

CHARACTERISTICS OF LIGNIN PRECIPITATED WITH ORGANIC ACIDS AS A SOURCE FOR VALORISATION OF CARBON PRODUCTS

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Lignin is a by-product of multiple lignocellulosic biomass derived industries. Hardwood and softwood lignin were obtained by precipitation from black liquor. The elemental analysis (EA) of the samples indicated that the sulphur content varied between the wood species, SW (softwood) organic acid precipitated samples showing the lowest sulphur content. FTIR showed differences in the intensities of the absorption peaks for each sample. TG analysis of the lignin samples in the presence of air revealed differences in the main degradation region of the TG/DTG curves. The type of organic acid used for precipitation appeared to influence the thermal degradation of the lignin samples. TG analysis under nitrogen resulted in carbon yields that were acceptable for the lignin samples to be considered as raw materials for carbon preparation. SEM images of the samples showed swelling in the lignin chars and revealed differences in the morphology of their structure, showing that different precipitation media would produce different carbon structures.

Keywords: lignin, precipitation, black liquor, valorisation, organic acids, thermogravimetric analysis, carbonisation, scanning electron microscopy

INTRODUCTION

The biorefinery concept dictates that the maximum value be drawn from biomass, rather than producing only a single product and discarding the rest of the biomass as waste.¹⁻³ Integrating biorefinery systems into current technologies, for example, in the kraft pulping process, would see mills achieving maximal usage of the biomass, as well as add to the product stream of the mill, thereby increasing profits. For example, instead of burning the whole biomass material for fuel purposes, the biomass can be pre-processing to isolate the hemicelluloses component for use in ethanol production, and thereafter the rest of the biomass could be utilized as solid fuel.⁴ ⁶ The kraft pulping process produces black liquor as a by-product. This by-product contains lignin, sugars, cooking chemicals, and extractives. In current kraft mills, the black liquor is processed in a recovery boiler to recover cooking chemicals, as well as to provide energy by combustion of the lignin. Ideally, this would render a kraft mill into a closed system. However, in older mills the capacity of the recovery boiler is limited,

consequently resulting in a bottleneck of black liquor processing, which in turn causes complications in the mill. Several methods have been proposed in recent years to replace recovery boilers with methods such as black liquor gasification, which could add more value to the mills to produce energy, as well as chemicals.⁷⁻⁹ Gasification of black liquor has a potential to produce electricity, chemicals, as well as fuels such as dimethyl ether, synthetic gas (syngas), methanol, hydrogen etc.⁹⁻¹¹ Another way to offload the excess black liquor would be to extract lignin. Due to its abundance, aromaticity, and carbon content, lignin has been identified as a resource that could have a high potential in the chemical industry, so much that it has been envisaged to be adequate enough to replace fossil fuel resources.¹²⁻¹⁴

Traditionally, lignin is obtained from black liquor by precipitation methods, involving the use of acids, mostly with sulphuric acid, and more recently with a combination of carbon dioxide and sulphuric acid.¹⁵⁻¹⁸ At pH ~4, complete lignin

precipitation has been observed by most researchers. The utilization of H₂SO₄ has also been shown to release foul gases such as SO₂ and/or H₂S during the precipitation experiments.^{19,20} The release of these environmentally unfriendly gases, when utilizing H₂SO₄ for lignin precipitation, could prove to be an inefficient acidification technology on an industrial scale. Therefore, it is worth exploring other acids for lignin precipitation that would have much greener consequences on the environment, especially when envisaging integrated biorefineries. Organic acids can be effective alternatives for lignin precipitation. Carbon based acids can serve as good precipitating agents because they would not introduce any objectionable elements during the precipitation process, thereby producing a 'greener' lignin product. Also, organic acids are not costly, as some of them are mostly by-products of other processes, and they are nontoxic.²¹ Poly-carboxylic acids, such as citric acid, have been shown to increase the mechanical properties of polymers, such as cellulose and regenerated protein fibres, by crosslinking the hydroxyl groups. Additionally, they have been utilized as non-polymeric fillers for size modification and porosity control of nanopowders.^{21,22} These characteristics could also be beneficial for lignin valorisation into carbon fibres and activated carbons, because polymer stability is essential for pre-treatment steps.^{23,24}

