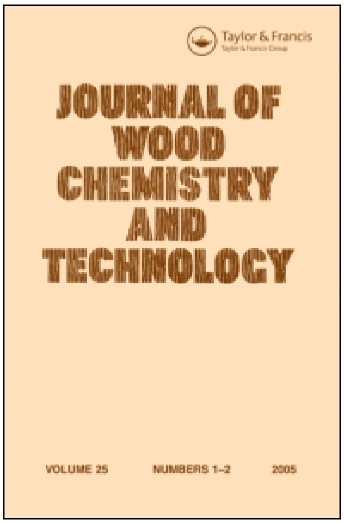

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FORMATION AND REACTION OF CONIFERYL ALCOHOL DURING ALKALINE PULPING

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Dedicated to Professor J. L. McCarthy on the occasion of his 70th birthday.

ABSTRACT

The formation and subsequent disappearance of coniferyl alcohol during kraft and soda-AQ (anthraquinone) pulping of western hemlock wood meal have been studied under isothermal condition. At 140°C, the amount of coniferyl alcohol generated increases to a sharp maximum (0.4% of total lignin in kraft and 1.9% in soda-AQ pulping) and then declines rapidly to low values. It was found that the disappearance of coniferyl alcohol was mainly due to condensation with other components of dissolved lignin. Nearly identical activation energies, 125 kJ mole^{-1} for kraft and 128 kJ mole^{-1} for soda-AQ pulping, were derived from the initial rates of coniferyl alcohol formation, conforming closely with the value 121 kJ mole^{-1} for the cleavage of phenolic β-ether model compounds in the kraft process.

INTRODUCTION

Coniferyl alcohol and analogous lignin structures have been postulated as intermediates in the degradation of p-hydroxy-arylglycerol-β-aryl ether units of lignin in kraft- and soda-AQ pulping. This postulate is based on the observation that model compounds

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representing such units are in part converted into coniferyl alcohol or related compounds, when treated under similar conditions[1-4]. However, the actual presence of coniferyl alcohol in kraft spent liquor was not demonstrated experimentally until 1980 by Gierer and Lindeberg[5]. The elusiveness of this intermediate is ascribable, according to Brunow and Miksche, to its instability in alkaline media at pulping temperature[6]. Various types of self-condensation mechanisms have been postulated on the basis of model compound studies[6-8] and it has also been suggested that these condensation products contribute to the formation of residual lignin in pulp[9]. Most recently, Mortimer[10] has shown that maximum concentrations of coniferyl alcohol are observed at low reaction temperatures (120-140°C). Interestingly enough, much larger amounts of coniferyl alcohol were generated in soda-AQ than in kraft pulpings (3.5 versus 0.4% of lignin).

In a previous paper[11], it was demonstrated that, in the kraft process, the initial delignification consisted of two kinetically distinguishable phases (ID_1 and ID_2) resulting in the dissolution of 13 and 11% of the original lignin, respectively. The ID_2-phase followed pseudo-first order kinetics with an activation energy of 73 kJ mole^{-1}. Since this value is significantly lower than the value 121 kJ mole^{-1} determined by Gierer and Ljunggren[12] for the cleavage of β-aryl ether bonds in phenolic model compounds, it was of interest to clarify the precise relationship between the formation of coniferyl alcohol and the initial phase delignification.

EXPERIMENTAL

Pulping Procedure

The pulping procedure described in the previous work[11], was applied to western hemlock wood meal using the following conditions in kraft pulping, effective alkali 20% as Na_2O, sulfidity

30%, wood to liquor ratio 10:1, 5 to 120 minutes at 100 to 150°C. In soda-AQ pulping similar conditions were applied, replacing sulfidity by 0.2% AQ charge.

Two-stage pulpings: Wood meal was cooked for 1 hr at 100°C (or, alternatively, 2 hrs at 120°C), filtered, washed with water and dried. The pre-cooked wood meal samples were treated with a fresh batch of cooking liquor at 120°C (or 140°C) for 5 ~ 120 minutes.

