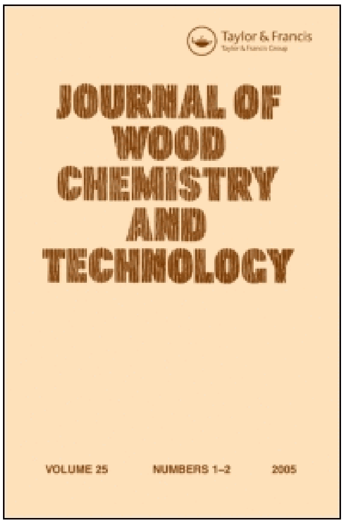

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Mechanistic Differences Between Kraft and Soda/AQ Pulping. Part 2: Results from Lignin Model Compounds

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Abstract: Data accumulated in our laboratory from the cooking of chips and bleaching of resulting pulps consistently pointed to a higher rate of lignin condensation during soda-AQ (SAQ) as compared to kraft pulping. The data also appear to indicate that the rate of condensation was higher at lower alkalinity and that the higher concentration of condensed structures in SAQ pulps is likely responsible for their poorer bleachability. Alkaline condensation reactions were investigated with four commercially available lignin model compounds: apocynol (AP), ethylguaiacol (EG), homovanillyl alcohol (HVA), and vinylguaicol (VG). The investigation of lignin model compounds (LMCs) indicated mechanistic differences that would explain the higher rate of lignin condensation for SAQ pulping as compared to the kraft pulping. Several research groups have reported that the rate of formation of coniferyl alcohol (CA) is 4–5 times higher for SAQ or kraft/AQ as compared to kraft pulping. The present investigation showed that secondary quinone methides from CA degradation products, such as vinylguaicol, participate in condensation reactions. A higher rate of condensation was observed in 0.1 M NaOH as compared to 0.6 M NaOH. Evidence was also found for carbohydrate-rich materials condensing with quinone methides.

Keywords: Alkaline pulping, lignin-carbohydrate condensation, lignin condensation, lignin model compounds, quinone methide

INTRODUCTION

As discussed in Part 1 of this series (this issue), the technical feasibility of black liquor gasification (BLG) would improve significantly if a non-sulfur pulping

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process were to replace kraft.[1−3] Therefore, research is being performed to improve the efficacy of soda-AQ (SAQ) pulping to a point where it becomes equal or superior to kraft. The probability of success is higher for hardwoods as compared to softwoods and as such most of the effort is focused on deciduous wood at the present time.

In the production of bleached hardwood pulps, the major disadvantage of the SAQ process as compared to kraft is poorer bleachability. The cooking of chips and bleaching of pulps were investigated in Part 1 of this series (this issue) and the results indicated that unbleached SAQ pulps contained more condensed lignin structures than kraft pulps.[1] Most of these condensed structures are less reactive to conventional bleaching chemicals[4,5] and their higher concentrations in SAQ pulps is the likely cause of their poorer bleachability. The objective of the present investigation is to elucidate alkaline condensation reactions amongst guaiacyl lignin model compounds (LMCs). Permanganate oxidation analyses of lignin from the SAQ pulping process have clearly indicated that condensation between guaiacyl units is much more significant than guaiacyl-syringyl or syringyl- syringyl condensation.[1,6]

MATERIALS AND METHODS

Lignin Model Compounds

The LMCs involved in this investigation are shown in Figure 1. LMCs **1–4** were all purchased from Aldrich Chemical Co.

Condensation Reactions

One or two LMCs were selected from among **1–4** and added to 60 ml of NaOH solution in 100 ml stainless steel autoclaves. The amount of each LMC was either 0.25 g or 0.50 g and NaOH concentration varied from 0.1–0.6 M. A small dose of Na_2S (0.1 g/l) was added as an oxygen scavenger when NaOH induced condensation was being investigated or a larger dose was added to simulate kraft cooking liquor. AQ was added by itself or in the form of AHQ obtained by reducing AQ with D-glucose. On no occasion were AQ and Na_2S added together. Each autoclave was sealed and placed in a 165°C oil bath for 60 min. After the reaction the autoclave was cooled by flowing cold water. The reaction mixture was acidified to pH$\sim$ 2 in a fumehood and extracted with dichloromethane (DCM). The DCM extract was concentrated to 20 ml and two 5 ml portions were set aside for Gas Chromatography (GC) and Gas Chromatography–Mass Spectroscopy (GC–MS) analyses while the remaining 10 ml was concentrated to $\sim$ 2 ml and use for solid sample introduction MS analysis.

