***UV/vis Lignin Analysis Neutral Spectra***

The neutral ultraviolet and visible (UV/vis) spectra were measured in a 2:1 2-methoxyethanol/water (v/v) solvent and according to standard literature procedures.[1] The UV/vis data was acquired using a Lambda 900 UV spectrometer. Briefly, the absorption spectra were recorded from 200 to 800 nm using a pathlength of 10 mm, a bandwidth of 1.0 nm and a scan speed of 250 nm/min. Only matched cuvettes were used when obtaining the spectra. The spectra were determined by adding 5 mL of the lignin solution (0.06 g/L in 2:1 v/v 2-methoxyethanol and deionized water) to 1 mL of phosphate buffer at pH 6.5. This lignin solution was placed in the sample cell. The reference cell was prepared by adding 5 mL of a solvent solution (2:1 v/v 2-methoxyethanol and deionized water) to 1 mL of phosphate buffer at pH 6.5.

***UV/vis Lignin Analysis for Ionization Spectra***

Kraft black liquor and residual lignins were characterized by differential UV/vis spectroscopy. The method is based on the difference in absorption between lignin in alkaline solution and lignin in neutral solution.[2] In alkaline solution, phenolic hydroxyl groups are ionized and the absorption changes towards longer wavelengths and higher intensities. By subtracting the spectrum derived from the neutral solution from that of the alkaline solution, an ionization difference spectrum, a $\Delta\varepsilon_i$-spectrum, is obtained. Typically for a double-beam spectrophotometer, the alkaline solution is placed in the sample cell and the neutral solution in the reference cell. In this way, the difference spectrum can be measured directly. For this research, the spectra of isolated lignins were measured in a 2:1 2-methoxyethanol/water (v/v) solvent. The UV/vis experiments were conducted according to standard literature methods.[3] The UV/vis data was acquired with a Lambda 900 UV spectrometer. Briefly, the absorption spectra were recorded from 200 nm to 800 nm using a pathlength of 10 mm, a bandwidth of 1.0 nm and a scan speed of 250 nm/min. Only matched cuvettes were used when obtaining the spectra. The spectra

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[1] *Lin, S.Y.; Ultraviolet Spectroscopy. In Methods in Lignin Chemistry, Lin, S.Y. and Dence, C.W., Editors. New York: Springer-Verlag. p. 217-232 (1992).*

[2] *Aulin-Erdtman, G.; Spectrographic Contributions to Lignin Chemistry V. Phenolic Groups in Spruce Lignin. Svensk Papperstidning* ***57*** *(20). p. 745-760. (1954); Goldschmid, O.; Determination of the Phenolic Hydroxyl Content of Lignin Preparations by Ultraviolet Spectrophotometry. Analytical Chemistry* ***26*** *(9). p. 1421-1423. (1954); Gärtner, A.; Gellerstedt, G. and Tamminen, T.; Determination of phenolic hydroxyl groups in residual lignin using a modified UV-method. Nordic Pulp & Paper Research Journal* ***14*** *(2). p. 163-170. (1999).*

[3] *Pasco, M.F. and Suckling, I.; Chromophore Changes During Oxygen Delignification of a Radiata Pine [Pinus radiata] Kraft Pulp. Appita Journal* ***51*** *(2). p. 138-146. (1998); Dyer, T.J. .; Ragauskas, A.J. Deconvoluting chromophore formation and removal during kraft pulping: influence of metal cations. Appita Journal (2006), 59(6), 452-458.*

were determined by adding 5 mL of the lignin solution (0.06 g/L in 1:1 v/v 2-methoxyethanol and deionized water) to 1 mL of either phosphate buffer at pH 6.5 (neutral spectra) or 0.6 M NaOH (for alkali spectra).

***Application UV/vis Analysis of Lignin***

A series of isolated kraft and residual lignins from the kraft, PS, AQ, and PS/AQ pulps were also analyzed employing differential UV/vis spectroscopy techniques. The UV/vis method is uniquely suited to monitor changes in conjugated phenolics. The ionization difference ($\Delta\varepsilon_i$) spectra are obtained by subtracting the spectrum of lignin recorded in neutral solution from that recorded in alkaline solution. The UV/vis difference spectra of the kraft and residual lignins are shown in Figure 1 and Figure 2, respectively. It is generally considered that the UV/vis absorption properties of etherified lignin units are unchanged in neutral and alkaline medium, whereas the absorption maximum bands of phenolic moieties shift to longer wavelengths at high pH due to the ionization of phenolic hydroxyl groups. Therefore, the differential UV/vis spectra recorded in the neutral and alkaline pH range provide a convenient means of estimating the phenolic hydroxyl groups.

Figure 1 and Figure 2 show that PS/AQ kraft and residual lignins had local maximum intensities at 250, 300, and 370 nm, while the other lignins had similar difference spectra. This indicates that PS/AQ kraft lignins contain a high amount of unconjugated phenolic lignin (i.e., peaks at 250 and 300 nm) and conjugated phenolic units (i.e., peak at 370 nm). Thus, kraft pulping with simultaneous addition of PS and AQ broke down the polymeric lignin matrix most significantly, implying a synergistic effect of PS and AQ on kraft pulping. These results are unexpected since prior work on lignin model compounds have shown that polysulfide readily reacts with lignin structures containing a conjugated double bond. For this reason, research is currently being conducted to further our understanding of this phenomenon. It seems that AQ and PS/AQ pulps have relatively high amounts of phenolic lignin units while in PS pulp the content of these kinds of structures is lowest. Almost no peak shifts were observed in the residual lignins from the polysulfide pulp.