Determination of Coniferyl Alcohol in Spent Liquor

The determinations of coniferyl alcohol in the spent liquors were performed using HPLC (Waters Associates Model U6K)[10]. After pulping, combined spent and washing liquors were adjusted to pH 9 by carbon dioxide gas and extracted with ethyl ether four times. The extract was washed with saturated NaCl and dried over anhydrous Na_2SO_4. The ethyl ether was removed on a rotary evaporator to yield a light brown oil. The extracted oil was dissolved in methanol and methyl guaiacol added as internal standard. Measured 3 μl quantities of the methanol solution were separated in a μ Bondapak TM/C_{18} column coupled to a UV detector monitoring at 280 mm. The mobile phase was 50% CH_3OH - H_2O. The retention time of coniferyl alcohol was 18.5 ± 0.1 minutes.

Isolation of Low Molecular Weight ID_1-Kraft Lignins

Western hemlock wood platelets (100 g o.d. with an average thickness of 0.7 mm) were treated in an autoclave with 1 ℓ of white liquor (effective alkali 20% as Na_2O, sulfidity 30%) for 1 hr at 100°C. The spent liquor was adjusted to pH 7 by acetic acid and extracted three times with $CHCl_3$. The extract was washed with water and dried over anhydrous Na_2SO_4. The $CHCl_3$ solution was concentrated on a rotary evaporator and poured into methanol. Precipitated inorganic sulfur was filtered off and methanol removed by distillation to yield a light brown oil (1.0 g, 3.4% on lignin).

Condensation of Coniferyl Alcohol

Coniferyl alcohol (10 mg), either alone or together with a sample of isolated ID_1-kraft lignin (20 mg) was dissolved in 10 ml of alkaline liquor (0.65 N NaOH, sulfidity varied from 0 to 100%) deaerated with nitrogen. An aliquot of each solution (8.0 ml) was transferred into a stainless steel autoclave having a volume of 10 ml. Air was replaced by nitrogen and the autoclaves sealed and heated in an oil bath at constant temperature. After 30 minutes the reaction was terminated by cooling. An aliquot of the reacted solution (5.0 ml) was adjusted to pH 9 by carbon dioxide and extracted with ethyl ether. The remaining coniferyl alcohol was determined in the extract by HPLC.

RESULTS AND DISCUSSION

Formation and Disappearance of Coniferyl Alcohol during Alkaline Pulping

The amounts of coniferyl alcohol (CA) produced in kraft pulping of western hemlock wood meal was determined at 100°, 120°, 140° and 150°C as a function of time and the results are shown in Figure 1. At 120°C, CA concentration increases during the first 60 minutes of pulping reaching a maximum corresponding to 0.25% of original lignin and then declines slowly. At 140°C, a substantially higher concentration level (0.42% on lignin) is reached after 10 minutes reaction time followed by a rapid decrease. It can be seen that CA released in the process is concurrently consumed in secondary reactions. These secondary processes are particularly fast at reaction temperatures of 140° and above. It was possible to demonstrate that the disappearance of CA from the reaction mixture was mainly due to condensation with lignin released in the ID_1-phase. When this lignin component was removed by treatment with kraft liquor at 100-120°C and the reaction continued using a fresh liquor charge, the CA subsequently released

