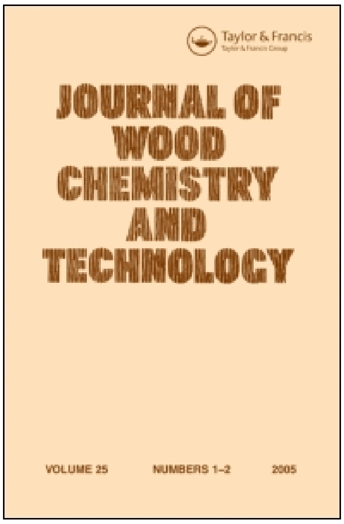

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COMPETING REACTIONS AFFECTING DELIGNIFICATION IN PULPING SYSTEMS

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ABSTRACT

Reactions of 1-(4-guaiacyl)-2-(*O*-guaiacyl)-1,5-pentanediol (**1**) provide information on the relative rates of pulping reactions that involve quinone methides (QM). The lignin model was treated with 2,6-xylenol, 1,5-anhydrocellobiitol, amylose, and amines; the levels of fragmentation and cyclization were determined. The results indicate that condensation reactions between the QM derived from **1** and phenolates or carbohydrates are much slower than fragmentation reactions of **1** with sulfide or anthrahydroquinone. The addition of amines to soda cooks of **1** provided little additional model fragmentation; instead, a vinyl ether was observed in substantial amounts.

INTRODUCTION

The reactions of 1-(4-guaiacyl)-2-(*O*-guaiacyl)-1,5-pentanediol (**1**) can be used to determine the relative delignification efficiencies of various pulping additives and combination of additives.[1,2] Here we report the reactions of model **1** with phenols, carbohydrates, and amines. The former two were examined because they are present in pulping liquors and their reactions with lignin quinone methide (QM) intermediates can lead to residual lignin products: phenol-lignin condensation and lignin-carbohy-

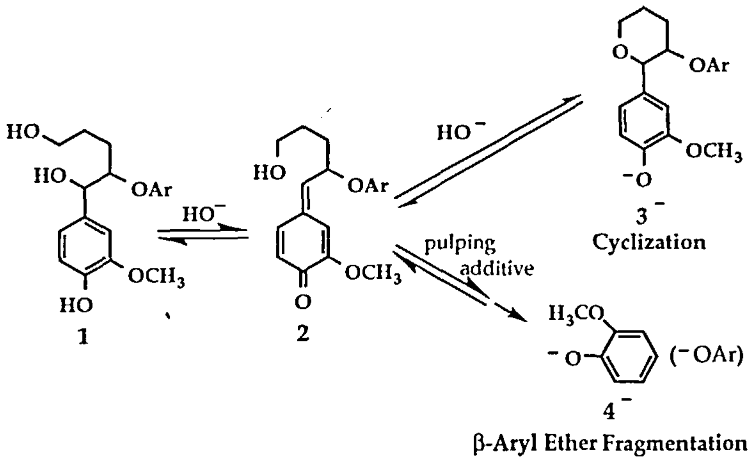


Figure 1. Competing parallel reactions for QM **2**: cyclization and fragmentation of model **1**.[1,2]

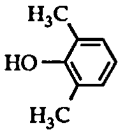
drate complex (LCC) products, respectively.[3,4] Amines were investigated because they have been reported to enhance delignification and produce strong pulps;[5] we wanted to rank their ability to fragment lignin with that of other pulping additives.

The rate of initial phase delignification is dominated by quinone methide formation.[2,6] The rates of subsequent steps are difficult to determine; yet, the rates of these steps are critical to the partitioning of QMs for productive β-aryl ether cleavage as opposed to undesirable reactions (i.e., vinyl ether formation and condensation reactions).[3] Relative QM reaction rates can be determined by analyzing the products from reactions of model **1**.[1,2] This model provides QM **2** when heated in alkali. The intermediate **2** cyclizes at a specific rate; other reactions, such as fragmentation to afford guaiacol (**4**), can be timed relative to the rate of cyclization (Fig. 1).[1,2] If the reaction of **2** is slow relative to cyclization, then only cyclized product **3** will be observed. If a specific reaction of **2** has a rate comparable to that of cyclization, you will see less cyclized product and (possibly, if stable) a new product or fragments.

