

Lignin Prepared by Ultrafiltration of Black Liquor: Investigation of Solubility, Viscosity, and Ash Content

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Technical lignin, which can be potentially obtained in large amounts as a by-product from kraft pulping, represents a potential resource for manufacturing fuels and chemicals. Upgrading of lignin, by lowering its molecular weight, is a valuable alternative to precipitation from black liquor, which occurs in the Lignoboost process. The solubility properties of Lignoboost lignin and filtered lignin in a number of technically feasible solvents were compared, and it was found that both lignins were dissolved in similar solvents. With the exception of furfural, the best lignin solvents generally were organic solvents miscible with water, such as methanol. It was possible to dissolve more filtered lignin in higher concentrations than Lignoboost lignin; additionally, the viscosities of the filtered lignin solutions were also considerably lower than those of Lignoboost lignin, especially at higher concentrations. Methods for non-organic component removal from filtrated lignin were tested, and it was concluded that several cold acidic treatments after dewatering can lower the ash content to values below 0.5% by weight.

Keywords: Lignin; Ultrafiltration; Liquid biofuel; Solubility; Viscosity; Ash content

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INTRODUCTION

The use of renewable raw materials as a replacement for fossil resources is necessary for several reasons, such as sustainability and minimizing environmental impacts on climate change (United Nations 1992). Because of the dependence on fossil fuels, *i.e.*, liquid fuel for combustion engines and plastics for consumption products, the question of exactly which combination of renewable resources should replace petroleum has become crucial. Ethanol obtained by fermentation is in many ways a perfect candidate, as it both can serve as fuel in Otto engines (a type of combustion engine often used in cars) and can be used as a raw material for plastics such as polyethylene *via* dehydration to ethylene (Wyman 1999). However, there are also problems with the concept of ethanol as a primary replacement for petroleum in bulk products. The best microbial strain for producing ethanol, baker's yeast (*Saccharomyces cerevisiae*), prefers glucose and other hexose monosaccharides as its carbon source (Kim *et al.* 2012). Excellent substrates for ethanol fermentation with *S. cerevisiae* include sucrose and starch (van Zyl *et al.* 2012). However, production of suitable plants for this substrate, *e.g.*, potato, sugar cane, corn, and sugar beet, competes directly with their use for food production (Spiertz and Ewert 2009).

A more attractive alternative is to use lignocellulose as a raw material, as reported by Baeyens *et al.* (2015). Wood, a lignocellulosic material, can be sustainably produced on

land that is not suitable for agriculture, and byproducts from agriculture, *i.e.* straw, also consist of lignocellulose (Abdeshshian *et al.* 2010). Typically, over one-third of lignocellulose materials consist of polysaccharides, such as cellulose, that can be converted to fermentable sugars (Sjöström 1993). Not surprisingly, much research and development efforts have focused on degrading cellulose into glucose for fermentation as second-generation ethanol (Baeyens *et al.* 2015). However, one problem with lignocellulosic biomass is that cellulose is resistant to degradation; this means that inhibitors for fermentation, such as furfural may be formed (Larsson *et al.* 1999). Thus, increased efforts for cellulose saccharification have focused on cellulose-degrading enzymes (Naik *et al.* 2010). This saccharification process produces a pure glucose stream as a product; however, this process is slow and consumes large amounts of enzymes, which has hindered its commercialization. Methods for increasing the degradation rate have been suggested (Wang *et al.* 2015). However, because cellulose is valuable both as a fiber and as a polymer, both in traditional paper products and in cellulose derivatives, it might appear less attractive to hydrolyze it into glucose.

A better alternative for lignocellulosic biomass as a source of fuels and chemical products may be to use *technical lignins*, such as the solubilized lignin contained in the spent liquors from kraft pulping (Sjöström 1993). Today, this dissolved material is primarily burned in the recovery boiler in the kraft pulp mill to generate energy and to recover the kraft cooking chemicals. However, there is room for removing a fraction of the lignin, and this may, in many cases, allow pulp mills that are chemical recovery limited (*e.g.*, recovery boiler bottleneck) to increase pulp production. A method for taking out lignin from the spent liquids of kraft pulping (black liquor) by a two-step precipitation method, *Lignoboost*, has been developed (Tomani 2009) and is presently commercialized. Many different applications have also been tested.

Lignin is generally more energy-rich than the carbohydrates in wood (McKendry 2002); however, this natural polymer is heterogenic and its structure is partly unknown (Boerjan *et al.* 2003). The structure becomes even more complex after its degradation during kraft pulping. Black liquor lignin consists of a mixture of organic oligomers with varying molecular weights and structure. Chemically, the oligomers are primarily hydrocarbons, rich in aromatic rings, double bonds, and oxygen. There is also some organically bound sulfur. This diverse complexity represents a problem for using the lignin for high-value applications. Dissolving lignin could be of central importance for processing the lignin into usable products. For example, if the lignin is dissolved, it can be fractionated by techniques such as ultrafiltration and chromatography into better-defined products, which can be used as feedstocks for other chemicals, materials, *etc.* Another interesting concept is that the double bonds in kraft lignin could be hydrogenated and the resulting material be cracked and refined, similar to petroleum, for producing liquid fuels in combustion engines. Thus, the solubility properties of prepared kraft lignin are of fundamental importance.

