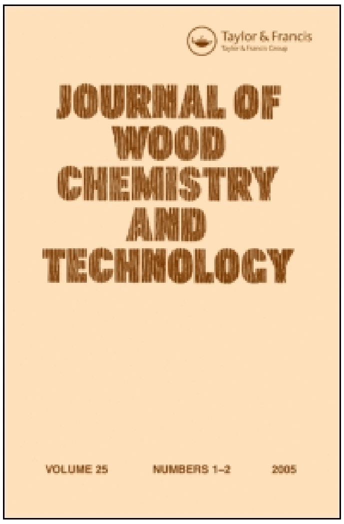

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# The Formation of Coniferyl Alcohol During Alkaline Delignification with Anthraquinone - Part II

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**To cite this Article** Mortimer, R. D.(1985) 'The Formation of Coniferyl Alcohol During Alkaline Delignification with Anthraquinone - Part II', Journal of Wood Chemistry and Technology, 5: 3, 347 — 361
**To link to this Article: DOI:** 10.1080/02773818508085198
**URL:** http://dx.doi.org/10.1080/02773818508085198

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 5(3), 347-361 (1985)

# THE FORMATION OF CONIFERYL ALCOHOL DURING ALKALINE DELIGNIFICATION WITH ANTHRAQUINONE — PART II.

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## ABSTRACT

Evidence has been gathered to demonstrate that coniferyl alcohol (CA) formation is predominantly a reaction of the initial phase of delignification. An attempt to link CA formation in the initial phase to the extent of delignification at the end of the cook indicated that the two processes were independent. Solutions of a commercial mixture of lignosulphonates also yielded CA when heated with alkali and catalysts like AQ. The relative effectiveness of certain redox catalysts to produce CA in this way correlates with their ability to accelerate the alkaline delignification of wood.

## INTRODUCTION

In the first part of this series, it was noted that coniferyl alcohol (CA) was produced in the cooking liquor of black spruce cooks during the initial phase of delignification[1]. Furthermore, it was demonstrated that the concentration of CA reached a maximum towards the end of the initial delignification phase and that this concentration increased dramatically when anthraquinone (AQ) was included in the cooking liquor. All of these observations have since been verified by independent researchers[2,3]. This report presents further characteristics of the initial phase reactions

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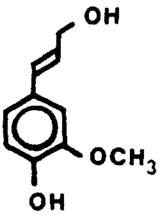


CONIFERYL ALCOHOL

and describes an attempt to link the formation of CA in the initial phase to the overall extent of delignification at the end of the cook.

## RESULTS AND DISCUSSION

### 1. Initial Phase Delignification

The effect of increasing AQ charge on the formation of CA was discussed previously[1]. Table 1 lists two sets of results which show not only the increase in the concentration of coniferyl alcohol with increasing AQ charge but also the corresponding decrease in lignin content of the woodmeal after the initial phase treatment. These results are consistent with Samuelson's observation of a catalytic effect of AQ on delignification at 120°C[4].

If one considers the extra lignin dissolved by adding AQ (21-30 mg) to the initial phase of a soda cook, the additional coniferyl alcohol formed represents at least 30-50% of that lignin. In other words, CA accounts for a significant portion of the lignin liberated by AQ in the initial phase. Whether CA is formed directly from lignin, thereby facilitating greater lignin release, or subsequently from soluble lignin fragments is not known. The former hypothesis, however, is consistent with the proposed mechanism of AQ action.

