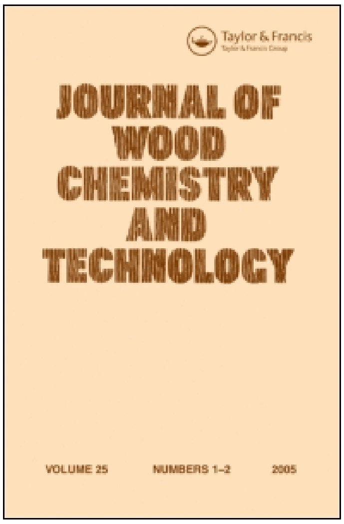

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THE EFFECT OF ANTHRAQUINONE AND ANTHRAHYDROQUINONE PENETRATION ON DELIGNIFICATION IN THE SODA PULPING OF NORWAY SPRUCE

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ABSTRACT

The extent of anthraquinone (AQ) penetration into handcut Norway spruce chips as a function of cooking time was examined through the combined use of ^{14}C-labelled AQ and various wood sectioning techniques. The results indicated that in the initial stage of the cook, the AQ was deposited mainly at or near the chip surfaces in contrast to the alkali which penetrated to the chip core. With increasing cooking time, free and/or combined AQ concentration at the transverse surface of the chips first decreased then increased both in this region and in the chip interior. This non-uniform distribution of AQ and alkali within the chips during the initial stage of pulping was also manifest by the Kappa number which increased significantly in proceeding from chip exterior to core.

A substantial reduction in Kappa number without sacrifice in yield was achieved by impregnating the chips with an alkaline solution of anthrahydroquinone prior to pulping with alkali as compared with AQ addition in the conventional manner. Subsequent experimentation led to the conclusion that the improved performance of AQ in this case was probably attributable to its more efficient use as a delignification "catalyst" as a result of its being dispersed throughout chips in its reduced form from the outset of pulping.

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INTRODUCTION

The results of previous studies reported by us[1] and others[2] have shown that the distribution of anthraquinone between the wood and liquor phases of a soda cook changes markedly as the digester is heated to the prescribed pulping temperature. This suggested that chemical and/or physical transformations taking place in the initial stages of the cook could have an important bearing on the performance of AQ as a delignification "catalyst", and therefore merited a closer scrutiny.

Accordingly, the experimental plan for this investigation consisted of making a series of short-term soda cooks with ^{14}C-labelled AQ, followed by an analysis to determine the condition of the AQ (i.e., whether it was free or chemically combined with a constituent of the wood) as a function of the depth of penetration into the chip. However, the initial findings made it desirable to modify this objective somewhat so as to place greater emphasis on exploring the relationship between delignification and the extent and uniformity of AQ penetration into chips.

RESULTS AND DISCUSSION

Penetration of ^{14}-C-Labelled AQ into Handcut Norway Spruce and Douglas Fir Chips

A mixture of technical Norway spruce (*Picea abies* Karst.) chips (95%) and handcut chips (5%) of 3-4 mm thickness were treated with alkali (20% NaOH) in the presence of 0.1% of ^{14}C-AQ for periods of up to 25 minutes and a maximum temperature of 170°C as described previously[1]. The cooked chips were blotted, and microtome sections (40-µm thickness) were successively cut from the cross-section surface to a depth of approximately 7 mm. The sections were combined into a series of fractions representing varying distances from the chip surface, and the label was determined by liquid scintillation counting. A parallel set of microtome sections was digested in a mixture of nitric and perchloric acids and the sodium content determined by atomic absorption spectrometry. When measured by radiolabel counting, the free and chemically combined forms of AQ are indistinguishable. Consequently, all stated "AQ" concentration values should be understood as representing the free and/or combined forms of AQ unless indicated otherwise.

The difference in penetration of ^{14}C-AQ and sodium into the handcut chips is illustrated by the plots in Fig. 1. The plots show that under conditions where the