The Royal Institute of Technology, in conjunction with CleanFlow Black AB, has developed a method for preparing lignin from kraft black liquor using ultrafiltration (Keyoumu *et al.* 2004; Helander *et al.* 2013). Presently, a pilot plant is under evaluation, and thus a novel type of technical lignin can be produced in large scale.

In this work, the solubility properties of *Lignoboost* and ultrafiltered CleanFlow Black lignin from the pilot plant were compared in technically significant solvents. The possibility of ash removal from the filtered lignin was also investigated.

EXPERIMENTAL

Materials

Technical lignins

Freeze-dried Lignoboost lignin (ash content 0.25%) was provided by Chalmers University, and filtered softwood kraft lignin (ash content 4%) was prepared by ultrafiltration of black liquor.

The ultra-filtrated lignin was prepared on CleanFlow Black's pilot plant located on a Swedish kraft mill pulping mixed softwood (*Picea abies* and *Pinus sylvestris*). The black liquor lignin was obtained by ultrafiltration followed by precipitation with carbon dioxide at pH 9 and 65 °C. The method is principally a larger scale version of the system described by Keyoumu *et al.* (2004) and used by Helander *et al.* (2013).

The ceramic filter with a nominal cut off of 5 kDa consists of 19 channels with a surface area of 816 cm². The membrane consists of ZrO₂ and is made by Altech Germany. The pilot plant produces 20 kg lignin per day and use weak black liquor. The high weight fraction is returned to the evaporation system.

Other materials

All the solvents used in this study were of analytical grade and purchased from Sigma Aldrich (USA). The centrifuge used was a Mini Spin Eppendorf from Eppendorf AG (Hamburg, Germany). The oven/furnace used for determining moisture and ash content was a M9-1200 from ML Furnaces Ltd. (Boughton, UK).

Methods

Dissolution experiments

Screening experiments with lignin solvents were conducted by attempting to dissolve 50 mg of lignin with 0.5 mL of polar, apolar solvents and water (Fig. 2), in a 2-mL pre-tared centrifugation tube. This was done both for Lignoboost lignin and low-molecular weight lignin. The samples, after shaking, were dissolved using constant magnetic stirring (300 rpm) at room temperature for roughly 2 h and visually examined for depth of color of solution, as well as the presence of undissolved material. Thereafter, the samples were centrifuged for 120 seconds at room temperature and 14×10^3 relative centrifugal force (rcf). The supernatant (Lignin to Liquid – L.t.L.) was poured out, whereas the solid fraction was washed with water by centrifugation under the same conditions. Finally, the residual pellet was dried at 50 °C overnight and weighed. To compare the solubility of Lignoboost and filtered lignin at higher concentrations, 400 mg of each lignin were mixed with 0.5 mL of the same solvents of previous experiment. The experimental set up and analysis were the same as for the screening experiment.

Viscosity measurements

The viscosity of the liquid fractions obtained after centrifugation was analyzed using a capillary viscometer. Each sample was sucked into a 0.5-mL glass pipette using a Peleus ball until the meniscus had reached the upper measurement mark. After the ball was removed, the solution drained from the pipet because of the hydrostatic pressure of the liquid column. Efflux times to reach the annular and lowest measurement mark ("0.0 mL and 0.9" mL) were measured manually using a stopwatch. The experiment was performed at room temperature. As references, the efflux times of water and glycerol were recorded. Viscosities were calculated using Eq. 1 (Expt 070):

$$\mu_{\text{solution}} = \frac{\rho_{\text{solution}} * \text{time}_{\text{solution}} * \mu_{\text{ref}}}{\rho_{\text{ref}} * \text{time}_{\text{ref}}} \quad (1)$$

where μ_{solution} is the viscosity of the sample, ρ_{solution} is the density of the sample, $\text{time}_{\text{solution}}$ is the flow time for the sample, μ_{ref} is the viscosity of the reference, ρ_{ref} is the density of the reference, and time_{ref} is the flow time for the reference.

Ash content removal

Filtered lignin produced at Aspa was tested for ash removal by proper and efficient washing. Roughly 2.2 g of finely ground lignin was washed with 50 mL of deionized water at pH 9.5, 1.5% acetic acid solution (pH 4), and 2% sulfuric acid solution (pH 1) at room temperature in a 100-mL beaker.

The lignin samples were magnetically stirred for 30 min and allowed to settle until phase separation occurred; lignin, when possible, was separated from the liquid and collected in a crucible. Lastly, water and both acidic solutions were tested as washing agents, also at their boiling points.

Scale-up of ash content removal

A batch of 20 kg of wet lignin was split into two buckets (10 L volume), and one drum (30 L volume) was filled with cold sulfuric acid solution (pH 4). The mixture was manually stirred and left to settle overnight. Water was removed by means of a Buchner funnel under vacuum, and the wet lignin collected was washed twice with cold H₂SO₄ solution (pH 4). The final washing was carried out using a more acidic H₂SO₄ solution (pH 2) that was cold. The lignin obtained after the last acidic wash was dried at 40 °C in a drying cabinet overnight.

Measuring ash content

An analytical balance was used to weigh 1 g of selected lignin samples (accurate to 0.1 mg) in a dried and pre-weighed 30-mL marked porcelain crucible. Samples were finely ground and carefully weighed. After moisture determination, which was carried out at 105 °C for 2 to 3 h and followed by 15 min of cooling in a desiccator, the dried samples were placed in a muffle furnace. To prevent overflowing and spattering in the furnace, the samples were kept at each intermediate 100 °C increment of temperature for 90 min before reaching the final temperature of 575 ± 10 °C. Afterwards, the samples were left in the furnace overnight for approximately 16 h; the crucibles were weighed after cooling them to room temperature in a desiccator for 1 h. The ash contents are expressed as percent ash in the sample, which is equal to the weight of the ash multiplied by 100 and this quantity divided by the weight of the original sample.

