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Fundamental Study of Relative Delignification Efficiencies (III): Organosolv Pulping

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## FUNDAMENTAL STUDY OF RELATIVE DELIGNIFICATION EFFICIENCIES (III): ORGANOSOLV PULPING

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### ABSTRACT

Reactions of a  $\beta$ -aryl ether lignin model compound (**1**) provide information on the relative rates of pulping reactions that involve quinone methides (QMs). The lignin model **1** was reacted under soda, kraft, soda/anthrahydroquinone (AHQ), and sulfite conditions in the presence of different levels of organic cosolvents. As previously observed in pure water systems, all alkaline reactions displayed the same lignin model disappearance rate, verifying that quinone methide formation was the rate-determining step. The addition of methanol did not affect  $\beta$ -aryl ether fragmentation efficiency for model **1** in the case of  $\text{HO}^-$ ,  $\text{HS}^-$ , and alkaline  $\text{SO}_3^{2-}$  additives. Isopropyl alcohol (IPA) slowed the disappearance rate of **1** for neutral sulfite and acid bisulfite cases;  $\beta$ -aryl ether fragmentation was marginally enhanced with neutral sulfite.  $\beta$ -Aryl ether scission was significantly improved when methanol was added to a soda/AHQ system. The enhancement of fragmentation correlated with the amount of methanol present. Several other solvents also displayed a response similar to methanol. The observed synergism in the AHQ/solvent cases is probably related to the unique electron transfer (radical) chemistry of the AHQ system. The solvents may act as radical scavengers and deactivate reactive free radicals that interfere with AHQ species, and/or alter the oxidation and reduction potentials of AHQ and QM species.

## INTRODUCTION

Pulping in organic solvents and organic/water mixtures has been examined as a way to lower odoriferous emissions, improve selectivity, and lower the effluent load associated with bleached pulps. Of particular interest are two processes that add small amounts of methanol (<20%) to pulping liquors: alkaline sulfite-anthraquinone-methanol (ASAM)<sup>1,2</sup> and soda-anthraquinone-methanol (organocell).<sup>1,3</sup> In comparison to their aqueous counterparts, the alcohol-reinforced pulping processes show increased delignification rates without negatively impacting the pulp's mechanical properties.<sup>1-4</sup>

The presence of organic solvents during alkaline pulping may aid the dissolution of lignin fragments and facilitate the delignification chemistry. The principal delignification mechanisms of solvent-reinforced pulping processes are generally believed to be similar to their aqueous counterparts.<sup>5</sup> However, little research work has been directed at studying the fundamentals of delignification during organosolv pulping to confirm this hypothesis.

There are reasons to believe that the chemistry might change in the presence of an organic solvent. Increased  $\beta$ -aryl ether fragmentation was observed by Sakai, et al., during bisulfite pulping of simple lignin models when isopropyl alcohol (IPA) was used.<sup>6</sup> While bisulfite ions in aqueous solution show little ability to transfer electrons to QMs at 135 or 150°C, the presence of IPA promotes such reactions.<sup>7</sup> Electron transfer reactions have been observed during the electrolysis of anthraquinone (AQ) and lignin model quinone methides (QMs) in various solvents.<sup>8</sup>

The goal of our study was to examine the effect of organic alcohols on the efficiency of  $\beta$ -aryl ether fragmentation of a lignin model (**1**) using soda, kraft, sulfite, sulfite/AQ and soda/AQ pulping conditions. Previous papers have used model **1** to qualitatively measure fragmentation efficiencies of traditional and modified pulping systems; details of the various reactions of model **1** and how QM reactions can be timed relative to cyclization of **1** to **3** (Fig. 1) are found in our earlier reports.<sup>9-11</sup>