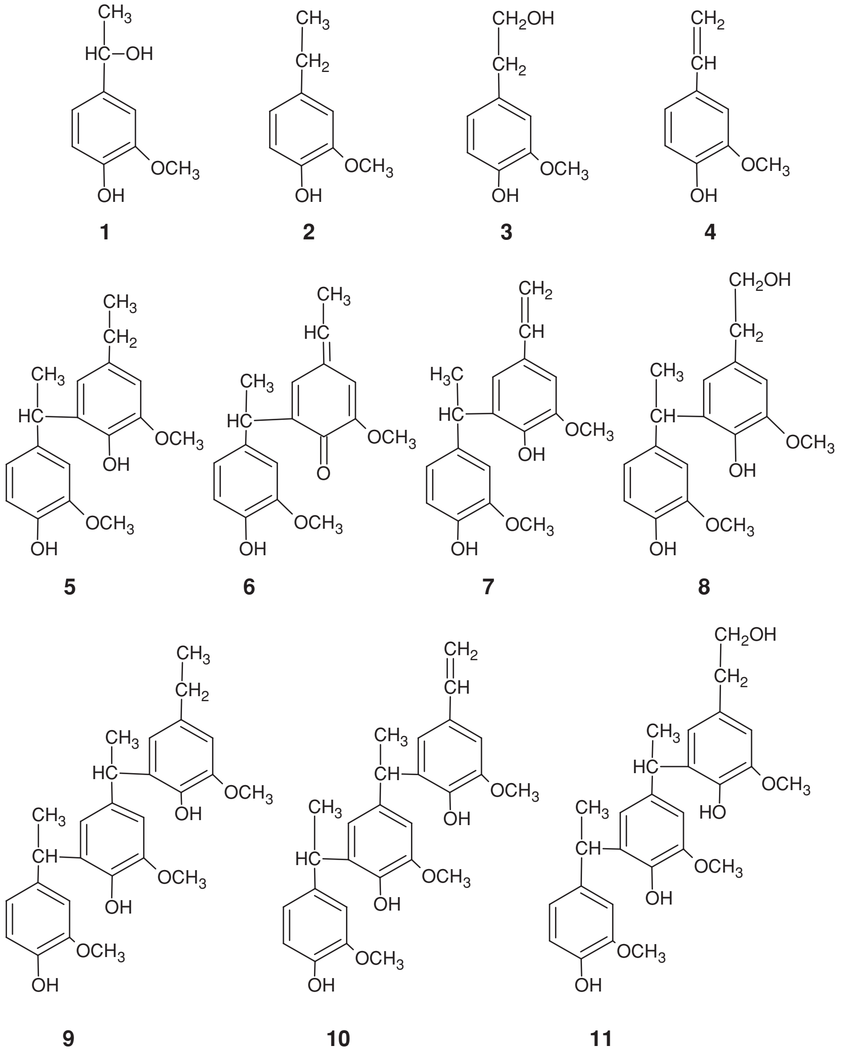

Figure 1. Lignin model compounds involved in this investigation.

GC, GC–MS, and MS Analyzes

The reaction products were analyzed on a HP 5890A gas chromatograph using a DB-17 or SE-30 column and with flame ionization detector. Either acetovanillone or homovanillyl alcohol (**3**) was used as the internal standard. A Hewlett Packard 5890 Series II GC fitted with a DB-5 column and interfaced with a Hewlett Packard 5989B mass spectrometer was used for GC–MS. Solid sample introduction MS was performed on a HP 5989B mass spectrometer operated at an electron impact energy of 70 eV and at the minimum temperature required for volatilization.

RESULTS AND DISCUSSION

Preliminary Results

When sugar maple chips were delignified by SAQ, the NaOH concentration decreased form an initial of ~ 1.0 M to ~ 0.5 M after the 90 min ramp time to165°C and to ~ 0.2 M after 2 h at that temperature. In the first experiment performed in duplicate, 0.5 g each of **1** and **2** were placed 60 ml of 0.4M NaOH along with 0.1 g/l of Na_2S added as O_2 scavenger. The mixtures were placed in a 165°C oil bath for 60 min (maximum temperature in the autoclaves was attained after ~ 5 min) then the autoclaves were removed and rapidly cooled. The products were acidified and extracted in dichloromethane (DCM). The reaction products were analyzed by GC–MS and solid sample introduction MS without derivatization. Two peaks were observed in the dimeric range when GC–MS analysis was performed using a DB5 column. The first peak eluted at ~ 25.0 min and its mass spectrum comprised of fragments with m/z: 302 (M^+ , 35), 287 (45), 178 (100), and 163 (76). The compound with this MS pattern is **5** in Figure 1. The MS is shown in Figure 2 and Pavlickova et al.[7] have

