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Fundamental Study of Relative Delignification Efficiencies (II): Effects of Phenols,
Carbohydrates, Amines and Reagent Combinations During Pulping

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FUNDAMENTAL STUDY OF RELATIVE DELIGNIFICATION EFFICIENCIES (II): EFFECTS OF PHENOLS, CARBOHYDRATES, AMINES AND REAGENT COMBINATIONS DURING PULPING

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ABSTRACT

Reactions of a β -aryl ether lignin model compound (1) provide information on the relative rates of pulping reactions that involve quinone methides (QM). The lignin model was reacted with 2,6-xylenol, 1,5-anhydrocellobiitol, amylose, reagent combinations, and amines. The results indicate that condensation reactions between QMs and phenolates or carbohydrates are much slower than fragmentation reactions with sulfide and anthrahydroquinone (AHQ). A sulfide/sulfite combination did not enhance β -aryl ether fragmentation; however, a sulfide/AHQ combination increased fragmentation synergistically. The addition of amines to soda cooks substantially increased the conversion of model 1 to a vinyl ether (9).

INTRODUCTION

Research efforts have intensified over the past several years to find alternatives and to make improvements to kraft pulping. There are primarily two factors driving this research: (a) to improve the selectivity of chemical pulping, and (b) to find more environmentally benign processes. Today, increased emphasis is being placed on selectively

extended delignification during pulping in order to reduce bleaching discharges.¹

Some modified kraft pulping systems, such as Super-BatchTM and RDHTM (rapid displacement heating), utilize black liquor during the initial heating and cooking stages to improve delignification uniformities.² Black liquor contains dissolved lignin and carbohydrate fragments that may affect β -aryl ether cleavage, an important delignification reaction. Dissolved organic fragments could undergo condensation reactions with lignin and form new linkages (i.e., C α -C γ ,³ and lignin-carbohydrate complex (LCC)⁴); such reactions inhibit delignification. These fragments could also increase delignification rates; Fullerton and co-workers have shown that reducing sugars can enhance alkaline β -aryl ether fragmentation of simple lignin models.⁵

Other modified pulping systems have used combinations of pulping reagents, including kraft/anthraquinone (AQ),⁶ kraft/polysulfide,⁷ kraft/polysulfide/AQ,⁸ and alkaline sulfite/AQ (ASAQ).^{9,10} The combination of alkaline sulfite and AQ has a synergistic effect; more β -aryl ether fragmentation is observed with the combination than either reagent can do separately.^{10,11} Several studies have investigated the accelerated delignification rates associated with the addition of amines to soda pulping processes.^{12,13} Soda/amine processes produce pulps that are stronger than kraft pulps at similar kappa numbers.¹³

Modified pulping processes still have a common feature with conventional kraft and soda/AQ pulping: the first step in delignification is dominated by quinone methide (QM) formation. The rates of subsequent steps are difficult to determine; however, 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 We sought to better understand what modifications to pulping may affect delignification efficiencies.

The study described herein examines the influence of dissolved organics (phenols and carbohydrates), combinations of reagents (sulfide/sulfite and sulfide/AQ), and various amines on the fragmentation/cyclization of model **1** (Fig. 1). The previous paper outlined the various

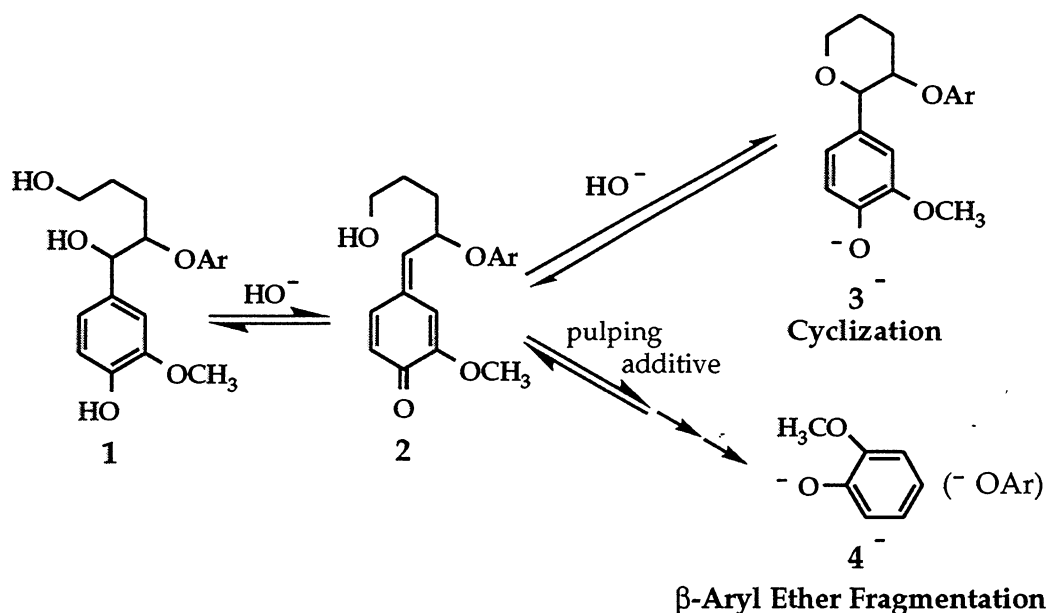


Figure 1. Competing parallel reactions for QM 2: cyclization and fragmentation of model 1.¹⁰

reactions of **1** and how QM reactions could be timed relative to cyclization of **1** to **3**.^{10,14} For the cases involving AQ, the AQ is reduced *in situ* to anthrahydroquinone (AHQ), the lignin active reagent in the AQ/AHQ redox pair.¹⁵