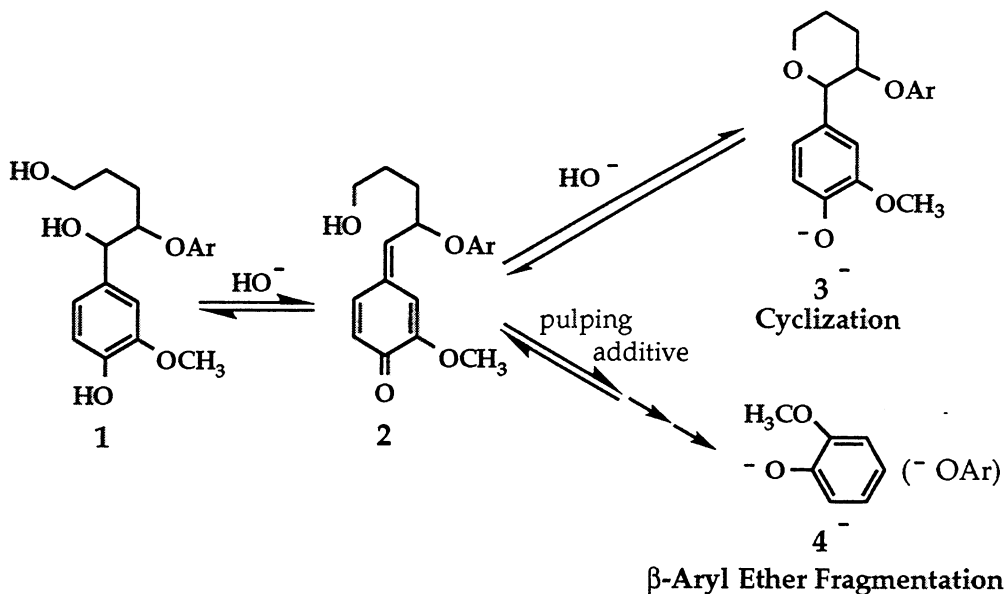


Figure 1. Competing parallel reactions for QM 2: cyclization and fragmentation reactions of model 1.<sup>9-11</sup>

## RESULTS

### Alcohol-Reinforced Soda, Kraft, and Alkaline Sulfite Reactions

Compound 1 was heated in water<sup>9</sup> and water/alcohol mixtures in sealed reaction vessels at 150°C for various time periods in the presence of 25 equiv. of NaOH, and 5 equiv. each of NaSH or Na<sub>2</sub>SO<sub>3</sub>. Alcohol-reinforced cooks consisted of 50% by volume alcohol. The results at various times are presented in Tables 1 and 2.

The product distribution from the methanol soda and kraft cooks, and isopropyl alcohol (IPA) alkaline sulfite cooks of model 1 showed little difference from their corresponding aqueous counterparts. The methanol soda cooks showed slightly lower amounts of cyclized compound 3 compared to an aqueous cook, whereas the methanol-reinforced kraft cooks showed the opposite trend. An IPA/soda cook gave a similar product distribution as the soda/methanol cook. The alcohol cooks did not enhance  $\beta$ -aryl ether fragmentation efficiencies of sulfide,

Table 1. Yield comparisons for aqueous<sup>9</sup> and alcohol-reinforced soda and kraft cooks with model 1, all with 25 equiv. of NaOH at 150°C. [5 equiv. NaSH for kraft; dashes indicate nondetectable by HPLC/UV.]

Reaction Time (min.)	Soda						Kraft			
	Aqueous			50% MeOH/50% H <sub>2</sub> O			50% IPA/50% H <sub>2</sub> O			
	Guaiacol (%)	Cyc. Cpd. 3 (%)	Guaiacol (%)	Cyc. Cpd. 3 (%)	Guaiacol (%)	Cyc. Cpd. 3 (%)	Guaiacol (%)	Cyc. Cpd. 3 (%)	Guaiacol (%)	
7.5	5	29	-	21	6	21	8	22	8	17
15	6	67	-	44	8	41	19	42	13	36
30	10	75	5	62	9	65	21	46	24	53
60	10	88	9	71	11	75	42	47	35	58
90	11	91	20	67	11	68	48	33	46	50

Table 2. Yield comparisons for aqueous<sup>9</sup> and alcohol-reinforced neutral and alkaline sulfite cooks with model 1 at 150°C. [5 equiv. Na<sub>2</sub>SO<sub>3</sub>; 25 equiv. NaOH for alkaline sulfite.]

