THE LIGNOFORCE SYSTEM™: A NEW PROCESS FOR THE PRODUCTION OF HIGH-QUALITY LIGNIN FROM BLACK LIQUOR

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ABSTRACT

Lignin can be precipitated and recovered from Kraft black liquor (BL) through the addition of an acidifying agent such as carbon dioxide, followed by filtration and washing. During this process, many researchers previously reported a high filtration resistance which affects lignin purity, cost, and productivity. To improve lignin filterability, FPInnovations developed the *LignoForce System*™, a patent-pending process in which the BL is oxidized under controlled conditions before the acidification step of conventional lignin recovery processes. Based on the data obtained, BL oxidation improves the filterability of the acid-precipitated lignin by providing suitable conditions with respect to pH (leads to a lower pH) and temperature (leads to a higher temperature) for lignin colloid agglomeration, leading to the formation of particles of a size and size distribution that are easy to filter and wash. In addition, it minimizes or eliminates total reduced sulphur (TRS) compounds, thereby leading to reduced TRS emissions during all steps associated with lignin precipitation, filtration, and washing. Furthermore, because the oxidation of TRS compounds and sugars consumes residual effective alkali (sodium hydroxide) in BL, the carbon dioxide and sulphuric acid requirements of the process are significantly reduced. An additional feature of the LignoForce process is the use of a filter press instead of a belt filter for lignin cake filtration and washing. No major difference in the chemical composition, molecular weight distribution, or main functional groups was found in the lignins produced using the LignoForce process compared with lignins produced by conventional methods. Based on the results obtained in laboratory studies, a lignin demonstration plant was designed and built at the Resolute – Thunder Bay mill for the production of 12.5 kg/h of high-quality lignin.

INTRODUCTION

During the kraft pulping process, lignin is removed from wood chips and, following brownstock washing, ends up in the spent pulping liquor (weak black liquor). This liquor is typically concentrated from approximately 15%–20% to 70%–80% solids using an evaporator train and then fired into a recovery boiler for the production of steam, electricity, and inorganic chemicals (in the form of smelt) for internal mill use. Over the last few years, North American pulp mills have been gradually increasing pulp production to the point that the calorific load on their recovery boilers has, in most cases, reached or exceeded the design limits. Expanding 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 easily be done by adding an acid to a portion of the black liquor flow, thereby precipitating out the lignin. Black liquor acidification is predominantly performed by using either carbon dioxide or a mineral acid (e.g., sulphuric acid) or a combination of the two to drop the pH of the black liquor from approximately 13–13.5 to 9–10. After acidification, the lignin is usually filtered using a belt filter or a filter press and washed with acid (e.g., sulphuric acid) and water to produce lignin of high purity (Fig. 1). In many cases, however, it is difficult to separate the lignin from the acidified black liquor solution. This problem appears to be related to the size of the lignin particles before filtration. As in other types of colloidal dispersions, lignin precipitation from black liquor is assumed to occur in two steps: nucleation and particle growth. The relative rate of these two steps ultimately determines the size of the precipitated lignin particles and consequently their filtration rate.


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In an effort to improve the filtration properties of acid-precipitated lignin slurries, a number of approaches have been considered, including filtration at high temperature (80°C–90°C), increased ionic strength, and reduced precipitation pH. Even though these approaches work to a certain extent, the filtration resistance is still quite high, leading to unreasonably low filtration rates and, in certain cases, to a lignin product of low dry solids content and purity. This, in turn, leads to the need for a large filtration area in the lignin filtration equipment, leading to high capital costs and increased drying costs for the lignin. A second problem associated with most lignin precipitation processes using acid is the large amount of acid (e.g., carbon dioxide and/or sulphuric acid) that is needed to induce the lignin to come out of solution or to be converted from the sodium to the hydrogen form (e.g., during suspension of the lignin cake in an acid solution or washing of the lignin with acid on the filter). A third problem is the emission of totally reduced sulphur (TRS) compounds during most stages of the process. These compounds include hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide, which are strongly odorous compounds with well-known negative effects on human health and other forms of life.