The objective of the current work was to investigate the thermal behaviour of lignin samples precipitated from kraft black liquor with three organic acids (formic, acetic, and citric acids). The purpose of utilizing organic acids was to avoid the negative effects of using sulphuric acid. The characteristics of the collected lignin samples were examined by elemental analysis (EA), Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), as well as scanning electron microscopy (SEM) after carbonisation.

EXPERIMENTAL

Lignin isolation

Hard- and softwood black liquor samples were obtained from a kraft mill in South Africa. The mill used mostly eucalyptus (80%) and some pine wood (20%) furnishes. The black liquor samples were stirred for 3 hours at room temperature to assure homogeneity in the bulk samples. Lignin was then isolated by precipitation with sulphuric acid (SA), as well as three organic acids, viz., formic (FA), citric (CA), and acetic (AA). An efficient procedure for precipitation, isolation and recovery of the lignin has been described in previous work.²⁵

Characterization

The lignin samples were dried in an oven at 70 °C overnight. Elemental analysis for carbon, hydrogen, nitrogen and sulphur (CHNS) was performed on a Perkin Elmer 2400-C instrument (Malaga, Spain), and O content was evaluated by difference. TG experiments were performed using a CI model Electronics Ltd. Thermobalance (Malaga, Spain). The initial sample weight was constantly adjusted to approx. 10-12 mg. A continuous gas (air or nitrogen) flow rate of 150 mL/min (STP) and a linear heating rate of 10 °C/min were used until a temperature of 900 °C was reached to obtain the TG and differential TG curves. The temperature signal for the controller was measured by means of a chromel-alumel thermocouple placed inside the reaction tube. The sample weight loss was continuously recorded in a microcomputer data acquisition system.

The lignin precipitates were characterized by Fourier transform infrared (FTIR) spectroscopy on a Bruker Optics Tensor 27 FT-IT spectrometer (Malaga, Spain): 50 scans, scanning range 4000-400 cm⁻¹ and a resolution of 4 cm⁻¹.

Scanning electron microscopy (SEM) micrographs were obtained by utilizing a JEOL JSM-6490LV instrument (Malaga, Spain).

RESULTS AND DISCUSSION

A representative elemental composition of the lignin samples precipitated from different acids is shown in Table 1. Elemental analysis showed a distribution of CHO that is commonly observed for lignin.²⁶⁻²⁸ The analyses of Alcell® lignin and a commercial kraft lignin (CKL) are also included for comparison. The CHO profile of the SW samples was closely related to that of Alcell® lignin, whereas that of HW was close to CKL, except for the oxygen content of the latter. Sulphur content in the samples is an important parameter to consider, because this could be a major concern for the environment when upscaling the precipitation reactions. The different acid HW precipitated lignin samples showed higher sulphur content than their SW counterparts. As expected, Alcell® lignin showed no sulphur content, while CKL showed higher sulphur content than SW and HW samples. Organic acids for this work were utilized with the expectation that they would result in lesser sulphur content in the lignin samples. However, it appears that acid strength, as well as wood type played a role. Compared with the SA samples, the organic acid samples showed lower sulphur content, except for the HWFA sample. The higher sulphur content may be due to differences in wood chemistry between HW and SW, where HW contains syringyl groups, which are not present in SW.

Thus, the sulphur (sulphites and sulphates) retained during the cooking process could react with the –OH groups of the syringyl to produce –SO₃H groups in the lignin samples. As observed in a previous work,²⁵ there is gas evolution (probably H₂S and CO₂) during the H₂SO₄ precipitation process, and CO₂ could be the main gas released for organic acids reactions. The release of CO₂ during organic acid precipitation could be observed as an added advantage as the gas can be captured and utilized as a precipitating agent as well.