RESULTS

Reactions of Model 1 with Phenols and Carbohydrates

Phenolate ions can condense with QMs to give α -aryl substituted products.^{3,16} We wondered whether alkaline condensation reactions of this type would be faster or slower than cyclization of model **1**. If faster, less cyclized product would be observed and a new product would appear. If slower, the amount of cyclization would be the same as a soda control. The phenol selected for study was 2,6-xylenol (**5**), a generally reactive phenol, which has been studied by others;¹⁶ the anticipated condensation reaction is shown in Figure 2.

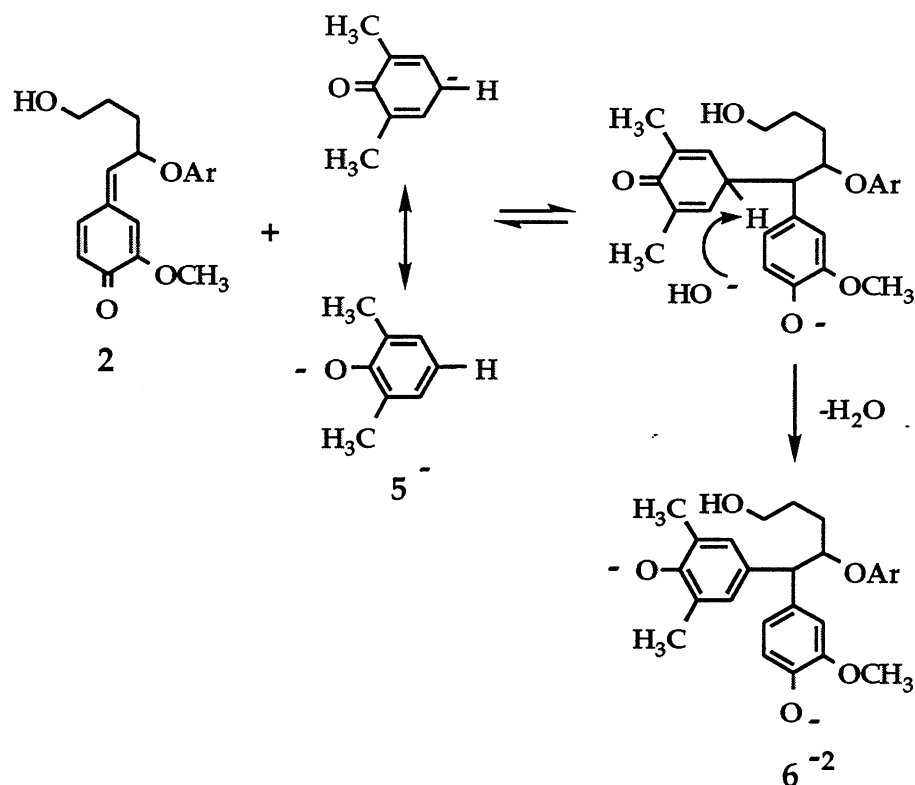


Figure 2. Possible condensation reaction of 2,6-xyleneol with model 1.

Heating model 1 at 150°C with 5 equiv. of 2,6-xyleneol in the presence of 25 equiv. of NaOH over a 90-min. period led to similar levels of cyclization as a soda control (Fig. 3). Disappearance of model 1 was somewhat slower than the control. We did not observe any condensation products, such as 6⁻². Guaiacol production was not quantified during 2,6-xyleneol runs since 2,6-xyleneol eluded at approximately the same time as guaiacol. Most of the material ($\geq 85\%$) was accounted for as either 1 or cyclized product 3; a similar balance ($\geq 87\%$) was seen with the soda cooks.¹⁰

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 alkali¹⁷ and a polymer with a reactive (reducing) end group.¹⁸ Ionized hydroxyl groups on compounds 7 or 8 could act as nucleophiles and attack QM 2 to form a "LCC."