One approach for addressing the problem of high filtration resistance is a process developed by STFI (now called Innventia) and licensed to Metso [1], which uses a first filter for the filtration of lignin in the sodium form, followed by suspension of the lignin cake in dilute sulphuric acid before filtration in a second filter. Another approach for addressing this problem, as well as several other problems associated with conventional processes, is a patent-pending process developed by FPInnovations and currently being commercialized by NORAM under the trade name *LignoForce Systems*™ [2] (Fig. 2). The purpose of this paper is to describe the impact of the BL oxidation step of the LignoForce process on filtration rate, chemical consumption, and lignin properties compared to the case in which the BL is not oxidized before lignin recovery.

EXPERIMENTAL

To improve the lignin filtration properties, the BL was oxidized under controlled conditions. The oxidized BL was then acidified, coagulated, and filtered, and the lignin was washed and dried in ways similar to other processes. Because the LignoForce process improves lignin filterability, only one filter press is required.

Following oxidation, lignin precipitation from black liquors received from different Canadian kraft mills was accomplished by sparging CO_2 into the black liquor solution. The precipitation temperature was kept between 70°C and 75°C. The addition of carbon dioxide was stopped when a pH of 9.5 – 10.0 was reached. After precipitation, the lignin slurry suspension was filtered using a commercial filter press from LAROX (Model PF 0.1 H2). A standard filter cloth from Tamfelt (S-2108-L1) was used [3]. The filtration cycle included the following steps: formation of the lignin cake, washing with sulphuric acid and water; pressing; and finally, air-drying. The filtration rate in $kg/m^2.h$ (kilograms of recovered lignin filtered per unit surface area per hour) was evaluated. The chemical requirements were also evaluated by measuring the consumption of carbon dioxide, sulphuric acid, and water usage.

The recovered lignin samples were analyzed for dry solids, calorific value, carbohydrates, UV-lignin, sodium, sulphur, and ash content. The morphology of the lignin samples was examined using a scanning electron microscope (SEM). The molecular weight (Mw) and molecular weight distribution (MWD) of lignin was measured using size exclusion chromatography (SEC) [4].

RESULTS AND DISCUSSION

Filtration Rate and Lignin Purity

The filtration rate was measured as the number of kilograms of recovered lignin filtered per unit surface area per hour. The recovered lignin samples were analyzed for dry solids, UV-lignin, and ash content. The results are presented in Table 1.

Particularly notable are the high filtration rates when the BL was oxidized using the LignoForce process compared to those without BL oxidation. As shown in Table 1, the filtration rate of lignin recovered from the oxidized BL was 1.25 to 2.5 times higher than that of lignin obtained from unoxidized BL.

Table 1 also shows that lignin obtained from the LignoForce process is sufficiently pure (low ash and high lignin content)