RESULTS AND DISCUSSION

A number of industrially feasible organic solvents were chosen for a screening experiment, where the crude lignin (Lignoboost) and the low-molecular weight lignin (CleanFlow lignin (also called filtered lignin)) were tested for their solubility in these

media. To evaluate the data and explain the outcomes using a scientific and theoretical approach, some preliminary calculations are necessary.

Solubility of Lignin

Calculation of Hildebrand parameters (δ values)

The solubility of a polymer, such as lignin, in a medium can be predicted qualitatively by the similarity in chemical groups between solvent and polymer, and quantitatively by solubility parameter comparisons. Therefore, to evaluate lignin solubility, Hildebrand parameters of lignin monomers guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) phenylpropane monomers have been calculated according to literature (Schuerch 1952). δ -values listed in Table 1 have been obtained summing up the square root of the ratio between Δe_i (energy of vaporization to the gas at zero pressure) and Δv_i (molar volume) of each monomer structural elements.

Table 1. δ -Value Calculation for Lignin Monomer Units

Atom/Group	Unit G		Unit H		Unit S	
	Δe_i	Δv_i	Δe_i	Δv_i	Δe_i	Δv_i
	cal/mol	cm ³ /mol	cal/mol	cm ³ /mol	cal/mol	cm ³ /mol
OH	7120	10	2 x 7120	2 x 10	7120	10
CH ₂	1180	16.1	1180	16.1	1180	16.1
C=	1030	-5.5			1030	-5.5
CH	820	-1.0	2 x 820	2 x (-1.0)	820	-1.0
Phenyl	7630	33.4	7630	14.4	7630	52.4
CH ₃	1125	33.5	2 x 1125	2 x 33.5		
O	2 x 800	2 x 3.8	3 x 800	3 x 3.8	2 x 800	2 x 3.8
Δv^*		18		18		18
Total	20505	112.1	29340	144.9	19380	97.2
$\delta = (\Sigma\Delta e_i / \Sigma\Delta v_i)^{0.5}$ (cal/cm ³) ^{0.5}	13.52		14.23		14.12	

*Correction factor for divergence in the v value (Wang *et al.* 2011)

Moreover, it has been reported by Ye *et al.* (2014) that the δ values of the repeating G, H, and S units were estimated to be 14.70, 14.05, and 12.83 (cal/cm³)^{1/2}, respectively. However, the real value of lignin depends on the ratio of the G, S, and H units, which can be determined by the conventional nitrobenzene oxidation method. Nevertheless, the calculated δ values in Table 1 are quite close to those reported by Ye *et al.* (2014) and in the range of most of the Hildebrand solubility parameter values reported in the literature for lignin. Generally speaking, the solubility parameter varies from 12 to 15.5 (cal/cm³)^{1/2}. Because softwood lignin is mostly composed of guaiacyl structures (not more than 5% syringyl structures are present), the expected value of δ should be very close to 14, according to the data shown in Table 1. Afterwards, using Eq. 2, the δ values of the most interesting lignin solvents in terms of price and availability, as well as biorefinery stream, have been calculated according to,

$$\delta = \sqrt{\frac{(\Delta H - RT) * \rho}{M_w}} \quad (2)$$

where δ is the Hildebrand solubility parameter value, ΔH is the heat (or enthalpy) of vaporization in cal/mol, T is the boiling point in K, ρ is the density in g/cm³, M_w is the molecular weight in g/mol, and R is the gas constant in cal/(mol·K). These values are reported in Table 2.

Table 2. Calculated δ Values of Solvents According to Hildebrand

Solvents	δ (cal/cm ³) ^{1/2}
H ₂ O	23.3
Methyl butenol (MBO)	8.78
Furfural	11.3
Furfuryl alcohol	12.5
Glycerol	16.6
Methanol	14.4
Acetic acid	9.95
Acetone	9.80
Ethanol 96%	12.1
Ethylene glycol	13.6
Cyclohexane	8.02
Formic acid	11.2
Heptane	7.39
Butanol	11.3
<i>p</i> -Dioxane 90%	9.81

Determination of Hansen parameters

Hansen parameters of lignin, together with the interaction radius (R_0), were found in the literature (Hansen 2007) and are listed in Fig. 1. Similarly, Table 3 shows the Hansen partial δ values and R_A (*i.e.*, solubility parameter distance) regarding the most interesting solvents, which were investigated by actual solubility experiments.

In Table 4, the solubility parameters of solvents investigated according to both theories are compared and listed in decreasing order; moreover, the best solvents for softwood lignin have been highlighted in bold font. They have Hildebrand solubility parameters (left side) approaching 14 (cal/cm³)^{1/2}, which corresponds closely to the value for lignin.

Similarly, according to Hansen (2007), the solvents able to dissolve lignin must have a relative energy difference, *i.e.*, RED (= R_A/R_0), that is less than or slightly greater than one.