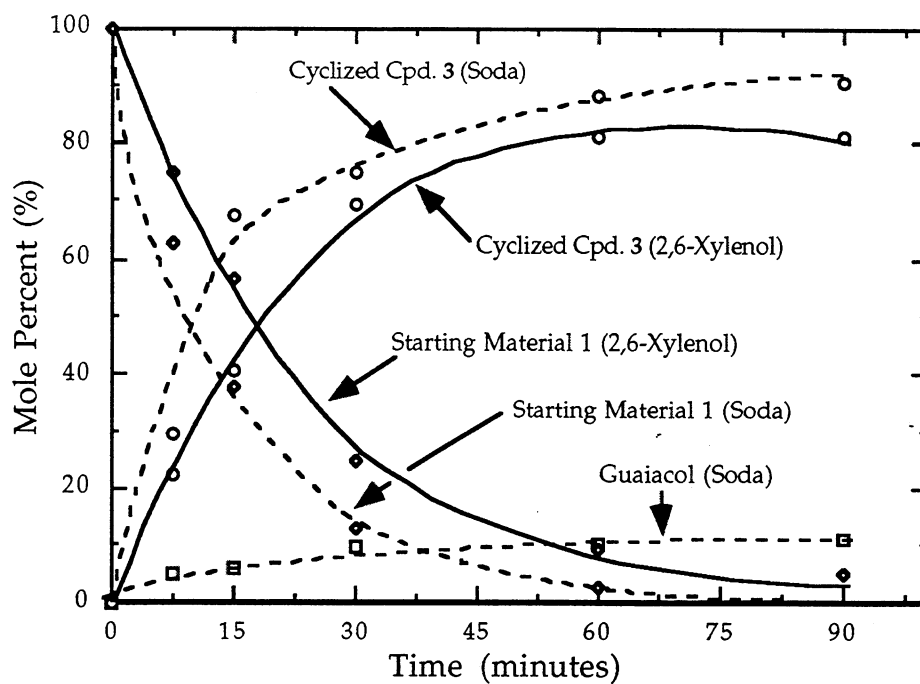


Figure 3. Yields of guaiacol 4 and cyclized cpd. 3 for 2,6-xylenol 5 (—) and soda (----) degradations of model cpd. 1 at 150°C.

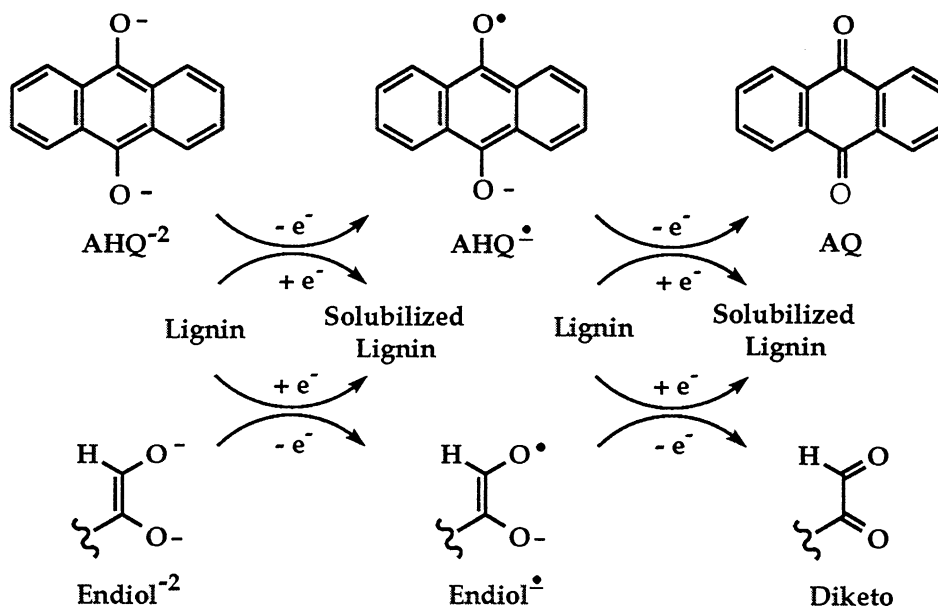
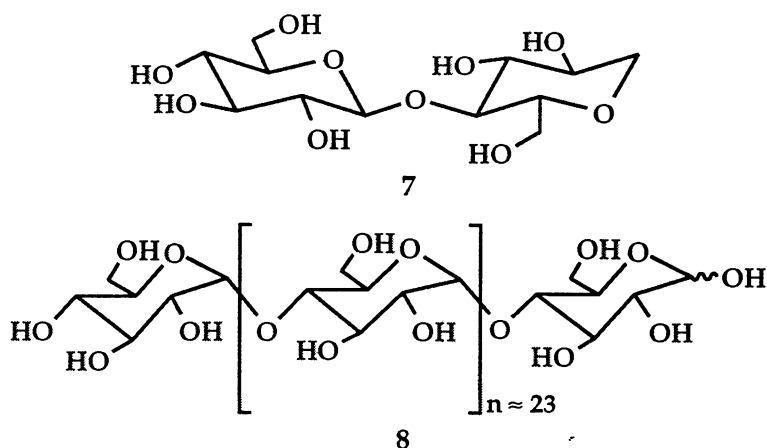


Figure 4. Possible fragmentation of lignin by the tautomerized forms of AQ and an aldose.¹⁵



Amylose degradation products might form adducts⁵ or electron transfer¹⁵ to a QM, either of which could lead to fragmentation (Fig. 4). Experiments were performed with 25 equiv. of NaOH and 5 equiv. of a carbohydrate model. [Amylose had an approximate molecular weight of 4068; 0.2 equiv. of **8** would produce roughly 5 equiv. of glucose if it completely degraded.]