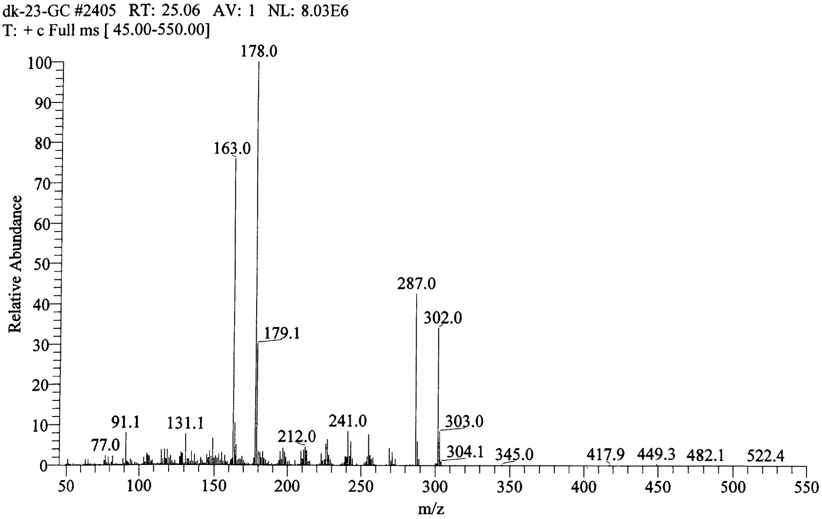

Figure 2. MS for a dimeric compound from GC-MS analysis of condensation products from **1** and **2**.

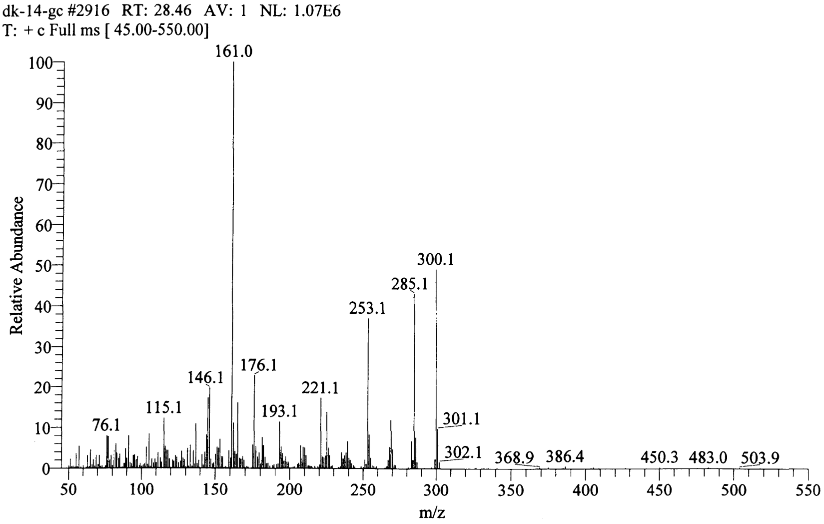

Figure 3. MS for second dimeric compound from GC-MS analysis of condensation products from **1** and **2**.

assigned fragments for all four of the major peaks. The second GC peak eluted at ~ 28.5 min and its mass spectrum comprised of fragments with m/z: 300 (M^+ , 50), 285 (46), 253 (40), 176 (24), and 161 (100). The m/z 300, 285, 176, and 161 fragments are all 2 m/z less than the corresponding fragments from **5**. This peak was assigned to **7** (Figure 1) and its MS is shown in Figure 3.

The solid sample introduction MS was dominated at m/z 300 & 302, 450 & 452, and 600 & 602 (Figure 4). The m/z 600 and 602 are the tetrameric analogs of m/z 300 & 302 while m/z 452 and 450 are **9** and **10** in Figure 1. Also when ethylguaiacol (EG; **2** in Figure 1) was replaced by homovanillyl alcohol (HVA; **3** in Figure 1), there was a corresponding increase of m/z 16 in the fragments with m/z of 302, 452, and 602 as compared to the MS spectrum involving ethylguaiacol (Figure 5). The reaction scheme in Figure 6 was proposed. A more detailed mechanism for the α -5 bond formation is given in Part 1 of this series (this issue).[1] The dimeric quinone methide or DQM (**6**) would result from condensation between two AP molecules. Pavlickova et al. interpreted their MS data and concluded that a DQM similar to **6** was generated when vanillyl alcohol was treated with hot alkali.[7]