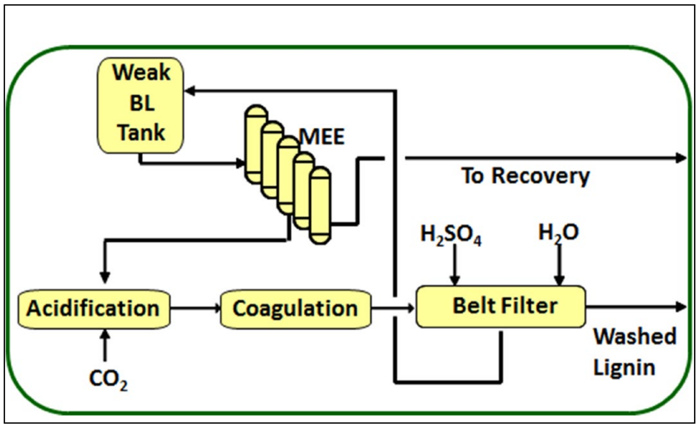

Fig. 1 - **Conventional process for lignin recovery from black liquor.**

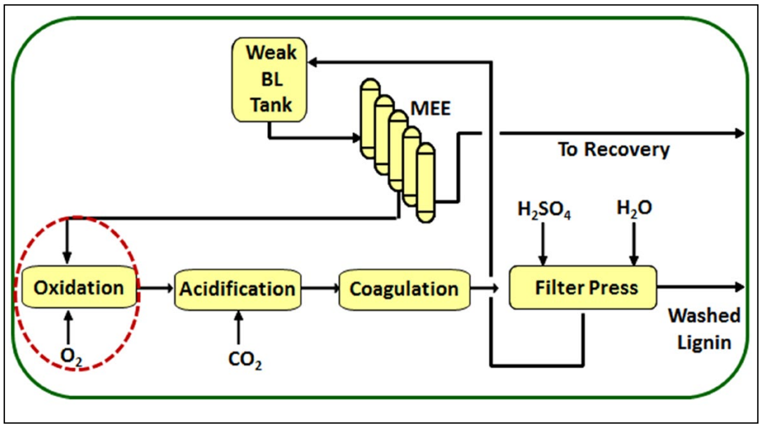

Fig. 2 - **LignoForce system for lignin recovery from black liquor.**

TABLE 1 *Filtration rate and lignin characteristics in the case of oxidized and unoxidized black liquor.*

	Without BL oxidation	With BL oxidation
Filtration rates (kg lignin/h.m^2)	0 – 80	100 – 200
Total solids (%)	30 – 58	60 – 62
Ash content (%)	0.2 – 15	0.1 – 0.7
UV lignin (%)	50 – 98	97 – 98
Lignin particle size (µm)	0.2 – 1	5 – 10

to be used as a fuel in the lime kiln (or in most other combustion processes) or in any one of several possible high-value applications. In the most demanding lignin application, the production of carbon fibre, ash levels below 0.1% are generally required. The lignin recovered from the oxidized BL came very close to meeting this specification, while that recovered from unoxidized BL did not. It is also worth noting here that, even though all liquors were diluted to approximately 30% dissolved solids upstream of the lignin precipitation reactor, the solids content of the lignin cake recovered from the oxidized BL was approximately 60%–62%. This suggests that the cost of drying the lignin to over 95% solids (if needed) will be relatively low.

Morphology of Lignin Recovered from Oxidized and Unoxidized BL

In an effort to identify the reason for the improved filtration rates, scanning electron microscopy (SEM) was used to evaluate the size and morphology of the lignin particles in the slurry as well as in the final lignin product recovered from the acidification of oxidized and unoxidized black liquors (Figs. 3 and 4).

Figure 3a shows that after acidification of the un-oxidized black liquor to pH 10 using carbon dioxide, the lignin slurry (before coagulation and filtration) is composed of very small lignin particles (approximately 0.2–0.5 µm). However, in the case of oxidized black liquor (Fig. 3b), the slurry appears to be composed of larger lignin particles (approximately 0.5 to 1 µm).

Similarly, the SEM images of the final lignin product from the untreated (un-oxidized) black liquor (Figure 4a), show small particles approximately 0.2–1.0 µm in diameter, whereas in the case of lignin derived from oxidized black liquor (Figure 4b), the SEM images show that the lignin is made up of larger particles of approximately 5–10 µm. This could explain the high filtration rate of the slurry recovered from the oxidized black liquor as compared to the un-oxidized one.

At the high pH of typical BLs, the repulsive forces between the ionized hydrophilic groups (mainly phenolic hydroxyl and carboxylate groups) stabilize the colloidal lignin and keep it in solution, thereby preventing lignin agglomeration and precipitation [5]. However, as the pH of the BL declines (e.g. when CO_2 is added), the dissociated phenolic hydroxyl groups on the lignin begin to accept protons resulting in a decline in the repulsive forces and the agglomeration of lignin to larger particles [5].