Cooks of model **1** with both carbohydrate models showed similar levels of cyclized product **3** as the soda control (Figs. 5 and 6). Model **1** disappearance was somewhat slower for both carbohydrate cooks than the soda control. Slightly higher levels of guaiacol were observed with amylose runs after 60 min.; however, the enhanced fragmentation of model dimers by reducing sugars, as seen by other,^{5,19} apparently was superseded in our case by the fast cyclization reaction. We did not observe any condensation products between model **1** and the two carbohydrate models.

Reactions of Model **1** with Kraft/Sulfite and Kraft/AHQ

Previous work with model **1** showed that sulfite/AHQ mixtures synergistically enhanced β -aryl ether cleavage;¹⁰ however, it is not known if sulfide (kraft)/sulfite combinations would behave similarly. Experiments were conducted to examine the possible enhancement of β -aryl ether cleavage with sulfide/sulfite mixtures (Table 1).

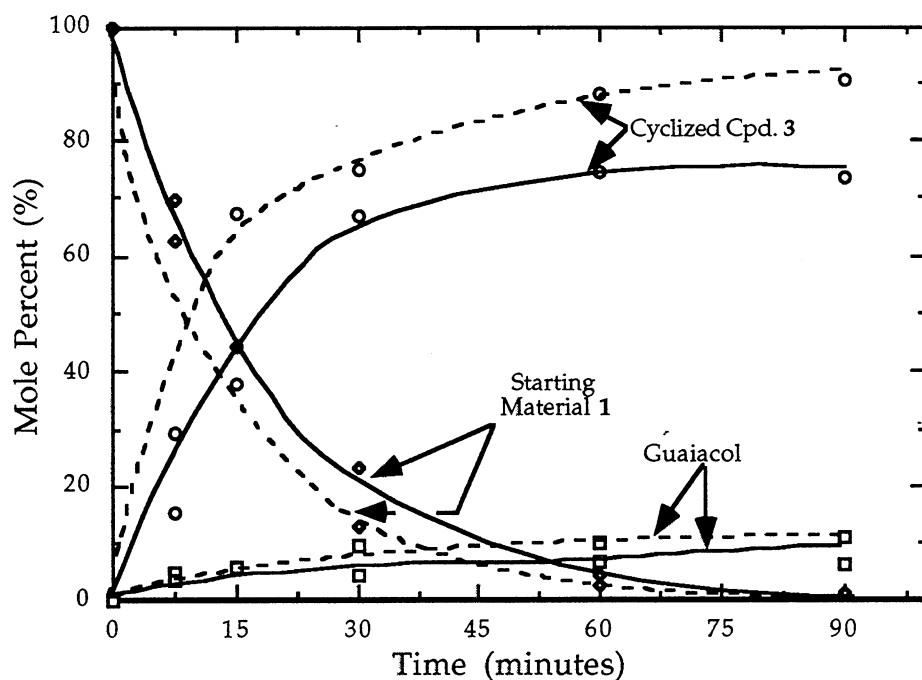


Figure 5. Yields of guaiacol 4 and cyclized cpd. 3 for 1,5-anhydrocellobitol 7 (—) and soda (---) degradations of model cpd. 1 at 150°C.

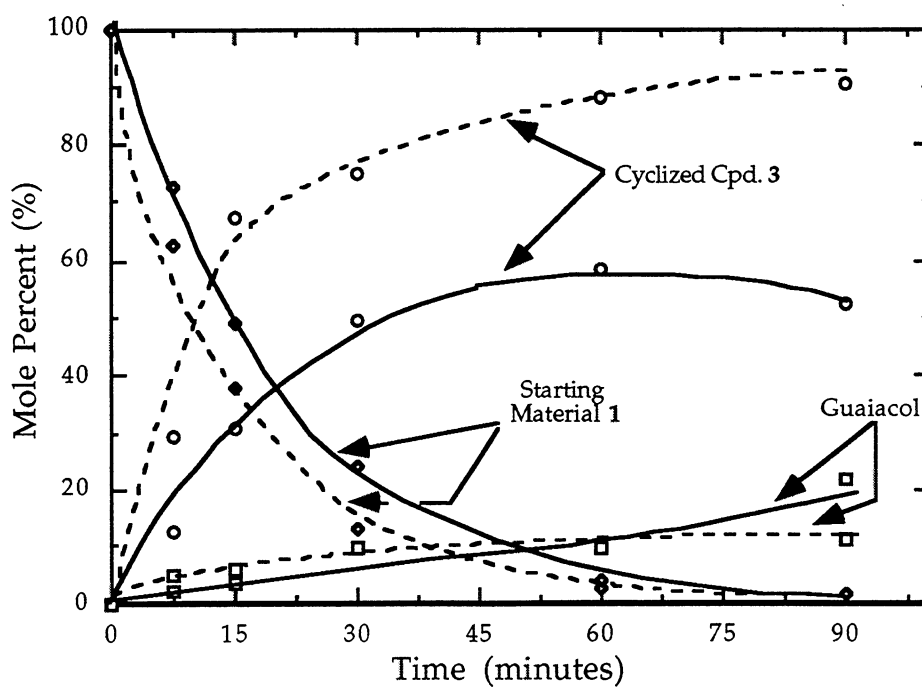


Figure 6. Yields of guaiacol 4 and cyclized cpd. 3 for amylose 8 (—) and soda (---) degradations of model cpd. 1 at 150°C.

