Kopra, Riku; Lähdeniemi, Annina; Dahl, Olli

Evaluating the lignin content in the fibreline of a birch kraft pulp mill with a TDS sensor

Published in:
APPITA Journal

Published: 01/01/2019

Document Version
Publisher's PDF, also known as Version of record

EVALUATING THE LIGNIN CONTENT IN THE FIBRELINE OF A BIRCH KRAFT PULP MILL WITH A TDS SENSOR

RIKU S. KOPRA[1], ANNINA M. LÄHDENIEMI[2] and OLLI P. DAHL[3]

[1]RDI Scientist, and corresponding author (Riku.Kopra@xamk.fi)
South-Eastern Finland University of Applied Sciences, Fibre Laboratory, Vipusenkatu 10, FI-57200 Savonlinna, Finland

[2] Researcher, [3] Professor, Aalto University,
School of Chemical Engineering, P.O. Box 16300, 00076 Aalto, Finland.

SUMMARY

In previous washing studies on brown stock and bleaching it has been shown that a refractometer can be used as an indicator of wash loss, since it measures the total dissolved solids (TDS) reliably.

This current study was performed on both the mill and laboratory scale. On the mill scale, lignin concentrations and also organic and inorganic materials in the hardwood fibre line were examined. On the laboratory scale, TDS concentration values using two different commercially available lignins with different concentrations in alkaline conditions were measured.

In the mill-scale tests of the fibre line it was noticed that the lignin content changed with the pulp and pulp suspension liquor streams during the various process steps, with a good relationship between lignin and total dissolved solids in the liquor streams. A very good relationship between dissolved lignin and organics (measured as COD) and a moderate correlation between dissolved lignin and inorganic material in the filtrates (measured as conductivity) in the different process steps were found.

In the laboratory tests, it was observed that differently processed lignins differ from one another and have different solubility behaviours. This phenomenon was also identified using a refractometer. These observations can help to better control the processes and improve their efficiency in the fibre line of a Kraft pulp mill. More research will be needed to prove all the findings however.

Keywords: Lignin, refractometer, total dissolved solids (TDS), chemical pulping, birch pulp, filtrate

INTRODUCTION

The relative composition of cellulose, hemicelluloses, lignin, and extractives varies greatly in different wood species, and the chemical composition of wood also varies quantitatively among tree species. Table 1 shows some values given as percentages of wood weight for each constituent in different wood species.

Table 1 Chemical comparison of various wood species (*1*)

Constituent [%]		Softwood		Hardwood	
		Scotts Pine (*Pinus sylvestris*)	Spruce (*Picea glauca*)	Silver Birch (*Betula verrucosa*)	Eucalyptus (*Eucalyptus camaldenisi*)
Cellulose		40.0	39.5	41.0	45.0
Hemicellulose	Glucomannan	16.0	17.2	2.3	3.1
	Glucuronoxylan	8.9	10.4	27.5	14.1
	Other polysaccarides	3.6	3.0	2.6	2.0
Lignin		27.7	27.5	22.0	31.3
Total Extractives		3.5	2.1	3.0	2.8

Lignin can be defined as a polyphenolic material arising primarily from the enzymic dehydrogenative polymerisation of three phenylpropanoid units: coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol, respectively *(2)*. Lignin classification is traditionally done according to the precursors of the polymer. Guaiacyl lignin (G) is typical of softwood species and is formed mostly of trans-coniferyl alcohol precursors, with the remainder consisting mainly of trans-*p*-coumaryl alcohol which contains *p*-hydroxyphenyl (H) units. In contrast, generally guaiacyl-syringyl (GS) lignins found in hardwood species are mainly composed of trans-coniferyl alcohol and trans-sinapyl alcohol type units in varying ratios.

The physical properties and chemical characteristics of lignin do not only vary between different wood species, but also according to the method of isolation. Moreover, the molecular structure and function groups differ for the various type of lignin. Hardwood lignin contains relatively more β-O-4 and less 5-5 and β-5 linkages than softwood lignin, although generally the most abundant linkage in lignin is β-O-4. The frequency of a β-O-4 linkage is approximately 45-50% of the phenylpropane units in softwood lignin, while being approximately 60-85% of the phenylpropane units in hardwood lignin (*3*).

Several industrially based technical lignins are by-products of chemical pulping. Kraft lignin (or sulfate lignin), alkali lignin (or soda lignin) and lignosulfonates are derived from the Kraft, soda-AQ, and sulfite pulping of wood, respectively. Most commonly, Kraft lignins are obtained from black liquor by precipitation with acid or by ultrafiltration. The LignoBoost lignin separation process, which has been

developed in co-operation between Chalmers University of Technology and Innventia and commercialised by Metso, is one example of this process of the precipitation of acid. The process is well-described in several publications (*4-6*). The procedure of the LignoBoost separation process is shown in Figure 1 (*7*).