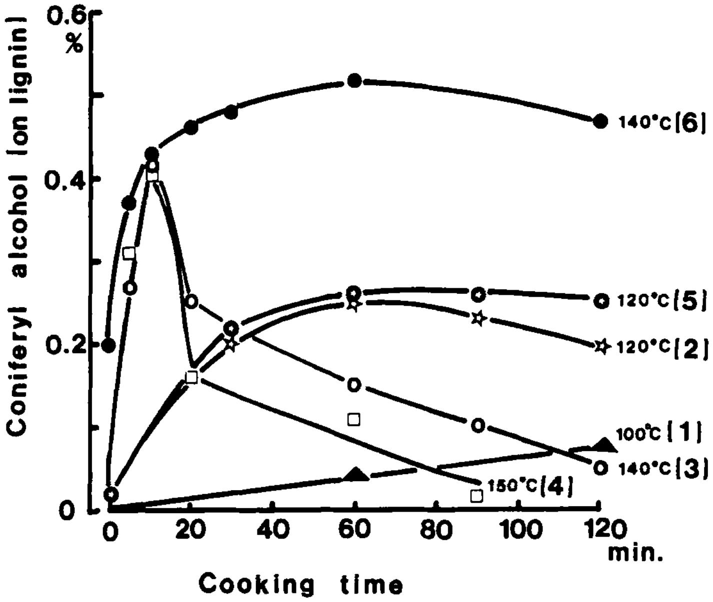


Figure 1. Formation and disappearance of coniferyl alcohol during initial kraft delignification. Curves 1 to 4, amounts of coniferyl alcohol determined for single stage delignification. Curves 5 and 6, cumulative amounts of coniferyl alcohol formed in two successive delignification steps. Curve 5: First stage, 1 h at 100°C. Curve 6: First stage, 1.5 h at 120°C.

showed hardly any tendency to decline. This is demonstrated by curves 5 and 6 in Figure 1, showing the sum of CA released in the two successive stages of kraft treatment. However, an additional factor also needs to be considered to account for the stability of the released CA in the two-stage process. The prevailing alkalinity is higher than in the single-stage process and this factor has been demonstrated by Gierer and Lindeberg[9] to retard CA decomposition.

Since Mortimer[10] has shown that soda-AQ pulping releases approximately five times more CA from softwood lignin than the kraft process, it was of interest to investigate the formation of CA in soda-AQ pulping under isothermal conditions. Rapid disappearance of CA, inititally formed, as a consequence of condensation with ID_1

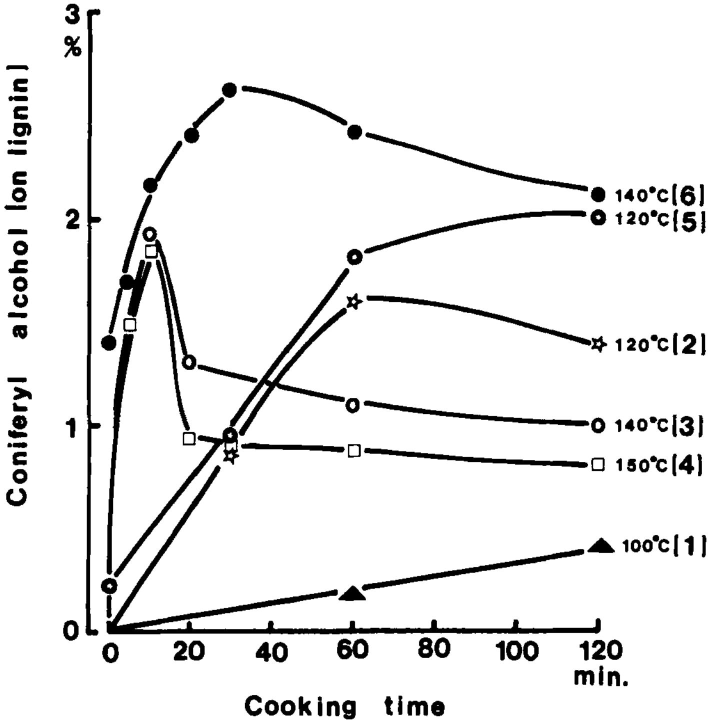


Figure 2. Formation and disappearance of coniferyl alcohol in initial soda-AQ pulping. Curves 1 to 4, single-stage delignifications. Curves 5 and 6, two-stage delignifications. First stages: Curve 5: 1 h at 100°C; Curve 6: 45 min at 120°C.

lignin was analogous to that observed in the initial kraft delignification as shown in Figure 2. In a two-stage treatment, a maximum of 2.7% of lignin was converted to CA.

In order to confirm the postulated condensation of CA with ID_1-lignin, an exploratory series of experiments was performed heating CA in alkaline pulping liquors at 140°C with and without the presence of added ID_1 lignin (LML), isolated from previous experiments. The results of these experiments are recorded in Table 1. It can be seen that the presence of low molecular weight lignin does indeed promote the destruction of CA.

Table 1. Effect of sulfidity and low molecular weight lignins (LML) addition on the consumption of coniferyl alcohol (cooking time 30 min at 140°C).