Table 1. Yield comparisons for kraft,¹⁰ alkaline sulfite,¹⁰ and kraft/sulfite cooks with model 1, all with 25 equiv. of NaOH at 150°C.

Time (min.)	HS ⁻ (equiv.)	SO ₃ ⁻² (equiv.)	% Yield at 150°C		
			Model 1	Guaiacol (6)	Cyc. Cpd. 3
30	-	5	24	9	45
30	5	-	16	25	49
30	5	5	20	31	55
60	-	5	8	9	65
60	5	-	5	42	47
60	5	5	8	45	45

Unlike alkaline sulfite/AHQ cooks, where sulfite addition to 2 equiv. of AHQ led to a predominance of fragmentation over cyclization,¹⁰ the addition of sulfite to kraft cooks did not change the product distribution. The presence of sulfite in kraft/sulfite cooks did not appreciably enhance guaiacol production at either 30 or 60 min. when compared to a kraft cook.¹⁰ [The material balance for the 30 min. sulfide/sulfite data was >100%; however, the product distribution is the same as the kraft system -- 2:3:6 (cpd. 1: guaiacol: cpd. 3).]

Model 1 was also used to probe the possible synergism between sulfide and AQ. Prior research with model 1 showed that 2 equiv. of AHQ to a soda cook afforded a product distribution similar to a kraft cook -- roughly equal amounts of fragmentation and cyclization over a 90-min. period.¹⁰ Kraft/AHQ cooks were conducted at 15 and 30 min. with 2 equiv. of AHQ, 5 equiv. of NaSH and 25 equiv. of NaOH (Fig. 7).

Approximately 10% of the guaiacol production in all three cooks can be attributed to the NaOH in the system;¹⁰ the remaining guaiacol yield must be due to the pulping additive. The guaiacol afforded in kraft/AHQ cooks was greater than the sum of kraft and soda/AHQ cooks at both times. Kraft and soda/AHQ cooks show a gradual increase in cyclized product 3 over time, whereas, the kraft/AHQ cooks showed little increase.

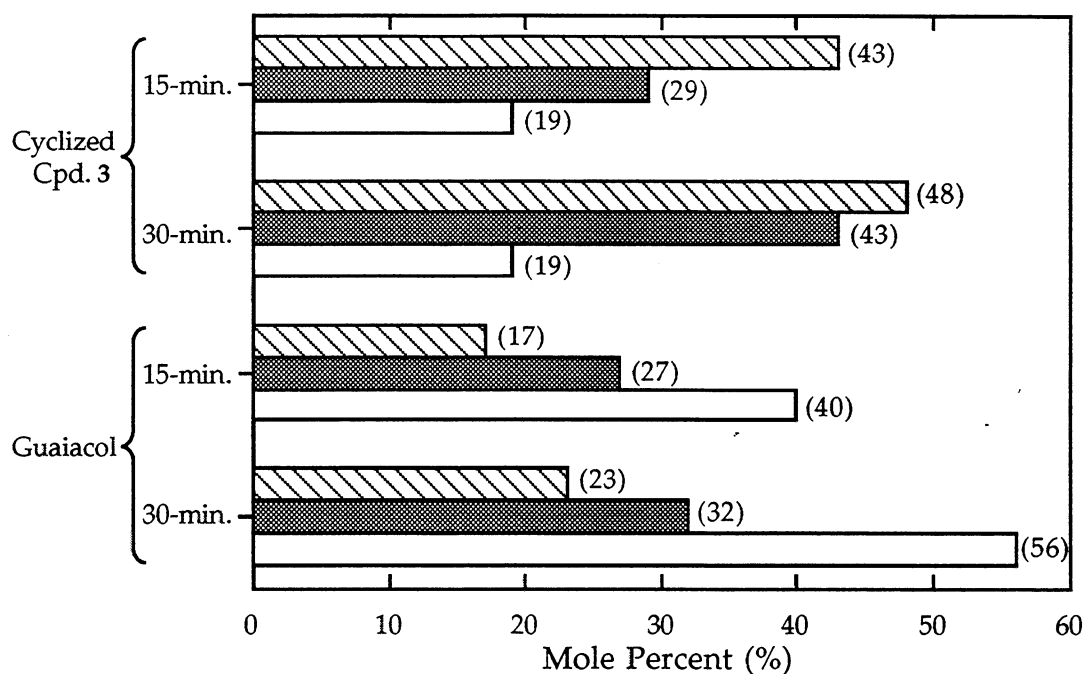


Figure 7. Yields of guaiacol 4 and cyclized cpd. 3 for kraft (▨), soda/AHQ (▤), and kraft/AHQ (□) degradation of **1** at 150°C. Yields in parenthesis. [25 equiv. NaOH, 5 equiv. NaSH, and 2 equiv. AHQ.]

