

FRACTIONATION AND CHARACTERISATION OF TECHNICAL AMMONIUM LIGNOSULPHONATE

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It is difficult to use lignin in any analytical methodology without reducing its considerable polydispersity by fractionation. An ammonium lignosulphonate sample was fractionated using a method of partial solubility in solutions of isopropanol increasingly diluted with distilled water, effectively fractionating by polarity. Selected fractions were characterised by gravimetric determination of the fractions, and determination of acid insoluble lignin, soluble lignin, and carbohydrate contents. Acid-insoluble lignin content was very low, and soluble lignin provided the majority of the lignin content, as should be expected from sulphonated lignin. Carbohydrate contents were also fairly low, the highest percentage at 14.5 being in Fraction 2, with the bulk lignin and Fraction 3 having 6.5% and 3.2%, respectively. Differences in the composition of each fraction support the efficacy of the fractionation process and permitted selection of fractions for use in subsequent studies.

Keywords: Lignosulphonate; Fractionation; Characterisation; Carbohydrate; Acid soluble; Acid insoluble

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INTRODUCTION

Commercially available technical lignins are by-products of chemical pulping. Early in the pulping process, small molecular weight lignin fragments are solubilised and removed from wood chips. Larger molecular weight fragments are removed as pulping continues. The result is a mixture of various lignin molecular fragment sizes. Sugars are also part of the mixture. The fragment sizes and sugar composition and content are dependent upon the pulping process. In this study powdered ammonium lignosulphonate from softwood was divided into smaller molecular weight distribution fractions to simplify later analysis. This process is referred to throughout this paper as fractionation and the products as fractions. The lignin was characterised by determining the gravimetric amount of each fraction in the whole, the carbohydrate content, and the acid insoluble and acid soluble contents.

Industrially, lignin is removed from spent liquor and/or fractionated using ultrafiltration. In ultrafiltration, membranes are used to remove solutes from solvents. Solute molecules are one to two orders of magnitude larger than the solvent molecules. Much research has been directed at improving ultrafiltration efficiency (Bansal et al.

1974; Bhattacharya et al. 2004). Ultrafiltration has been shown to be effective in producing lignosulphonate fractions for research purposes (Zhor 2004).

Lin (1992) reported methods for fractional precipitation of lignin from kraft and sulphite processes. Lignosulphonates were firstly reacted with a long-chain alkyl amine to form a complex, which was removed from the solution with an organic solvent. The lignin was recovered from the complex by increasing the pH in aqueous solution. Addition of the alkyl amine in steps permitted fractionation of the lignin by sulphonic acid content. Lin reported that high molecular weight, low sulphonic acid fractions were extracted first. Ringena et al. (2006) compared lignin fractionation by amine extraction and by ultrafiltration. As well as being time consuming and solvent consuming, they cited incomplete removal of the amine during the back-extraction process as one of the disadvantages of amine extraction. Ultrafiltration was lauded for rapid separation with the added advantage of providing some molecular weight distribution information without additional analysis. Difficulties with ultrafiltration included formation of a gel and membrane fouling. In their work, ultrafiltration yielded a higher recovery of the original lignin, but retained more of the sugars and inorganic materials than amine extraction. Pouteau (2003) stated that soxhlet extraction of lignin, compared to other methods in the literature, was a notably a suitable method to prepare large samples.

Glasser et al. (1974) found that lignin sulphonates could be separated into narrower molecular weight dispersity fractions using liquid column chromatography with mixtures of alcohols and distilled water as eluent. Starting with ethanol, they obtained low molecular weight fractions, which were marked visually by their yellow colour. By slowly increasing the water content, they obtained increasingly higher molecular weight, brown, fractions. They were not able to eliminate the sugar component from the lignin in the lowest molecular weight fraction. Luh and Frederick (1992), in their study of phase behavior of sodium lignosulphonates in ethanol and water mixtures, also designated the yellowish lignin solution to be the low molecular weight fraction.