TABLE 1. The Effect of AQ Charge In The Initial Phase[1]

| AQ, mg | CA, mg/L | CA, % on o.d. wood | Lignin,[2] % | Yield, % |
|---|---|---|---|---|
| 0 | 49 | 0.05 | 29.9 | 79.3 |
| 0.4 | 172 | 0.17 | 29.6 | 82.7 |
| 1.8 | 258 | 0.26 | 29.3 | 82.4 |
| 3.9 | 384 | 0.38 | 29.2 | 77.8 |
| 11.4 | 580 | 0.58 | 28.6 | 78.5 |
| 21.2 | 655 | 0.66 | 28.3 | 78.6 |
| 80.0 | n.d. | n.d. | 26.8 | 80.3 |
| | | | | |
| 0 | 58 | 0.06 | 29.4 | 81.0 |
| 0.4 | 118 | 0.12 | 29.4 | 80.7 |
| 1.5 | 266 | 0.27 | 28.9 | 83.5 |
| 6.0 | 437 | 0.44 | 28.2 | 79.8 |
| 12.0 | 481 | 0.48 | 28.2 | 79.8 |
| 30.0 | 668 | 0.67 | 27.5 | 82.9 |

[1] Black spruce woodmeal (28.0% lignin), 15g o.d., L/W=10 L/kg, 0.3N NaOH, 80-145°C in 73 minutes.

[2] Klason + UV lignin content of cooked woodmeal.

[3] n.d. = not determined

## 2. The Topochemistry of CA Formation

If initial phase delignification occurs predominantly in the secondary wall lignin[6] and if the coniferyl alcohol formation is a characteristic of the initial phase delignification, then it follows that coniferyl alcohol is formed predominantly from the secondary wall. Whiting et al.[7] have succeeded in separating tissue fractions from the secondary wall and the middle lamella. Duplicate samples of each fraction, as well as of the original spruce whole woodmeal, were cooked under the mild conditions of the initial phase and the concentrations of coniferyl alcohol in the final liquor were measured by HPLC[1]. The results are listed in Table 2. The middle lamella fraction produced 14-16 times less CA than did the secondary wall fraction on the basis of the lignin contents. The whole woodmeal produced slightly less than the secondary wall, a result which is consistent with the relative

TABLE 2. Topochemistry of CA Formation[1]

| Starting Material | Lignin, % | Coniferyl alcohol<br>Conc., mg/L | Coniferyl alcohol<br>Yield based on lignin, % |
|---|---|---|---|
| Whole Spruce Wood | 27 | 379 | 1.40 |
| | | 415 | 1.54 |
| Secondary Wall | 22 | 347 | 1.58 |
| | | 380 | 1.73 |
| Middle Lamella | 60 | 59 | 0.10 |
| | | 74 | 0.12 |

[1] Duplicate cooks; see Experimental Section.

proportion of secondary wall and middle lamella lignin in the original wood and with their corresponding reactivities.

## 3. The Effect of the Cation on Formation of CA

Maass et al.[8,9] demonstrated many years ago that the cation used to prepare the alkaline cooking liquor could influence the overall rate of reaction; i.e., $Li^+ < Na^+ < K^+$, and Mortimer and Fleming recently confirmed that indeed NaOH solutions delignify much faster than LiOH solutions[10]. However, when only the initial phase of the cook was considered, the cation influenced neither CA formation nor the extent of delignification (Table 3).

## 4. The Effect of Wood Species on CA Formation

The previous preliminary observation that sinapyl alcohol (SA) as well as coniferyl alcohol was formed in the cooking liquor during the initial phase of hardwood pulping[1] has now been confirmed. The HPLC method had a detection limit of 5 mg/L for sinapyl alcohol in spent liquor; no peak for sinapyl alcohol was

TABLE 3. Effect of Cation in the Initial Phase[1,2]

| Cation | CA conc., mg/L | Klason + UV lignin, % |
|---|---|---|
| Lithium | 526 | 28.0 |
| | 562 | 27.8 |
| Sodium | 598 | 27.7 |
| | 534 | 28.2 |
| Potassium | 517 | 27.7 |
| | 592 | 27.5 |

[1] Cooking conditions: Black spruce woodmeal (20-40 mesh, 7.4 g o.d.), 0.14% AQ, L/W=13.6 L/kg, 0.3N $OH^-$, 85-125°C in 43 min and 60 min at 125°C.