Reaction Time (min.)	Neutral Sulfite						Alkaline Sulfite			
	Aqueous			50% IPA/50% H <sub>2</sub> O			Aqueous			
	Guaiacol (%)	Cyc. Cpd. 3 (%)	Adduct 4 (%)	Guaiacol (%)	Cyc. Cpd. 3 (%)	Adduct 4 (%)	Guaiacol (%)	Cyc. Cpd. 3 (%)	Guaiacol (%)	
7.5	-	-	22	-	-	9	6	16	7	27
15	-	7	45	-	10	22	8	32	6	47
30	-	11	68	4	15	30	9	45	9	70
60	-	15	80	7	29	40	9	65	9	81
90	-	11	91	9	35	44	10	73	10	91

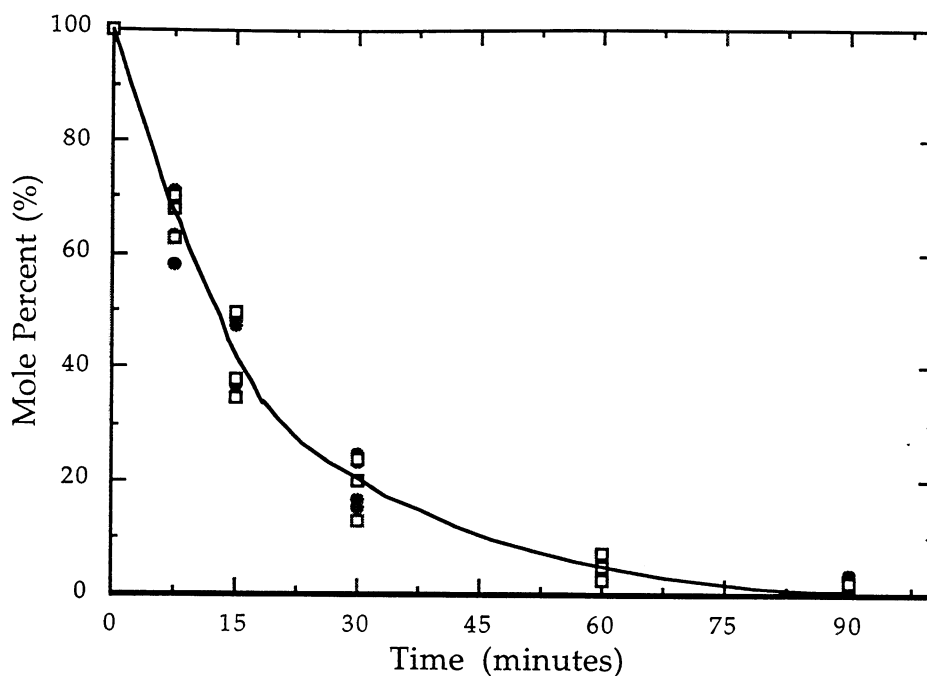


Figure 2. Disappearance of 1 as a function of time at 150°C for aqueous<sup>9</sup> (□) and alcohol-reinforced (●) cooks under soda, kraft, and alkaline sulfite conditions. [Corresponds to Tables 1 and 2.]

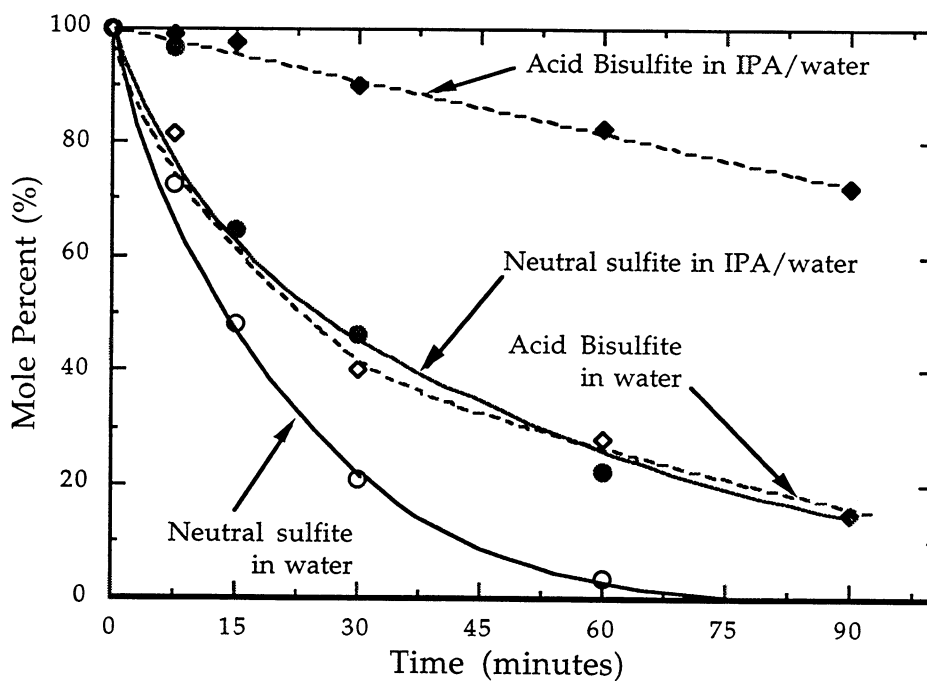
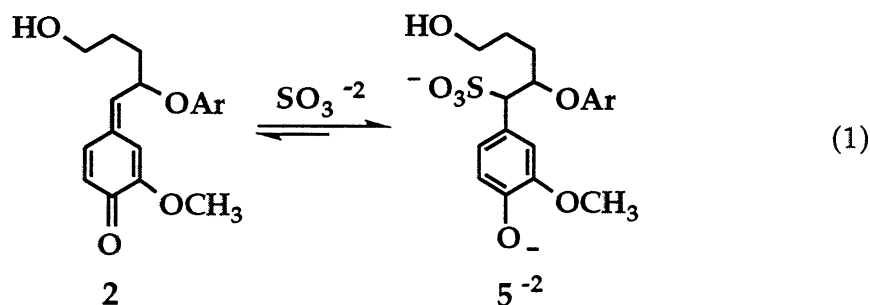


