DETERMINATION OF LIGNIN IN *PINUS RADIATA* NEUTRAL SULPHITE-ANTHRAQUINONE PULPING LIQUORS BY ULTRAVIOLET ABSORBANCE MEASUREMENT AT 280 NM

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ABSTRACT

The neutral sulphite-anthraquinone delignification of *Pinus radiata* D. Don samples is readily followed by determining the variation in absorbance at 280 nm of (diluted) pulping liquor with cooking time. The 280 nm wavelength, despite its low absorption maximum, is preferable to that of the 205 nm wavelength used in a previous study since it is less prone to interference by changes in pH, or liquor oxidation. Excellent correlations between liquor absorbance at 280 nm and the amount of lignin dissolved in liquor were obtained for a number of cooks (and for three digester systems). The results showed that the extent of lignin removal and sodium sulphite concentration (or amount consumed) were linearly correlated, and indicated that absorbance at 280 nm, when combined with other procedures, could be used to examine the kinetics of neutral sulphite-anthraquinone pulping.

Keywords: neutral sulphite-anthraquinone pulping; sodium sulphite; lignin; ultraviolet absorbance; *Pinus radiata*.

INTRODUCTION

Two procedures for the determination of lignin in *P. radiata* neutral sulphite-anthraquinone (NS-AQ) pulping liquors by ultraviolet absorbance are compared in this paper. The use of anthraquinone (AQ) as a catalyst in alkaline pulping and in neutral sulphite pulping is well established. The processes, practice, and mechanisms have been extensively reviewed (Goyal 1997). In previous studies on the neutral NS-AQ pulping of *P. radiata* corewood and slabwood samples at the New Zealand Forest Research Institute (Uprichard & Okayama 1984) ultraviolet absorbance measurements on process liquors at absorption maximum of approximately 205 nm were used to follow the course of delignification in some cooks. These studies showed that during pulping the extent of lignin removal and sodium sulphite consumption were linearly correlated, and indicated that the

absorbance technique might be used to examine process kinetics. More detailed studies on the ultraviolet absorbance of NS-AQ liquors resulted in the improved analytical procedure using the absorption maximum of 280 nm described in this paper. Some kinetic studies on *P. radiata* wood chips are described in a later note (Uprichard *et al*. 2004). Eagle & McDonough (1988) who studied the NS-AQ delignification of loblolly pine (*Pinus taeda* L.) used thin wood shavings in their investigations: they made detailed studies of the kinetics and developed a mathematical model of the process.

The ultraviolet spectra of lignin and its derivatives have been examined by many authors. An excellent review of earlier studies on lignin ultraviolet spectra has been given by Goldschmid (1971). His review showed that some of the difficulties encountered in the determination of lignin by ultraviolet absorbance measurement in process liquors were caused by interference and/or interaction between substrates such as carbohydrates, present in the lignin-containing samples being examined: variation in pH also influenced the position and intensity of absorbance peaks. The present paper compares the results of NS-AQ lignin absorbance measurements on pulping liquors at wavelengths of 205 nm and 280 nm respectively, and shows how absorbance methods can be used to follow the progress of delignification. Initial absorbance studies involved the attempted removal of sulphur dioxide by acidification of cooking liquor samples, or by direct oxidation of sulphite ion, prior to lignin determination by ultraviolet absorbance at approximately 205 nm.

MATERIAL AND METHODS
Wood Chips

Air-dry *P. radiata* slabwood chips were used in an initial study of ultraviolet absorption of NS-AQ liquor; however, air-dry *P. radiata* corewood chips were generally used for pulping. The corewood chips had basic density of 370 kg/m^3, 1.7% dichloromethane extractives based on oven-dry (o.d.) extractive-free wood, and 26.9% Klason lignin content based on oven-dry wood, and came from the same batch as that used by Uprichard & Okayama (1984). The screened wood chips used for pulping had passed through a screen with 32-mm circular apertures, and then through an 8-mm slotted screen, and were those retained on a screen with 19-mm apertures. The wood chips were soaked in water overnight prior to pulping.

Neutral Sulphite-AQ Pulping

The pulps were prepared from wood chips using one of the following digester systems:

(i) A 20-litre circulatory stainless steel Haato digester equipped with four stainless mesh baskets, which had a charge of 1600 g o.d. wood chips equally distributed between the baskets;

(ii) A stainless steel Weverk 10-litre rotating autoclave which used a charge of 1000 g o.d. wood chips; or

(iii) A Stalsvet multi-unit polyethylene glycol heated digester equipped with six 2-litre stainless steel vessels, each of which contained a charge of 250 g o.d. wood chips.