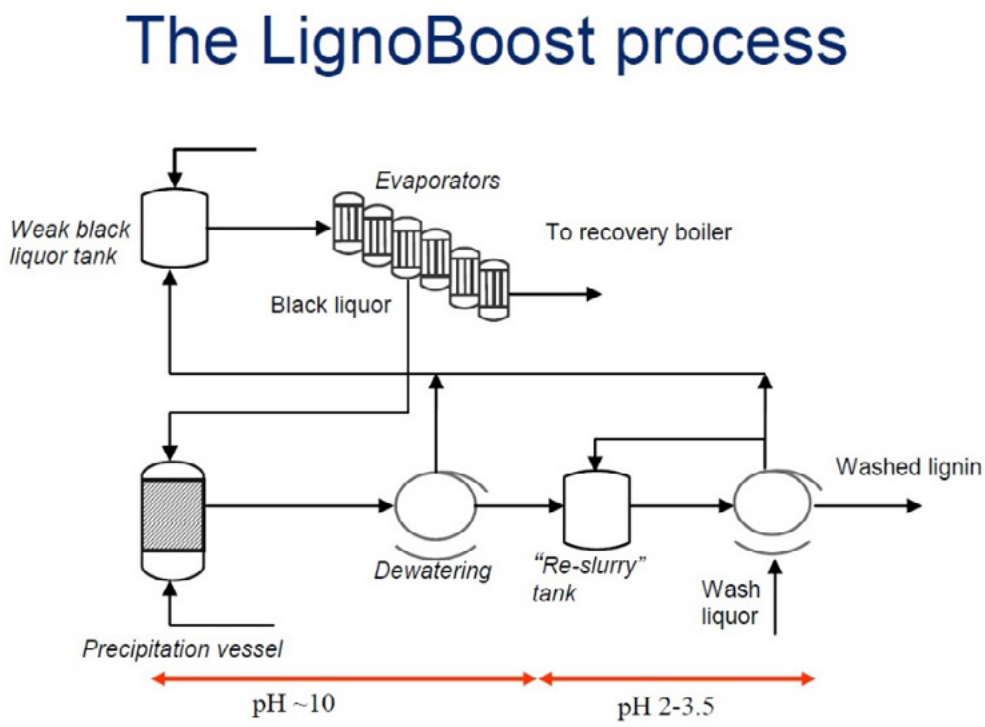

Fig. 1. Isolation process of lignin (*7*).

When the raw material or concentration of the lignin changes in the biorefinery recovery process or pH conditions change, for example in the pulp mill's oxygen delignification or lignin precipitation and purification process, concentration measurements are required to monitor the quality of the lignin and the performance of the process steps.

In this study the traditional refractive index technique is used to measure the concentration of various lignin-containing solutions. Normally the reactivity and physico-chemical properties of lignins are partly governed by their molar mass distribution. Recent developments in industrial refractometers for continuous in-line measurement for TDS as well as in-line adsorption UV (-VIS) measurement for dissolved lignin opens up new possibilities for measuring and analysing, for example, the performance of a washing line and oxygen delignification (*8-10*).

EXPERIMENTAL

Materials and methods

The experiments for this study were carried out in a Scandinavian pulp mill's fibre line and in the Fibre Laboratory of South-Eastern Finland University of Applied Sciences. This section presents the pulp mill fibre line's measurement points, the measurements and test arrangements.

The hardwood (HW) (mainly *Betula pendula* and *Betula pubescens*) pulp fibre line consists of a continuous digester with a high heat washer in its lower section, an atmospheric diffuser (AD), one drum displacement (DD) washer before 1-stage oxygen delignification and two DD washers after the oxygen stage, and D_0, EOP, D_1, D_2 sequenced bleaching with washing by DD washers after all bleaching sequences. Production was about 2000 a.d. metric tons/day during research, the Kappa target after digester was 17 and after oxygen delignification 11 (the hexenuronic acids (hexa) contribution to Kappa number being 5-6). Pulp samples were taken from the washer's outlet pulp. Consistency after high heat and AD was about 10% and after the DD washers about 15%. The fibre line and sample points are shown in Figure 2.