Figure 3. Disappearance of 1 as a function of time at 150°C for aqueous<sup>9</sup> (○, ◇) and IPA-reinforced (●, ◆) cooks under neutral sulfite (○, ●) and acid bisulfite (◇, ◆) conditions.

hydrosulfide, and hydroxide ions. Also, the disappearance rate of **1** in soda, kraft, and alkaline sulfite cooks was not affected when 50% of the water was replaced with methanol or IPA (Fig. 2).

### Alcohol-Reinforced Neutral Sulfite and Acid Bisulfite Reactions

Neutral sulfite (pH ~8.5) and acid bisulfite (pH ~4.5) cooks, employing 5 equiv. of Na<sub>2</sub>SO<sub>3</sub>, were performed with model **1** using aqueous<sup>9</sup> and IPA/water solutions. A 50% IPA neutral sulfite cooks did not substantially increase β-aryl ether fragmentation of model **1** (Table 2); the presence of IPA promoted the cyclization and retarded α-sulfonation (cpd. **5**, Eq. 1). Experimental results from IPA-reinforced acid bisulfite cooks also showed little β-aryl fragmentation (<16% after 300 min). Both alcohol-reinforced sulfite systems showed a slower disappearance rate of **1** than the corresponding aqueous system (Fig. 3).



### Alkaline Sulfite/AHQ/Methanol and AHQ/Alcohol Reactions

Model **1** was subjected to methanol-reinforced alkaline sulfite-AHQ (ASAM) conditions; anthrahydroquinone (AHQ) is the reduced form of AQ. The results are compared to previous experiments with aqueous alkaline sulfite/AHQ<sup>9,10</sup> (Fig. 4). The ASAM cook at a 50% methanol substitution level greatly augmented β-aryl ether scission over its aqueous counterpart; little cyclization of model **1** was observed. The disappearance rate of **1** was not affected by the methanol addition.