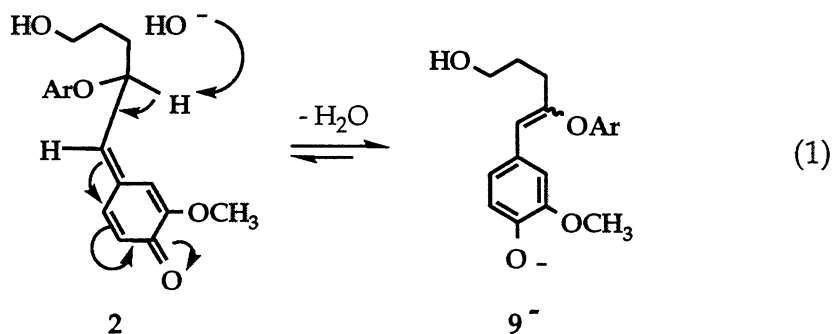
Reactions of Model **1** with Soda/Amines

Past pulping studies have indicated increased delignification rates when amines were added to soda cooks.^{12,13} This could be the result of a fast reaction between the amines and lignin QMs;²⁰ therefore, we examined the reactions of various amines with model **1** (Table 2). 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**.

Vinyl ether **9** is produced in small amounts ($\leq 10\%$) during the soda cooks of model **1**.¹⁰ Vinyl ethers can be generated by C β -proton abstraction from the intermediate QM **2** (Eq. 1); enolization reactions of this type are commonly observed when lignin models are heated with NaOH.^{16,21-23} Compound **9** was not detected in measurable quantities in soda/AHQ, kraft, and alkaline sulfite cooks of model **1**. Vinyl ethers have been shown to be the predominate product when β -aryl models were subjected to alkaline amine treatments.²⁴⁻²⁶

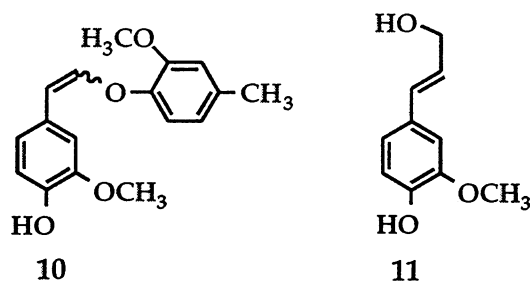
Table 2. Yield comparisons for soda¹⁰ and various soda/amine cooks with model **1**, all with 25 equiv. of NaOH at 150°C.

Additive (5 equiv.)	% Yield after 60 min. at 150°C			
	Model 1	Guaiacol (6)	Cpd. 9	Cyc. Cpd. 3
Soda (Control)	3	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



Several pieces of evidence were used to prove the existence of **9** in both soda and soda/amine cooks. The eluting LC signal (from both soda and soda/amine cooks) has a UV spectrum very similar to vinyl ether **10**²³ and coniferyl alcohol **11**. All three compounds have styrene-like structures, and elute at approximately the same time on the LC. 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^{27,28} or model **1**.¹⁰

Cis/trans vinyl ether **9** was synthesized by treating **1** with 0.1 M NaOCH₃ in CH₃OH at 150°C for 4 hrs; similar conditions have been employed to prepare other vinyl ethers.²³ The vinyl ethers formed had



identical elution times and UV spectra as the LC signals detected during the soda and soda/amine cooks. Along with 9, the NaOCH₃ reactions also produced substantial quantities of cyclized compound 3 and an unknown component suspected to be an α-OCH₃ adduct²³ of model 1. We were unable to isolate 9 by column chromatography. When the product mixture was hydrogenated, the LC signal for compound 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 starting material, indicating a saturated side chain.²⁹

DISCUSSION

The disappearance rate of 1 for 2,6-xyleneol (5), 1,5-anhydrocellobitol (7), and amylose (8) cooks was marginally slower than soda (control) cooks. All the cooks initially started with 25 equiv. of NaOH; the xyleneol and carbohydrates consumed some of the available alkali during the cooks.³⁰ The lower alkali levels may have slowed the disappearance rate of model 1 and the formation of QM 2 when compared to the control.

Condensation reactions between model 1 and 2,6-xyleneol were not observed; such reactions must be slow compared to the cyclization reaction of model 1. Our results agree with previous condensation studies. Gierer and Ljunggren noted that 2,6-xyleneol reacts quantitatively with simple β-aryl ether models to form a condensation product (similar to 6, Fig. 2) in the presence of NaOH.¹⁶ They also observed that 2,6-xyleneol ions do not compete well with sulfide ions for QMs in experiments where both were present in equal amounts; however, condensation

products became prevalent when 2,6-xylenol was in a ten-fold excess of sulfide ions. Gierer and Ljunggren determined that the rate of QM sulfidation was ~13 times greater than the rate of QM condensation.¹⁶ Assuming a similar reactivity difference exists for compound **1** and knowing that rates of sulfide-induced fragmentation and cyclization of **1** are similar, we expect that condensation reactions of **1** with 2,6-xylenol should not be competitive with cyclization; indeed, none were observed.