[2] Duplicate cooks.

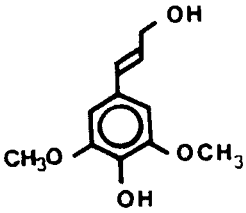
TABLE 4. Formation of Coniferyl and Sinapyl Alcohols[1,2]

| Wood Species | Concentration, mg/L | |
|---|---|---|
| | Coniferyl Alcohol | Sinapyl Alcohol |
| Trembling Aspen | 220 | 178 |
| | 223 | n.d. |
| White Birch | 265 | 234 |
| | 227 | n.d. |
| Western Red Cedar | 685 | <5 |
| | 524 | n.d. |
| Balsam Fir | 555 | <5 |
| | 620 | n.d. |
| Jack Pine | 695 | <5 |
| | 566 | n.d. |
| Black Spruce | 474 | <5 |

[1] Cooking conditions: woodmeal (40-60 mesh, 20 g o.d.), 0.2% AQ, L/W=10 L/kg, 0.4N NaOH, 21-145°C in 82 min.

[2] Duplicate cooks; n.d. = not determined.

found in softwood liquors. In addition, coniferyl alcohol was found in the cooking liquors from a variety of softwoods and hardwoods by HPLC as noted in Table 4. It is interesting that the concentrations of coniferyl and sinapyl alcohols are roughly equal from hardwoods and that the sum of the two is similar to the concentration of coniferyl alcohol found from softwoods. This does not necessarily refute the view that the secondary wall lignin in hardwoods is primarily syringyl as the detailed structure of this lignin is unknown.



SINAPYL ALCOHOL

## 5. The Effect of Additive Efficiency on CA Formation

The ability of certain quinones to accelerate delignification to a greater extent than others is, according to Werthemann[11], usually due to their differences in 'xylophilicity' or attraction to wood. An additive with greater xylophilicity is a better accelerator. It was suggested that the greater efficiency was due to better adsorption of the additive on the wood surface. Table 5 lists the concentrations of coniferyl alcohol measured in the liquors from the cooking of black spruce woodmeal with quinones of different efficiencies.

The concentration of coniferyl alcohol was found to increase with the increasing pulping efficiency of the various additives.

TABLE 5. The Effect of Additive Efficiency on CA Formation[1]

| Additive | Relative Efficiency[2] | CA conc., mg/L |
|---|---|---|
| nil | 0 | 35 |
| 1,4-naphthoquinone | 0.1 | 67 |
| AMS | 0.45 | 161 |
| 1,5-diamino-AQ | 0.7 | 339 |
| AQ | 1.0 | 362 |
| 2-methyl-AQ | 1.1 | 540 |

[1] Cooking conditions: Black spruce woodmeal (40-60 mesh, 10 g o.d.), all additives equimolar to 0.1% AQ charge, L/W=10 L/kg, 0.4N NaOH, 85-125°C in 48 min. and 60 min. at 125°C.

[2] References 5 and 12.

Curiously, the same order of coniferyl alcohol production was found even when the starting material was an aqueous solution of lignosulphonates (Figure 1). The concentration of coniferyl alcohol increased linearly with the r-value (a term defined by Werthemann to express the efficiency of an additive relative to AQ whose r-value is 1). The significance of the result shown in Figure 1 lies in the fact that the reaction mixture for these experiments appeared to be homogeneous; i.e., there was no wood surface on which a xylophilic catalyst might be adsorbed. This suggests that if the relative efficiency of an additive is due to its degree of adsorption, then adsorption on the lignin macromolecule itself may be more important than on the wood surface generally. Further work is needed to assure that lignin micelles are not involved.