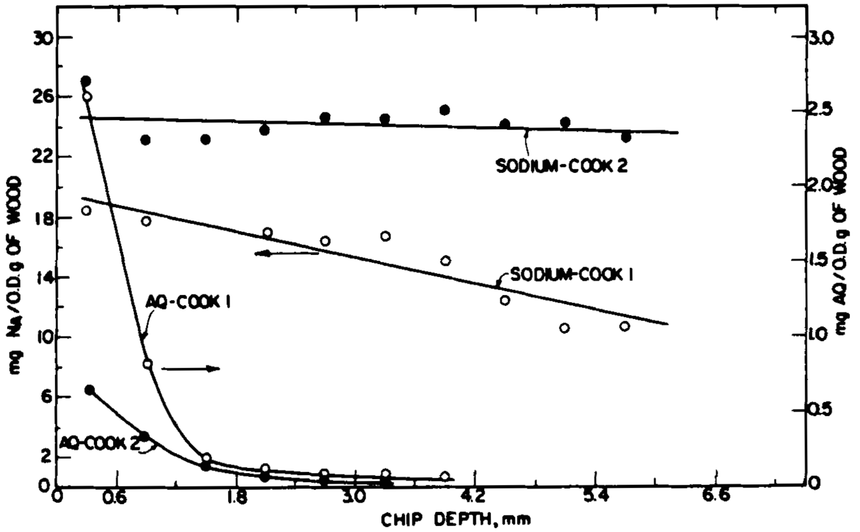

Figure 1. Sodium and anthraquinone penetration of Norway spruce chips in soda-AQ pulping. Cooking conditions: 300g o.d. chips (moisture content of handcut chips, 24.0%), 20% NaOH, 0.1% AQ, L/W = 5:1; cook 1, 15 min to 83°C; cook 2, 30 min to 125°C.

sodium had penetrated essentially to the core of the chip, AQ penetration was mainly confined to a depth of 2 mm or less in the longitudinal direction. A similar ^{14}C-AQ distribution profile was noted by Cameron et al[3] in their treatment of eucalypts and P. radiata with AQ under NSSC pulping conditions.

No attempt was made to measure AQ penetration at the radial and tangential surfaces of the chips. However, penetration at these surfaces was judged to be very small in the short-term cooks in view of the fact that the two plots in Fig. 1 show the AQ concentration tailing off to essentially zero in progressing from the surface of the chip to the core. The lower extent of penetration in the radial and tangential directions as compared to that in the longitudinal direction is a trend frequently reported in the literature (e.g.[4-7]).

The plot in Fig. 1 corresponding to AQ shows that after heating the handcut chips to 83°C over a 15-min period, the concentration of AQ at or near the cross-sectional surface was 2.0-2.5 mg/g of o.d. wood or approximately 2-2.5 times the concentration expected had all of the applied AQ been distributed uniformly throughout the chip. With increasing pulping time and higher temperature, the concentration of the AQ in the vicinity of the cross-sectional surface was observed to decrease markedly (Fig. 1). This initial transferral of AQ from the wood phase to the liquor phase in the initial stages of a soda-AQ cook has been similarly noted by Fleming et al[2], who credited the phenomenon to the reduction of free AQ to anthrahydroquinone (AHQ), which is soluble in the alkaline medium.

The fact that penetration of sodium hydroxide into the chip far exceeded that of AQ in the initial phase of the cook implies that only a fairly narrow zone bordering the chip surfaces actually experienced soda-AQ pulping while a major portion of the chip essentially underwent conventional soda pulping. As a consequence, the presumption was that the benefits of AQ with respect to enhanced delignification were not fully achieved. The validity of the supposition is reinforced by the data in Table 1. Thus, sections cut from soda-AQ pulped handcut chips showed progressive increases in Kappa number paralleling the decrease in AQ concentration in proceeding from surface to core. On the other hand, the Kappa numbers of the pulps from the corresponding zones cut from soda-pulped chips were virtually the same, reflecting the uniform penetration and delignification of the chips by alkali.

The data in Table 1 further show that pulps from the outer and inner zones of the chips produced in soda-AQ pulping had significantly lower Kappa numbers than the corresponding zones of chips obtained by soda pulping. Comparison of the Kappa numbers of the pulps pre-

TABLE 1

Kappa Number Gradient in Progressing from Chip Surface to Core in the soda-AQ pulping[a] of Norway Spruce

Cook Type	Total Pulp Yield, %	Kappa Number[b] Outer Zone	Inner Zone	Core
Soda-AQ[c]	61.6	96	115	134
Soda	65.0	126	135	129

[a] Pulping Conditions: 300 g (o.d. basis), 5% handcut, 95% commercial chips; 20% NaOH, 0.1% AQ, L/W = 5/1; 30 min to temp, 60 min at 170°C; cooked chips disintegrated in Waring blender, washed and screened.

[b] Measured on handcut chips using TAPPI Standard Method T236 os-76 modified to accommodate small samples average error, 5%).

[c] Average of two experiments.

[d] The "outer" and "inner" zone fractions contain material from all surfaces of the chips, thus each represents a "shell" of penetration distance.

pared from chip cores in each case revealed that the soda-AQ pulp had a slightly higher Kappa number, although the difference is probably not experimentally significant. This observation is consistent with the low concentration of free and/or combined AQ found in the chip cores of the soda-AQ pulp (see Fig. 1 and Table 2).

A determination of the behavior of AQ in a full length cook with respect to chip penetration could not be made using the method of microtome sectioning since pulping beyond 75 minutes rendered the chips too soft to be cut successfully using this technique. To overcome this problem, a series of soda-^{14}C-AQ cooks of widely varying length was made. The handcut chips were once again arbitrarily sectioned into inner, outer and core portions and the radioactivity of each zone measured. The results compiled in Table 2 confirm the trend noted earlier in which AQ concentration at the chip surface decreased as the digester temperature was increased to 125°C. With increasing cooking time, the concentration of AQ (free and combined forms) in the outer zone once again increased while the AQ in the inner and core zones continued to increase. Although a generally similar trend might be observed in the cores of commercial chips, the expectation is that the relative distributions of AQ in the various chip zones would differ from those measured in the handcut chips as a consequence of the "destructuring" accompanying the breakdown of wood in a commercial chipper.