Pulps were generally prepared using between 20% and 35% neutral sulphite based on oven-dry wood, with the same ratio of sodium sulphite : sodium carbonate of 4.86 : 1 in all

cooks. Pulps were prepared using 0.1% AQ at a liquor to wood ratio of 4:1 or 5:1, using the following schedule: 180 minutes to maximum temperature (generally 175°C) and up to 210 minutes at maximum cooking temperature. Pulps of yield 77–53% o.d. wood were prepared by varying time at temperature from 0 to 210 minutes. Pulps of between 57% and 75% yield were generally defibred using a 200-mm Bauer disc refiner at 0.25 mm, and those of lower yield by high-speed stirring. Yields were determined in the usual way (Uprichard & Okayama 1984). Kappa numbers were determined on screened pulps by a half-scale modification of Appita Standard P201m-77.

Cooking Liquor Sampling and Sulphite Measurements

The progress of delignification and sulphite consumption during pulping was followed by taking small samples of liquor for analysis (30 ml from the Haato circulatory digester, or about 15 ml from the Weverk rotary digester), generally at 30-minute intervals from the time at maximum temperature, until the end of the cook. Large samples of final cooking liquor from the Weverk digester (about 3 litres) were also collected from some cooks for studies on liquor stability and lignin analysis procedures. The changes in sodium sulphite concentration in cooking liquor with time at maximum temperature were determined by the Palmrose iodate method (CPPA Standard J1), generally by using a 2-ml sample of liquor. Pulps and liquor sampling were done at the end of cooks made using the Stalsvet 2-litre vessels for similar time periods to those described above.

Ultraviolet Absorption Measurements

Lignin was determined by diluting liquor samples (10 μl or 15 μl) to 100 ml and measuring the absorbance of the dilute solutions at the 205 nm range in a 10-mm cell using a Perkin-Elmer spectrophotometer. In comparative studies on the effects of liquor treatment on ultraviolet absorption, it proved useful to dilute samples over a range of dilution ratios (a dilution by volume of 1 in 5 is termed a dilution ratio of 0.2), and compare the effects of treatment at these levels. In some cooks, lignin content was also determined from the absorption at 280 nm, by diluting samples of 100 μl to 100 ml, and determining absorption as described above.

The effects of liquor treatments (designed to remove sulphite ion before spectral analysis) on ultraviolet absorption of lignin solutions were also assessed. The purpose of these various studies, which are summarised below, was to improve the lignin analysis procedure. The spectra of sodium sulphite solutions, and some cooking liquor samples which contained added sodium sulphite, were also examined. Attempts to reduce sodium sulphite concentration in pulping liquor samples (or solutions of sodium sulphite) included (a) acidification of liquor and removal of sulphur dioxide by heating the solution of sulphurous acid (and attempted removal of sulphur dioxide by bubbling nitrogen gas through the solution), and (b) oxidation of sulphite ion to sulphate.

(a) Acidification of liquor

(i)   A sample of the pulping liquor (50 ml) was titrated with 1 M hydrochloric acid to pH 3, and much of the liberated sulphur dioxide (its presence was tested by starch-iodide paper) was removed by heating for 10 to 15 minutes. Heating of the acidified solution

for about 20 minutes gave rise to a brown precipitate (presumably lignin): on treatment of the cooled acidified mixture with 1 M sodium hydroxide, the brown solid dissolved. Some minor modifications to this procedure, and their effects on ultraviolet absorption spectra, are described later.

(ii) Treatment of the acidified pulp liquor with oxygen-free nitrogen gas at a flow rate of 700 ml/min (for 15 or 45 minutes) had little effect on the absorbance of the diluted solutions.

(b) Sulphite ion oxidation

Sodium sulphite solution (10 ml of a 56.7 g/litre solution) was adjusted to pH 3 with dilute hydrochloric acid, and about 5 ml of potassium iodide solution were added. The solution was titrated with 0.5 M iodine until colourless (starch) and made up to 100 ml (Solution A). Samples of this solution at dilution ratios 0.5, 0.75, and 1.0 respectively after further dilution for absorbance measurement ($10\,\mu l/100\,ml$) had absorbance values of 0.21, 0.28, and 0.39 respectively at about 205 nm, showing that the sulphate ion absorbed in the same region as that of the sulphite ion. The sulphite ion had an absorbance peak at 195 nm.

RESULTS AND DISCUSSION

Ultraviolet Absorption Studies on Neutral Sulphite-AQ Lignin

The pulping liquor used for initial studies was final liquor from a NS-AQ cook of slabwood chips made using the Haato digester (28% sodium sulphite, 4 : 1 liquor to wood ratio, 210 minutes at 175°C). The pulp had Kappa number 54 and was obtained in 54.2% yield. The changes in sodium sulphite concentration of the liquor and lignin content of the pulp (based on oven-dry wood) with time at maximum temperature (Table 1) showed similar trends to those found earlier (Uprichard & Okayama 1984). The liquor from this cook was used for studies on liquor stability, and was also used to assess the suitability of the absorbance maximum at about 205 nm as a measure of dissolved lignin.