The equilibrium (top left in Figure 6) between **6** and the phenolate of **7**[8,9] was of great interest because vinylguaiacol (VG; **4** in Figure 1) is actually generated in alkaline pulping of wood as one of the degradation products of coniferyl alcohol or CA.[8,10] The yield of CA is 4–5 times higher in SAQ or kraft/AQ black liquor as compared to kraft black liquor when softwoods are delignified.[8,11] The CA concentration is approximately 10 times higher when

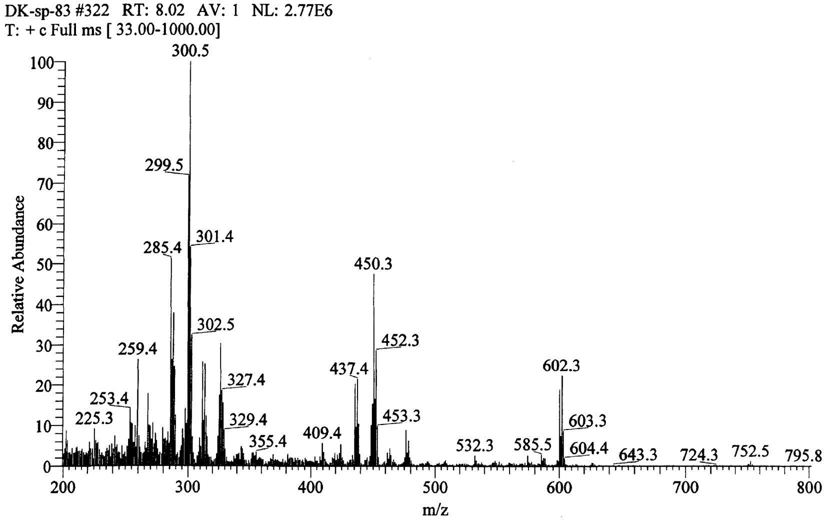

Figure 4. Solid sample introduction MS data for condensation products from **1** and **2**.

SAQ or kraft/AQ is compared to soda pulping.[8,10] Because the equilibrium between **6** and **7** is actually operative, the quinone-methide (QM) from **1** is a likely intermediate for the condensation reaction in kraft and SAQ pulping processes. The reaction scheme in Figure 6 suggests that **4** could condense

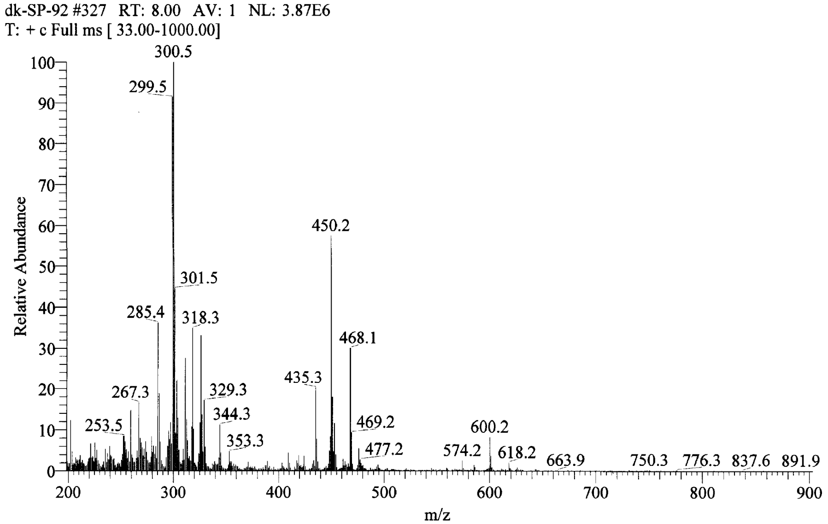

Figure 5. Solid sample introduction MS data for condensation products from **1** and **3**.