δ_d [MPa] ^{0.5}	δ_p [MPa] ^{0.5}	δ_h [MPa] ^{0.5}	R_0
21.9	14.1	16.9	13.7

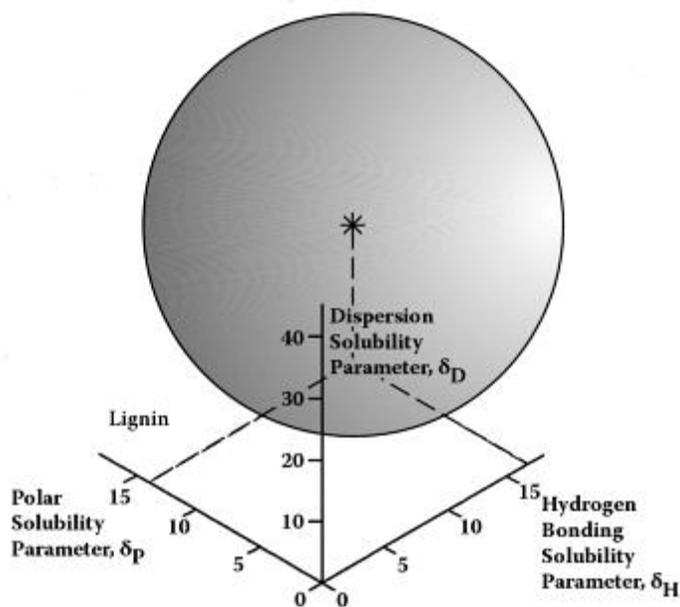


Fig. 1. Hansen's partial solubility parameters and R_0 (left), and space (right) for lignin (Hansen 2007)

Table 3. Solvents' Hansen Partial Solubility Parameters (δ_d , δ_p , and δ_h) and Solubility Parameter Distance (R_A)

Solvents	δ_d [MPa] ^{0.5}	δ_p [MPa] ^{0.5}	δ_h [MPa] ^{0.5}	R_A
Methanol	15.1	12.3	22.3	14.74
Cyclohexane	16.8	0.0	0.2	24.12
Acetic acid	14.5	8.0	13.5	16.36
Butanol	16.0	5.7	15.8	14.53
Acetone	15.5	10.4	7.0	16.60
Ethanol	15.8	8.8	19.4	13.53
Ethylene glycol	17.0	11.0	26.0	13.73
Glycerol	17.4	12.1	29.3	15.45
Furfural	18.6	14.9	7.0	11.93
Water	15.6	16.0	42.3	28.42
Furfuryl alcohol	17.4	7.6	15.1	11.25
Heptane	15.3	0.0	0.0	25.66
<i>p</i> -Dioxane 90%	19.0	1.8	7.4	16.59
Formic acid	14.3	11.9	16.6	15.36

As can be seen, both sets of data show that the lignin was hydrophobic and that apolar solvents (heptane, cyclohexane) were unable to dissolve the lignin. On the other hand, polarity and hydrogen bonding ability seemed to play a crucial role in lignin dissolution. To some extent, this is an expected outcome, which confirms what has been reported in the literature (Duval *et al.* 2015)

Table 4. Best Solvent for Lignin (bold) according to Hildebrand's δ (left) and Hansen's RED number (right)

Solvents	δ (cal/cm ³) ^{1/2}	Solvents	RED
Water	23.27	Water	2.07
Glycerol	16.59	Heptane	1.87
Methanol	14.42	Cyclohexane	1.76
Ethylene glycol	13.63	Acetone	1.21
Furfuryl alcohol	12.49	<i>p</i> -Dioxane 90%	1.21
Ethanol 96%	12.10	Acetic acid	1.19
Butanol	11.33	Glycerol	1.13
Furfural	11.32	Formic acid	1.12
Acetic acid	9.95	Methanol	1.08
Formic acid	11.2	Butanol	1.06
<i>p</i> -Dioxane 90%	9.81	Ethylene glycol	1.00
Acetone	9.80	Ethanol	0.99
Cyclohexane	8.03	Furfural	0.87
Heptane	7.39	Furfuryl alcohol	0.82

Filtered vs. Lignoboost lignin

As a result of screening experiments carried out at low lignin concentration (roughly 10% by weight), it was observed that the filtered lignin was more soluble than the Lignoboost lignin (Figs. 2 and 3). Furthermore, apolar solvents were clearly poor media for lignin dissolution, except for *p*-dioxane, which dissolved both Lignoboost and low-molecular weight lignin (*i.e.*, filtered lignin) with the same efficiency (Fig. 2). Glycerol is a polar solvent and is able to hydrogen bond; nonetheless, this solvent did not dissolve the lignin at all. Aliphatic alcohols, together with the apolar nature of the aliphatic chain, have differing abilities to dissolve lignin.

It has been observed that the number of carbon atoms in the aliphatic alcohols affects lignin dissolution. To put it in different terms, butanol is a longer molecule and has less mobility than methanol; additionally, butanol has more steric hindrances *versus* methanol to surround lignin moieties. Finally, the high polarity of furfural and the hydrogen bonding ability of furfuryl alcohol illustrates that these solvents are very promising to dissolve lignin for biorefinery applications. However, condensation and curing reactions that occur with these solvents, which are accelerated by increased temperature with acidic environments, make them more interesting for use with green plastic engineering rather than fuel generation (Dongre *et al.* 2015).