Gardon and Mason (1955) noted that a fraction's methoxyl content increases with increasing molecular weight and sulphur content decreases with increasing molecular weight. Sulphur content in lignosulphonates is present in the form of sulphonic acid groups. The low molecular weight fractions are therefore the most polar, and the higher molecular weight fractions are less polar. This characteristic could be used in development of simpler means of fractionation. Thring and Griffin (1995) in their work with fractionation of kraft lignin with ethyl acetate and methanol used the differing hydrogen bonding capabilities of the solvents to extract differing molecular weight lignins from the original widely polydisperse mixture. Their method was based on the work of Schuerch (1952), who found that kraft lignin could be extracted into molecular weight fractions by differences in solubility parameter. This is a characteristic of a solvent which may be modified by mixing solvents.

Because of the inhomogeneity of lignin from differing sources and pulping systems, once a lignin sample is fractionated, it is necessary to characterise the lignin to provide an estimation of purity and a basis of comparison between studies. Gardon and Mason (1955) had difficulty establishing the endpoint of lignin dialysis filtration. They stated that determination of lignin purity is difficult because many characterisation

parameters, i.e. reducing power, sulphur content, neutralization equivalent weight, and methoxyl content vary with changes in molecular weight. They speculated that other non-lignin chemical moieties that also carry methoxyl groups may be present, especially in low molecular weight fractions, and so using methoxyl content as the sole means of characterisation may be misleading. Another way to characterise lignin is to determine the acid-insoluble and soluble lignin content and the sugar content. Acid insoluble lignin is lignin that remains as residue after hydrolysis with concentrated sulphuric acid. This is one of the classical methods of lignin determination (Sarkenen 1963). Soluble lignin is the lignin remaining dissolved in the filtrate from acid insoluble lignin preparation, as determined by UV spectroscopy at 280 nm (Dence 1992). Together, the acid insoluble and soluble determinations quantify the lignin content of a sample. The remainder is expected to be sugars and extraneous materials. These methods, however, are also not without their difficulties. Lignins in general and lignosulphonates in particular have proven to be difficult to characterize, resulting from lack of a suitable calibration standard (Kaar and Brink 1991; Fengel and Wegener 1983), as a result of sample history and evidence that the acid insoluble lignin method measures acidic degradation of lignin rather than solubility of lignin in acid (Kaar and Brink 1991; Yasuda et al 2001), and species composition (Yasuda et al 2001; Maekawa et al 1989; Gosselink and van Dam 2004; Fengel and Wegener 1983). Klason and acid soluble lignin determination and carbohydrate and nitrogen content determination methods, however, were found to be 'reliable and reproducible' in a round robin test described by Gosselink et al. (2004). Newer methods such as Fourier-transform infra-red (FT-IR) are increasingly utilized (Boeriu et al 2004; Alonso 2001) and eliminate the effects of carbohydrate and extractive contaminants, but introduce their own difficulties such as overlapping bands, which require advanced statistical techniques such as principal component analysis, and differing band intensities that may be lignin isolation method dependent (Quintana et al 2008).

Hoyt and Goheen (1971) suggested that sugars comprise up to 20% of the apparent lignin recovered from spent sulphite liquor. In their quest for a lignin suitable for the Lederer-Manesse reaction with formaldehyde, Alonso et al. (2001) characterised several lignins using a variety of techniques. They determined lignin content of their samples using an ultra-violet absorption method and found that their softwood ammonium lignosulphonate sample had a lignin content of 79.57% with 6.2% ash. While reporting the kinetics of the methylation of their ammonium lignosulphonate sample, Peng et al. (1993) described the lignin and carbohydrate contents as 62.32% and 10.13%, respectively. Methodological details were not given. Calvé and Fréchet (1983) compared the influence of carbohydrates on the binding efficiency of ammonium lignosulphonate, which had 68% lignin content and 22% reducing sugars. El Mansouri and Salvadó (2006) characterised kraft, soda anthraquinone, organosolv, ethanol, and spent sulphite lignins to determine which was best suited to adhesive production. Acid insoluble lignin content for lignins other than spent sulphite varied from 61.2% for kraft lignin to 92.3% for organosolv lignin. Carbohydrate content for the same lignins ranged from 1.16% for organosolv to 22.37% for ethanol. Lignosulphonate content of spent sulphite lignin was 56.5%. Carbohydrate content was not determined for spent sulphite