Carbohydrate condensation reactions with QMs also appeared slower than the cyclization reaction of model **1**. Both the ionized propyl hydroxyl side chain of QM **2** and the ionized hydroxyl groups of the carbohydrates should have similar reactivities with QM **2**; however, the alkoxide side chain has a "higher effective concentration" due to its close proximity to the C α (similar to neighboring group effect).³ This effect could explain why cyclization took precedence over LCC formation.

The addition of amylose to a soda cook did not greatly 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.¹⁴ Reactive amylose degradation products, such as enediols, are labile in hot alkali.^{19,31} The concentration of enediols during the cook of model **1** was probably too low to compete with the cyclization reaction.

The combination of sulfide and AHQ substantially improve β -aryl ether fragmentation and suppressed cyclization of model **1** better than either component alone. In order to determine possible synergistic effects, we have separated the guaiacol yield given in Table 3 into two categories: (a) guaiacol from alkali reactions (column 2), and (b) guaiacol from additive reactions (column 3). For additive combinations (entries 6-8), a predicted guaiacol yield is estimated from each individual additive (column 4). The data analysis indicates that the kraft/AHQ combination synergistically enhances β -aryl ether fragmentation, similar to the alkaline sulfite/AHQ system.¹⁰ A previous AQ solubility study indicated that sulfide ions can slowly reduce AQ to AHQ $^{\cdot-}$ or AHQ $^{2-}$.³² Sulfide ions could have reduced AQ to AHQ anions during the kraft/AHQ cooks

Table 3. Guaiacol yield comparisons at 30 min. for various pulping systems for model 1, all with 25 equiv. of NaOH at 150°C.

Additive (equiv.)	Observed	Guaiacol (%)		
		NaOH ^a	Additive ^b	Predicted ^c
1. Control [Soda]	10			
2. Alk. sulfite (5)	9	10	0	
3. Kraft (5)	25	10	15	
4. Soda/AHQ (5)	82	10	72	
5. Soda/AHQ (2)	32	10	22	
6. Alk. sulfite (5)/AHQ (2)	46	10	0 + 22	32
7. Kraft (5)/AHQ (2)	56	10	15 + 22	47
8. Kraft (5)/Sulfite (5)	26 ^d	10	15 + 0	25

^aAssumed yield due to NaOH in the system (entry 1); ^bGuaiacol due to additive(s); ^cPredicted values for entries 6-8 by summing NaOH and additive columns; ^dValue has been normalized from Table 2.

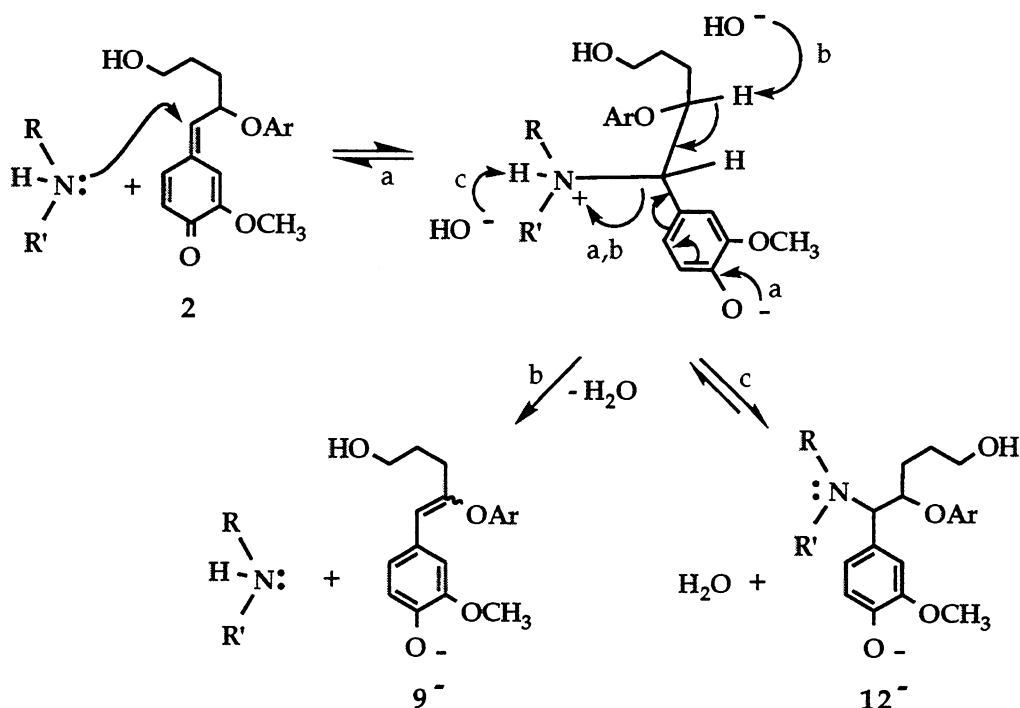


Figure 8. Reactions of amines with QM 2. [R and R' correspond to various functional groups for amines listed in Table 2.]

of model **1**; however, the reduction was not complete, since only 56% fragmentation was observed after 30 min. If the conversion was efficient, the amount of fragmentation should have resembled the soda/AHQ cooks with 5 equiv. of AHQ (i.e., 82%¹⁰).

