molecular weight distribution (MWD) of the various lignins were measured using Size Exclusion Chromatography (SEC).<sup>25-26</sup> These parameters were quantified by measuring: a) Mw – the weight average molar mass (or molecular weight) obtained by measuring the total mass of each polymer chain of particular length, summing up these masses and dividing by the total mass of the sample, b) Mn – the number average molar mass (or molecular weight) which represents the common arithmetic mean, and c) the ratio Mw/Mn – the polydispersity (or heterogeneity) index of a polymer, which provides a rough measure of the breadth of molar mass distribution. Differential scanning calorimetry (DSC) was used to measure the glass transition temperature of the various lignins produced, while thermogravimetric analysis (TGA) was used to measure the initial and final decomposition temperatures.

The well-characterized kraft lignin was used to substitute 30, 40 and 50% phenol in the formulation of LPF resins. The LPF resins were prepared by reacting lignin with phenol and formaldehyde, under alkaline conditions. Plywood panels consisting of three layers were prepared using three different resins, and tested according to the existing Canadian Standards. The plywood shear strength was evaluated after soaking and/or boil-dry-boil treatments.

## RESULTS AND DISCUSSION

### Purity of lignin recovered using a filter press vs. a belt filter

As shown in Table 1, the lignin recovered from either filter press or belt filter was sufficiently pure to be used as a fuel in the lime kiln (or in most other combustion processes) or in any one of the several possible high-value applications.

Particularly notable is the low ash content of these lignins. In the most demanding lignin application, the production of carbon fiber, ash levels below 0.1% are generally

required. Three of four lignins came very close to meeting this specification, while only one did not correspond. In all cases, the lignin content of the final cake was very high. It is also worth mentioning here that, even if all liquors were diluted to about 30% dissolved solids prior to the lignin precipitation reaction, the solids content of

the lignin cake recovered from the filter press was of about 61%. This suggests that the cost of drying lignin to over 95% solids (if needed) will be relatively low. However, the lignin cake recovered from the belt filter was much lower in solids than the one filtered through the filter press (32-35% solids).

Table 1  
Chemical and physico-chemical analysis of lignins recovered from a filter press (lignins 1 and 2) and a belt filter (lignins 3 and 4)

	Filter press		Belt filter	
	Lignin 1	Lignin 2	Lignin 3	Lignin 4
Total solids, %	60.30	61.40	35.40	32.20
Ash, %	0.15	0.72	0.06	0.14
Na, %	< 0.01	0.15	< 0.01	< 0.01
S, %	1.70	1.40	1.46	1.37
Organics, %	99.85	99.28	99.90	99.90
UV-lignin, %	97.20	98.40	99.00	97.90
Carbohydrates, %	1.67	1.57	4.35	3.27
Calorific value, BTU/lb	12111	11872	12060	12010
Glass transition temp., °C	150		156	
Decomposition temp., °C	220		264	