Representative TG curves, under air atmosphere, obtained for lignin precipitated with different acid media are shown in Figure 1 (A – TGs and B – DTGs). All four different lignins showed a behaviour typical of general TG profiles of lignins, although some differences were

observed for each lignin. The DTG profiles make it possible to better observe the different temperatures where decompositions occur. For the SW samples, it can be observed that the DTG curves show clear decomposition regions for all samples; SWSA displayed main decomposition between 260-490 °C; for SWFA the decomposition shifted to 310-550 °C. For the SWAA sample, double decomposition peaks were observed between 290-460 °C, as well as between 480-640 °C. Finally, for the SWCA samples, decomposition occurred between 290-610 °C. The differences in the DTG curves for the decomposition of the samples observed provide a clear indication that precipitation with organic acids has different effects on kraft lignin, as well as a larger range of decomposition.

Table 1

Elemental and immediate analyses of commercial kraft lignin, Alcell® lignin, and kraft lignin samples precipitates with H₂SO₄ and organic acids

Lignin sample	% C	% H	% O	% N	% S	% Ash (db)	% Volatile matter (db)	% Fixed carbon (db)	% Char yield
HWSA	58.44	5.12	31.77	0.22	4.43	1.58	69.82	28.59	30.17
HWFA	57.52	5.44	30.97	0.21	5.84	2.81	63.26	33.92	36.73
HWAA	52.49	5.34	38.62	0.17	3.37	3.74	64.36	31.89	35.64
HWCA	52.37	5.19	40.54	0.19	1.71	2.81	61.27	35.92	38.73
SWSA	62.52	6.00	28.32	0.24	2.92	0	66.86	33.14	33.13
SWFA	63.38	6.06	29.04	0.21	1.29	2.49	73.83	23.68	26.17
SWAA	61.78	6.00	30.85	0.20	1.16	2.05	67.24	30.70	32.75
SWCA	63.57	6.05	28.43	0.25	1.70	1.37	59.43	39.20	40.57
CKL	52.08	4.85	40.13	0.15	2.80	12.60	75.03	12.37	24.97
Alcell®	65.91	6.28	27.57	0.24	0	0	66.44	33.56	33.56

db – dry basis, HW – hardwood, SW – softwood, SA – sulphuric acid, FA – formic acid, AA – acetic acid, CA – citric acid, CKL – commercial kraft lignin

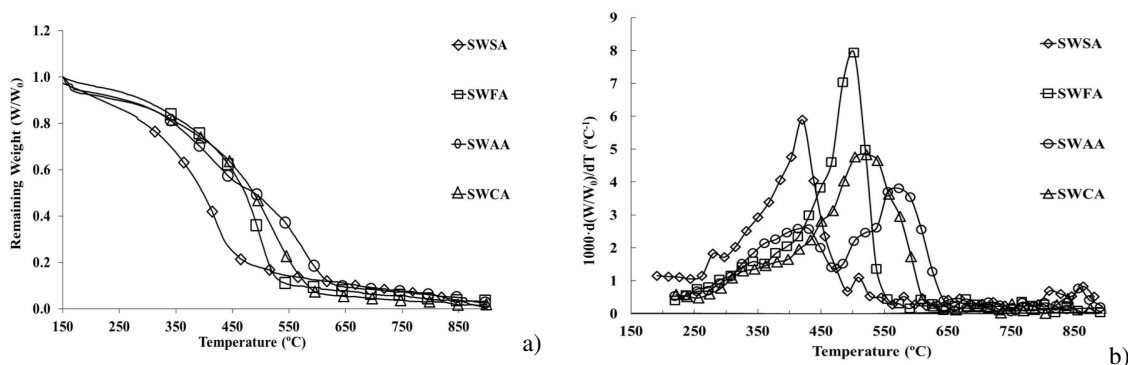


Figure 1: (a) TG and (b) DTG profiles obtained in air atmosphere for softwood kraft lignin precipitated with SA, FA, AA and CA