The absorbance of liquor at various levels of dilution was measured immediately, and after storage at 4°C overnight (Table 2). The liquor at dilution ratio of 0.2 to 1.0 was further diluted by dissolving 15 µl in 100 ml of distilled water for absorbance measurement. Dilution ratio and absorbance at 205 nm, as expected, were highly correlated and some differences were obtained between the absorbance of fresh and stored samples. However, these differences were not consistent with respect to high and low dilution ratios, although the overall trends were similar for both fresh and stored samples.

TABLE 1–Variation in sodium sulphite liquor concentration with cooking time at maximum temperature (Haato digester). Pulp yield 54%.

	Time (minutes at max. temperature 175°C)						
	0	30	60	90	120	150	210
Lignin (% o.d. wood at 202 nm)	15.4	10.4	8.2	7.1	6.6	5.9	4.5
Sodium sulphite concentration (g/litre)	40.8	28.8	22.3	17.0	12.4	11.3	8.7

TABLE 2–Variation in ultraviolet absorbance of NS-AQ liquor (210 minutes at 175°C) with dilution
ratio and overnight storage time.

Haato digester, final liquor sample (fresh liquor only) 0	Initial dilution ratio* 0	Absorbance max. (~205 nm) range –	Mean absorbance[†] (~205 nm) 0
1	0.2	0.29–0.31	0.30 (0.35)
2	0.4	0.63–0.66	0.64 (0.65)
3	0.6	0.99–1.00	1.00 (0.98)
4	0.8	1.38–1.41	1.40 (1.28)
5	1.0	1.74–1.79	1.76 (1.66)

* The samples were further diluted from 15 µl to 100 ml, and have been corrected for a blank value.
[†] The first set of mean absorbance values were obtained on fresh liquor samples, and those in
parentheses on liquor samples stored in the refrigerator overnight.

It seemed likely that some of the observed variability within and between sets of
analyses might be related to aerial oxidation of sodium sulphite. The prospects of removing
sulphite ion either by acidification and loss of sulphur dioxide by heating and/or nitrogen
gas displacement, or by direct oxidation of sulphite ion, were therefore examined. The
absorbance of untreated liquor samples at various dilution ratios (after final dilution of
15 µl to 100 ml) are compared in Table 3 with samples which had been acidified and heated,
or acidified and gasified with nitrogen at reasonably high flow rate. The treated samples
have somewhat lower absorbance than those of the untreated liquor samples, but all sets
showed similar trends. Since it proved difficult to devise a simple and reproducible
procedure for removal of all the sulphur dioxide present, the acidification route was not
explored further.

Sodium sulphite has a well-defined absorption maximum at 195 nm but, unlike lignin,
has no absorption at 280 nm. The high level of variability in the absorbance of the sulphite
solutions at 195 nm (Table 4) was somewhat surprising, and may be related to their well-

TABLE 3–Comparison of absorbances of pulp liquor and acidified pulp liquor samples (at 15 µl to
100 ml dilution).

Dilution ratio	Liquor	Liquor acidified and:	
		(a) heated	(b) nitrogen-gas treated
0.2	0.35	0.31	0.33
0.4	0.65	0.60	0.60
0.6	0.98	0.93	0.96
0.8	1.28	1.23	1.29
1.0	1.66	1.61	1.65

TABLE 4–Absorbance values of sodium sulphite solutions at 195 nm.

Sodium sulphite (approximate % w/v)	Absorbance at 195 nm
1.25×10^{-3}	0.36. 0.33. 0.39, 0.39, 0.44, 0.36
2.5×10^{-3}	0.62, 0.74, 0.61, 0.78, 0.71
5.0×10^{-3}	1.05, 0.95, 1.20, 1.05, 1.02

known ease of oxidation (or ultraviolet detector sensitivity). The addition of 5% sulphite ion solutions to pulp liquor samples had little effect on ultraviolet absorbance, the effects being generally similar to that of aqueous dilution. These initial results suggested that for NS-AQ lignin analyses, the well-known absorption peak at 280 nm, despite its low intensity, had more potential.

Cooking data, and absorbance measurements at 202 nm and 280 nm respectively, for the slabwood NS-AQ pulp of 54.2% yield and Kappa number 54 prepared in the Haato digester, are given in Table 5. The estimates of lignin content in the final pulp based on oven-dry wood (the product of pulp lignin content times yield fraction) (Table 1) were based on the equation obtained in earlier studies by Uprichard & Okayama (1984), where K is Kappa number, and Klason lignin content of pulp:

$$\text{Lignin}_{klason} = 0.1767 \text{ K} - 3.6687$$

The estimates of lignin content were obtained graphically from linear plots based on lignin absorbance values of zero at wood lignin content of 27.2% and their respective values (at 205 nm and 280 nm) at lignin content of 3.2%. The results show that determination of lignin content by absorbance at 280 nm tends to give somewhat higher estimates of lignin content than that determined from the absorbance at lower wavelength, as was confirmed in later studies.