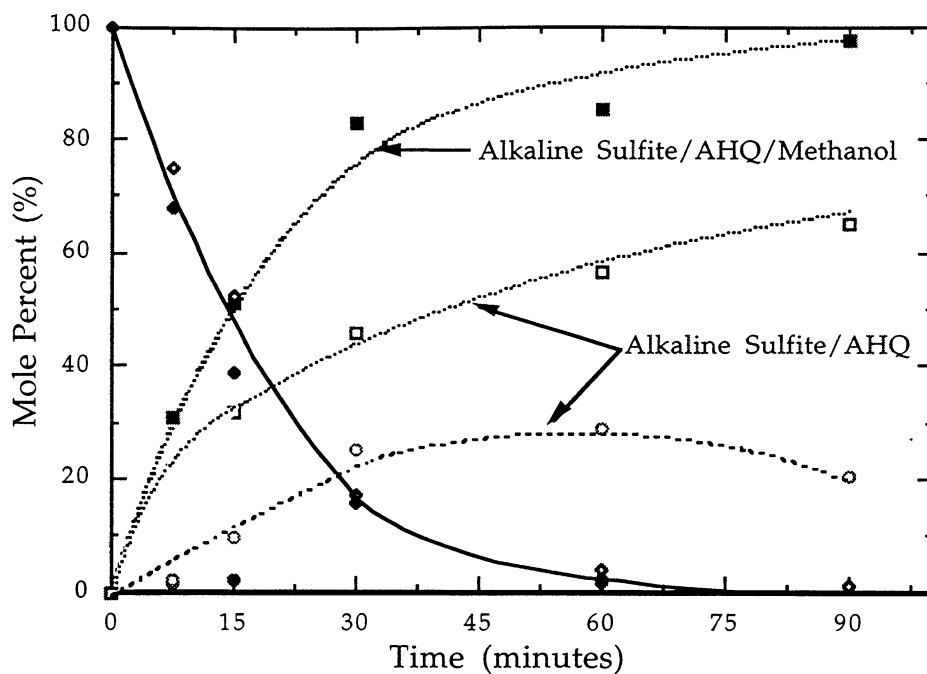


Figure 4. Yields of guaiacol 4 (····), and cyclized cpd. 3 (----) for aqueous<sup>9,10</sup> (□, ○, ◊) and methanol-reinforced (■, ●, ◆) alkaline sulfite/AHQ degradations of model cpd. 1 (—) at 150°C.

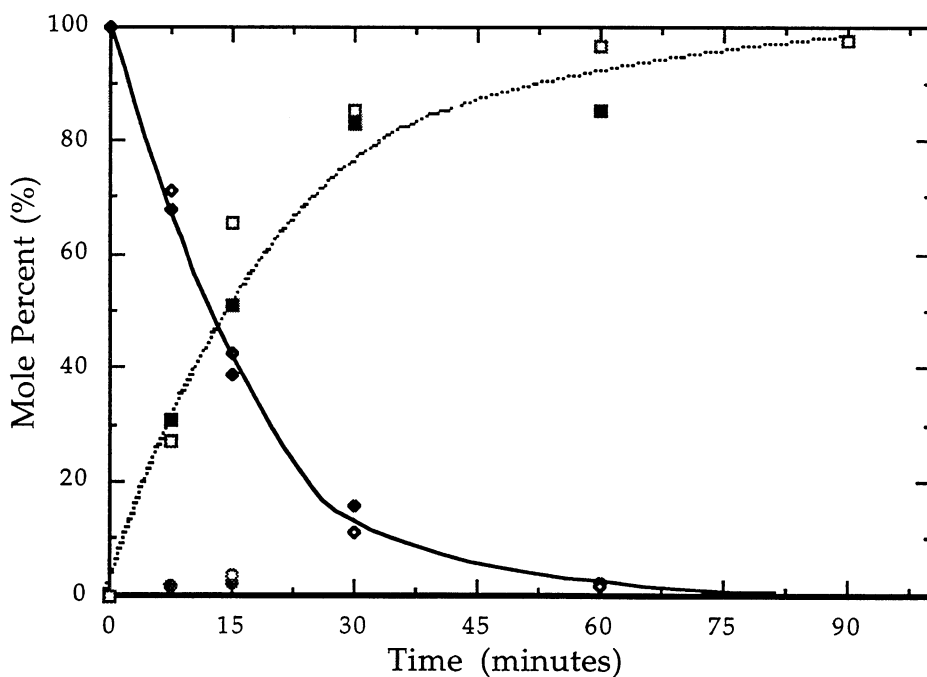


Figure 5. Yields of guaiacol 4 (····) and cyclized cpd. 3 (----) for methanol-reinforced alkaline sulfite/AHQ (■, ●, ◆) and soda/AHQ<sup>9,10</sup> (□, ○, ◊) degradations of model cpd. 1 (—) at 150°C.