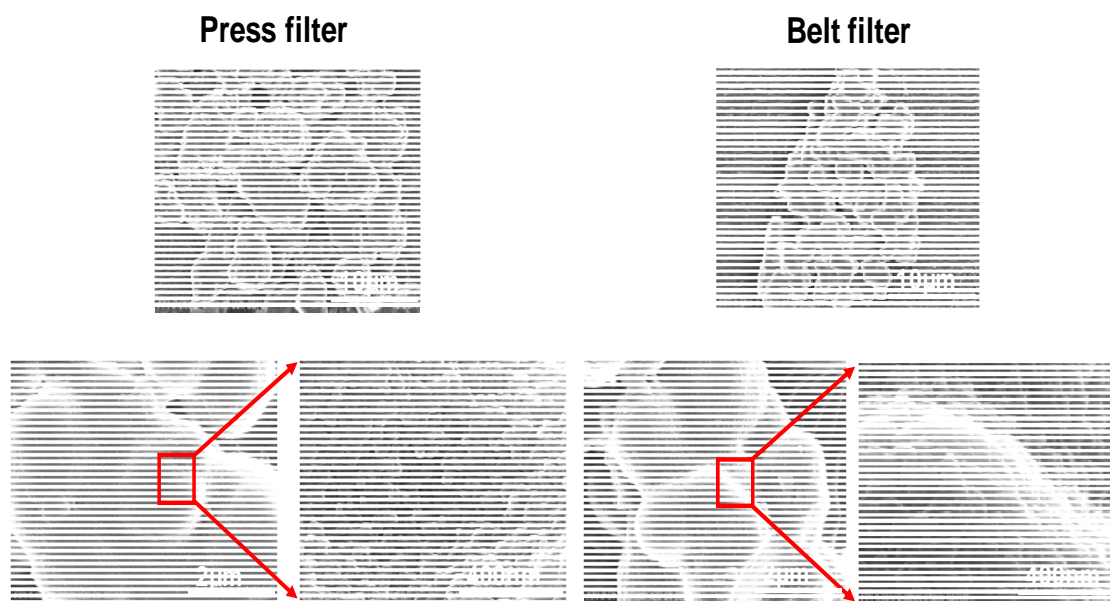


Figure 1: SEM images of lignin recovered from black liquor after acidification to pH 10 using carbon dioxide, followed by coagulation and filtration using a filter press or a belt filter

Table 1 shows that the lignins recovered from the filter press and belt filter have almost the same glass transition temperature (150 and 156 °C, respectively). However, the

lignin recovered from the belt filter has a slightly higher decomposition temperature compared to that recovered from the filter press.

The thermal properties of lignin, like those of any other polymer, are very important in relation to its processability, *e.g.* the maximum temperature at which a polymer may be used (as they are often used in structural materials where mechanical properties may be of paramount importance), as well as the product yield (*e.g.*, in the production of carbon fibers one wishes to maximize lignin conversion to the desired product, while avoiding lignin decomposition).

#### Morphology of lignin recovered using a filter press *vs.* a belt filter

The lignin samples obtained by processing the black liquors received from Thunder Bay mill were examined on a Scanning Electron Microscope (Fig. 1).

The SEM images showed no major morphological differences between the lignin recovered from black liquor using a filter press or a belt filter. Small particles of about 5 to 7  $\mu\text{m}$  in diameter were observed. The shape of the particles is mostly spherical or oblong. In addition, some surface bumps are visible on the large particles, indicating the presence of sub-particles of about 50 nm in size within the larger ones.

#### Average MW and MWD of lignin recovered using a filter press *vs.* a belt filter

Table 2 lists the Mw, Mn and Mw/Mn values of lignins recovered from black liquor using a filter press and a belt filter.

Table 2  
Mw and MWD of various lignins recovered from black liquor solutions using a filter press (lignins 1 and 2) or a belt filter (lignins 3 and 4)

		Filter press		Belt filter	
		Lignin 1	Lignin 2	Lignin 3	Lignin 4
MALLS detector	Mw	9030	11590	8660	8870
	Mn	2570	5400	3130	3030
	Mw/Mn	3.51	2.15	2.76	2.93
UV detector	Mw	5563	6717	5417	5192
	Mn	1232	1314	1304	1276
	Mw/Mn	4.52	5.11	4.15	4.07

Table 3  
Chemical requirements of the lignin recovery processes employing a filter press (with and without a lignin re-slurrying step) or a belt filter

	Filter press		Belt filter
	With lignin re-slurrying step	Without lignin re-slurrying step	Continuous process
Filtration rate (kg of lignin/h.m <sup>2</sup> )	55-57	100-240	20-34
CO <sub>2</sub> rate (kg of lignin/h.m <sup>2</sup> )		0.2-0.3	0.2-0.3
H <sub>2</sub> SO <sub>4</sub> rate (kg of lignin/h.m <sup>2</sup> )		0.3-0.4	0.2-0.3
Water rate (kg of lignin/h.m <sup>2</sup> )		10-15	6-12