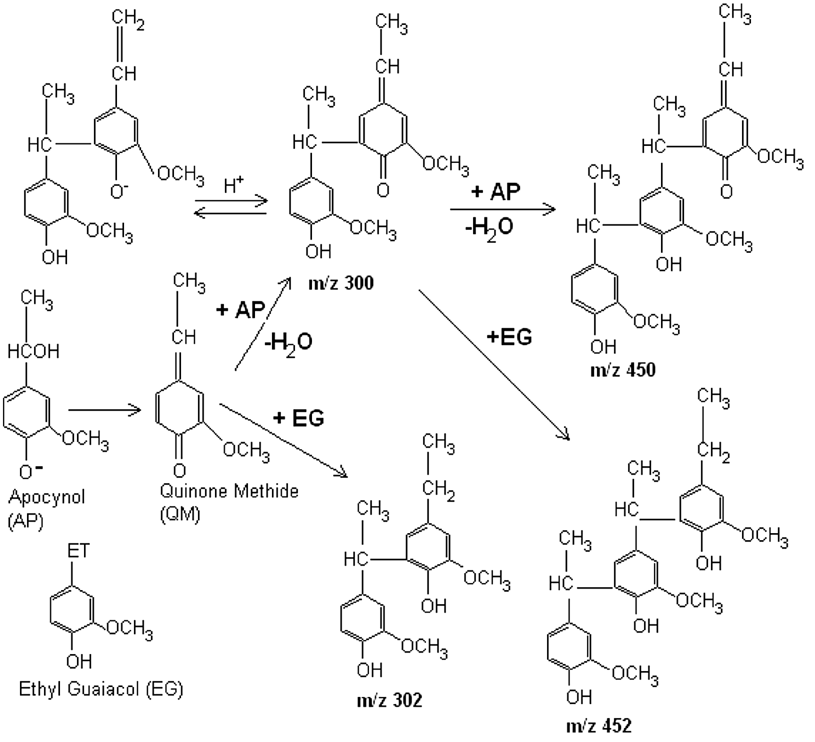

Figure 6. Reaction scheme proposed for alkaline condensation of **1** (AP) and **2** (EG).

with one lignin oligomer at the C-5 position and with another at the α -carbon position. If 4–5 times as much **4** is generated in SAQ as compared to kraft pulping then that may be an explanation for more condensed structures in SAQ pulps. To confirm that the equilibrium is actually operative **1** (AP) was replaced with **4** (VG) and identical dimeric products were obtained when condensation with EG was performed (Figure 7). The solid sample introduction MS data for condensation products were nearly identical when **4** (VG) was used instead of **1** (AP) in reaction with EG.

Effect of Sulfide and AHQ

Quantitative and semi-quantitative analyses of the condensation products were performed using 0.25 g each of **1** and **2**. Reaction products were identical to those in Figure 6 but it did appear that% molar yield (based on **1**) of **5–7** was ~ 20% lower than those when 0. 5 g each of these model compounds were used. The results suggest that the addition of a high concentration of sulfide or

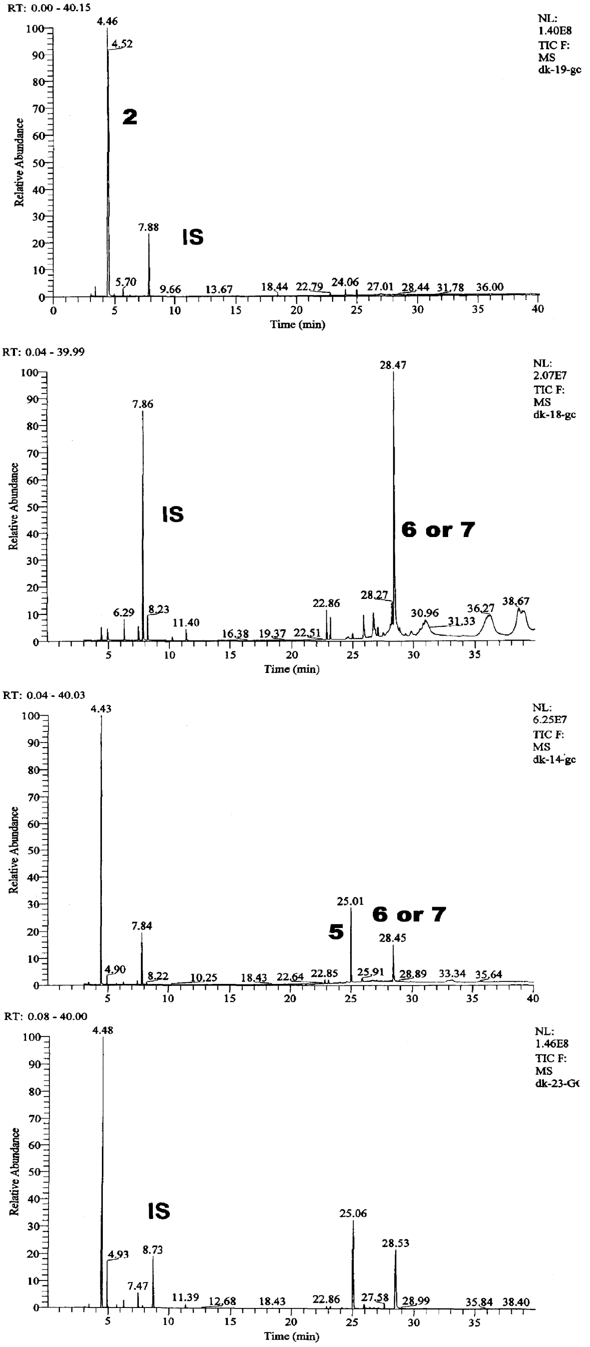

Figure 7. Chromatograms (GC/MS) for alkaline condensation of (top to bottom): EG only, AP only, AP + EG, and VG + AP.