TABLE 5–Lignin content in pulp as a percentage of oven-dry wood.

Cook time at 175°C (min.)	Sodium sulphite concentration (g/litre)	Lignin absorbance*		Lignin (% o.d. wood)	
		at 202 nm	at 280 nm	at 202 nm	at 280 nm
0	40.8	0.90	0.09	15.4	17.4
30	28.8	1.26	0.13	10.4	12.7
60	22.3	1.41	0.15	8.2	10.3
90	17.0	1.49	0.17	7.1	8.0
120	12.4	1.53	0.17	6.6	8.0
150	11.3	1.58	0.18	5.9	6.8
180	7.8	1.62	0.19	5.3	5.6
210	8.7	1.68	0.20	4.5	4.5

* Lignin absorbances at dilution of 15 µl / 100 ml, and calculated lignin contents based on oven-dry wood. The pulp made in the Haato digester had yield 54.2% and a Kappa number of 54.

Lignin Dissolution Rate: Comparison of Procedures

The general effectiveness of absorbance (at 280 nm) of cooking liquor for determining the extent of delignification was assessed by comparing the results of a series of cooks made on *P. radiata* corewood using the Stalsvet multi-unit digester with those obtained using the same set of conditions in the Weverk rotary digester. Pulps were made using the same chemical charge (35% sodium sulphite : 7.2% sodium carbonate and 0.1% AQ based on oven-dry wood), liquor to wood ratio (5:1), and time to maximum temperature (180 minutes to 175°C). In the Stalsvet series, pulp yield, pulp Kappa number, and cooking liquor absorbance were determined for pulps obtained after delignification at maximum temperature for 0, 30, 60, 90, and 180 minutes, respectively (Table 6). The results obtained were compared with liquor samples taken at the same time periods from the Weverk rotary

TABLE 6—Comparison of NS-AQ delignification rates in the multi-unit Stalsvet digester and the Weverk rotary digester, using the same cooking conditions of 180 minutes to 175°C, chemical charge and liquor to wood ratio of 5:1. Sodium sulphite concentration at start of cook 70 g/litre.

| | | Stalsvet multi-unit digester | | | | | | | Weverk rotary digester | | |
Pulp No.	Time at 175°C (min)	Sodium sulphite concentration (g/litre)	Yield (%)	Kappa number	Lignin (% o.d. wood based on Kappa No.)	Lignin (% o.d. wood) at 280 nm	Absorbance at 280 nm*	Pulp No.	Sodium sulphite concentration (g/litre)	Absorbance at 280 nm*	Lignin (% o.d. wood in pulp)
3601	0	48.3	75.0	122.3	15.2	17.1	0.37	4600	49.4	0.43	16.0
	30	37.1	63.7	86.1	8.9	9.7	0.62		37.6	0.63	10.4
	60	32.8	57.7	67.6	6.2	7.6	0.69		32.4	0.74	7.3
	90	30.2	57.2	56.5	5.0	5.8	0.75		29.5	0.80	5.6
	180	24.3	52.8	41.2	3.2	3.18	0.84		23.4	0.88	3.4

* Absorbance measurements at 280 nm were made on solutions containing 100 µl cooking liquor in 100 ml distilled water.

digester, in which yield was determined at the end of the cook (180 minutes at 175°C), and the extent of delignification was determined by absorbance of the liquor samples at 280 nm.

The pulping data (Table 6) show that delignification rates in the Stalsvet and Weverk digesters were generally similar. These cooks which used two different digester types were of a preliminary nature, but showed substantial agreement. On this basis it was concluded that ultraviolet absorption measurements at 280 nm of diluted cooking liquors (at 1 in 1000 dilution) gave a useful indication of the extent of delignification.

Relationships Between Pulping Variables

The various pulping variables — sodium sulphite concentration, liquor to wood ratio, maximum temperature, and cooking time at maximum temperature — were explored in a series of cooks made using the Stalsvet 2-litre digesters. Pulp yield and Kappa number were determined in the usual way, and the extent of delignification was also followed by the determination of ultraviolet absorbance measurements at 280 nm. The results of these experiments are summarised in Table 7.