The AQ penetration experiments performed on handcut Norway spruce chips were repeated with Douglas fir (Pseudotsuga taxifolia Britt.). In this latter situation, chips handcut from both heartwood and sapwood portions of the wood (5%) were added individually to commercial wholewood chips (95%) and pulped with alkali

TABLE 2

Distribution of ^{14}C-AQ[a] into Handcut Norway Spruce Chips as a Function of Cooking[b] Time

Cooking Time, min To temp	 At temp (170°C)	AQ[a], mg/g of pulp Outer Zone[c]	 Inner Zone[c]	 Core[c]
30 (110°)	0	0.28	0.10	
45 (131°)	0	0.27	0.11	0.07
60	0	0.22	0.17	0.08
60	15	0.24	0.23	0.09
60	30	0.42	0.27	0.18
60	45	0.36	0.25	0.16

[a] Free and/or combined.

[b] Pulping conditions are described in footnote a, Table 1.

[c] See footnote d, Table 1.

in the presence of AQ for a relatively short period.

The microtoming and radiolabel counting procedures duplicated those used with the spruce. The results compiled in Table 3 confirm the generally recognized[9] poor penetrability associated with the heartwood of Douglas fir. The poor penetrability of the Douglas fir sapwood by ^{14}C-AQ in comparison with that of the Norway spruce wholewood (see Table 3) was somewhat surprising, however.

As anticipated, the restricted penetration of the AQ into the Douglas fir heartwood was evidenced, following soda and soda-AQ pulping, by the yield/Kappa number data in Table 4 which show AQ to be much more effective in promoting the delignification of spruce wholewood than of Douglas fir heartwood.

Soda Pulping of Norway Spruce Pre-impregnated with AHQ

Evidence presented in the preceding section (Fig. 1 and Table 1) indicated that, in the soda-AQ pulping of Norway spruce, delignification as measured by Kappa

TABLE 3

The Penetration of ^{14}C-Labelled Anthraquinone in the Longitudinal Direction of Handcut Douglas Fir Heartwood and Sapwood Chips in Soda-AQ Pulping[a]

		Mg AQ[b]/g o.d. pulp					
Material	Cooking Schedule	Penetration, mm	0.5	1.0	1.5	2.0	3.0
Douglas fir heartwood	15 min to 85°C		Trace[c]	0	0	0	0
Douglas fir heartwood	30 min to 116°C		0.44	0.10	Trace	Trace	0
Douglas fir sapwood	15 min to 83°C		0.17	0.10	Trace	0	0
Norway spruce wholewood	15 min to 85°C		1.70	1.05	0.25	0.15	0

[a] Cooking conditions: 300 g of chips (o.d. basis), moisture contents of handcut chips: heartwood, 24.4%, sapwood 31.8%, 20% NaOH, 0.1% AQ, L/W = 5:1.

[b] Free and/or combined.

[c] Trace = < 0.1 mg of AQ/g o.d. pulp.

TABLE 4

Comparison of Soda and Soda-AQ Pulping[a] of Douglas Fir Heartwood and Norway Spruce Wholewood

Material	Soda Cook Total Yield,%	 Kappa No.	Soda-AQ Cook Total Yield,%	 Kappa No.
Douglas fir heartwood	51.1	98.6	48.9	58.4
Norway spruce wholewood	54.0	96.9	50.9	44.9

[a]Cooking conditions: 300 g (o.d. basis) of commercial chips, 20% NaOH, 0.1% AQ, L/W = 5:1, 0.5 hr to and 2.5 hr at 170°.

number reduction was considerably more extensive on the surface of the chips than in their cores. This finding was attributed to the more limited penetration of the chips by AQ as compared to sodium hydroxide, and suggested that a more extensive reduction of Kappa number could be achieved if the AQ were uniformly dispersed throughout the chip prior to cooking.

To test this supposition, the AQ was first reduced to anthrahydroquinone (AHQ) with glucose, and an aqueous alkaline solution of AHQ was used as the impregnation system. As shown by the data in Table 5, this pre-impregnation treatment was successful to the degree that the AHQ was found to have penetrated to the chip cores. On the other hand, an approximately 10-fold AHQ concentration gradient was observed in proceeding from chip surface to chip center.