Sulfite addition to the kraft cooks of **1** did not significantly improve the fragmentation efficiency (Table 3). Initially, we wondered if sulfite ions could regenerate sulfide ions (HS^-) from elemental sulfur (S°); the latter can be generated from thiirane intermediates that are part of the fragmentation chemistry.³ Regenerated sulfide ions could later attack QMs and lead to an overall increase β -aryl ether cleavage (similar to the kraft/AHQ system). A previous study with a simpler lignin model has shown that increased levels of sulfide increase β -aryl ether cleavage.²⁷ Fleming, et al., have suggested that HS^- can be partially regenerated from S° during a kraft cook.³³ However, our results indicate that the sulfite ion is unable to reduce S° to HS^- .

The addition of amines to soda cooks of model **1** did not improve the amount of β -aryl ether fragmentation. Instead, model **1** was efficiently converted to cyclized compound **3** and vinyl ether **9**. The formation of **9** is probably a higher energy process;^{22,27} very little is formed during soda cooks of model **1**.¹⁰ The soda/amine combination appears to provide an alternative method for vinyl ether generation, besides C_β -proton abstraction from a QM (Eq. 1).

Amines are known to undergo nucleophilic addition to QMs and form adducts^{20,24} (Fig. 8; path c, **12**⁻); however, we did not observe any adducts. Low levels of adducts were observed at 170°C during Obst's soda/amine study with lignin models.²⁴ Obst noted that amine adducts (synthesized from the reactions of QMs and amines at 40°C) were unstable when subjected to heating in alkali at 170°C.²⁴ The lone electron pair on the amine adduct could become protonated (reverse of path c). The resulting positively charged nitrogen is electron-withdrawing and increases the acidity of the C_β -proton; alkali can abstract the C_β -proton and cause a Hofmann-like elimination³⁴ to form a vinyl ether (path b).

Soda/amine and kraft pulping of **1** have some similarities. In both cases model **1** gave similar levels of cyclized product **3** and degradation

products (vinyl ethers for soda/amine and guaiacol for kraft). Amines do not appear to promote β -aryl ether fragmentation from phenolic structures; instead, amines produce vinyl ether structures that are more resistant to alkaline pulping conditions.^{3,23}

It is surprising that amines have shown accelerated delignification rates in comparison to kraft.^{12,13} The fast rates may be due to other factors. Studies performed by Wallis have indicated that amines may interact with non-phenolic structure in lignin to promote lignin fragmentation reactions.²⁶ Kubes, et al., have suggested that amines increase delignification rates by changing the redox potential of cooking liquor.³⁵ On a percentage basis, amines are not as efficient delignification reagents as sulfide; most soda/amine pulping processes use ~40% (o.d. wood) amine^{12,13} compared to ~7 % sulfide for kraft.

CONCLUSIONS

The condensation reactions between QM 2 and organic fragments are much slower than fragmentation of QM 2 by efficient pulping reagents, such as AHQ and sulfide ions. β -Aryl ether scission was synergistically enhanced when AHQ was added to a kraft cook; the cause is probably related to a redox cycle between AQ and sulfide ions. The addition of sodium sulfite to a kraft cook of model 1 did not improve the fragmentation efficiency or affect the product distribution. 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.

EXPERIMENTAL

General Analytical Procedures

The equipment, model reagent amounts, model 1 degradation procedure, product analysis by reverse phase liquid chromatography, and most of the compound characterization have been previously de-

scribed.^{10,36} 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 partial characterization of vinyl ether **9** are 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**³⁶ dissolved in 1 M NaOCH₃/CH₃OH. An additional 2.5 mL of 1 M NaOCH₃ 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 a sample was analyzed by reversed phase liquid chromatography.¹⁰ 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 -OCH₃ adduct of **1** based on previous vinyl ether synthesis with 1 M NaOCH₃²³ (retention time of 2.4 min.). The combined solutions were evaporated to yield light brown crystals.

Several unsuccessful attempts were made to separate compound **9** from the crude product mixture using column chromatography with CH₂Cl₂/CH₃CH₂OH and hexane/CH₂Cl₂ solvent systems. Approximately 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 using reversed phase liquid chromatography with 33% (v/v) aq. CH₃OH flowing at 0.450 mL/min. Vinyl ether **9** (retention time 4.1 min.) was not observed in the hydrogenated sample. Instead, a new LC signal was observed at 3.6 min. with a UV spectrum similar to compound **1**, indicating 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]¹⁰ during product analyses of various model **1** reactions.

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