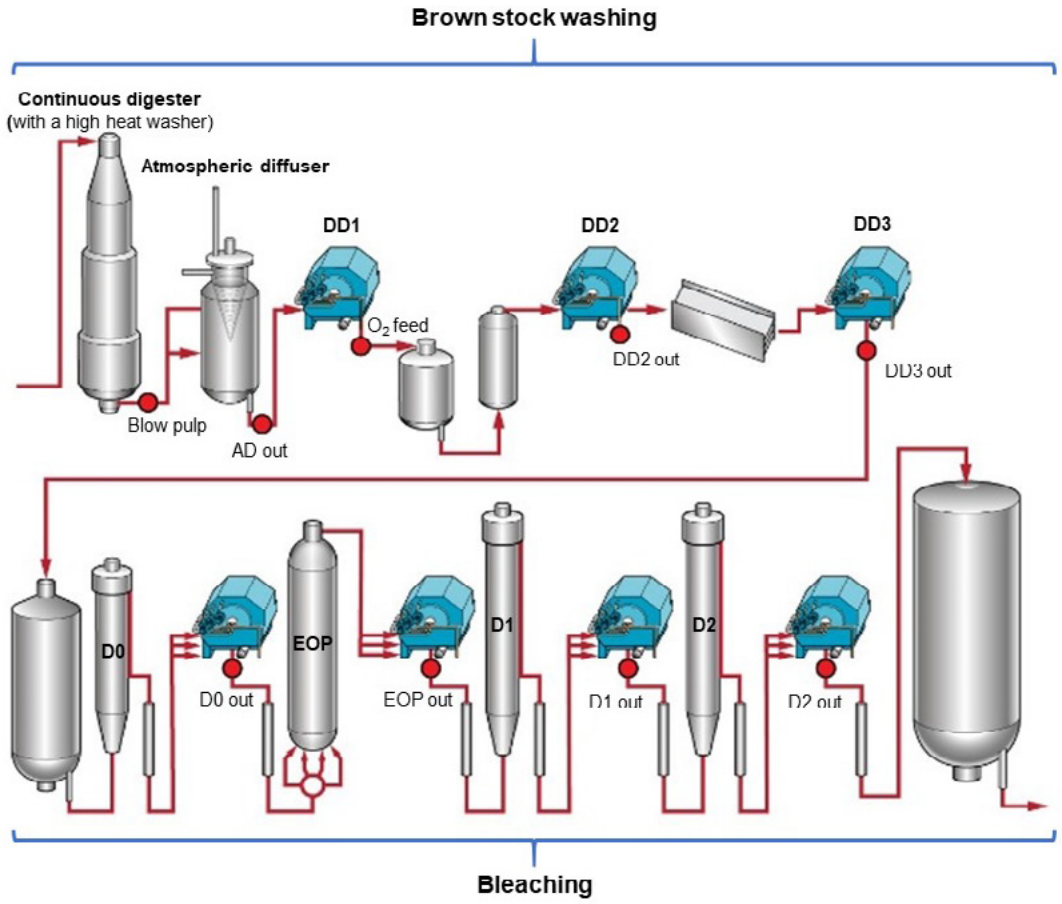

Fig. 2. Pulp samples (red points) of hardwood pulp fibre line, 650,000 a.d.metric tons/year.

In the laboratory tests, the solubility behaviour of the two different Kraft-based lignins in different pH solutions was tested and the amount of dissolved lignin concentration was measured using the portable refractometer. In Kraft lignin case A the LignoBoost separation process was used and in case B the separation method was unknown (commercial Aldrich lignin), but the end pH of the lignin was controlled to 6.5.

Measurement units: process refractometer

The refractometer measures liquid concentration based on measuring the refractive index. Refractive index measurement is actually a measurement of the speed of light in a medium. The speed of light in a medium depends on the medium itself, the temperature and the wavelength. The refractive index depends on the concentration of dissolved solids. In general, the larger the molecular size of the dissolved solids, the greater the refractive index per concentration unit (*11*). The measurement accuracy is not influenced by particles, bubbles, fibres, colour or temperature changes in the process medium (*12*). The laboratory reference temperature is usually 20°C or 25°C. Due to the wavelength dependency, the refractive index is measured using monochromatic light. The principle behind the measurement of dissolved dry solid content through refraction has been presented in detail in earlier studies (*13-15*). Normally refractometers are installed directly in the process, but in this study, we used a portable refractometer, Figure 3, which has been presented by Kopra et al. (*16*).

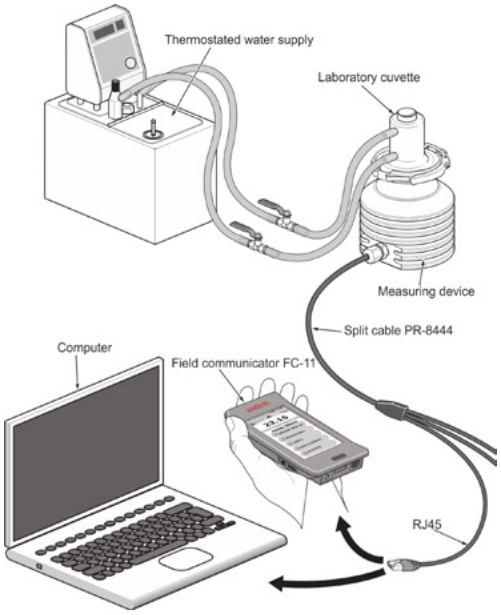

Fig. 3. Test arrangements using a refractometer in a laboratory with a single sample

Analytical determinations

Analyses were made to define the chemical situation of the fibre line. The samples were analysed using the following methods:

- Determination of dry matter content (analytical) (ISO 638 "Paper, board and pulps—determination of dry matter content—oven-drying method")
- Determination of dry matter content (on-site), refractometer or portable refractometer
- Conductivity (on-site), conductometer (Mettler Toledo; Columbus, OH, USA)

- COD liquor samples, filtrated using 1000 µm paper and analysed in a COD analyser (ISO 15705 "Water quality determination of the chemical oxygen demand index [ST-COD] small-scale sealed-tube method")
- Dissolved lignin, ultraviolet (UV) measurement at 280 nm, UV 2550 Spectrophotometer (Shimadzu Corp.) using an absorptivity value of 19.8 L/(g·cm)
- Pulps (ISO 302 "Determination of Kappa number")

RESULTS AND DISCUSSION

Mill tests

Table 2 shows the concentrations of different measurements of the Scandinavian hardwood pulp mill's fibre line.