The effect of the AHQ pre-impregnation treatment on Kappa number reduction over a range of AHQ contents is compared to that resulting from standard soda-AQ cooking in Fig. 2. The pulp yields corresponding to the Kappa number data varied irregularly with the im-

Table 5

The Penetration of ^{14}C-Labelled AHQ in the Longitudinal Direction of Handcut Norway Spruce Chips During Pre-impregnation Treatments[a]

Penetration, mm	% AQ (AHQ) on Chips
0.6	0.69
0.6-1.2	0.31
1.2-2.4	0.09
2.4-4.0	0.06
4.0-5.8	0.06
5.8-8.0	0.06

[a] Handcut blocks (10 mm thick, 25 mm wide and of variable length) were evacuated then soaked in a 13.3 g/l NaOH solution of ^{14}C-AHQ (0.6% on o.d. weight of chips) under nitrogen for 5 days; L/W = 5:1; ^{14}C-AQ (AHQ) uptake: 0.11% based on o.d. wood or 18% of applied.

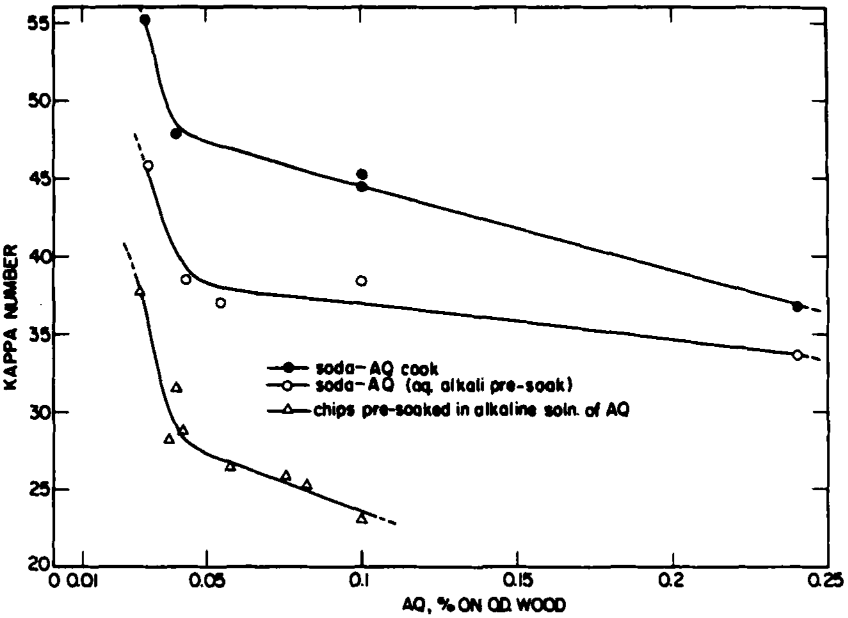

Figure 2. The effect of AHQ dosage on Kappa number in the soda-AHQ pulping of Norway spruce.

pregnation of increasing amounts of AHQ, but the average of all the cooks was essentially the same as the average yield for the soda-AQ cooks (see Table 6). As a comparison of the plots in Fig. 2 indicates, a significant portion of the Kappa number reduction resulting from the AHQ pre-impregnation treatment can be credited to the effect of the AHQ over and above that contributed by the alkali alone. Data in Table 6 further reveal that an alkali pre-soak followed by the addition of AHQ to the cook was far less successful in mediating a Kappa number reduction without sacrifice of pulp yield than when the AHQ was introduced into the wood prior to pulping. In this connection, Fullerton[9] similarly observed that replacement of AQ by AHQ provided no advantage with respect to Kappa number reduction in the pulping of *Pinus radiata*.

The strength properties of pulps prepared from wood pre-impregnated with AHQ are listed in Table 7. These data indicate a modest over-all gain in strength for the pulps prepared from the wood pre-impregnated with AHQ compared to pulps prepared by conventional soda-AQ pulping under equivalent conditions. This effect can be rationalized largely on the basis of Kappa number differences, the Kappa numbers of the pulps from the AHQ pre-impregnated chips being 30-50% lower than those of comparable conventional soda-AQ pulps.

Although the involvement of AHQ as the species actually responsible for promoting delignification in soda-AQ pulping is now generally accepted, the present investigation has demonstrated that further refinements in the mode of application of this chemical are required in order to exploit its benefits to the fullest degree. In seeking to explain the reason for the benefi-

TABLE 6

Comparison of Soda Pulping[a] of Norway Spruce Pre-impregnated[b] with AHQ Prior to Heating with Conventional Soda-AQ Pulping

Cook Description	AQ or AHQ, % based on o.d. wood	Kappa No.	Yield, %
Pre-impregnation of chips with NaOH solution of AHQ	0.028	37.8	
	0.038	28.1	
	0.040	31.6	average: 50.2 average deviation: ±1.1%
	0.042	28.8	
	0.057	27.5	
	0.075	26.1	
	0.082	25.1	
	0.10	23.2	
Pre-soak in aq NaOH AQ added prior to cooking	0.031	45.9	49.5
	0.043	38.5	47.0
	0.054	36.0	46.4
Pre-soak in aq NaOH AHQ added prior to cook	0.10	38.5	51.6
Standard Soda-AQ	0.030	55.2	
	0.040	47.9	average: 50.0 average deviation: ±1.3%
	0.10	44.9	
	0.24	36.8	
Standard Soda	-	96.9	54.0

[a] Cooking conditions: 300 g o.d. chips, 20% NaOH, L/W = 5:1, 30 min to and 150 min at 170°C

[b] Chips were evacuated and soaked in a aqueous NaOH solution containing AQ (amount calculated to be 6 times the desired % on wood) and glucose under nitrogen for 5 days at room temperature, L/W = 5:1. (Details described in Experimental section).