## 6. The Relationship between CA Formation in the Initial Phase of Delignification and Overall Delignification

The influence of initial phase reactions on the later stages of delignification is a subject of interest to a number of re-

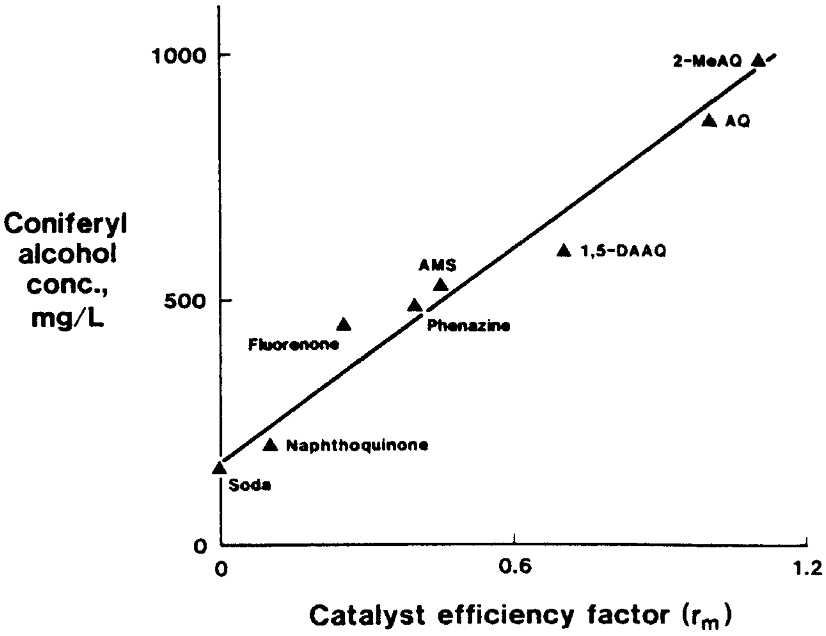


FIGURE 1. The effect of catalyst efficiency ($r_m$) on the formation of coniferyl alcohol from an alkaline solution of lignosulphonate under initial phase pulping conditions. The terms 1,5 DAAQ and AMS refer to 1,5-diaminoanthraquinone and sodium anthraquinone-2-sulphonate, respectively.

searchers[13-15]. Axegard and Wiken[15], for example, reported that AQ in the initial phase reduced the amount of residual lignin in the final phase. In the present work, two experiments were done to attempt to establish a link between the coniferyl alcohol formed in the initial phase and the extent of delignification in the bulk phase.

As noted before[1], woodmeal produced approximately sixty percent more coniferyl alcohol in the initial phase than wood chips

TABLE 6. Effect of Wood Size on Final Kappa Number[1]

| Set | Kappa Number[2] Woodmeal | Wood Chips |
|---|---|---|
| 1 | 47.2 ± 0.8 | 53.3 ± 1.4 |
| 2 | 41.9 ± 2.9 | 52.4 ± 2.0 |

[1] Cooking conditions: Black spruce, L/W = 10 L/kg, 1.0N NaOH, 0.1% AQ, 20-40 mesh woodmeal, 90 min to temp. (170°C), H-factor = 1400

[2] Duplicate cooks for each set.

under identical conditions. Table 6 shows however that the difference in the final Kappa numbers towards the end of the bulk phase of delignification was rather small.

Although the woodmeal gave both a higher yield of CA and a lower Kappa number than the wood chips, the difference in the Kappa numbers represented only 0.5-0.8% difference in lignin on an o.d. wood basis. Judging by the results in Table 1, this difference is probably generated in the initial phase of delignification and not in the bulk phase.