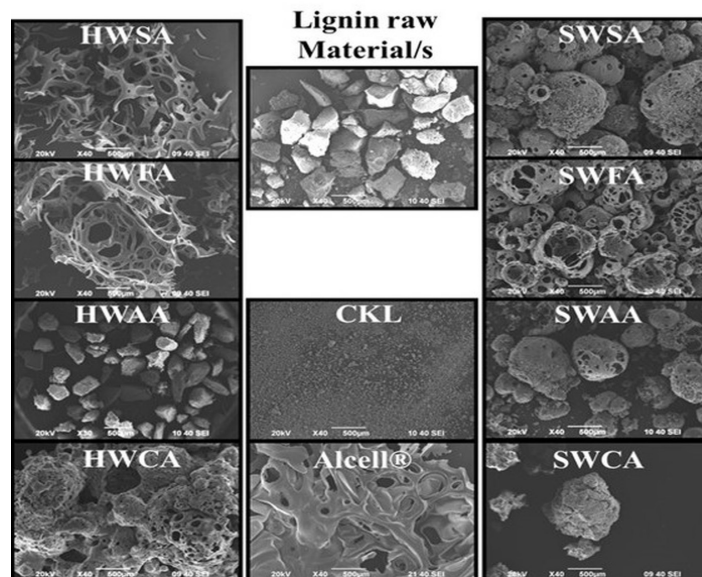


Figure 2: SEM micrographs of carbonized lignin samples

To assess the suitability of the obtained lignin samples as potential precursors for carbon materials, similar TG analyses were performed for all samples, however in this case under nitrogen environment, to measure the volatile matter, the fixed carbon content, and the char yield of each sample on a dry basis (db) (shown in Table 1). The results for fixed carbon content and char yields were sufficient to consider the lignins as good prospects for future processing into valuable carbon products.^{27,29} The lignin samples also exhibited expansion and/or swelling at the end of each experiment, as illustrated in the SEM micrographs (Figure 2). The micrographs of the lignin samples prior to thermal treatment under nitrogen displayed similar granular structures as the particle size remained constant for all HW and SW samples. However, after carbonization, the samples displayed different morphologies. Differences in the swelling of the samples were observed, and this is a commonly observed behaviour for lignin samples, typically showing cracks and cavities, where the volume of particles increases, indicating plastic deformation by cavitation.³⁰ Due to their high ash content, HWAA and CKL samples showed no signs of swelling, which agrees with the work reported by Rodríguez-Mirasol *et al.*,²⁷ who observed that above 2.5% ash content, lignin tends not to swell when carbonized. However, as can be observed for

the HWSA, HWFA and HWCA samples, there are structural modifications that are different from cavitation and are closely related to the Alcell lignin carbonized sample. This observation could further support the deduction that organic acids modified kraft lignin during precipitation.

FTIR was performed to analyse the differences in the functional groups of the different lignin samples obtained (Figure 3). The FTIR spectrum of commercial kraft lignin (CKL) was utilized as a reference, since the hardwood and softwood black liquor samples in this work were obtained from a kraft mill. The fingerprint region where lignin functional groups are commonly observed is around $1800\text{--}900\text{ cm}^{-1}$. There were subtle differences, mainly in the intensity of the absorption peaks, observed in the spectra in Figure 3 for each lignin sample when compared to each other individually, as well as with the CKL. For this reason, the peak intensities observed for the lignin samples were sufficient to enable differentiation among the samples.

The HW and SW samples also had common peaks between them (approx. $1600, 1525, 1440, 1217, 1034$ and 910 cm^{-1}), which represented the common features of the backbone monomers (guaiacyl and syringyl) of a lignin molecule. The main IR peaks observed in the lignin samples were assigned as shown in Table 2.