It is well known that oxidation reactions (e.g. TRS compounds to oxidized sulphur species and sugars to sugar acids) generate heat (exothermic reactions). In addition, the reaction of any acid with a base (e.g. sugar acids with residual sodium hydroxide) also generates heat. With increasing temperature, the degree of dissociation of the lignin charged groups (e.g. phenolic groups) decreases, leading to increased lignin colloid agglomeration and coagulation to form larger lignin particles (and larger particles lead to higher filtration rates). Furthermore, since the heat produced by the oxidation and neutralization reactions is generated *in-situ*, it is distributed in a homogeneous fashion throughout the solution. As a result, the creation of lignin particle nucleation sites is likely to be uniform throughout the BL solution, ultimately resulting in lignin particles of higher size distribution compared to conventional process in which BL is heated using conventional approaches. In addition, since during the oxidation step, sugars are converted to organic acids and total reduced sulphur (TRS) compounds are oxidized to non-volatile compounds such as sulfuric acid, methane sulphonic acid and dimethyl sulphone, the emission of odorous compounds is mostly eliminated. The extent of pH reduction was found to be related to the extent of BL oxidation and the rate of pH decline was found to slow down significantly as the carbonate-bicarbonate buffering effect became significant[5]. It should be pointed out here that despite the larger particle size, the lignin produced from the oxidized black

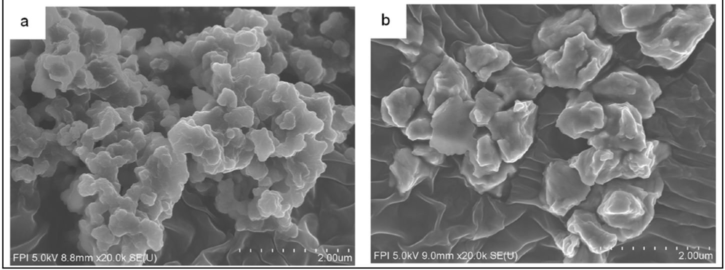

Fig. 3 - **SEM images of lignin in lignin slurry obtained from: a) un-oxidized and b) oxidized black liquor solution after acidification to pH 10 using carbon dioxide.**

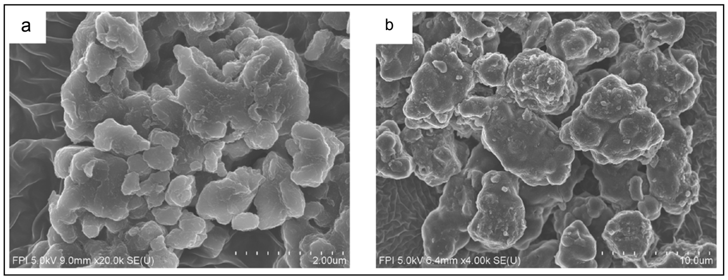

Fig. 4 - **SEM images of lignin product recovered from: a) un-oxidized and b) oxidized black liquor solution after acidification to pH 10 using carbon dioxide, followed by coagulation, filtration, and washing.**

liquor was purer than the lignin produced from untreated black liquor (Table 1). The ash content was quite low, approximately 0.1%–0.7%, compared to 0.2%–15% for the lignin produced from untreated black liquor. Its lignin content was 97%–98%, compared to 50%–98% for the lignin produced from untreated black liquor.

Chemical Requirements

Table 2 compares the carbon dioxide and sulphuric acid consumption of the conventional process versus the LignoForce lignin recovery process at the same washing rate.

As shown in Table 2, following black liquor oxidation, the carbon dioxide needed to reach the target pH of 9.5–10 for lignin precipitation was reduced significantly. Furthermore, it was found that black liquor oxidation led to reduced sulphuric acid requirements during the washing step and reduced TRS emissions during all steps associated with lignin precipitation, filtration, and washing. As discussed in the previous section, these reductions in acid requirements can be explained by the oxidation of TRS compounds, some of which are known to consume sodium hydroxide (e.g. sulphide to sulphate), as well as oxidation of organics to organic acids present in black liquor and, in particular, of carbohydrates which, upon oxidation, generate carboxylic acid groups which consume alkalinity in the residual black liquor.