A second experiment was done to investigate the effect of the alkali concentration in the initial phase on the formation of CA at 145°C and on the final Kappa number at an H-factor of 1400. The previous publication[1] had noted that the CA concentration decreased as the initial alkali concentration increased above 0.3N NaOH. Was this due to formation of less CA or did it reflect an increase in the rate of CA degradation/condensation reactions? Indeed, Kondo and Sarkanen[2] have shown that CA in the presence of wood reacts with wood degradation products that are generated even earlier in the cook than CA. They have not demonstrated, however,

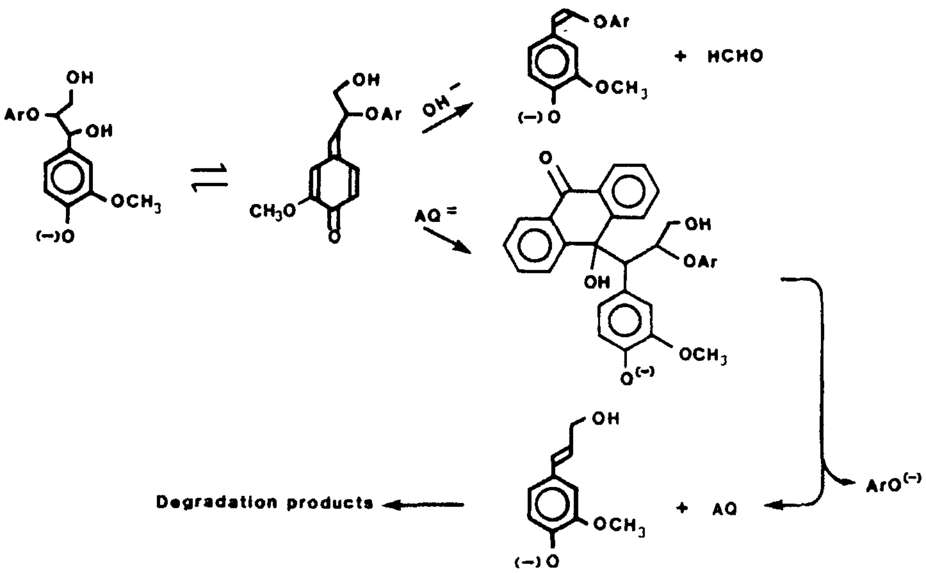


FIGURE 2. The proposed mechanism to explain the accelerating effect of AQ on alkaline delignification.

that this reaction is alkali-dependent.

On the other hand, Gierer and Lindeberg[16] have found that CA alone is more stable at higher alkali concentrations; hence, the decrease in CA noted previously[1] could simply have reflected a lower production of CA. This decline in CA concentration at higher alkali concentrations may be due to increasing competition between the AQ di-anion and the hydroxide anion for the quinone methide (see Figure 2). Reaction of the quinone methide with hydroxide is thought to lead to vinyl ether formation, not to CA formation. This hypothesis was examined by splitting the alkali charge of one cook into two parts such that the initial phase was cooked at a low alkali charge. Then, at the end of the initial phase, the overall charge was equalized to that in the control

TABLE 7. The Influence of Initial Phase Alkali Charge on CA Formation and Final Kappa Number[1]

| | Control | Split Charge |
|---|---|---|
| Total NaOH Charge, moles | 0.24 | 0.24 |
| Initial NaOH Charge, moles | 0.24 | 0.10 |
| Added NaOH Charge, moles | 0 ($H_2O$ only) | 0.14 |
| AQ, % on o.d. wood | 0.1 | 0.1 |
| L/W Ratio, L/kg | 4 | 4 |
| H-factor | 1400 | 1400 |
| <u>Results</u> | | |
| CA conc.,[2] mg/L | 480 | 690 |
| Final AQ conc., mg/L | 62 | 52 |
| Final NaOH conc., $\underline{N}$ | 0.50 | 0.49 |
| Kappa | 52 | 51 |
| Yield, % | 50 | 50 |
| Rejects, % | 0.3 | 0.8 |

[1] Cooking conditions: both the cooks were interrupted after 145°C during the rise-to-temp., the bombs were chilled, the contents sampled, the additions made and then the cooks were completed. The results reported are average values from three separate experiments with standard deviations of 6% in all cases.

[2] Measured at the end of the initial phase.

experiment which did not have its alkali charge split. The cooks were identical in all other respects. The work of Axegard and Wiken[15] indicates that splitting the alkali charge will itself not generate a difference in the final pulp.