Figure 2 summarizes the results obtained from lignin dissolution with the different solvents. The number reported over each column stands for the amount of dissolved lignin obtained (*i.e.*, L.t.L.) after dissolution and centrifugation. The values in parentheses beside the solvent name in Fig. 2 are the weight/volume ratio of the solvent/lignin mixture.

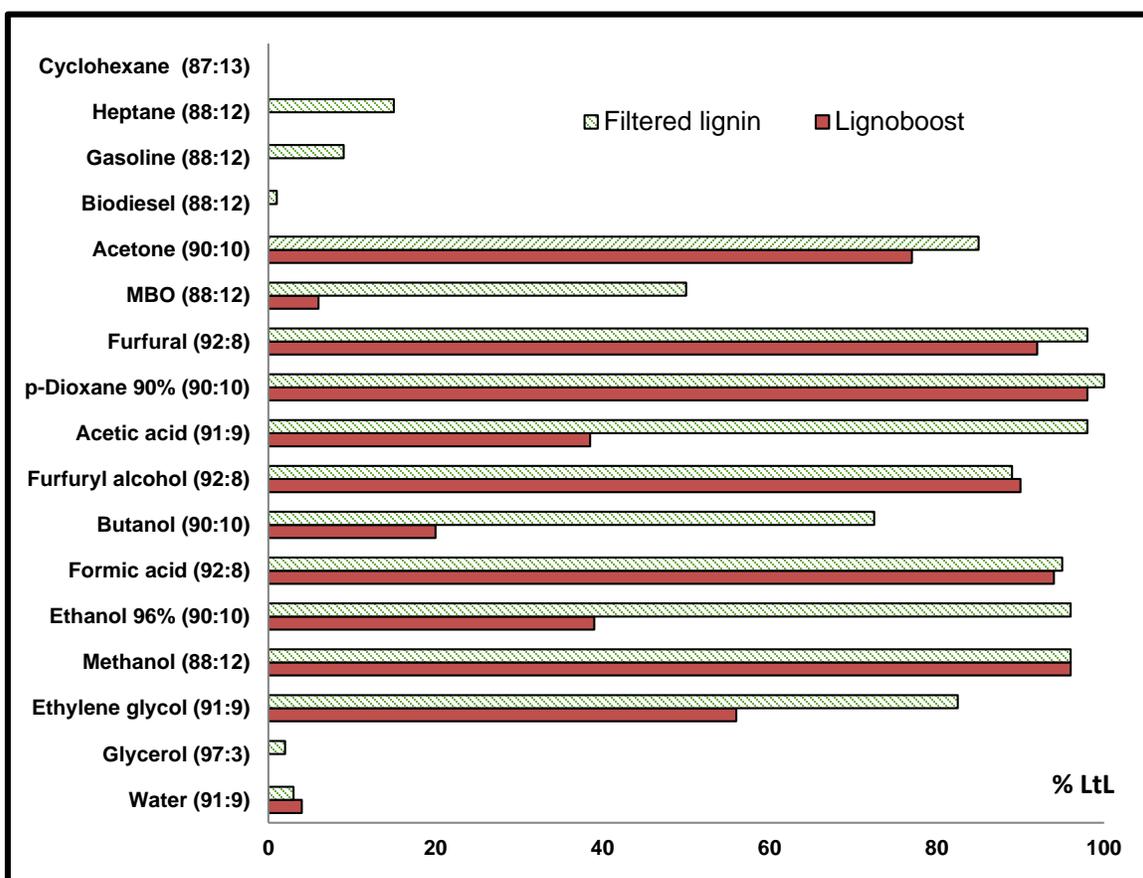


Fig. 2. Screening of organic solvents used to dissolve Lignoboost lignin and filtered lignin at low concentrations

Generally during the dissolution process, it was observed that good lignin solvents, which turned out to be miscible with water, resulted in darker (almost black) solutions than the original solvent's color. Furthermore, the observed increase in the solvent's viscosity was obviously caused by lignin dissolution. Conversely, poor lignin solvents, such as cyclohexane and heptanes, maintained their original solvent viscosity and color. As expected, the non-polar nature of solvents such as gasoline and cyclohexane resulted in low L.t.L. values. Lastly, it was observed that mixing glycerol and lignin together created a heterogeneous suspension in which the solid lignin particles were dispersed throughout the liquid phase.

The last set of solubility experiments focused on the ability of the best solvents to dissolve lignin at higher concentrations. Figure 3 illustrates that low-molecular weight lignin (*i.e.*, filtered lignin) exhibited higher solubility in all the solvents tried than the Lignoboost lignin. The lower degree of polymerization of the ultrafiltrated lignin *versus* the Lignoboost lignin allows the solvent molecules to better solvate these lignins.

Furthermore, lower-molecular weight lignin fractions are soluble in solvents with a wider range of solubility parameters and hydrogen bonding capacities than higher-molecular weight lignin fractions. This was the case observed for acetic acid and butanol.