	Consumption of Coniferyl Alcohol (%)	
Sulfidity (%)	No LML	With LML
0	40.4	80.5
30	64.8	89.4
100	84.5	-

On the other hand it should be noted that the disappearance rate of CA is quite high even in the absence of low molecular weight lignin. As demonstrated in earlier studies by Gierer and Lindeberg[5] and by Mortimer[10], contributing processes probably consist of conversions of CA to such products as vinyl guaiacol, isoeugenol and condensation products. An increase in sulfidity appears to further promote the destruction of CA, in conformity with observations by Gierer and Lindeberg.

The instability of CA at 140°C, demonstrated by results in Table 1, has also significance in the interpretation of results shown in Figures 1 to 3. For example, in the second-stage soda-AQ pulping (curve 6, Figure 2), the CA concentration appears to remain approximately constant after 30 minutes reaction time. In view of the instability of CA at 140°, the constant concentration is likely to be caused by a steady-state condition, that is, by approximately equal formation and destruction rates of CA. On this basis, the amount of CA released during the total reaction period could be much higher than the peak value 2.7% on original lignin. A steady-state condition could also explain the flat portions of curves 3 and 4 in Figure 2, as well as that of the kraft curve 6 in Figure 1. However, the steady-state hypothesis is probably not sufficient to account for the much lower yields of CA in the kraft process as compared with

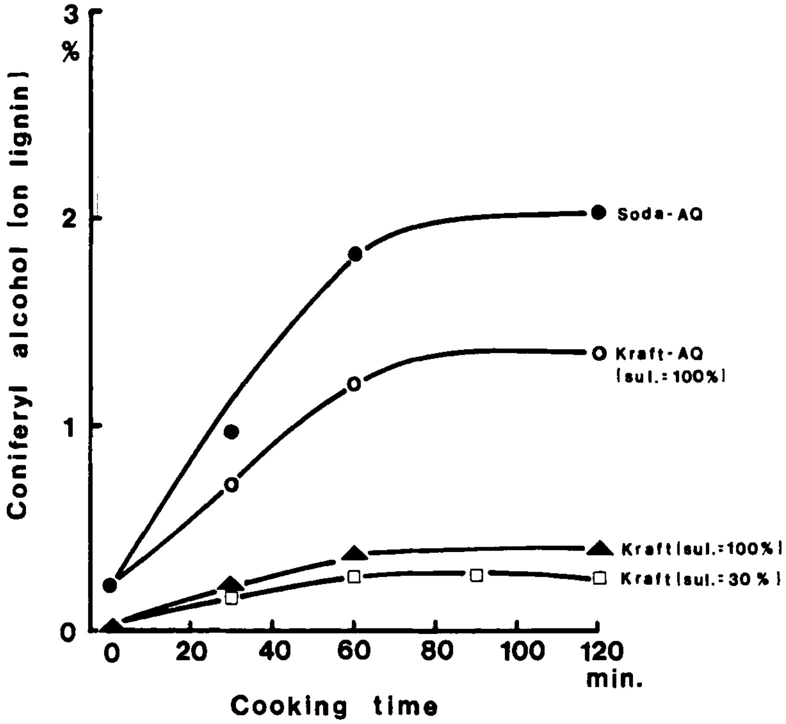


Figure 3. Formation of coniferyl alcohol in kraft, kraft-AQ and soda-AQ delignifications at 120°C. Prior to each run, ID_1-lignin was removed by 1 h treatment at 100°C.

the soda-AQ delignification. The possibility that, in the kraft process, only a fraction of cleaved phenolic β-ether structures is actually converted to CA should be considered as a potential explanation for the low yields.

Kinetics of Coniferyl Alcohol Formation

Gierer and Ljunggren[12] have determined the activation energy for the cleavage of β-ether linkages in phenolic guaiacylglycerol-β-aryl ether model compounds under kraft pulping conditions obtaining the value 121 kJ $mole^{-1}$. If it is assumed that CA released in the kraft pulping of wood is derived from analogous structures, the activation energy for this process should be of the same magnitude.

The formation kinetics of CA are, of course, complicated by the subsequent condensation processes and consequently, one is forced to resort to the estimation of initial release rates at different reaction temperatures in order to obtain an approximate value for the activation energy. Since the initial release rates were found to be practically identical in one- and two-stage pulpings, this approach was considered to be an adequate one. The activation energy plot based on these reaction temperatures is shown in Figure 4 and conforms with the value 125 kJ $mole^{-1}$ which is very close to the model study by Gierer and Ljunggren. An almost identical activation energy, 128 kJ $mole^{-1}$, was obtained for the CA formation rate in soda-AQ pulping irrespective of the substantially higher rates of reaction at any given temperature.