Kappa number and pulp yield

There was an excellent linear correlation between pulp Kappa number and pulp yield (Fig. 1) as has been found previously (Uprichard & Okayama 1984). The respective Kappa number (K) *versus* pulp yield correlation (Y), and the corresponding yield and Kappa number correlation (Fig. 2) are listed below:

    (i) $K = 3.6566\ Y - 150.22$ $R^2 = 0.9647$

    (ii) $Y = 0.2638\ K + 41.876$ $R^2 = 0.9647$

The results are similar in form, but show some minor differences from those obtained in the earlier investigation using undried wood chips (Uprichard & Okayama 1984), as would be expected. The correlations are shown for two reasons; firstly because they indicate the good agreement between related variables (a measure of the data quality), and secondly because they were used to some extent in some kinetic studies of the NS-AQ process as applied to *P. radiata*.

Sodium sulphite concentration and lignin dissolution

For an individual series of cooks — for example, 4607 — there was an excellent linear correlation between sodium sulphite concentration and the percentage of lignin in wood, and degree of delignification over the major delignification period (Fig. 3). This had been observed earlier (as sodium sulphite consumption) by Uprichard & Okayama (1984). Relationships of this type between sodium sulphite concentration and lignin concentration in wood with cooking time and temperature proved useful in the kinetic studies of Eagle & McDonough (1988).

Lignin absorbance as a measure of dissolved lignin

There was an excellent linear correlation between the level of dissolved lignin in neutral sulphite-AQ pulp liquor and its ultraviolet absorbance (after appropriate dilution), as is

TABLE 7–Cooking data for NS-AQ pulps prepared using the Stalsvet 2-litre vessels under a variety of conditions

Pulp No.	Chemicals* Na₂SO₃: Na₂CO₃ (%)	Sodium sulphite (g/litre)	Liquid to wood ratio	Time to max. temp. (min)	Maximum temp. (°C)	Time at max. temp. (min)	Yield (% total)	Kappa No.	Lignin in pulp (% o.d. wood)†	Lignin in solution (% in o.d. wood)†	Absorbance of cooking liquor at 280 nm	Na₂SO₃ in cooking liquor (g/litre)	pH of cooking liquor
3601	35.0: 7.2	70.0	5:1	180	175	0	75.0	122.3	13.46	13.44‡	0.37	48.3	NA
						30	63.7	86.1	7.35	19.55	0.62	37.1	NA
						60	57.7	67.6	4.78	22.2	0.69	32.8	NA
						90	57.2	56.5	3.61	23.29	0.73	30.2	NA
						180	52.8	41.2	1.91	24.99	0.84	24.3	NA
4602	35.0: 7.2	87.5	4:1	180	175	0	73.2	114	12.06	14.84	0.51	57.6	9.33
						60	60.7	69	5.17	21.73	0.90	39.4	9.23
						90	60.2	62	4.39	22.51	0.85	33.7	9.13
						180	55.0	44.6	2.32	2.58	0.90	22.2	9.00
4603	25.0:5.14	50.0	5:1	180	175	0	79.9	130	15.42	NA	NA	25.8	9.02
						30	68.8	101	9.75	NA	NA	17.3	9.10
						60	66.4	88	7.89	NA	NA	14.0	9.00
						90	62.3	72	5.64	NA	NA	11.4	8.98
						150	59.8	63	4.46	NA	NA	7.0	8.87
4605	25.0: 5.14	62.5	4:1	180	175	0	76.1	129	14.55	12.35	0.46	29.5	8.83
						30	68.2	98	9.30	17.6	0.69	20.5	8.85
						60	64.4	79	6.63	20.27	0.83	15.7	8.78
						90	61.6	70	5.36	21.54	0.90	12.0	8.65
						150	58.1	60	4.03	22.87	0.97	8.1	8.45
4606	30.0: 6.17	60.0	5:1	180	175	0	72.0	124	13.13	NA	NA	29.3	9.08
						30	67.6	97	9.11	NA	NA	22.6	8.95-
						60	64.4	83	7.08	NA	NA	15.6	8.85
						90	59.9	71	5.32	NA	NA	15.1	8.76
						180	55.0	54.8	3.31	NA	NA	12.7	8.71

TABLE 7–cont.