Molecular Weight (Mw) and Molecular Weight Distribution (MWD)

To evaluate the effect of black liquor oxidation on lignin structure, the Mw and MWD of lignin were measured using size exclusion chromatography (SEC). The results are presented in Table 3.

From the results presented in Table 3, it appears that there was no major change in the lignin molecular weight because no large differences were seen in Mw, Mn and by extension, Mw/Mn, when the lignin was produced from un-oxidized or oxidized black liquor, or even when the lignin was converted from the sodium to the hydrogen form in these two cases.

TABLE 2 *Chemical requirements of the two lignin recovery processes (with and without black liquor oxidation).*

	Without BL oxidation	With BL oxidation
CO_2 consumption (kg/kg of lignin)	0.50 – 0.60	0.2 – 0.4
H_2SO_4 consumption (kg/kg of lignin)	0.30 – 0.40	0.2 – 0.3
Water usage (L/kg of lignin)	10 –15	10 –15

TABLE 3 *Mw, Mn and MWD of lignin (in sodium and hydrogen form) recovered from oxidized and un-oxidized black liquor solutions.*

		Without BL oxidation		With BL oxidation	
		Na-lignin	H-lignin	Na-lignin	H-lignin
MALLS detector	Mw	**11060**	**11040**	**10330**	**11200**
	Mn	6547	5139	4881	5698
	Mw/Mn	1.69	2.15	2.12	1.97
UV detector	Mw	**4206**	**4425**	**4880**	**5212**
	Mn	1143	1224	1300	1416
	Mw/Mn	3.68	3.62	3.75	3.68

TABLE 4 *^{31}P NMR analysis of hydroxyl groups in lignins recovered from oxidized and unoxidized BL.*

	Without BL oxidation	With BL oxidation
Carboxylic, mmol/g	0.26	0.31
Aliphatic, mmol/g	1.75	1.87
Phenolic, mmol/g	2.07	1.98
Condensed units, mmol/g	1.49	1.72
Total OH groups, mmol/g	5.57	5.88

As shown in Table 3, the molecular weight obtained by the MALLS detector is approximately two times higher than that obtained by the UV detector. This is consistent with the literature and seems to occur because, in the latter case, the calculation of Mw and Mn is based on a calibration conducted with polystyrene standards having a linear structure. Because 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, Mw and Mn as 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 deviation of lignin structure from linearity [4].

Functional Groups

^{31}P NMR analysis was used to determine the main functional groups of the lignins produced. These results are shown in Table 4.

As shown in Table 4, the number of carboxylic acid groups, aliphatic hydroxyl groups, phenolic hydroxyl groups, and condensed units is almost the same for lignin recovered from oxidized and unoxidized BL. Given the large number of phenolic groups in the lignins produced from both processes, they are expected to be suitable for use in the manufacture of phenolic resins. The same applies to the use of these lignins in the manufacture of polyurethane foams, where a large number of primary hydroxyl (aliphatic) groups is required.

CONCLUSIONS

The black liquor oxidation step used by the LignoForce System™ was shown to lead to an increase in lignin slurry filtration rates (under both alkaline and acidic conditions) without compromising lignin purity or affecting lignin structure and chemistry (e.g., lignin MWD and functional groups). In addition, this process was found to reduce acid requirements during the lignin precipitation and washing steps while minimizing or eliminating TRS emissions from all processing steps. Based on the results obtained, a lignin demonstration plant was built by FPInnovations at the Resolute Thunder Bay mill for the production of 12.5 kg/h of high-quality lignin.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the technical assistance provided by Pak-Yan Wong of FPInnovations and the financial support provided by Natural Resources Canada (NRCAN) and the Centre for Research and Innovation in the BioEconomy (CRIBE).

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