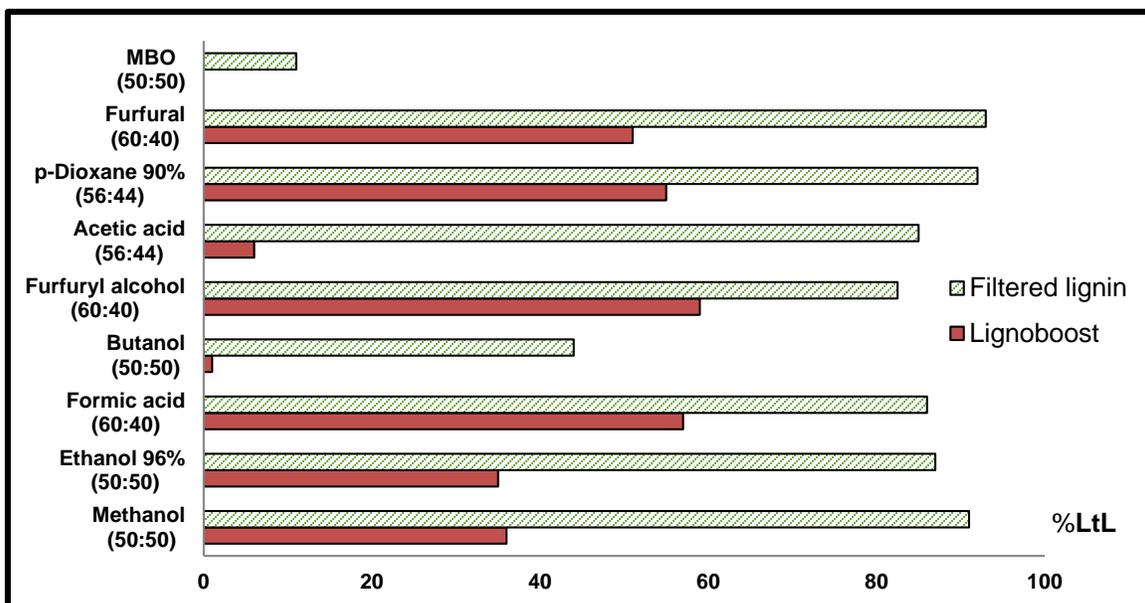


Fig. 3. Comparison of solvents' ability to dissolve Lignoboost and filtered lignin at high concentrations

Lignin Solution Viscosity Analysis

Solution viscosity is a crucial parameter for handling, processing, and transporting a liquid. Dynamic viscosity values (in centipoises) of 50 mg of lignin in 0.5-mL solutions were measured from previous dissolution experiments. As shown in Fig. 4, at this low lignin concentration value, the viscosity of almost all solvent solutions seemed unaffected by the dissolved lignin.

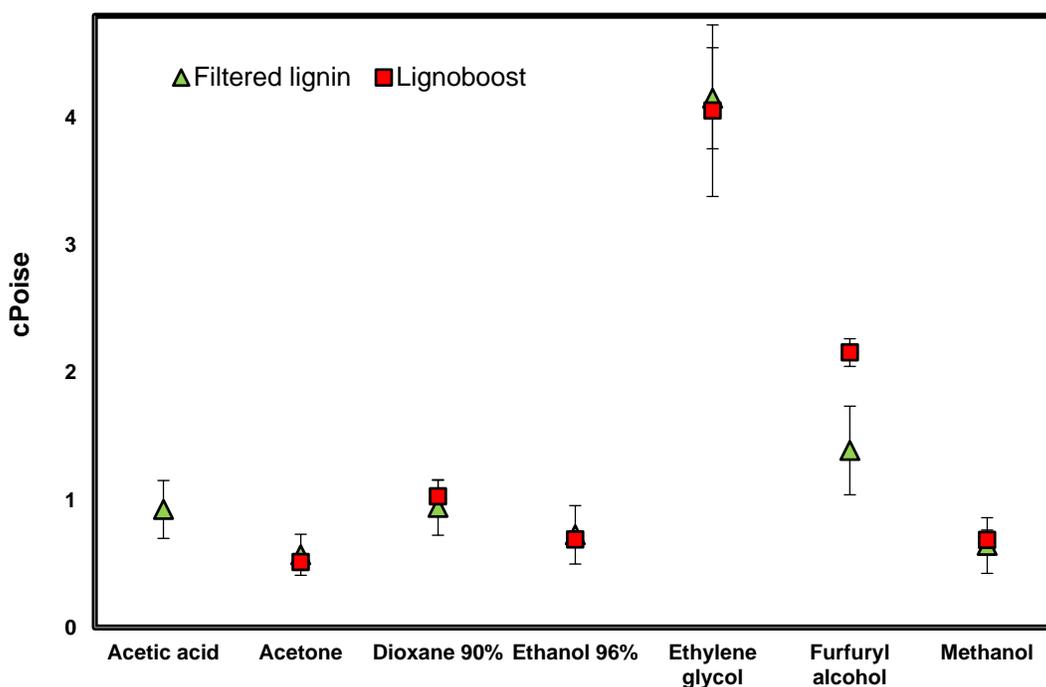


Fig. 4. Measured capillary viscosity values of solutions with low lignin concentration made from Lignoboost and filtered lignin

The viscosities of these solutions were lower than water (as the reference) and quite similar to their respective solvent without dissolved lignin. On the other hand, lignin solutions with furfuryl alcohol or ethylene glycol were roughly two and four times more viscous than water, respectively. Furthermore, lignin solutions obtained from filtered lignin were always, even if in some cases only slightly, less viscous than those obtained from Lignoboost lignin. However, as shown in Fig. 5, higher concentrations of lignin in the solvents resulted in a larger viscosity gap between the filtered and Lignoboost lignins. The solution viscosities of Lignoboost lignin were approximately an order of magnitude higher than those obtained from filtered lignin. Unsurprisingly, the highest viscosity values were obtained from the densest solvents, such as furfural and furfuryl alcohol, respectively, with the Lignoboost lignin. Thus, it is clear that there is an advantage to using filtered lignin whose concentration, in a suitable solvent, can be tailored to a targeted viscosity range. For instance, this could allow a lignin-based liquid fuel to be pumped. Finally, looking at the filtered lignin line in Fig. 5, it can be observed that the viscosity of the methanol solution is markedly lower than that of the others. For instance, furfural and acetic acid solutions are, respectively, five and eight times more viscous than the methanol solutions of filtered lignin.