Table 2. Measured results of hardwood fibre line

Sample	Kappa Number	Dissolved Lignin [mg/L]	TDS by lab. Ref. [%]	COD [mg/L]	Conductivity [mS/cm]	TDS by lab (105°C) [%]
Blowpulp	17.4	26880	6.74	65400	47.30	7.68
AD out	17.2	10480	3.39	28400	28.10	4.10
O_2 feed	15.9	4495	2.27	13400	25.00	2.90
DD2 out	12.8	580	0.43	3700	4.22	0.49
DD3 out	12.7	115	0.14	1510	0.67	0.09
D_o out	4.3	730	0.40	2930	4.11	0.42
EOP out	3.9	105	0.18	778	1.72	0.15
D_1 out	0.9	63	0.16	655	1.55	0.12
D_2 out	0.7	16	0.09	172	0.25	0.02

Figure 4 shows the progress of lignin concentration in the fibre line both in the pulp and in the filtrate. Lignin in the pulp is estimated from the Kappa number, using a factor of 6.7. At the beginning of the brown stock washing line under very alkaline conditions, there is a large amount of lignin in the filtrate part of the mass flow. As the pH decreases and the filtrate purifies, the difference in the lignin content of the filtrate and pulp rapidly increases. Because pulp samples are from the washers' discharge pulp, the effect of counter-current washing is also shown in the filtrate section. It is beneficial that there are large tanks in which the concentration differences can be equalised between pulp and filtrates through diffusion. It can

also be seen from the figure that the oxygen phase of the experiment mill works a little ineffectively and most of the lignin can be removed from the pulp in the bleaching. In a previous study (*17*), it was found that the oxygen phase Kappa reduction moderately follows the change in the TDS over the oxygen reactor.

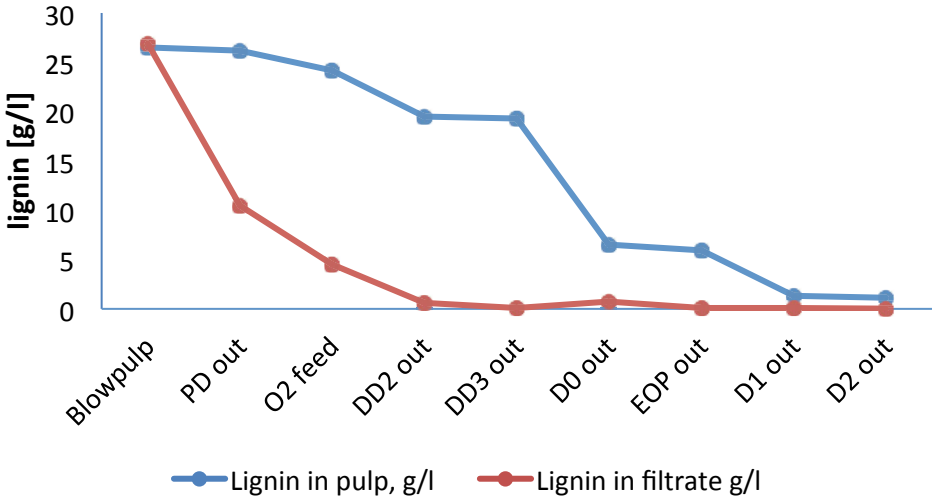

Fig. 4. Lignin concentration in the hardwood fibre line in the pulp and filtrate parts

Figure 5 shows the relative proportion of dissolved lignin to dissolved solids. After cooking, about a third of the pulp filtrate fractions TDS content is lignin. The relative proportion begins to decrease and eventually at the end of bleaching, it is at 5%. At the beginning of bleaching, the filtrate is slightly dirtier than at the end of brown stock washing (BSW). At the end of BSW pure water or condensate is used for washing and in the bleaching, all the acid filtrates of the bleaching line accumulate into the D_0 stage. The aim of BSW is to recover lignin as effectively as possible to get lignin into the recovery boiler and not to the waste-water treatment system.

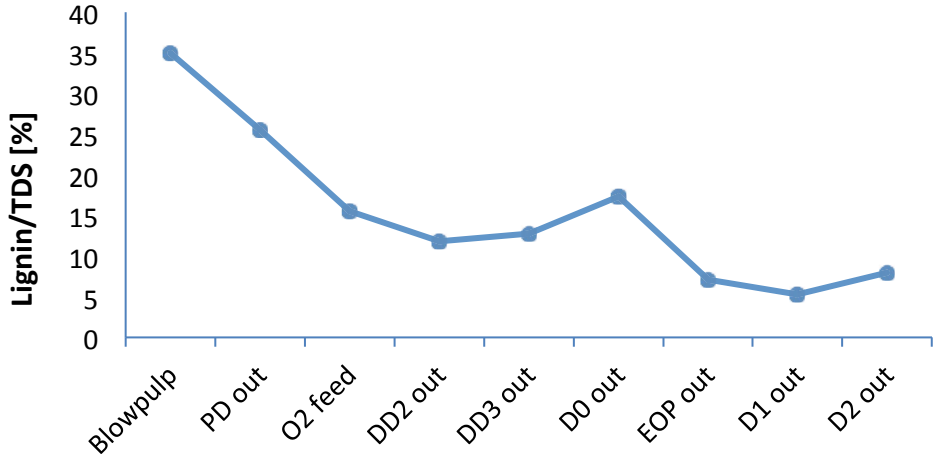

Fig. 5. Relative proportion of dissolved lignin in the dissolved solids measured from the hardwood fibre line