TABLE 7

The Strength Properties of Soda-AQ Pulps Prepared from Norway Spruce Pre-soaked in Alkaline Solutions of Anthrahydroquinone

Pretreatment[a]	Cook[b]	Total Yield, %	Kappa No.	Burst Index[c] kPa m^2/g	Tear Index[c] mNm^2/g	Tensile Index[c] Nm/g
0.1% AHQ/ aq NaOH	Soda	51.6	23.2	8.60	12.8	102.8
0.03% AHQ/ aq NaOH	Soda	51.4	37.8	6.27	15.2	75.4
Aq NaOH	0.1% AQ/Soda	51.6	38.5	7.33	11.9	94.3
Aq NaOH	0.03% AQ/Soda	49.5	45.9	5.50	16.6	63.7
None	0.1% AQ/Soda	50.9	44.9	7.04	11.5	89.3
None	0.03% AQ/Soda	50.1	55.2	5.50	14.8	60.8

[a] Pre-treatment conditions: See footnote b, Table 6.

[b] Cooking conditions: 20% NaOH, L/W = 5:1, 0.5 hr to and 2.5 hr at 170°C.

[c] Pulps beaten to 320 ml CSF in a PFI mill.

cial effect of the AHQ pre-soak on delignification during the ensuing pulping treatment, the possibility that a chemical reaction between the AHQ and wood occurred during the prolonged pre-impregnation treatment was tested for by performing the pre-soak at both higher (50°C) and lower (4°C) temperatures. However, this explanation was subsequently rejected when it was determined that the Kappa numbers and yields of the pulps corresponding to these pre-soak conditions were identical to those found when the pre-soak was performed at ambient temperatures.

Alternatively, an AHQ pre-soak may disperse the chemical throughout the chips and make it available for use prior to the initation of delignification reactions. In conventional soda-AQ pulping, the AQ or AHQ first has to penetrate the chip structure before it can perform its role as "catalyst." In this latter situation, the possibility exists that some of the AQ (AHQ) may not penetrate to reactive lignin sites prior to becoming "inactivated" through reactions with solubilized wood components present in the pulping liquor. Thus, the latter process appears to be inherently less efficient than in the situation where the AQ (AHQ) is in close proximity to the reaction site. This supposition is consistent with the observation that, in the case of the cook preceded by an AHQ pre-soak of the wood, a smaller application of AHQ provided greater benefits in terms of Kappa number reduction than a larger amount of AQ supplied to the wood externally as in a conventional soda-AQ cook.

Distribution of Free and Combined AQ in the Pulp and Pulping Liquor in the Soda-AQ Pulping of Norway Spruce

As originally planned, the study was to include a determination of the extent of reaction of AQ with wood constituents as a function of the depth of AQ penetration. This was to be accomplished by solvent-extracting microtome sections of chips pulped in the presence of ^{14}C-labelled AQ and subsequently measuring the free (i.e., uncombined) AQ by HPLC and the total of free and combined AQ contents of the wood sections by radiolabel measurement following combustion to CO_2. However, the limited penetration of the chips by AQ under conditions where they were still rigid enough to be microtomed negated this approach. As an alternative, the proportions of free and combined AQ in the whole chips and in the cooking liquors were determined for both abbreviated and normal length cooks.

As shown by the plot in Fig. 3, the proportion of free AQ in the pulp decreases essentially linearly over the entire pulping period irrespective of differences in the initial rate of heating. Fleming et al (2) similarly observed a progressive decrease in the amount of AQ contained in the chloroform extract of the pulped chips in the later stages of the cook. As indicated by the plot in Fig. 3, less than 10% of the initial charge of AQ is free at the end of the cook. This value agrees well with results reported by Fleming et al (2), but is about half that reported by Algar et al (14) for a cook employing twice as much AQ (i.e., 0.2%).