Pulp No.	Chemicals* Na₂SO₃: Na₂CO₃ (%)	Sodium sulphite (g/litre)	Liquid to wood ratio	Time to max. temp. (min)	Maximum temp. (°C)	Time at max. temp. (min)	Yield (% total)	Kappa No.	Lignin in pulp (% o.d. wood)†	Lignin in solution (% in o.d. wood)†	Absorbance of cooking liquor at 280 nm	Na₂SO₃ in cooking liquor (g/litre)	pH of cooking liquor
4607	30.0: 6.17	75.0	4:1	180	175	0	71.4	123	12.90	14.0	0.54	41.5	9.24
						30	65.7	95	8.62	18.28	0.77	30.3	9.15
						60	62.4	77	6.20	20.7	0.87	24.8	9.08
						90	58.1	66	4.64	22.26	0.94	21.3	8.96
						180	53.2	49.8	2.73	24.17	1.02	14.3	9.00
4608	20.0:4.11	50.0	4:1	180	175	0	78.6	141	16.70	10.2	0.44	23.7	8.61
						30	70.6	111	11.26	15.64	0.72	11.5	8.74
						60	66.7	95	8.75	18.15	0.78	7.8	8.63
						90	64.6	84	7.22	19.68	0.85	4.7	8.52
						150	62.6	75.9	6.10	NA	NA	1.9	8.16
4614	30.0: 6.17	75.0	4:1	180	185	0	65.5	96	8.70	18.20	0.75	29.5	9.19
						30	58.6	70	5.10	21.8	0.90	21.5	8.93
						60	56.3	55	3.41	23.49	0.98	17.0	8.74
						90	53.9	48	2.59	24.31	1.03	13.4	8.43
						120	53.3	45.6	2.34	NA	NA	12.2	8.42
4615	30.0: 6.17	75.0	4:1	180	165	0	76.8	132	16.9	10.0	0.45	45.2	9.02
						0	NA	113	14.9		0.62	35.1	8.99
						60	NA	98	10.2		0.70	31.5	8.98
						120	NA	82	7.3		0.83	25.2	8.94
						180	59.2	65.6	4.7		0.87	22.5	8.85

* 0.1% AQ in all cooks

† Klason lignin, based on Kappa number and yield fraction. Lignin ₖₗₐₛₒₙ = (0.1767 K – 3.6687) × Yield fraction

‡ Absorbance values of liquors of cooks 3601 prepared using liquor to wood ratio of 5:1 need to be multiplied by 1.25 for comparison with those of cooks 4602 made at lower liquor to wood ratio of 4:1.
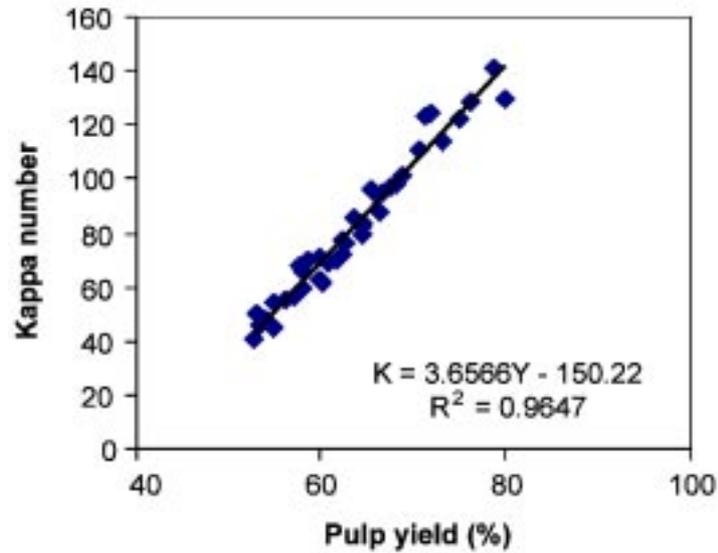
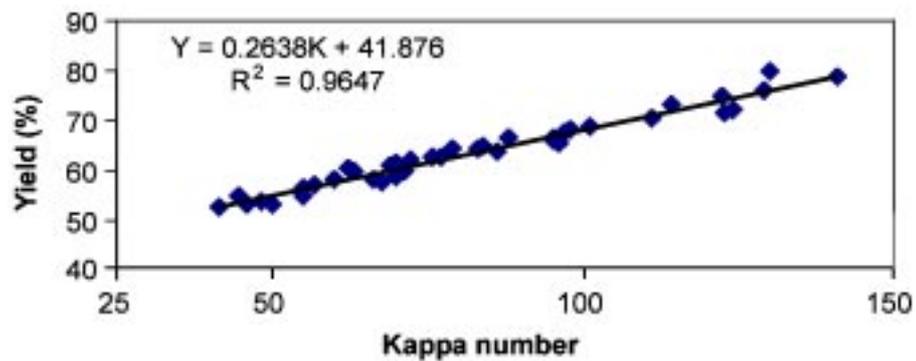FIG. 1–Relationship between Kappa number and pulp yield.