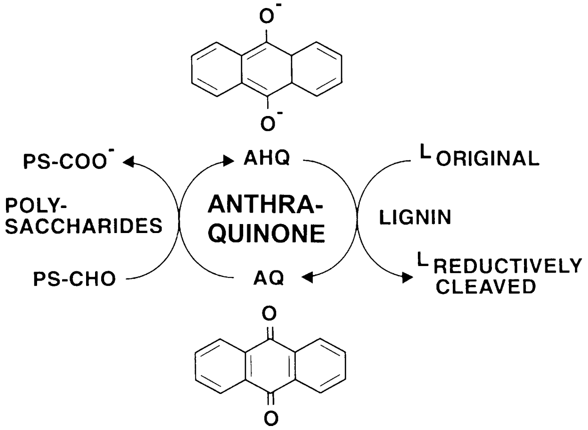

Figure 8. Redox cycle between AQ and AHQ.

anthrahydroquinone (AHQ; generated from AQ reduction by glucose) did not decrease the yield of condensed products. The redox cycle where AHQ adds to a QM and cause cleavage of the adjacent β-O-4 bond with the concurrent formation of AQ is shown in Figure 8. When 0.25 g each of **1** (1.49 mmoles) and **2** (1.64 mmoles) were used along with (1) 0.4 M NaOH + 0.1 g/l Na_2S (0.0013 M), (2) 0.32 M NaOH + 0.8 M Na_2S, and (3) 0.4 M NaOH + 0.225 g AQ + 0.3g D-glucose, the molar yield of **5** were 0.38 mmoles (dimeric basis), 0.37 mmoles, and 0.39 mmoles, respectively. The yield of **6** or **7** was fairly constant at 0.13 mmoles of dimer. One of the major tenets of our rationale for this research was that the typical concentration of S^{2-} /HS^- in kraft pulping was ~ 0.16 M (Na_2S application of 4.0% Na_2O; 4:1 L:W ratio) while the initial AQ concentration in SAQ was ~ 0.0012M (0.1% AQ, MW = 208). The maximum possible concentration of AHQ would be the initial AQ concentration. Therefore, there was a much higher sulfide concentration to interact with QM (Figure 6) and retard condensation reactions. It was observed that there was no difference in dimeric yields or no new products by GC–MS or solid sample introduction MS when low or high sulfide concentration or AQ/glucose was added to the solution of LMCs for the condensation reaction. Also, all the results for the reaction mixtures of the LMCs in 0.4 M NaOH solution without sulfide or AQ /glucose (straight alkali) or NaOH/AQ without glucose were nearly identical to those above. If sulfide anion reduces the rate of the condensation reaction as compared to AHQ, it probably does so by generating less intermediates like CA which are the major sources of secondary QM that would be involved in condensation reactions later in the cook.

A major difference between kraft and SAQ pulping appears to be products from the cleavage of β-O-4 bonds. In the kraft reaction mechanism, S^{2-} /HS^- adds to the QM, cleaves the adjacent β-O-4 bond, and form a thiirane structure

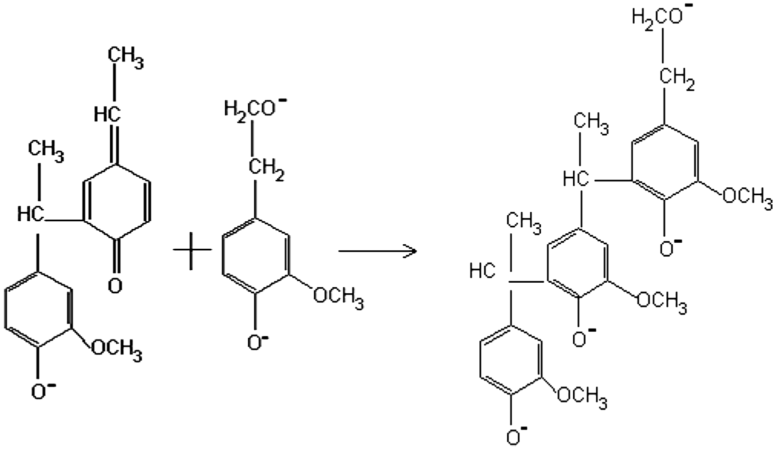

Figure 9. Condensation between charged species at higher alkalinity.