Figure 6a presents the relation between the dissolved lignin content and TDS content measured in the laboratory using a portable refractometer for HW pulp filtrates. Figure 6b shows the correlation between dissolved lignin and conductivity content. Figure 6c shows the correlation between dissolved lignin and COD respectively. The results indicate that measurement of dissolved organics and inorganics by a refractometer has excellent correlation with dissolved lignin (R^2 0.9723, checked from xy-graph) because of the high portion of organic matter present in the filtrates. The correlation of conductivity with dissolved lignin is satisfactory with HW (R^2 0.8854). The correlation of dissolved lignin and conductivity was worse at the beginning of the fibre line before the oxygen stage, indicating that the organic material washed away better than the inorganic in the experimental mill. Lignin, which caused significant organic load, also followed the COD value levels (HW, R^2 0.9976). For the COD and dissolved lignin analysis, the samples were diluted with plenty of water, which in turn can cause measurement errors and make real-time measurements difficult to implement.

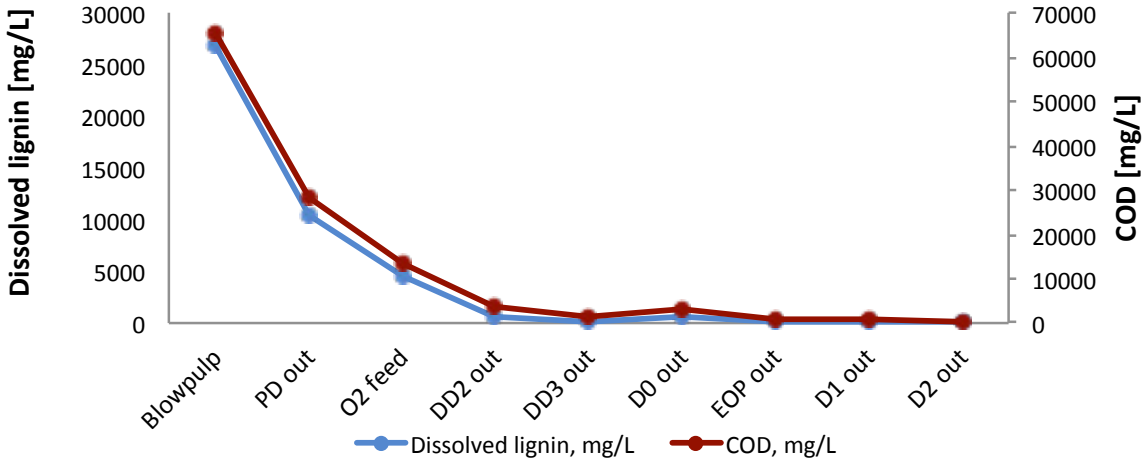

Fig. 6a. Dissolved lignin versus TDS measured by portable refractometer

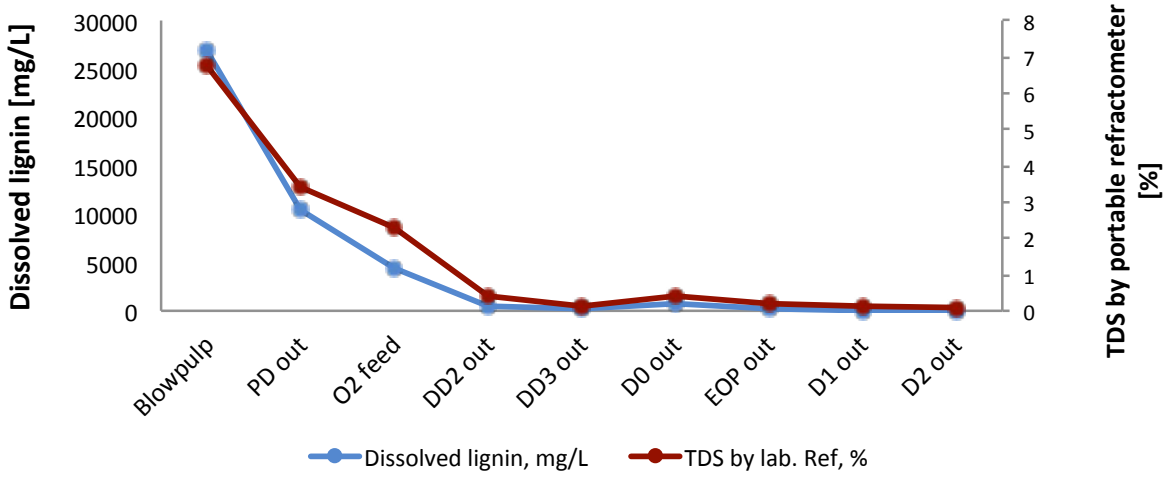

Fig. 6b. Dissolved lignin versus conductivity

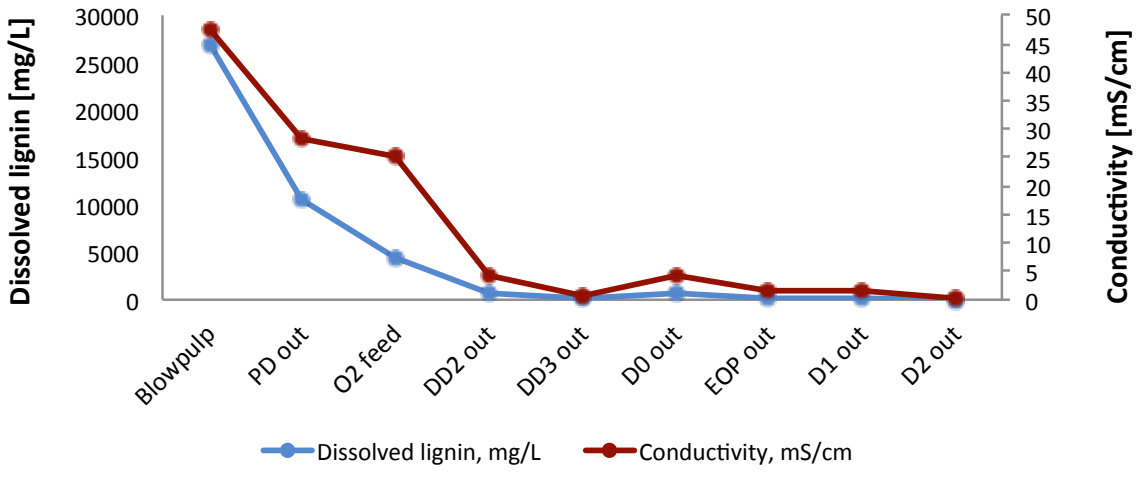

Fig. 6c. Dissolved lignin versus COD

Laboratory test

Figure 7 shows that the addition of lignin A and B to the strong alkali behaved almost linearly and at the same rate in the TDS measurement. However, the higher the lignin dosage, the higher the values obtained with lignin A. Both lignins were well-soluble in 0.1M NaOH.

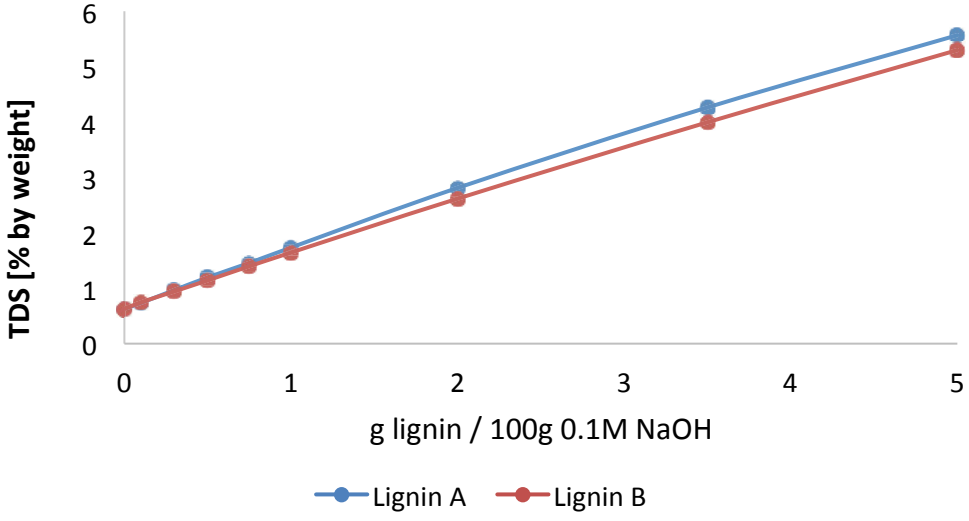

Fig. 7. Changes in the TDS concentration of two different Kraft lignins in alkaline solution measured using a portable refractometer

Figure 8 shows the effect of alkali concentration on the pH of lignin A and B (1g lignin/100 mL NaOH). From Figure 7, it can be seen that lignin A decreases more in pH than B. As previously described, A is industrially prepared using sulfuric acid and is not supposed to be treated as being as pure as commercial lignin B.