FIG. 2–Relationship between pulp yield percentage and Kappa number

shown for the 4:1 liquor-to-wood cooks of 4605, 4607, 4608, and 4614 in Fig. 4. It can be seen in Fig. 4 (for example) that at absorbance 0.5, 12.4% of the lignin present in the wood has been dissolved. In Fig. 5 the corresponding lignin percentage in oven-dry wood *versus* ultraviolet absorbance indicates the change in the lignin present in the wood chips with increased delignification; the data shown in the previous Figure are also presented in a format more appropriate for modelling purposes. These results suggested that ultraviolet absorbance at 280 nm could be used to follow the course of delignification in some NS-AQ pulps prepared using the Weverk digester, the early stages of the cook being of most interest.
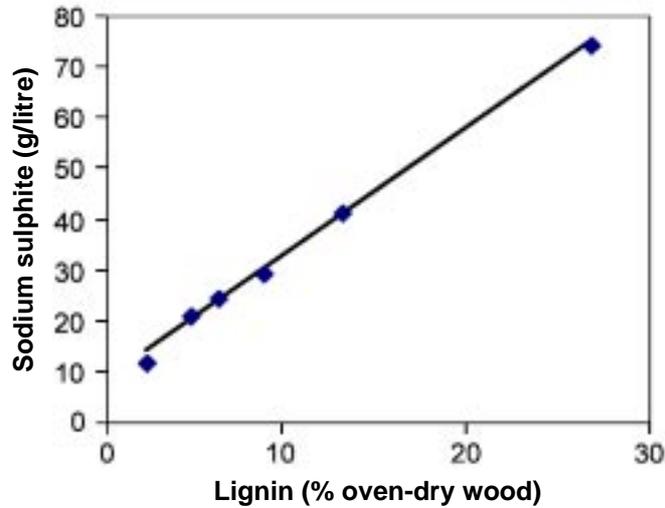
FIG. 3–Variation in lignin content with sodium sulphite concentration during the period at maximum temperature, 175°C.
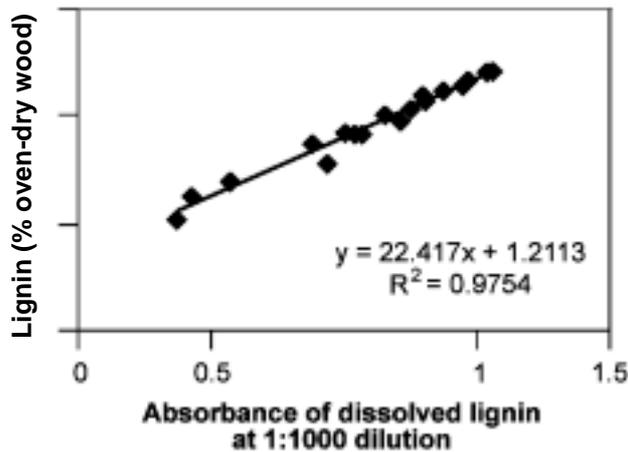

FIG. 4–Relationship between dissolved lignin as a percentage of oven-dry wood in pulp liquor and liquor absorbance at 280 nm.

Effects of Initial Chip Moisture Content on Delignification

All of the pulps examined in this investigation had been prepared from chips which had been air-dried and then soaked in water overnight prior to cooking, a procedure which had been used earlier on air-dry chips from the same source (Kibblewhite & Okayama 1986; Kibblewhite 1988). The liquor absorbance data for cooks made using the Weverk rotary digester, the liquor of which could be sampled at intervals without stopping the cook, are given in Table 8. It is apparent from the absorbance data that little delignification occurred

TABLE 8–Cooking data for NS-AQ pulps prepared using the Weverk rotary digester which was sampled at intervals throughout the cook.

Pulp No.	Na_2SO_3 (g/litre) (0.1% AQ)	Liquor to wood ratio	Total time to max. temp. (min)	Time from cook start to max. temp. (min)	Max. temp. (°C)	Cooking time at max. temp. (min)	Na_2SO_3 (g/litre)	Yield (%)	Kappa No.	Absorbance at 280 nm	pH
4600	70.0	5:1	180	180	175	0	49.4	-	-	0.43	-
						30	37.6	-	-	0.63	-
						60	32.4	-	-	0.74	-
						90	29.5	-	-	0.89	-
						180	23.4	53.0	42.9	0.88	-
4601	87.5	4:1	180	0	175		103	-		0	
				120			91.9	-		0.03	
				180		0	62.0	-		0.47	
						30	43.4	-		0.70	
						60	38.8	-		0.95	
						90	33.3	-		1.04	
						180	23.8	52.4		1.13	
4604	50.0	5:1	180	0	175		53.2			0	10.29
				120			44.4			0.02	9.63
						0	26.3			0.36	9.06
						30	15.9			0.59	9.11
						60	8.4	NA		0.57	9.09
						90	6.4			0.75	9.01
						150	5.0			0.84	8.86
4609	75.0	4:1	180	60	175		78.6			0.01	10.19
				120			72.8			0.02	9.57
				180		0	43.4			0.52	9.07
						30	29.6			0.81	9.11
						60	20.3			0.95	9.03
						90	16.8			1.03	8.98
						180	10.9	54.0	45.7	1.15	8.90

TABLE 8–cont.