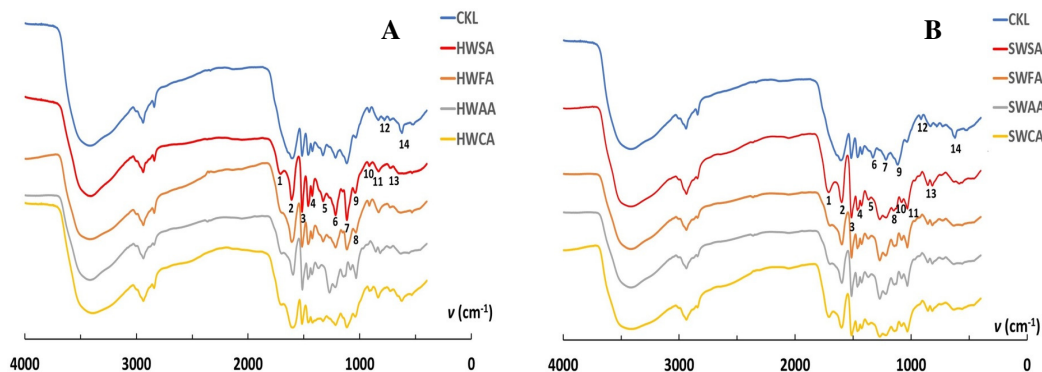


Figure 3: FTIR spectra of HW (A) and SW (B) acid precipitated lignin samples with CKL as reference spectrum

Table 2
FTIR absorption frequency assignments for peaks numbered in Figure 3

Peak #	Wavenumber (cm ⁻¹)	Assignments
1	1710	Ethers, methoxy
2	1606	Aromatic skeletal
3, 4	1514, 1458	methyl and methylene deformation
5	1421	C-H aromatic stretching with
6	1330	Ethers, methoxy
7	1215	Carbonyl deformation
8	1114	Deformation C-H or S-O (sulphate)
9	1033	C-H deformation in G-unit
10	914	Aromatic skeletal
11, 12, 13	829, 721, 612	Typical of S-O bond stretching
14	621	Sulphate O-S-O deformation

CONCLUSION

Precipitation of lignin from kraft black liquor using organic acid instead of sulphuric acid or carbon dioxide results in lignin samples with different physical and chemical characteristics from those of lignins produced using inorganic acids. The lignin samples had lower sulphur content, especially the lignin from softwood kraft black liquor. Sulphuric and formic acid precipitated lignin samples displayed major weight losses during thermal decomposition, while acetic and citric acid precipitated samples showed the least weight losses. The samples with an ash content higher than 2.5% showed no modifications after carbonization. FTIR spectra showed that the lignins had similar functional groups. However, there were differences in absorption peak intensities, peak sharpening and broadening in each of the samples. The fixed carbon content and char yields from the carbonized lignins showed that the precipitated lignin samples in this work are

good biomass for further processing into valuable compounds.

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REFERENCES

- ¹ B. Antizar-Ladislao and J. L. Turrion-Gomez, *Biofuel. Bioprod. Biorefin.*, **2**, 5455 (2008).
- ² J. H. Clark, F. E. I. Deswarte and T. J. Farmer, *Biofuel. Bioprod. Biorefin.*, **3**, 72 (2009).
- ³ M. F. Demirbas, *Appl. Energ.*, **86**, S151 (2009).
- ⁴ P. Sassner and G. Zacchi, *Biotechnol. Biofuels*, **1**, 1 (2008).
- ⁵ R. Wooley, M. Ruth, D. Glassner and J. Sheehan, *Biotechnol. Prog.*, **15**, 794 (1999).
- ⁶ M. Galbe and G. Zacchi, *Appl. Microbiol. Biotechnol.*, **59**, 618 (2002).