The previously-described effects produced by AHQ pre-impregnation prompted an examination of chips following pulping to determine the effect of such a pretreatment on the proportions of free and combined AQ. As evidenced by the lower plot in Fig. 3, the pre-impregnation of AHQ had the initial effect of reducing the percentage of free AQ to approximately 23%, compared to the 87% observed when AQ was added to the cooking liquor in the conventional manner. However, at the

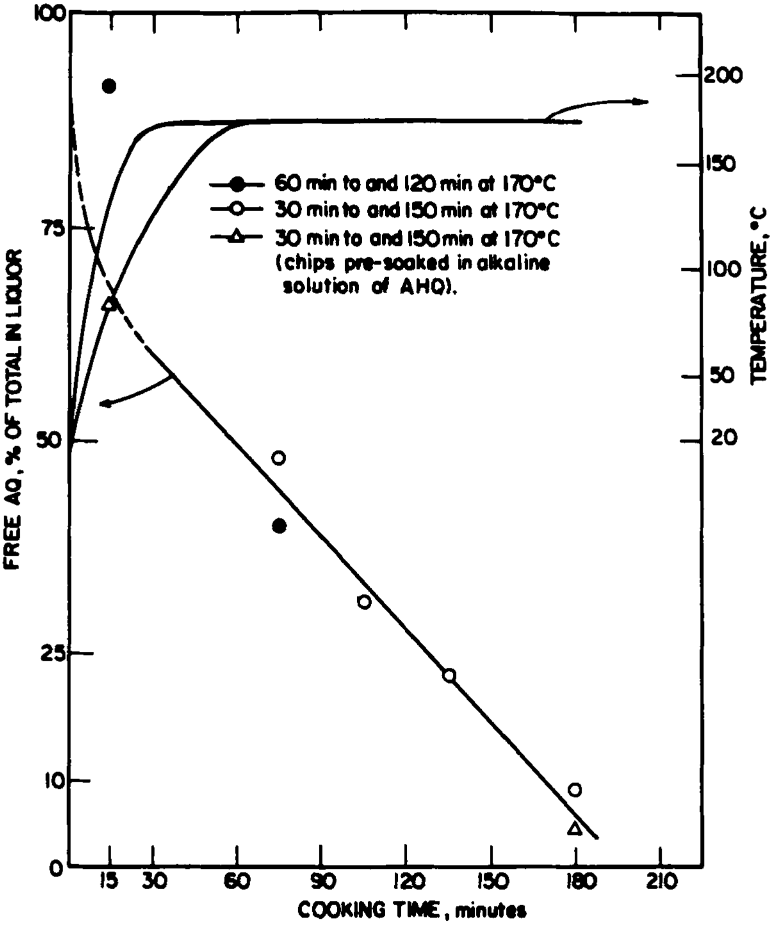

Figure 3. Effect of cooking time on the proportion of uncombined AQ in the pulp in the soda AQ pulping of Norway spruce. Cooking conditions: 300g (o.d. basis) of chips (original or pre-impregnated), 0.1% AQ, 20% NaOH, L/W = 4:1; Pre-impregnation conditions: 300g (o.d. basis) of chips, 0.6% AQ, 3.0g of glucose, 20g NaOH/1.5, 5 days, room temperature.

conclusion of the cook, the fraction of free AQ was the same in both cases. The result obtained when the chips were pre-impregnated with AHQ and subjected to a short cook was not duplicated when the AHQ was external to the chips at the outset of cooking.

The variation in the proportion of free AQ in the pulping liquor over the course of the cook is shown in Fig. 4. The profile of this plot is similar to that found for the corresponding pulp (Fig. 3) in that the percentage of free AQ decreased uniformly throughout the greater part of the cook. A similar trend was observed by Fleming et al (2) for total (free + combined) AQ and by Algar et al (14) for free AQ alone in the case of pulping liquors corresponding to the intermediate and late stages of soda-AQ pulping. The apparent initial decrease in free AQ in the liquor evidenced by the plot in Fig. 4 suggests the possibility that AQ (most likely in the reduced form) had reacted with a component of the wood at or near the chip surface, forming structures which soon thereafter were released to the cooking liquor in the form of low-molecular weight lignin- and/or carbohydrate-AQ derivatives.

The proportion of free AQ in the liquor generated in the cook in which the chips were pre-soaked with AHQ was essentially the same as when AQ was added to the wood in the conventional way. This finding is in contrast to the effect produced in the pulp where the amount of free AQ was distinctly lower under the same conditions. This is not unexpected in view of the difference in the availability of the wood components to the AQ (AHQ) in each situation.

Interpretation of the Changes in AQ Distribution

Based on the foregoing, the following sequences can be visualized as characterizing the overall be-