The results in Table 7 confirmed that the coniferyl alcohol concentration in the initial phase was higher at the lower hydroxide concentration. The pulp properties at the end of the second stage, however, were the same. There was no evidence that the extent of coniferyl alcohol formation in the initial stage, as determined by the initial alkali charge, had any influence on the later stage of delignification.

The lower concentration of residual AQ in the spent liquor from the cook with the split alkali charge is interesting. It may reflect a greater AQ activity in this cook than in the control cook that leads to AQ consumption but not to delignification. The same effect was noticed in the woodmeal vs. wood chips cook; the liquor from the woodmeal cook had only 80% of the residual AQ found in the liquor from the wood chips cook. The reason for this is presently unknown.

## CONCLUSIONS

Coniferyl alcohol has been found during the early stage of alkaline pulping in the cooking liquors of all wood species examined including softwoods and hardwoods. In addition, sinapyl alcohol has been found in the liquors from the hardwood cooks in approximately equal proportion to coniferyl alcohol.

The formation of coniferyl alcohol in black spruce soda cooks has a number of characteristics in common with initial phase delignification, namely, it: exhibits no cation effect (unlike bulk delignification), is independent of hydroxide concentration above a certain minimum concentration, occurs predominantly in the secondary wall, and appears to be complete by the time the cook reaches 150°C.

Efficient redox catalysts like AQ give both high CA yields and good delignification. Initial experiments, however, show no direct link between the extent of CA formation in the initial phase, as determined by varying the initial alkali charge or the wood particle size, and the extent of delignification at the end of the complete cook. If the mechanism presently accepted for kraft pulping[17], in which CA is an important end product, is correct then the formation of CA during the bulk delignification phase of the cooking cycle needs to be demonstrated.

## EXPERIMENTAL

The source of chemical standards, the general cooking techniques and the method of coniferyl alcohol analysis by HPLC were described in the previous publication[1]. Sinapyl alcohol was analyzed by the same method as that used for coniferyl alcohol; the retention time was a few minutes longer. Methyl p-hydroxy benzoate (100 mg/L) was used as internal standard.

### Cooking Cell Wall Fractions

Into a 1 mL Reacti-vial (Pierce Chem. Co.) was first placed 0.225 mg of AQ (added as a solution in acetonitrile then evaporated at room temp.) then 15.0 mg of the tissue fraction, 2.0 mg of glucose and 0.15 mL of 0.5N NaOH. The vial was sealed with a Teflon-lined cap and immersed in the oilbath at 80°C. The temperature of the bath was raised to 125°C over 45 min at which point the vial was removed and chilled in cold water. Any vial which leaked was discarded. The contents of the vials were diluted (5x) with 5% acetic acid in methanol and centrifuged for 25 min. The supernatant was analyzed by HPLC as described[1].

### Cooking Lignosulphonates

Into a 5 mL Reacti-vial (Pierce Chem. Co.) was placed 0.5 g of Marasperse N-22 (American Can Co.), 0.1 g of glucose, 5 mL of 1.0N NaOH and 1.33 mg of AQ (other additives were equimolar to AQ). The sealed vial was then heated at 125°C for 30 min. After cooling, an aliquot of the liquor was diluted 1:5 with acetic acid-methanol (10% v/v), filtered and analyzed by HPLC.

### Miscellaneous

Residual AQ in spent liquors was analyzed by HPLC using the acetonitrile extraction method[18].

Klason lignin was determined according to TAPPI T222 os 74 and UV lignin according to TAPPI UM250.

## ACKNOWLEDGMENTS

Once again I am indebted to Mr. P.Y. Wong for his careful experimental work. A special note of thanks is due to Drs. P. Whiting and D.A.I. Goring for their generous donation of wood tissue fractions and to Dr. N.G. Lewis for the sample of pure sinapyl alcohol.

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