RESULTS

Reactions of Model 1 with Phenols and Carbohydrates

The phenol selected for reaction with model **1** was 2,6-xylenol (**5**). This phenol has been studied by others and is generally considered to be a highly reactive phenol in alkaline systems.[7] The anticipated product from a condensation reaction[3,7] of **5** with QM **2** would be **6**.



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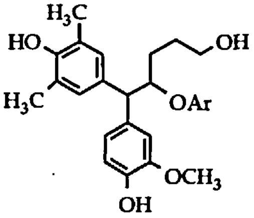

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Heating model **1** at 150°C with 5 equiv. of 2,6-xylenol and 25 equiv. of NaOH over a 90-min. period led to similar levels of cyclization as a soda control (Fig. 2). Disappearance of model **1** was somewhat slower than the control. We did not observe any condensation products, such as **6**. Guaiacol production was not quantified during 2,6-xylenol runs since 2,6-xylenol eluted at approximately the same time as guaiacol. Most of the material (≥ 85%) was accounted for as either **1** or cyclized product **3**; a similar balance (≥ 87%) was seen with the soda cooks.[2a,2d]

An analogous study was done with 1,5-anhydrocellobiitol (**7**) and amylose (**8**). These carbohydrates were selected because they are water soluble and cover a broad range of structure: a disaccharide that is relatively stable in alkali[8] and a polymer with a reactive (reducing) end group.[9] Ionized hydroxyl groups on compounds **7** or **8** could act as nucleophiles and attack QM **2** to form an LCC.

Experiments were performed with 25 equiv. of NaOH and 5 equiv. of carbohydrate model **7** or 0.2 equiv. of amylose (molecular weight of ~4068 = ~5 equiv. of glucose monomer). Cooks of model **1** with both carbohydrate models showed a dominance of cyclized product **3**; the amount of

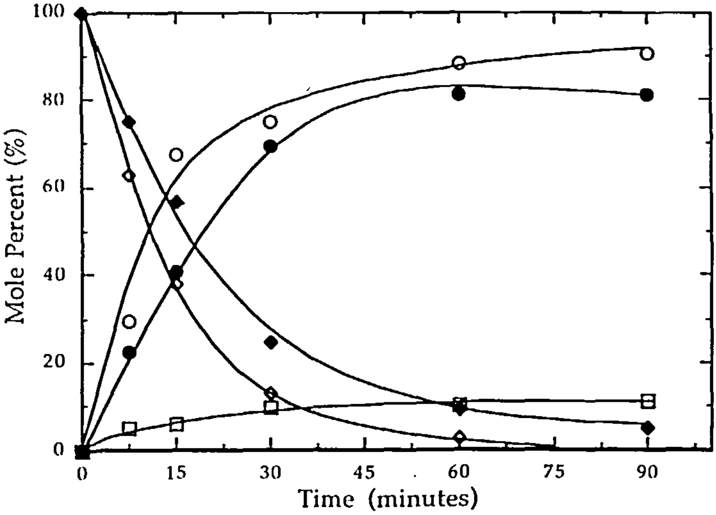
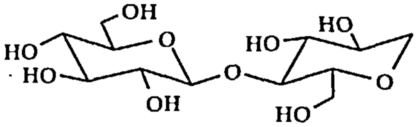


Figure 2. Yields of guaiacol 4 (□) and cyclized cpd. 3 (○;●) for 2,6-xylenol 5 (●;◆) and soda (□;○;◇) degradations of model 1 (◇;◆) at 150°C.



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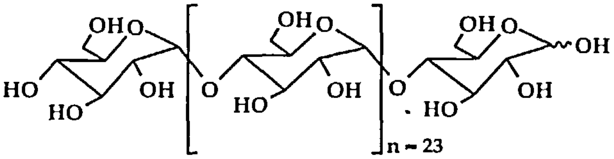

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fragmentation was low and similar to the soda control (Figs. 3 and 4). Model 1 disappeared somewhat slower than the soda control for both carbohydrate cooks. Condensation products between model 1 and the carbohydrate models were not observed; however, the lower material balance with amylose suggests the occurrence of side reactions.