on the C_9 unit containing the original QM.[12] The thiirane is slowly hydrolyzed, forming several sulfur-free compounds, including a small amount of CA. In the SAQ mechanism, AHQ adds to the QM, the β-O-4 bond is cleaved with the simultaneous generation of AQ and a relatively high yield of CA.[12] The higher concentration of CA and its degradation products in the SAQ process cause a higher rate of condensation in the late stages of cooking.

Effect of Alkalinity

The effect of alkalinity on the rate of condensation was investigated with **2** being replaces by **3**. The LMCs **1** and **3** were treated with 0.6 M and 0.1 M NaOH solutions in duplicate. The assumption was that the reaction in Figure 9 would occur more slowly at the higher alkalinity due to more repulsion of the anions. When 0.25 g of **1** and **3** (each 1.49 mmol) were allowed to react in the 0.1 M and 0.6 M NaOH solutions, the yields of condensed products **8** were 0.27 mmoles for the former and 0.21 mmoles for the latter, respectively. The yield of **7** was 0.25 mmoles in both the 0.1 M and 0.6 M NaOH solutions. In the solid sample introduction MS analysis, the ratio of total ion count for m/z 468 (**11** in Figure 1) to m/z 300 (**7** in Figure 1) was 0.058 and 0.065 for 0.1 M NaOH and 0.042 and 0.046 for 0.6 M NaOH. The reaction in Figure 9 occurred to a greater extent in the 0.1M NaOH solution and it can be interpreted that less dissociation of the terminal CH_2OH group and less repulsion of the two reactants occurred at the lower alkalinity. The results of these condensation reactions of LMCs are consistent with our belief that lignin condensation occurs under low alkalinity conditions during the later stages of SAQ pulping

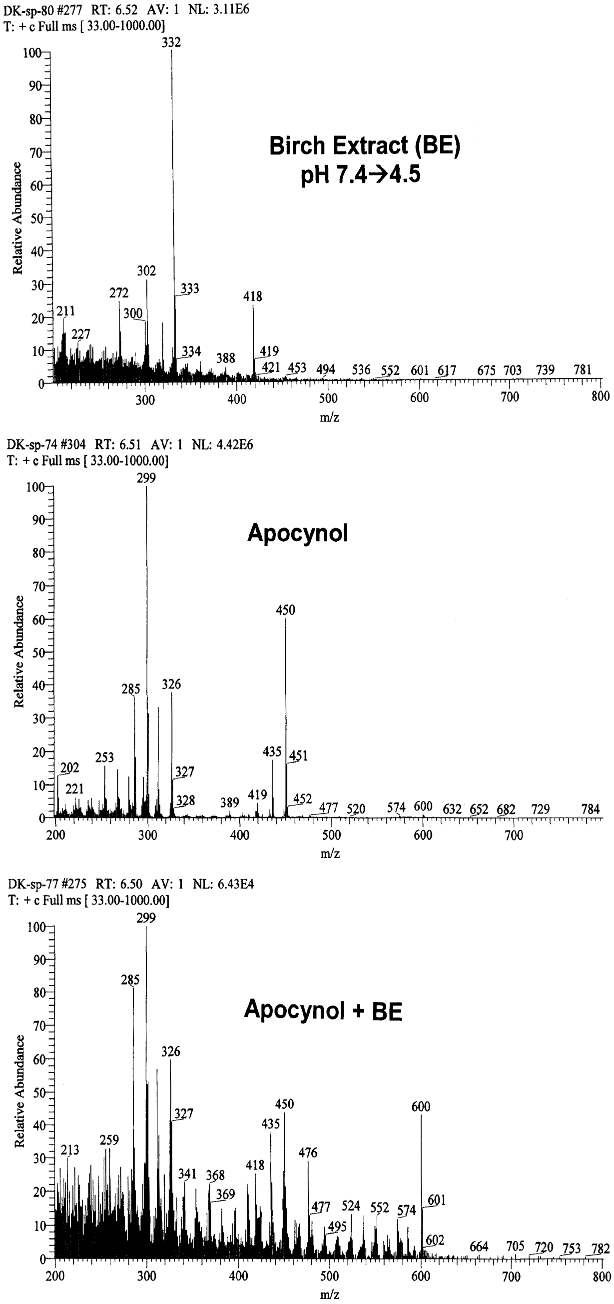

Figure 10. Solid sample introduction MS of alkaline condensation products from birch extract, apocynol, and a combination of the two.

and is harmful to bleachability. In Part 1 of the series (this issue) we showed that one strategy for improved bleachability is increasing the alkalinity and/or shortening the SAQ cooking time.[1]

Can Acid or Near-Neutral Pre-Extraction of Chips Retard Condensation during SAQ Cooking?