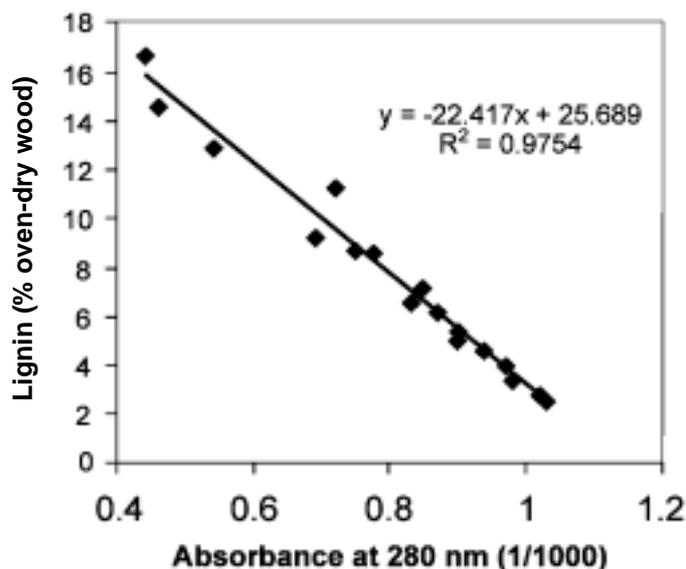| Pulp No.	Na$_2$SO$_3$ (g/litre) (0.1% AQ)	Liquor to wood ratio	Total time to max. temp. (min)	Time from cook start to max. temp. (min)	Max. temp. (°C)	Cooking time at max. temp. (min)	Na$_2$SO$_3$ (g/litre)	Yield (%)	Kappa No.	Absorbance at 280 nm	pH
4610	62.5	4:1	180	60	175		70.2			0	10.15
				120			59.9			0.03	9.45
			0	180		0	32.0			0.45	8.92
						30	19.6	58.7	60.3	0.80	9.03
						60	11.1			0.90	9.01
						90	7.6			1.02	8.90
						150	3.3			1.11	8.74
4611	50	4:1	180	60	175		54.7			0.01	10.12
				120			46.7			0.03	9.33
				180		0	21.4			0.48	8.7
						30	9.4	61.9	85.4	0.75	8.89
						60	4.1			0.88	8.83
						90	1.3			0.96	8.54
						150	0.4			1.05	8.25
4612	75.0	4:1	180	60	185		83.6			0	10.13
				120			69.6			0.06	9.35
				180		0	36.0			0.68	9.08
						30	20.0	52.9	45.8	1.05	8.98
						60	13.0			1.14	8.84
						90	9.7			1.19	8.78
						120	8.0			1.23	8.77
4613	75.0	4:1	180	60	165		85.4			0.01	10.35
				120			75.0			0.02	9.71
				180		0	53.4			0.35	9.12
						30	39.5			0.60	9.23
						60	31.5	60.6	65.6	0.77	9.24
						90	26.9			0.89	9.23
						120	21.7			0.96	9.18
						150	17.9			1.01	9.16
						180	14.3			1.12	NA

FIG. 5–Relationship between lignin percentage of oven-dry wood and liquor absorbance at 280 nm.

during the first 120 minutes of the cook. The sulphite analyses during this period of the cook are also higher than would be expected if there was adequate diffusion between the liquor in wood chips and free liquor.

The results show that there was poor mixing of the water associated with the chips and the added liquor, although there was considerable uptake of water within the wood chips during the pre-soaking stage. They also show that there was poor diffusion of sulphite liquor within the wood chips in the early stages of the cook.

Kibblewhite (Kibblewhite & Okayama 1986; Kibblewhite 1988) had previously found that there were some small differences between the levels of delignification obtained on air-dried wood chips treated with water and then sulphite solution before cooking (as described above) when compared with those obtained in the earlier studies by Uprichard & Okayama (1984) who had used undried moist wood chips.

The results of this investigation show that the wood chip wetting procedure is clearly undesirable when applied to NS-AQ cooks with their relatively low pH, although it has been used with success on alkaline cooking liquours (J.A.Lloyd pers. comm.).

DISCUSSION

This investigation showed that the course of neutral sulphite-anthraquinone delignification may be followed by taking small samples of the pulping liquor and determining their absorbance at 280 nm (after appropriate dilution). This wavelength despite its low absorption maximum was preferable to the 205 nm used in a previous study because it is less prone to error caused by possible interference by sulphite and other ions.

Removal of sulphite by acidification or oxidation did not improve the reproducibility of the 205 nm measurements.

It was shown by using the absorbance procedure that the treatment of air-dry wood chips with water prior to NS-AQ cooking is undesirable, since there was little measurable delignification until the cooking temperature was between 120° and 175°C.

Excellent linear correlations between liquor absorbance at 280 nm and the amount of lignin dissolved in pulping liquor were obtained for cooks in three digesters. The linear correlations between the amount of lignin remaining in the wood chips and sodium sulphite concentration showed that there were prospects for the development of a mathematical model of the process as shown earlier by Eagle & McDonough (1988).

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