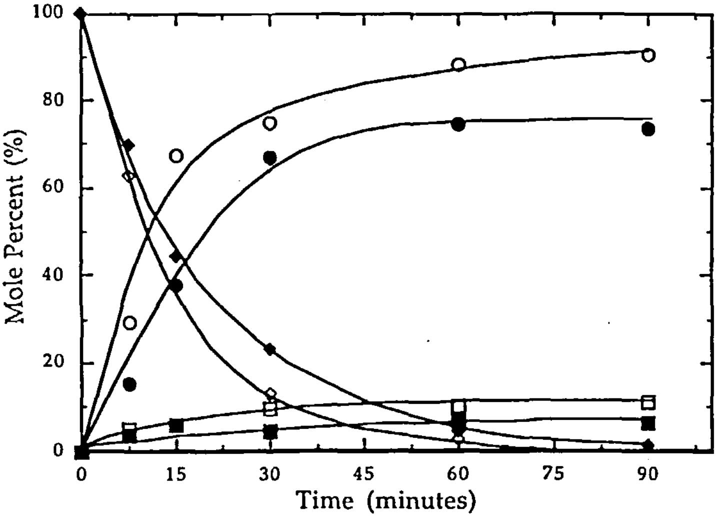


Figure 3. Yields of guaiacol 4 (□;■) and cyclized cpd. 3 (○;●) for 1,5-anhydrocellobiitol 7 (■;●;◆) and soda (□;○;◇) degradations of model 1 (◇;◆) at 150°C.

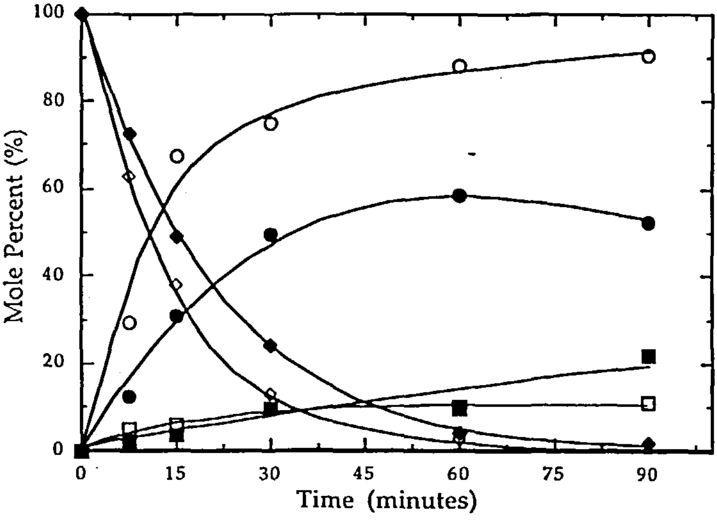


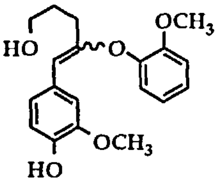
Figure 4. Yields of guaiacol 4 (□;■) and cyclized cpd. 3 (○;●) for amylose 8 (■;●;◆) and soda (□;○;◇) degradations of model 1 (◇;◆) at 150°C.

Reactions of Model 1 with Soda/Amines

The product composition from reacting various amines with model 1 for 1 hour are given in Table 1. Only small amounts of β-aryl ether fragmentation were observed in the soda/amine runs. The two predominate products formed were cyclized product 3 and vinyl ether 9.

Table 1. Yield comparisons for soda[2a] and various soda/amine cooks with model 1, all with 25 equiv. of NaOH at 150°C.

Additive	% Yield after 60 min. at 150°C			
(5 equiv.)	Model 1	Guaiacol (4)	Cpd. 9	Cyc. Cpd. 3
Soda (Control)	3	10	≤ 10	88
Ethyl Amine	3	20	46	40
Diethyl Amine	2	15	32	43
Diisopropyl Amine	2	14	27	62
Ethanol Amine	2	21	47	47
Diethanol Amine	1	19	47	47
Ethylene Diamine	2	17	38	56



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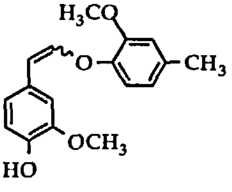

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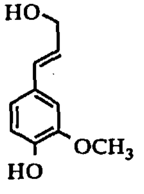

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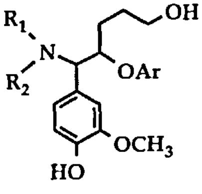

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The vinyl ether 9 (a mixture of cis/trans isomers) could not be isolated and characterized as pure compounds; however, several pieces of evidence pointed to the presence of 9 in the soda and soda/amine cooks of 1. First, there is considerable literature precedence to expect vinyl ether products.[7,10-14] They can be generated by Cβ-proton abstraction by base from the intermediate QM 2; enolization reactions of this type are commonly observed when lignin models are heated with NaOH.[7,10,11] Vinyl ethers have been shown to be the predominate product when β-aryl models were subjected to alkaline amine treatments.[12-14]