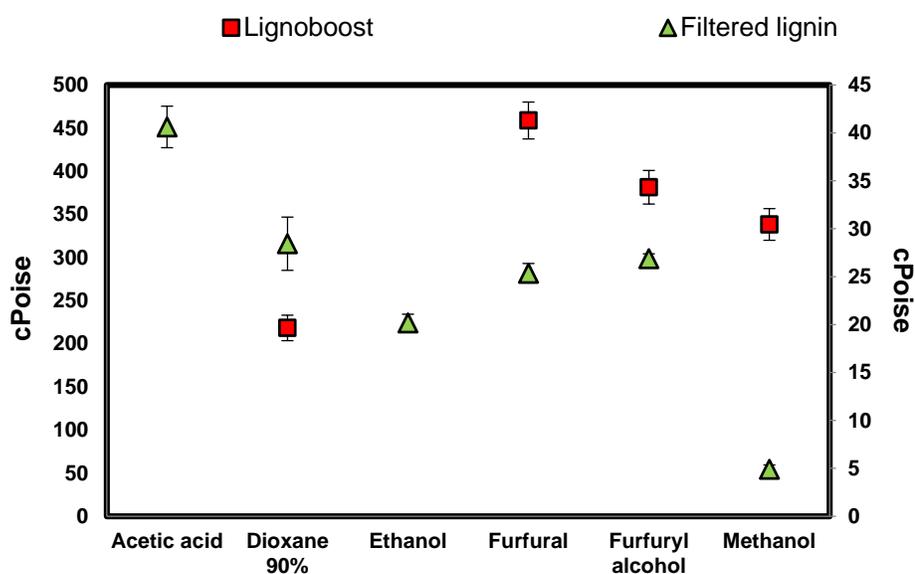


Fig. 5. Measured capillary viscosity values of high lignin concentration solutions made from Lignoboost (left y-axis) and filtered lignin (right y-axis)

In Figs. 4 and 5, there are some absent data for certain solvents. This was due to the following reasons:

- When less than ideal solvents were used to dissolve Lignoboost lignin, low L.t.L volumes were obtained; these limited volumes were not enough to run capillary viscometer tests. This was directly related to the experimental set-up employed, where a 2-mL centrifugation tube was used as the mixing environment.
- Very viscous solutions could not be compared in terms of timing to the reference solvent (glycerol) because they were unable to flow in a narrow 0.5-mL pipette.

Finally, it must be noted that subjective observation errors or differences in the measured capillary efflux times led to increasing reproducibility uncertainties, as well as to certain systematic errors. Nonetheless, the results obtained in this study illustrate the indisputable advantages of using low-molecular weight lignin (*i.e.*, filtered lignin), as it yielded higher solubilities in various solvents with lower solution viscosities.

Reducing Ash Content

During a preliminary experiment (Fig. 6), it was discovered that black liquor contained most of the inorganic salts responsible for lignin ash formation. This experiment was critical to deciding which bench-top strategies to choose to scale up to process 20-kg (wet weight) batches of lignin. Experimental data confirmed that efficiently removing and replacing black liquor with cold acidic water was the best washing process for minimizing inorganic ash. Figure 6 shows that unwashed kraft lignin produced at Aspa Bruk and precipitated at pH 9 had an ash content that was slightly less than 15% (*i.e.*, represented by the black datum point). Lignin washes performed at room temperature showed that the lower pH washes with water resulted in lower ash levels in the recovered lignin. This observation was an expected result and agrees with our previous work with the Lignoboost process (Axegård 2007)

Lignin washing that was performed at higher temperatures resulted in increased difficulties of separating the solid lignin from the wash water. In particular, for the sample dissolved in deionized water, after cooling, lignin redissolved in particles small enough that they could not settle. Filtration was impossible because of clogging of the filter cake together with swelling of particles. For this reason, the ash content data for this sample was not reported.

Looking at Fig. 6, the trends show that if samples are washed at higher temperature, the ash content is always lower than those washed at room temperature. This outcome might be explained by the fact that mobility and diffusion of ions such as Na^+ are more efficient.