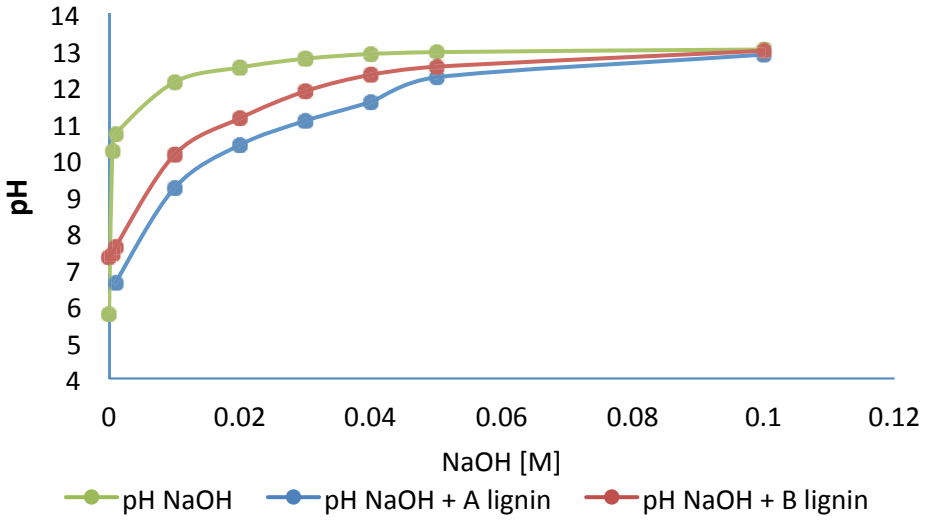

Fig. 8. Effect of alkali concentration on the pH of NaOH, NaOH lignin A and B solutions

Figure 9 shows how these alkali/lignin solutions are displayed in the TDS measurement. It can be seen that when the alkali concentration decreases, the dissolving of lignin A weakens strongly. Lignin B dissolves moderately well even in deionised water. Figure 10 shows the critical pH range at which the dissolving of lignin A begins to deteriorate. The critical pH value of 10.5 is the same as that at which the lignin begins to adhere to the fibre in the brown stock washing area.

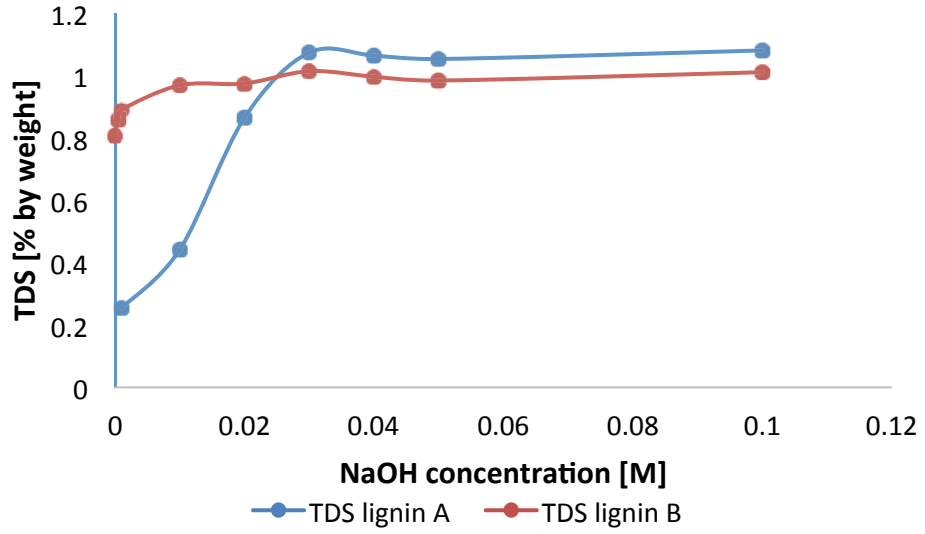

Fig. 9. Effect of alkali/lignin solution concentration on TDS measurement

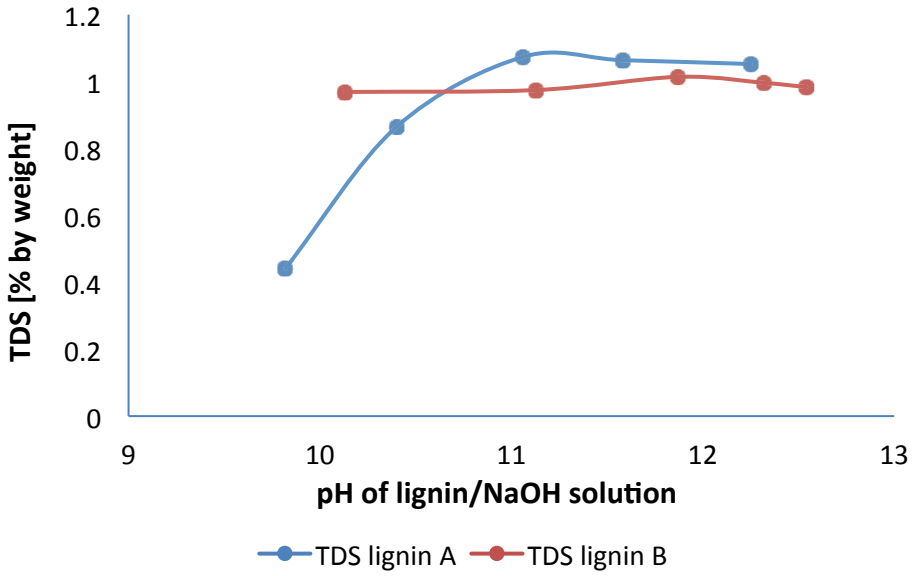

Fig. 10. Effect of pH on dissolving of lignin A and B

The results above show that, although the refractometer measures the total dissolved solids as a sum parameter, this has a good correlation with the dissolved lignin in the wash liquors. This is due to the high proportion of lignin in the filtrates and its high refractive index, while alcohol and acids have a much lower refractive index (*15*).