Our LC method of analysis employed a full wavelength UV detector; thus, UV spectra for the eluting components were obtained. The two signals assigned to cis/trans vinyl ether **9** had UV spectra and LC retention times very similar to vinyl ether **10**[11] and coniferyl alcohol **11**, two other styrene structures that we analyzed. [Compounds **9-11** all have strong absorbance peaks at 280 and 310 nm which are indicative of a C_α-C_β double bond conjugated with the aromatic ring.[15]] The LC signal was not considered to be related to coniferyl alcohol; such structures are typically very reactive and are not observed in measurable quantities for kraft or for soda/AHQ cooks of lignin dimers[6b,16] or model **1**.[2a,2d]

Cis/trans vinyl ether **9** was synthesized by treating **1** with 0.1 M $NaOCH_3$ in CH_3OH at 150°C for 4 hrs; similar conditions have been employed to prepare other vinyl ethers.[11] The cis/trans vinyl ethers formed had identical elution times and UV spectra as the LC signals detected during the soda/amine cooks. Along with **9**, the $NaOCH_3$ reactions also produced substantial quantities of cyclized compound **3** and an unknown component suspected to be an α-OCH_3 adduct[11] of **1**. When the product mixture was hydrogenated, the LC signal for **9** disappeared and a new signal appeared with a slightly shorter retention time than **9**. The UV spectrum of the new signal was similar to **1** (without the strong absorbance peaks at 280 and 310 nm), indicating a saturated side chain.[16]

DISCUSSION

The disappearance rate of **1** for 2,6-xylenol (**5**), 1,5-anhydrocellobiitol (**7**), and amylose (**8**) cooks was marginally slower than soda (control) cooks. All the cooks initially started with 25 equiv. of NaOH; the xylenol and carbohydrates consumed some of the available alkali during the cooks.[17] The lower alkali levels may have slowed the disappearance rate of model **1** and the formation of QM **2** when compared to the control.

The reaction of model **1** with 2,6-xylenol produced high amounts of cyclization, no observable condensed products, and a good material balance. The data indicate that condensation reactions did not occur. Our results agree with previous studies. Gierer and Ljunggren report that 2,6-xylenol reacts quantitatively with simple β-aryl ether models to form a condensation product (similar to 6) in the presence of NaOH; however, the rate of 2,6-xylenol condensation was ~13 times less than sulfide-induced fragmentation the model.[7] Assuming a similar reactivity difference exists for compound 1 and knowing that rates of sulfide-induced fragmentation and cyclization of 1 are similar,[2a] it is logical that condensation reactions of 1 with 2,6-xylenol would not be competitive with cyclization.

The expected carbohydrates reactions with model 1 were twofold: bond formation to C_α of QM 2 to give an LCC[4] and, in the case of amylose (a reducing sugar), possibly enhanced fragmentation.[18,19] It is impossible to rule out LCC formation, since we do not know how such products would respond to the LC analysis and there is some unaccountable material. However, based on the high levels of 3 observed, we can conclude that carbohydrate condensation reactions were not prominent. The condensation rate must be notably slower than cyclization.

The addition of amylose to a soda cook did not enhance β-aryl ether cleavage of model 1 versus cyclization. This result agrees with our previous finding that glucose addition to a model 1 soda cook did not increase fragmentation.[1] Reactive amylose degradation products, such as enediols, are labile in hot alkali.[19,20] Their concentration during the cook of model 1 was probably too low to compete with the cyclization.

Amine additions to soda cooks of 1 did not improve the amount of β-aryl ether cleavage. Instead, model 1 was efficiently converted to cyclized compound 3 and vinyl ether 9. The vinyl ether formation must be a relatively fast reaction in the amine case, since it competes favorably with cyclization. In contrast, vinyl ether 9 was produced in very minor amounts in a soda treatment of 1 and was not detected with good delignification systems, such as soda/AHQ, kraft, and alkaline sulfite.[2] In these cases, the vinyl ether is mostly likely formed by C_β-proton abstraction by NaOH -- a reaction that is relatively slow compared to cyclization or scission. The amines obviously produce vinyl ethers in a different way.

Amines are known to add to QMs and form adducts (similar to 12);[12,21] however, we did not observe adducts. Low levels of adducts were observed at 170°C during Obst's soda/amine study with lignin models.[12] Obst noted that amine adducts (synthesized by reactioning QMs and amines at 40°C) were unstable when subjected to alkali at 170°C.[12] The enhanced amounts of vinyl ether products observed here and by others when using amines may be related to elimination reactions of the adducts.