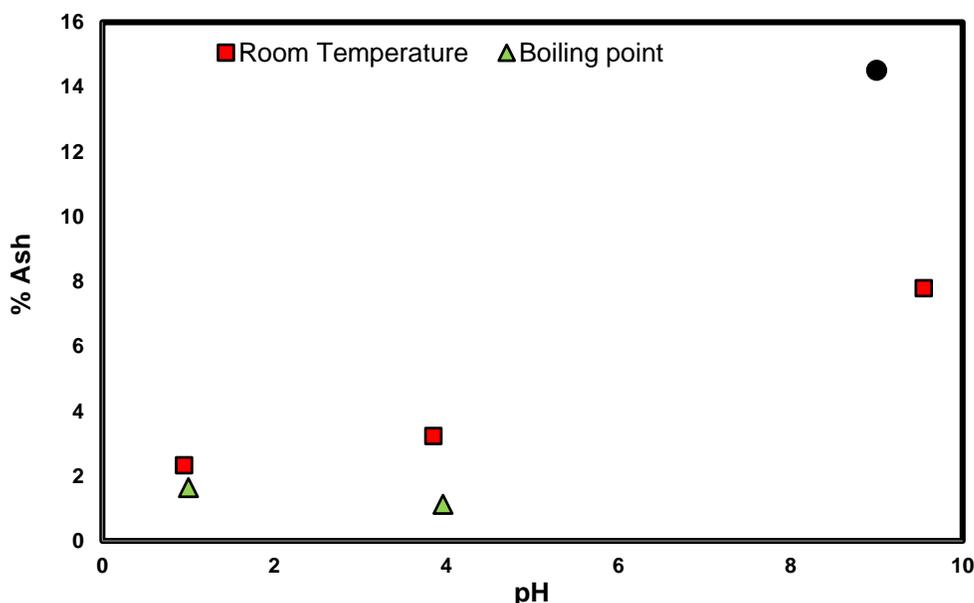


Fig. 6. Wash curves obtained at different pH values at room temperature and at 100 °C. Lignin used was precipitated at pH 9 after black liquor ultrafiltration through a ceramic membrane with a nominal cut off of 5 kDa (denoted above by the black datum point).

Figure 7 illustrates the composition of the lignin produced from the first large run at the pilot plant facility at Aspa Burk, before and after it was washed. As can be seen, the work done was markedly efficient: the ash content was lowered by nearly two orders of magnitude, reaching a value of less than 0.5%. Factors that are critical to lignin washing, besides wash water pH and temperature, include the following:

- *Size of lignin particles.* Increasing surface area by reducing the size of lignin particles is crucial to quick and even ion exchange.
- *Volume of wash water.* The wash liquor volume must be at least two times the volume of supernatant in each washing step. This observation agrees with our previous work with the Lignoboost method (Axegård 2007).
- *Time of washing.* The amount of time needed for lignin washing is inversely proportional to wash temperature. However, a time period between 12 and 24 h, in each step, appeared to be enough time to ion exchange the lignin into its protonated form.
- *Number of washing steps.* A new amount of clean, acidified water is needed when the washing liquor becomes saturated. The result shown in Fig. 7 (right) was obtained after using four separate washing steps. As a demonstration of this, with one washing less, the ash content for the batch described was ten times higher.



Fig. 7. Initial lignin composition (left graph) of the first batch (≈ 20 kg) of lignin produced at Aspa Burk. Final composition (right graph) after several acidic washings of the initial batch

Finally, it was observed that when the “reference” unwashed lignin samples were heated to analyze their ash content, the formation of char occurred frequently. Because these were unwashed samples, it is very likely that the access of oxygen to organic material is hindered by the presence of salts such as sodium. However, when the incombusted samples were reheated at 575 °C, char disappeared, providing reliable reference data. For this reason, preparing a finely grounded sample of less than 1 g has been shown to be helpful to limit char formation.



Fig. 8. Examples of char formation

Technical Significance

The lignin obtained by the ultrafiltration of black liquor displayed superior properties over the unfractionated lignin in terms of solubility and lower viscosity, which leads to easy handling of the material. Thus, the processing steps of the ultrafiltered lignin, such as fractionation, chemical modification, and hydrogenation, will be enhanced. The high solubility of ultrafiltration lignin in furfural has a special interest, as this chemical is used for the manufacture of resins. Dissolved lignin can work as a filler or modifier in these resins.

A potential problem associated with black liquor lignin in many different applications is the ash content. However, washing the lignin with acidified water, such as carbon dioxide (from the lime kiln) dissolved in water, presents an industrially feasible method: firstly carbon dioxide is available in kraft mills, and secondly it does not disturb the sulphur sodium balance by not adding any non-process elements to the chemical recovery system (Tomani 2009).

Furthermore, to lower the ash content, it would seem advantageous if the lignin is precipitated with carbonic acid instead of sulfuric acid, thus avoiding formation of sulfur based compounds such as sulfides and oxides.

Thus, ultrafiltration can be a technically interesting way of obtaining technical lignin as it is or in combination with ways of fractionating lignin based on selective acid precipitation or extraction with organic solvents (Cui *et al.* 2014; Lourencon *et al.* 2015; Dodd *et al.* 2015).

CONCLUSIONS

1. Black liquor lignin is generally soluble in moderately polar solvents, such as ethanol, acetic acid, and methanol, whereas highly polar solvents, such as water, and apolar solvents, such as hexane, are poor solvents for such lignin.

2. Furfural stands out as a good lignin solvent in spite of its low hydrophilicity; part of furfural's lignin dissolving capacity may be due to the solvent's ring structure.
3. The novel type of low-molecular weight black liquor lignin from filtration (CleanFlow) and unfractionated black liquor lignin (Lignoboost) were generally soluble in the same solvents. However, the low-molecular weight lignin could be more easily dissolved in good lignin solvents at considerably higher concentrations.
4. The viscosities of the lignin solutions made from filtered lignins were lower than solutions of unfractionated lignins at the same concentration levels. This was especially the case when high concentrations of lignins were dissolved.
5. Lower ash contents can be obtained by dewatering the precipitated lignin, followed by several cold acidic washes.

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