lignin. Glennie (1971) reported that lignosulphonates may also contain sugar acids, sulphonated sugars, alcohols, aldehydes, terpenes, lignans, sulphite, and sulphite salts. Gellerstedt's group (1994) used pyrolysis gas chromatography-mass spectrometry to examine structural properties of lignin from birch kraft liquor. They found that much less than expected (about one-third) of the material isolated from pulping liquor was lignin. The remainder was furanoic structures, which were believed to have arisen from degradation of hemicelluloses. Birch has a high hemicellulose content (Barton and Brownell 1981). Furans are produced commercially by hydrolysis of pentosans under a pressurised and acidic environment, similar to the environment found during kraft pulping, so it is not unreasonable to believe that furanoic structures may be produced during the pulping process. Their work reinforced the need to characterise lignin used in research. Recent research has suggested that the carbohydrates in lignins may be bound into lignin-carbohydrate complexes rather than present as free sugars (Lawoko *et al.* 2005, 2006; Choi *et al.* 2007). This may be the reason that many researchers have reported difficulty completely removing sugar from lignin samples.

EXPERIMENTAL

Materials

Softwood ammonium lignosulphonate was provided by Tembec Inc. Isopropanol was locally obtained.

Methods

Based on the literature above, and using the solubility chart of Teas (1968) as a guide, mixtures of isopropanol increasingly diluted with water were used to sequentially extract ammonium lignosulphonate from a thimble in a soxhlet apparatus at ambient temperature.

A predetermined mass of lignosulphonate was poured into a cellulose extraction thimble and placed inside the reservoir of a soxhlet. In order to avoid changes to the lignin from excess heat, a manual extraction at room temperature, until lignin no longer dissolved into the solution, was performed using firstly 100% isopropanol, followed by the isopropanol-water ratio solutions 100:0, 80:20, 60:40, 40:60, 0:100, resulting in fractions referred to as Fraction 1 through Fraction 5, respectively. Each solution was concentrated using rotary evaporation, with care taken to ensure that the solution temperature did not exceed 50°C (it was generally between 27°C and 35°C) until the solution was reduced to a few millilitres. Fifty degrees Celsius was chosen as the upper temperature limit to coincide with the temperature used in the Lin method. Solutions were then placed into weighing boats and allowed to evaporate to dryness in the fume hood, except for Fractions 1 and 2, which were evaporated to dryness with the rotary evaporator. Five fractions resulted.

Gravimetric determinations were made by weighing each fraction and calculating its percentage contribution to the total lignin sample. Determination of Klason (acid-insoluble) and UV (soluble) lignin and carbohydrate contents were made by FPIInnovations-Paprican, Pointe Claire, Quebec, Canada. FPIInnovations-Paprican

performed carbohydrate analysis according to TAPPI test method 249 cm-85. They identified individual sugars using gas chromatography. Acid insoluble lignin was determined according to TAPPI test method T 222 om-88. Soluble lignin was determined by the absorbance of the filtrate from acid-insoluble determination at 205 nm in a spectrophotometer.

RESULTS AND DISCUSSION

The 100:0 isopropanol: distilled water solution was barely visibly coloured until concentrated. The 100:0 and 20:80 solutions were amber or straw yellow, corresponding well to low molecular weight fractions as reported previously in the literature (Glasser et al. 1974; Luh and Frederick 1992). The 40:60 and 60:40 solutions were the brown colour typical of lignin. At dryness, most fractions reduced easily to glassy shards. The 100:0 and 80:20 fractions were difficult to dry, suggesting that they consisted of low molecular weight molecules with sulphonic acid groups sterically accessible to solvents. No residual alcohol was apparent.