Measuring does not measure one substance in the brown stock washing line, but, for example, in oxygen delignification, it can successfully monitor the degree of lignin delignification. The company BTG has further developed lignin-specific on-line measurement (*18-19*). In addition, Valmet, for example, has measurement methods which analyse the lignin content.

CONCLUSIONS

The mill-scale results indicate that the refractometer can be used for reliably measuring the change of total dissolved solids (TDS) at various process stages of a pulp mill. Combining the mill-scale knowledge and laboratory-scale results, it can be concluded that at some points of the fibre line (such as oxygen delignification), it can also be used as an indirect policing meter to avoid harmful lignin re-deposition into the fibres.

ACKNOWLEDGEMENTS

This study was initiated under a contract between the South-Eastern Finland University of Applied Sciences, K-Patents OY, Stora Enso Oyj and Aalto University. This research was partially funded as part of a larger

research project (NewPro) by Business Finland – the Finnish Funding Agency for Innovation, the European Regional Development Fund (ERDF) and partner companies. The authors thank Liz Dexter for editing the manuscript and thank Sakari Toivakainen (TOIHAN Company) and Anu Pihlajaniemi for helping with the data analysis. The authors are grateful to all the participants involved with this study.

REFERENCES

(1) Sjöström, E. – **Wood Chemistry Fundamentals and Applications** (2nd edition): Academic Press, San Diego, CA (1993).

(2) Stenius, P., Gullichsen, J. and Paulapuro, H. – **Papermaking Science and Technology, Book 3. Forest Products Chemistry**. Fapet Oy, Jyväskylä (2000).

(3) Chen, C.L. – Lignins: Occurrence in Woody Tissues, Isolation, Reactions, and Structure. In **Wood Structure and Composition**. Lewin, M., Goldstein, I.S. (Eds), Marcel Dekker, New York, p 183 (1991).

(4) Öhman, F. – Precipitation and separation of lignin from kraft black liquor, Doctoral dissertation, Chalmers University of Technology, Gothenburg, Sweden, ISBN 91-7291-742-3 (2006)

(5) Wallmo, H. – *Lignin extraction from Black Liquor, precipitation, filtration and washing*, Doctoral dissertation, Chalmers University of Technology, Gothenburg, Sweden, ISBN 978-91-7385-151-0 (2008).

(6) Tomani, P. – The LignoBoost Process, *Cellulose Chem. Technol.* **44**(1-3): 53 (2010).

(7) Theliander, H. – The LignoBoost Process: Solubility of Lignin, *Proc. Tappi PEERS Conf*., Norfolk, VA, USA (2010).

(8) Kopra, R., Helttunen, J., Tervola, P., Tirri, T. and Dahl, O. – Refractive index measurements for brown stock washing loss – mill investigations, *Appita J*. **63**(2): 131 (2010).

(9) Andersson, N., Wilke, C., Biazzo, T., van Fleet, R., Germgård, U. – A new sensor and novel control concept for optimized fiberline operation, *10th Research Forum on Recycling*, Green Bay, Wisconsin, USA, (2013).

(10) Tervola, P. – New method for estimating chemical pulp washer efficiency using online data reconciliation, *Appita J.* **71**(2): 136 (2018).

(11) Silla, E. Arnau, A. and Tunon, I . – Fundamental principles governing solvent use, In **Handbook of Solvents** (Second Edition), Wypych, G (Ed)., Volume 1, ISBN 9781927885383 (2014).

(12) Sherman, R.E. and Rhodes, L.J. - Chapter 14 Refractive index analyzers, In **Analytical Instrumentation: Practical Guides for Measurement and Control,** Instrument Society of America, USA (1996).

(13) Kopra R., Tirri, T., Dahl, O. – Refractive index measurements for brown stock washing loss – laboratory investigations, *Appita J.* **61**(5): 408 (2008).

(14) Kopra R., Karjalainen S., Tirri T. and Dahl O. – Optimization of pressure filter performance using refractometer – Mill investigations, *Appita J.* **65**(1):49 (2011).

(15) Kopra R. – *Application of the refractometer in the measurement and monitoring of brown stock washing,* Doctoral dissertation, Aalto University, Espoo, Finland, p. 51. (2015).

(16) Kopra, R., Karjalainen, S. and Dahl O. – Portable refractometer for mill total dissolved solids (TDS) measurement, *Proc. ABTCP Conf*., Sao Paulo, Brazil (2018).

(17) Kopra, R., Mutikainen H., Dahl O. – Using online bubble size and total dissolved solids (TDS) measurements to investigate the performance of oxygen delignification. *Tappi J.* **17**(6):339 (2018).

(18) Andersson, N., Wilke, C., van Fleet, R., Mathur, A and Germgård, U. – On the impact of dissolved lignin in oxygen delignification and chlorine dioxide stages, *Proc. Tappi PEERS Conf*., Atlanta, GA, USA (2015).

(19) Andersson, N., Wilke, C., Mathur, A and Germgård, U. – Fast and accurate online measurement of differentiated lignin and HexA kappa numbers leads to improved fiberline control, *Proc. Tappi PEERS Conf.,* Portland, OR, USA (2018).

Original manuscript received 20 March 2019, accepted 13 June 2019