One of the significant new discoveries related to SAQ pulping is that a mild acid pre-extraction of the chips ($\sim$ 3% mass removal)[3,13] or a moderate near-neutral pre-extraction ($\sim$ 10% mass removal)[14] can both decrease the SAQ cooking time and improve bleachability. When chips are given such a pretreatment the free liquor is normally drained off and fresh cooking liquor added. The most straight-forward interpretation as to how the pretreatment could retard subsequent condensation reactions would be that the pretreatment effluent contains dissolved material that if not removed would have participated in condensation reactions under alkaline conditions. To investigate this possibility, we performed a hot water extraction on loblolly pine (*Pinus Taeda*) chips (60 min to 160°C, 60 min at 160°C, 4:1 L:W, end pH 3.4), collected the effluent and evaporated it to dryness. Approximately 50% of the lignin was removed from the dry extract by refluxing it in DCM. When this extract with a lignin content of $\sim$ 6 wt% was added along with AP (**1**) and alkaline condensation reactions were allowed to occur, many new peaks were observed in the solid sample introduction MS of the condensation products that were not products for the alkaline treatment of AP alone or extract alone. The experiment was repeated using paper birch (*Betula pepyrifera*). The same extraction conditions (end pH 3.2) and DCM reflux were used. The extraction of birch with 0.05 M sodium acetate was then performed using the same temperature profile (pH 7.4 to 4.5). The amounts of extracted materials removed from pine and birch chips by acidic extraction were $\sim$ 15% and $\sim$ 20%, respectively while $\sim$ 12% was removed from birch by the near neutral extraction. The near neutral birch effluent was added directly to alkaline AP ($\sim$ 0.3 g of dissolved solid and 0.25 g of AP), and condensation reaction was allowed to occur, and again in the solid sample introduction MS, new peaks were observed. The MS results are shown in Figure 10 and it was concluded that there new peaks at m/z 341, 356, 368, 382, 396, and 524. This is base total ion counts for these fragments, which were high only in the case of AP + birch effluent but not AP or birch effluent alone. It appears that condensation precursors were removed from the wood chips by pre-extraction stages carried out in the pH range of 3.0–7.4.

CONCLUSIONS

Four commercially available lignin model compounds (LMCs) were used to investigate alkaline lignin condensation reactions. Condensation between carbohydrate-rich wood extract and the QM from apocynol was also investigated. The results provide an explanation for the observation in Part 1 of this series (this issue)[1] that there is a higher rate of condensation reactions in SAQ as compared to kraft pulping. The rate of formation of coniferyl alcohol is reported to be 4–5 times higher during SAQ as compared to kraft pulping[8,11] and vinylguaicol (VG) has been identified as one of the degradation products of CA.[8,10] In the kraft reaction mechanism, S^{2-} /HS^{-} adds to the QM, cleaves the adjacent β-O-4 bond, and form a thiirane structure on the C_9 unit containing the original QM.[12] The thiirane is slowly hydrolyzed, forming several sulfur-free compounds, including a small amount of CA. In the SAQ mechanism, AHQ adds to the QM, the β-O-4 bond is cleaved with the simultaneous generation of AQ and a relatively high yield of CA.[12] It was shown that VG condenses with other monomers at both its C-5 and α -C positions to generate trimers. If it is assumed that there are more CA degradation products in SAQ pulping then one would expect a higher rate of condensation. Condensation experiments involving apocynol and homovanillyl alcohol demonstrated that $\sim$ 50% more trimers were obtained at an initial NaOH concentration of 0.1 M as compared to 0.6 M. A plausible reaction scheme is included to explain the result.

Hot water and sodium acetate solutions were used to extract 12–20% of the extracted materials from pine and birch chips. The dissolved solids in these extracts participated in condensation reactions with apocynol. It can be deduced that if chips are given a hot water or near-neutral pre-extraction and 75% of extract is discarded then less condensation reactions would be expected to occur during subsequent SAQ pulping. This phenomenon may be a partial explanation as to why these pre-extractions accelerate subsequent SAQ pulping and improve bleachability.

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