SEC analysis evidenced some differences in the Mw, Mn values and, by extension, in Mw/Mn, in the lignins filtered using a belt filter *vs.* a filter press. The average MW of lignin recovered from the belt filter was slightly lower than that of the lignin recovered from the filter press – which could be due to the higher water content of lignin produced using the belt filter, as compared to the filter press. On drying these two lignins, a higher amount of low Mw dissolved/colloidal lignin is likely to remain

on the precipitated lignin recovered from the belt filter, compared to the filter press. As shown in Table 2, the molecular weight obtained by the MALLS detector is about two times higher than the one obtained by the UV detector. This is consistent with the literature and appears to be due to the fact that, in the latter case, the calculation of Mw and Mn is based on a calibration conducted with polystyrene standards of linear structure. Since lignin is not a linear polymer, the results obtained are of value

only for comparative purposes and do not necessarily reflect the true Mw of lignin. On the other hand, the Mw and Mn values measured by the MALLS detector do not require the use of calibration standards, thereby providing a more accurate measurement of these two parameters. The difference in the values obtained by the two techniques can be regarded as a measure of the lignin structure deviation from linearity.<sup>26</sup>

### Filtration rates and chemical requirements

The consumption of carbon dioxide, sulfuric acid and wash water is summarized in Table 3. As shown in the table, less water and sulfuric acid were needed when using the belt filter. However, the filtration rate obtained with the belt filter was very low, compared to the one obtained with the filter press.

### Plywood sample evaluation

The plywood shear strength of panels prepared with different LPF resins was

evaluated after subjecting the plywood specimens to soaking and boil-dry-boil treatments. The results are presented in Figure 2. As shown in the figure, following the soaking treatment, the plywood panels made with a commercial and a FPIInnovations PF resin had plywood shear strengths lower than the specific standard value of 2500 KPa. However, the panels made with lignin-based PF resin demonstrated plywood shear strengths higher than the standard value. Following the more rigorous boil-dry-boil treatment, the shear strength of the plywood panels made with the lignin-based PF resin at 40 and 50% phenol substitution levels was lower, compared to the specified standard value of 2500 KPa, but still higher than or comparable to the control resins. These results indicate that lignin can replace up to 30% phenol in a phenol formaldehyde adhesive, causing no major change in plywood strength properties.

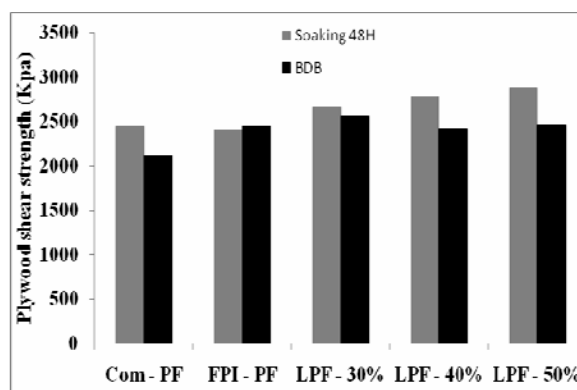


Figure 2: Plywood shear strength of panels prepared with PF and LPF resins, after soaking and BDB treatments. The LPF resins were prepared at 30, 40 and 50% phenol substitution levels

### CONCLUSIONS

No major differences were observed in the physico-chemical properties of lignins produced using a belt filter *vs.* a filter press. The solids content of lignin and the filtration rate obtained with the filter press were significantly higher than those obtained with the belt filter. Based on the above results, the filter press was preferred in a lignin demonstration plant, which is currently being installed at the Abitibi Bowater – Thunder Bay mill. It was demonstrated that kraft lignin can replace up to 30% of the phenol present in the phenol formaldehyde resins

used for plywood preparation, with no major changes in plywood strength properties.

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