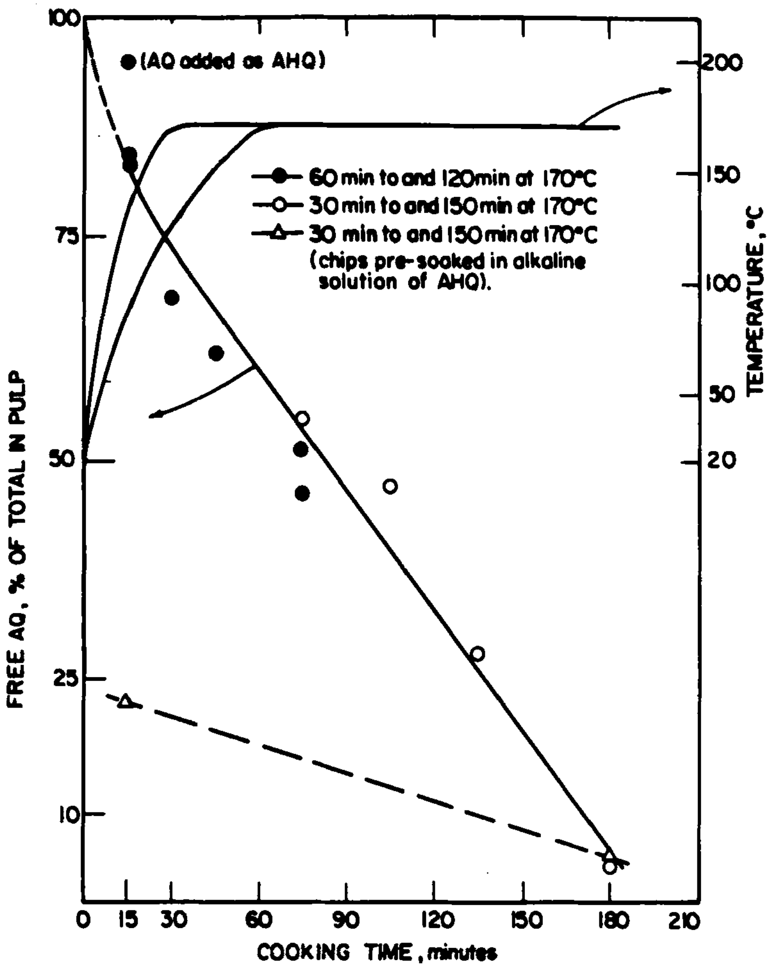

Figure 4. Effect of cooking time on the proportion of uncombined AQ in the liquor in the soda-AQ pulping of Norway spruce.
Cooking and pre-impregnation conditions: see caption for Figure 3.

havior of AQ in soda-AQ cooking: prior to and during the initial heating period, a sizeable portion of the AQ is deposited on or very near the chip surfaces. With continued heating, the AQ is reduced by the carbohydrate (e.g. [12-14]) and lignin[13] components to anthrahydroquinone which is soluble in alkali and diffuses from the chip surfaces into the pulping liquor. Even at this early stage of the cook there is evidence indicating that as much as 15-30% of the AHQ or possibly its reduction product, anthrone[15], is chemically combined with carbohydrate and/or lignin fragments, both in the chips and in the free-circulating cooking liquor.

In the 90-120°C temperature range, a significant fraction of the AQ (AHQ) penetrates the chips to a greater depth than initially, probably as a result of the AQ being present in an alkali-soluble form (i.e., as AHQ) and as a result of the chip structure having been broken down sufficiently to permit greater access to the AHQ. The amount of free and combined AQ (AHQ) in the pulp continues to increase with further heating up to a maximum and thereafter steadily decreases throughout the remainder of the cook. This latter trend probably is indicative of further chip disintegration in combination with the fragmentation of AHQ- or anthrone-containing lignin and carbohydrate material to dimensions sufficiently small to diffuse out of the chip into the free-circulating liquor. The AQ (AHQ) content in both the solid (i.e., chip) and liquor phases decreases almost linearly with cooking time in this stage of the cook and at nearly the same rate until consumption is almost complete.

SUMMARY

The results of the investigation reported herein

have served to re-emphasize the importance of AQ being in its reduced (AHQ) form as a prerequisite for exerting a beneficial effect on delignification. It was further shown that the benefits of AQ with respect to Kappa number reduction at a given yield can be enhanced if a practical way of pre-penetrating the chips with AHQ prior to pulping could be found. There is, moreover, a likelihood that further gains in Kappa number reduction can be achieved through refinement of the pre-soaking and pulping procedures used in the present study.

EXPERIMENTAL

Materials

Norway spruce chips (48.6% solids) were prepared in-house using a 12-knife Carthage Chipper. Coastal Douglas fir chips and wood discs used for the preparation of handcut chips and blocks were supplied by the Crown Zellerbach Company. The solids contents of the sapwood and heartwood handcut chips were 68.2% and 75.6%, respectively. The handcut chips had an average thickness of 3 mm (2-5 mm range), were 25 mm wide and of variable length. Handcut blocks were 10 mm thick. Materials were stored at 4°C under a chloroform atmosphere.

^{14}C-Labelled AQ was prepared as described previously[1]. The unlabelled AQ was of reagent grade quality which in some cases had been previously recrystallized from either chloroform or ethanol. Visually, the labelled and unlabelled materials appeared to be of nearly identical particle size.