Based on our results, the accelerated delignification rates by amines, in comparison to kraft,[5] are not due to enhanced fragmentation of QMs. Other explanations have been offered: enhanced fragmentation of non-phenolic structures[14] and changes in cooking liquor redox potentials.[22] Amines are not too efficient; most soda/amine pulping processes use ~40% (o.d. wood) concentration of amine,[5] compared to ~7 % sulfide for kraft.[17]

CONCLUSIONS

The reactions of model **1** confirm that condensation reactions of quinone methides with carbohydrates and phenols are much slower than fragmentation reactions by efficient pulping reagents, such as AHQ and sulfide. The addition of amines to soda cooks of model **1** did not promote β-aryl ether fragmentation; instead, the amines provided substantial quantities of vinyl ether products. The rate of this latter reaction is comparable to the rapid cyclization reaction that is characteristic of model **1**.

EXPERIMENTAL

The equipment, model reagent amounts, model **1** degradation procedure, product analysis by reverse phase liquid chromatography, and the characterization of **1**, **3**, and **4** have been previously described.[1,2,23] All pulping reactions used 0.015 mmoles (= 1 equiv.) of **1** and 25 equiv. of NaOH and 5 equiv. of pulping additive(s), except were noted. The synthesis and characterization of vinyl ether **9** is described below.

5-(3-Methoxy-4-hydroxyphenyl)-4-(2-methoxyphenoxy)-4-penten-1-ol (9)

To five 4.5 mL pressure vessels (bombs) was added 1 mL of a 0.015 M solution of model **1**[23] dissolved in 1 M $NaOCH_3/CH_3OH$. An additional 2.5 mL of 1 M $NaOCH_3$ solution was added to each bomb. The bombs were sealed, agitated in a 150°C fluidized sand bath for 4 hr, removed, quenched in ice water and emptied. The combined solutions were acidified

Our LC method of analysis employed a full wavelength UV detector; thus, UV spectra for the eluting components were obtained. The two signals assigned to cis/trans vinyl ether **9** had UV spectra and LC retention times very similar to vinyl ether **10**[11] and coniferyl alcohol **11**, two other styrene structures that we analyzed. [Compounds **9-11** all have strong absorbance peaks at 280 and 310 nm which are indicative of a C_α-C_β double bond conjugated with the aromatic ring.[15]] The LC signal was not considered to be related to coniferyl alcohol; such structures are typically very reactive and are not observed in measurable quantities for kraft or soda/AHQ cooks of lignin dimers[6b,16] or model **1**.[2a,2d]

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General Analytical Procedures

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2.5 mL of 1 M $NaOCH_3$ solution was added to each bomb. The bombs were sealed, agitated in a 150°C fluidized sand bath for 4 hr, removed, quenched in ice water and emptied. The combined solutions were acidified to pH 5 and analyzed by reversed phase liquid chromatography (LC).[2a,2d] Vinyl ether **9** was a mixture of cis and trans isomers which had retention times of 3.8 and 4.1 min. The crude product mixture consisted of ~45% vinyl ether **9**, ~30% of cyclized compound **3**, and 25% of an unknown compound suspected to be the α-OCH_3 adduct of **1** based on previous vinyl ether synthesis with 1 M $NaOCH_3$[12] (retention time of 2.4 min.). The combined solutions were evaporated to yield light brown crystals.

Several unsuccessful attempts were made to separate **9** from the crude product mixture using column chromatography and elution with CH_2Cl_2/ CH_3CH_2OH and hexane/CH_2Cl_2. Roughly 10 mg of the crude product mixture was dissolved in 20 mL of 0.3 M NaOH; the resulting solution was subjected to low-pressure catalytic hydrogenation. The solution was analyzed before and after hydrogenation by LC (33% (v/v) aq. CH_3OH flowing at 0.450 mL/min). The hydrogenated sample showed no vinyl ether **9** (ret. time 4.1 min.) but, instead, a new LC signal at 3.6 min. having a UV spectrum similar to compound **1**, indicative of a saturated side chain. Since pure samples of compound **9** were unavailable, we used a response factor of 1.0 to the internal standard [β-(O-guaiacyl)-α-(4-guaiacyl) ethanol][2a,2d] during product analyses of various model **1** reactions.

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