- ⁷ M. Naqvi, J. Yan and M. Fröling, *Bioresour. Technol.*, **101**, 937 (2010).
- ⁸ T. Bludowsky and D. W. Agar, *Chem. Eng. Res. Des.*, **87**, 1328 (2009).
- ⁹ M. Naqvi, J. Yan and E. Dahlquist, *Bioresour. Technol.*, **101**, 8001 (2010).
- ¹⁰ M. Naqvi, J. Yan and E. Dahlquist, *Appl. Energ.*, **90**, 24 (2012).
- ¹¹ A. V. Neimark, K. S. W. Sing and M. Thommes, in “Handbook of Heterogeneous Catalysis”, edited by G. Ertl, H. Knözinger, F. Schuth and J. Weitkamp, Wiley Online Library, 2008, pp. 721-738.
- ¹² H. Wallmo, M. Wimby and A. Larsson, *Procs. Tappi Engineering, Pulping and Environmental Conference*, Tennessee, October 11-14, 2009, pp. 1-5.
- ¹³ D. Ibarra, J. C. del Río, A. Gutiérrez, I. M. Rodríguez, J. Romero *et al.*, *Enzyme Microb. Technol.*, **35**, 173 (2004).
- ¹⁴ A. J. Ragauskas, M. Nagy, D. H. Kim, C. A. Eckert, J. P. Hallett *et al.*, *Ind. Biotech.*, **2**, 55 (2006).
- ¹⁵ R. Alén, P. Patja and E. Sjöström, *TAPPI J.*, **62**, 108 (1979).
- ¹⁶ A. García, A. Toledano, L. Serrano, I. Egüés, M. González *et al.*, *Sep. Purif. Technol.*, **68**, 193 (2009).
- ¹⁷ P. Tomani, *Cellulose Chem. Technol.*, **44**, 53 (2010).
- ¹⁸ W. Zhu and H. Theliander, *Procs. ISWFPC 16th International Symposium on Wood, Fiber and Pulping Chemistry*, Tianjin, 2011, pp. 195-199.
- ¹⁹ V. C. Uloth and J. T. Wearing, *Pulp Pap.-Can.*, **90**, T310 (1989).
- ²⁰ M. Helander, H. Theliander, M. Lawoko, G. Henriksson, L. Zhang *et al.*, *BioResources*, **8**, 2270 (2013).
- ²¹ N. Reddy and Y. Yang, *Food Chem.*, **118**, 702 (2009).
- ²² D. Wyrzykowski, E. Hebanowska, G. Nowak-Wiczak, M. Makowski and L. Chmurzynski, *J. Therm. Anal. Calorim.*, **104**, 731 (2011).
- ²³ R. Ruiz-Rosas, J. Bedia, M. Lallave, I. G. Loscertales, A. Barrero *et al.*, *Carbon*, **48**, 696 (2010).
- ²⁴ J. M. Rosas, R. Berenguer, M. J. Valero-Romero, J. Rodríguez-Mirasol and T. Cordero, *Front. Mater.*, **1**, 1 (2014).
- ²⁵ M. Namane, B. B. Sithole and D. Ramjugernath, *J. Sci. Ind. Res.*, **74**, 571 (2015).
- ²⁶ D. Montané, V. Torné-Fernández and V. Fierro, *Chem. Eng. J.*, **106**, 1 (2005).
- ²⁷ J. Rodríguez-Mirasol, T. Cordero and J. J. Rodríguez, *Carbon*, **31**, 87 (1993).
- ²⁸ J. M. Rodríguez-Maroto, F. Garcia, J. Rodriguez-Mirasol, T. Cordero, R. Suau *et al.*, *J. Environ. Sci. Health A*, **A28**, 651 (1993).
- ²⁹ F. Kifani-Sahban, A. Kifani, L. Belkbir, A. Zoulalian, J. Arauzo *et al.*, *Thermochim. Acta*, **298**, 199 (1997).
- ³⁰ S. Sebbahi, A. Ahmido, F. Kifani-Sahban, S. El Hajjaji and A. Zoulalian, *J. Eng.*, **2014**, 1 (2014).