Pretreatment of Norway Spruce Chips in an Aqueous Alkaline Solution of Anthrahydroquinone (AHQ)

Six g of sodium hydroxide was dissolved in 1400 ml of distilled water and heated to 80°C under nitrogen. Six times the required amount of AQ (0.2-1.8 g) on o.d. wood basis was dispersed in 100 ml of an aqueous 30 g/l solution of glucose and added to the sodium hydroxide solution. After 45 minutes the hot reaction mixture was added under vacuum to 300 g (o.d. basis) of Norway spruce chips which had been pre-evacuated for one hour with a vacuum pump. Soaking was continued under nitrogen for five days at room temperature except for two experiments where pre-soak temperatures of 4 and 50°C were used. In control experiments, the pre-soak liquor consisted of a hot aqueous sodium hydroxide solution of glucose with AQ being added in the pulping stage.

After soaking, the chips or blocks were drained, rinsed with water, air-dried overnight, thoroughly washed again to remove residual alkali, and re-dried. The AQ (AHQ) distribution in the soaked chips was measured in a parallel experiment using an aqueous alkaline solution of ^{14}C-AHQ as the pre-soak liquor (see section on Penetration Experiments).

Penetration Experiments

Pulped or pre-soaked handcut chips or blocks were microtomed along the fiber axes into 20 or 40 μm slices using an American Optical Co. Model 860 microtome. Two mm of wood was removed from each radial and tangential face of the handcut blocks before microtoming. The slices were combined into fractions representing 0.2 to 0.6 mm increments of cut depth and air-dried prior to further treatment.

Alternatively, for chips too soft to microtome, the digested wood was sectioned with a razor blade. Slices were removed from all faces of the chip, 0.5 mm thick from the radial and tangential surfaces, 2 mm from the cross-section surface. The sectioning process was performed twice on each of 25 handcut chips and materials of equivalent chip penetration distance were combined, yielding the fractions designated "outer" and "inner" zones. The remaining portions of the chips constituted the "core" fraction.

Extraction of Liquors and Pulps

Prior to extraction, each liquor was thoroughly aerated to oxidize any AHQ present to AQ and treated with sodium hydroxide to lessen emulsification. A 25-ml sample of spent liquor was extracted with 3 x 25 ml of chloroform. The combined extracts were concentrated at 40°C in a rotary evaporator to a final volume of 25 ml. Two or three ml of the concentrate were evaporated to dryness while being heated under a stream of nitrogen. For liquid scintillation counting, the dried sample was reconstituted directly with scintillation cocktail; for liquid chromotography, the sample was dissolved in acetonitrile. Pulps were extracted with acetonitrile following the procedure described by Armentrout[16].

Liquid Scintillation Counting

Most measurements of radioactivity in pulp and liquor samples were performed using methods described previously[1]. Air-dried microtome slices were crushed, weighed, and mixed directly with scintillation cocktail for counting. Small amounts of water were added to liquor samples to aid gel formation in the cocktail.

In certain cases, 2-ml samples of the spent liquors or 0.25 g samples of air-dried pulps were combusted in a Packard Instruments Model B306 sample oxidizer in preparation for radiolabel counting. The carbon dioxide absorbent was National Diagnostics Carbamate and the scintillation solution was National Diagnostics Oxosol 306. ^{14}C-Labelled AQ radioactivity standards, in the solid form or as dioxane solutions, were prepared and used for determining the specific activity recovered by the sample oxidizer. The scintillation counting efficiency was calculated using the channel ratio method, a quench curve was generated by repeated counting of a vial containing ^{14}C-toluene quenched by successive additions of either carbamate or nitromethane.

High Performance Liquid Chromatographic Determination of AQ

Liquid chromatography procedures for determining AQ were based on published methods[16-18]. The instrumentation consisted of a Waters Model ALC 202 liquid chromatograph equipped with a 254 nm detector, a 6000 psi pump, and a Valco 6-port injection valve.

Acetonitrile or dioxane solutions of the extract residue or AQ standards were filtered through a 0.45 µm Nylon 66 Ultipore filter prior to injection. The mobile phase was 10% (v/v) water in methanol. The column system consisted of an Alltech standard guard column packed with Perisorb RP-18 followed by a 30 cm x 4.6 mm (i.d.) stainless steel column packed with Lichrosorb RP-18 (5µm). Retention time was about 9 min.

Sodium Analysis

Microtomed slices of the chips were digested with a mixture of nitric and perchloric acids and the resulting solutions analyzed by flame emission with a Perkin-Elmer Model 360 atomic absorption spectrophotometer. A calibration curve was generated by diluting Fisher Scientific atomic absorption sodium standard solution as required.

Pulp Testing

Pulp samples were beaten in a PFI mill at a 0.15

mm clearance. Handsheets were prepared and tested as prescribed in the appropriate TAPPI standards. In some instances, the Kappa number determination was modified as follows in order to accommodate the small amounts of pulp sample available for the test: Fifty or 25 ml of 0.1N potassium permanganate solution was applied to the pulp samples; the remaining reagent volumes were adjusted proportionately to account for the different initial volumes. Calculations were performed as prescribed in TAPPI standard T236 os-76 except in determining the correction factor. The actual permanganate consumption, "p", was multiplied by 2 or 4, respectively, and this figure used to find "f", but not in the actual Kappa number calculation.

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