Gravimetric quantitative determination of the fraction proportions provided the information summarised in Table 1:

Table 1. Quantitative Gravimetric Lignin Fractions in the Sample

Fraction	Solvent	Proportion in Lignin Sample (%)
1	100:0 isopropanol:water	0.2
2	80:20 isopropanol:water	16.95
3	60:40 isopropanol:water	84.35
4	40:60 isopropanol:water	0.3
5	0:100 isopropanol:water	0.04

Fractions 1, 4, and 5 comprised only a small part of the sample. Since Fractions 2 and 3 made up the bulk of the sample, they would be expected to play the most significant role in subsequent use of the lignin. It was noted that the total percentages exceeded 100%. Fractions 1 and 2 were highly hygroscopic, and it is likely that, although apparently dry, the samples still contained some water.

FPIinnovations-Paprican tests gave the results presented in Table 2 for acid-insoluble lignin, soluble lignin, and carbohydrate contents of the bulk lignin and Fractions 2 and 3.

Table 2. Carbohydrate, Klason and Soluble Lignin Content of Bulk Lignin and Fractions 2 and 3

Sample	Carbohydrate (%)	Klason Lignin (%)	Soluble Lignin (%)
ALS – bulk	6.8	0.43	50.7
Fraction 2	14.5	5.84	41.6
Fraction 3	3.2	0.38	52.2

The sulphonated nature of the lignin under study and resulting solubility in ionic solutions is in harmony with the finding that the acid-insoluble lignin fraction of the samples was small and soluble lignin was large. The carbohydrate content of 6.8% for the bulk lignin, though slightly lower than other reported values, was within expected limits. The spent sulphite liquor had originally been concentrated by ultrafiltration, and it was possible that many of the expected free carbohydrates were already removed. Of the samples tested, carbohydrate concentration was high in Fraction 2, and very low in Fraction 3. Soluble lignin was much lower in Fraction 2 than in Fraction 3. The current findings conform with the literature as described above.

Sugars identified are listed in Table 3.

Table 3. Identity of Carbohydrates Found in Bulk Lignin and Fractions 2 and 3

Sugar	Bulk Lignin (%)	Fraction 2 (%)	Fraction 3 (%)
Arabinan	1.0	5.5	0.4
Xylan	1.4	1.7	0.7
Mannan	1.4	4.2	0.8
Galactan	0.9	2.2	0.5
Glucan	2.1	1.2	0.6

Concentrations of the different carbohydrates were similar to one another in the bulk lignin and in Fraction 3. Fraction 2 had a higher carbohydrate content and much higher concentrations of arabinan and mannan than Fraction 3 or bulk lignin. Since free carbohydrates were not expected in these samples, it may be that the carbohydrates were bonded to the lignin. Lawoko et al. (2005) studied lignin-carbohydrate complexes in lignin resulting from kraft pulping and found that softwood lignin tended to be associated with glucomannan or xylan carbohydrates. They later (2006) studied sulphite softwood pulp lignins and found glucan-lignin complexes, glucomannan-lignin complexes, and xylan-lignin-glucomannan complexes. An independent group (Choi et al. 2007) studied spruce (*Picea abies*, A. Dietr.) unbleached pulps from three pulping methods and concluded that carbohydrates were bonded to lignin via benzyl-ether bonds and that galactose and mannose were most likely to be the affiliated carbohydrates. The lignin presently under study contained high levels of mannan and arabinan. If the carbohydrates found in these samples are the result of lignin-carbohydrate complexes, clearly mannan and arabinan are involved.

CONCLUSIONS

1. Fractionation by partial solubility in isopropanol was found to be a simple, yet effective means of preparative lignin separation.
2. Each fraction was qualitatively different from the others and each succeeding fraction, by comparison of qualitative attributes against the literature, was of higher molecular weight than that preceding.
3. A higher than expected proportion of the lignin was found in Fraction 3. As expected, carbohydrates concentrations were higher in Fraction 2 and sparingly found in Fraction 3. Although carbohydrates were equally distributed in bulk lignin and

Fraction 3, Fraction 2 contained higher concentrations of arabinan and mannan. As expected from sulphite lignin, most of the lignin found was of the soluble rather than the acid insoluble form.

4. For preparative scale lignin fractionation, the method described here not only yielded five unique fractions, it also prepared the fractions for further analysis.

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