These ionization difference spectra are also useful in analyzing the chromophore content of residual and dissolved kraft lignins. The peak centered around 370 nm in the $\Delta\varepsilon_i$ spectrum of dissolved and residual kraft lignin is composed of peaks due to phenolic *o,p*-dihydroxystilbenes ($\lambda_{max}$ = 378 nm), *p,p*-dihydroxystilbenes ($\lambda_{max}$ = 356 nm), phenolic α-carbonyl units ($\lambda_{max}$ >>350nm) and possible other chromophores. The data in Figure 1 suggests that an increase in phenolic α-carbonyl structures in the dissolved lignin from PS, AQ, and PS/AQ pulps, with PS/AQ dissolved lignin having the greatest concentration of such structures. Meanwhile, the residual lignins suggest different trends. The data in Figure 2 suggests that the residual lignin from PS pulps has the lowest amount of phenolic α-carbonyl structures compared to conventional kraft, AQ, and PS/AQ residual lignins. Meanwhile, the residual lignins from the AQ and PS/AQ pulps contained more of these functionalities than the conventional kraft residual lignin. Coincidentally, the chromophore index and brightness follow similar trends as seen with the phenolic α-carbonyl functionalities; that is, as the chromophore index increases, the phenolic α-

carbonyl structures also increase in concentration. For this reason, such structures may be important contributors to the chromophore index of conventional kraft, PS, AQ, and PS/AQ kraft pulps.

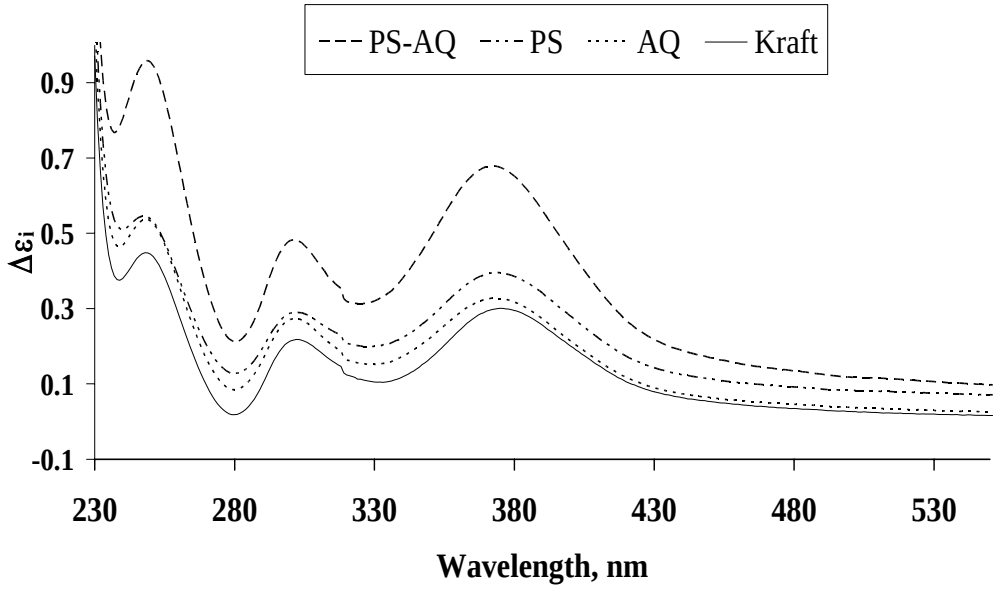


**Figure 1. Differential ionization UV/vis spectra of kraft, PS, AQ, and PS/AQ kraft dissolved lignins.**

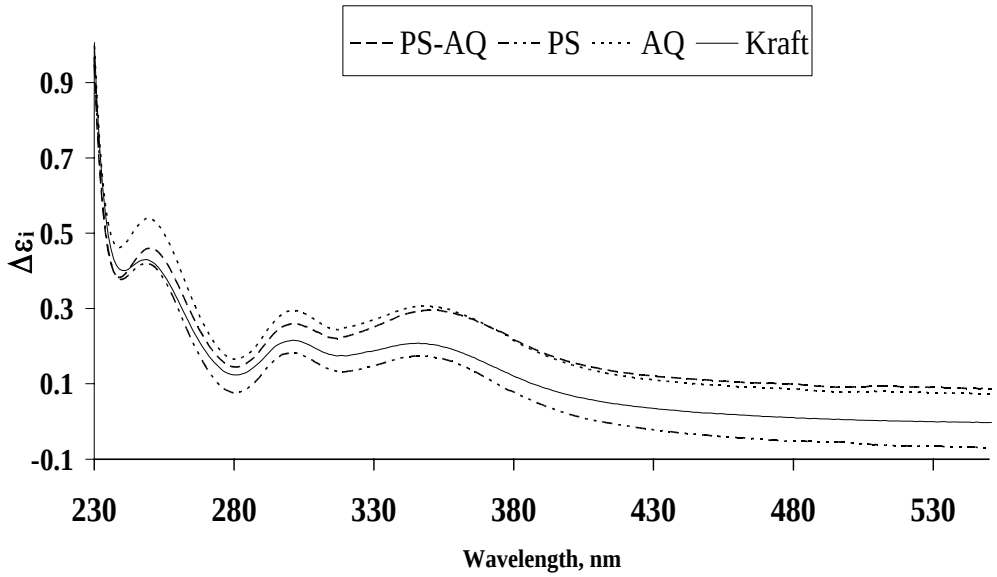


**Figure 2. Differential ionization UV/vis spectra of kraft, PS, AQ, and PS/AQ residual lignins.**