The observed activation energies are significantly higher than the value 73 kJ $mole^{-1}$ for the ID_2-delignification phase, reported in an earlier paper[11], and support the contention that coniferyl alcohol is, in all likelihood, formed from terminal aryl glycerol-β-aryl ether units. If this is true, the rate determining step in the coniferyl alcohol formation, both in kraft- and soda-AQ processes, is likely to be the conversion to a quinone methide structure, and the activation energy 128 kJ $mole^{-1}$ accordingly should be characteristic for this conversion. On this basis, identical rates of CA formation could be expected for kraft- and soda-AQ processes. Since this is not the case, it is probable that, in the kraft process, only a part of phenolic guaiacylglycerol-β-aryl ether structures is actually converted to coniferyl alcohol, as suggested earlier in this paper.

To account for the low activation energy of the ID_2-delignification phase, it should be noted that the bulk of lignin dissolved in this phase is in the form of oligomeric fragments. It was proposed in the previous paper[11] that these products may stem

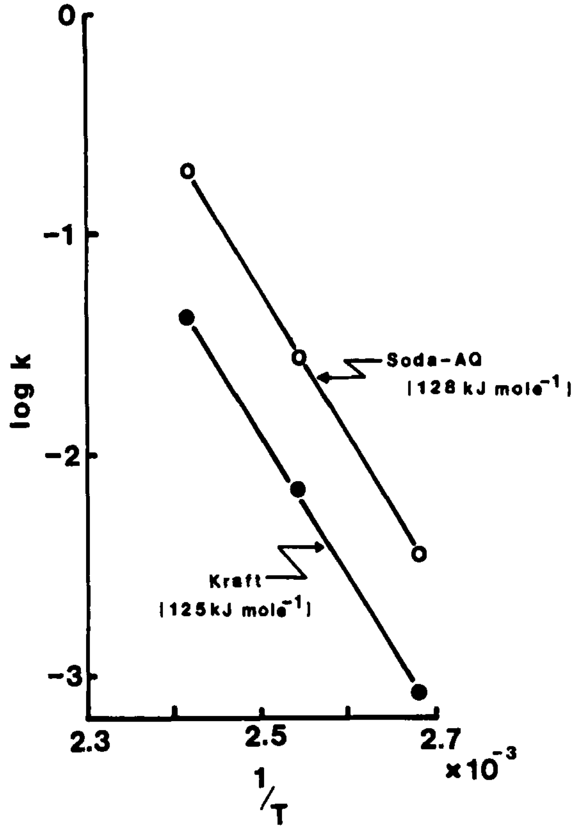
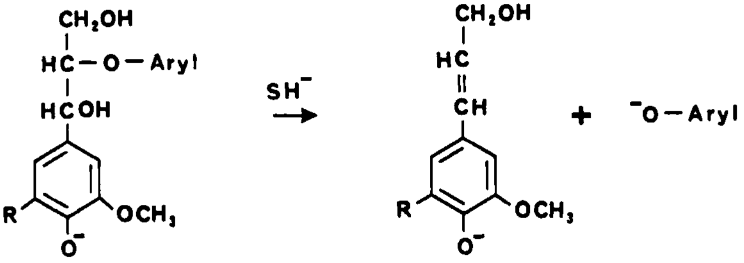


Figure 4. Activation energy plots for the initial rates of formation of coniferyl alcohol in kraft- and soda-AQ pulpings.



1a: R=H
1b: R=(GP)$_n$

2a: R=H
2b: R=(GP)$_n$

Figure 5. Types of phenolic β-aryl ether structures reactive in initial delignification. Type 1a: Terminal unit, Type 1b: Nonterminal unit. GP = Guaiacyl propane unit. n = number of guaiacyl propane units in sequence.

from non-terminal phenolic β-aryl ether structures 1b (Figure 5), if it is assumed that the bulky 5-substituent group would lower the activation energy of the conversion to the corresponding quinone methide. This hypothesis requires, of course, confirmation from appropriate model compound studies.

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