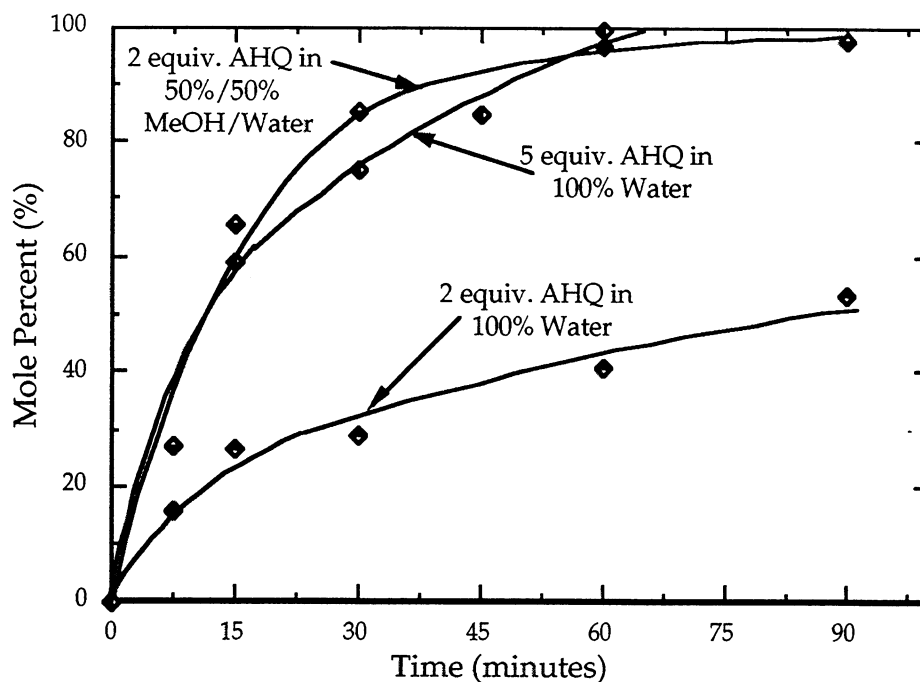


Figure 6. Yields of guaiacol 3 as a function of time for aqueous<sup>9,10</sup> and alcohol reinforced soda/AHQ cooks of model compound 1 at 150°C. [All cooks had 25 equiv. NaOH.]

Several methanol-reinforced soda/AHQ experiments were performed as controls to ASAM cooks (Fig. 5). The soda/AHQ/methanol cooks showed identical appearance of guaiacol and disappearance of model 1 when compared to ASAM. The results indicated that the increased fragmentation seen during the ASAM cooks was primarily due to a synergistic interaction between methanol and AHQ. Methanol-reinforced soda/AHQ cooks with 2 equiv. of AHQ is as efficient at  $\beta$ -aryl ether cleavage as 5 equiv. of AHQ in totally aqueous system (Fig. 6).

Additional experiments were performed with the soda/AHQ/methanol system to examine the effects of methanol substitution level (Fig. 7). The rate of fragmentation (guaiacol production) of the model increased as the amount of methanol used increased from 0 to 50%; correspondingly, the level of cyclization decreased (Fig. 7).

Several other organic solvents were tested with the soda/AHQ system at 12.5% substitution level and 60 min for model 1 (Fig. 8). A similar product distribution was observed for the lower molecular

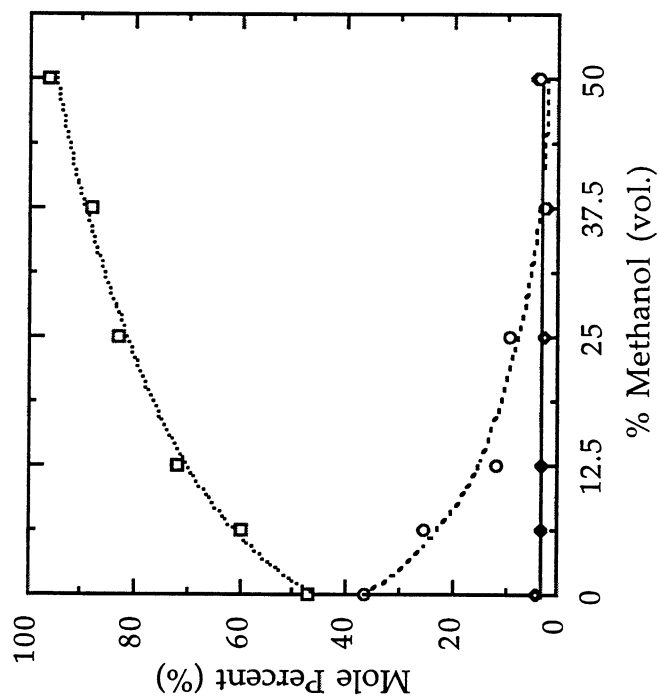
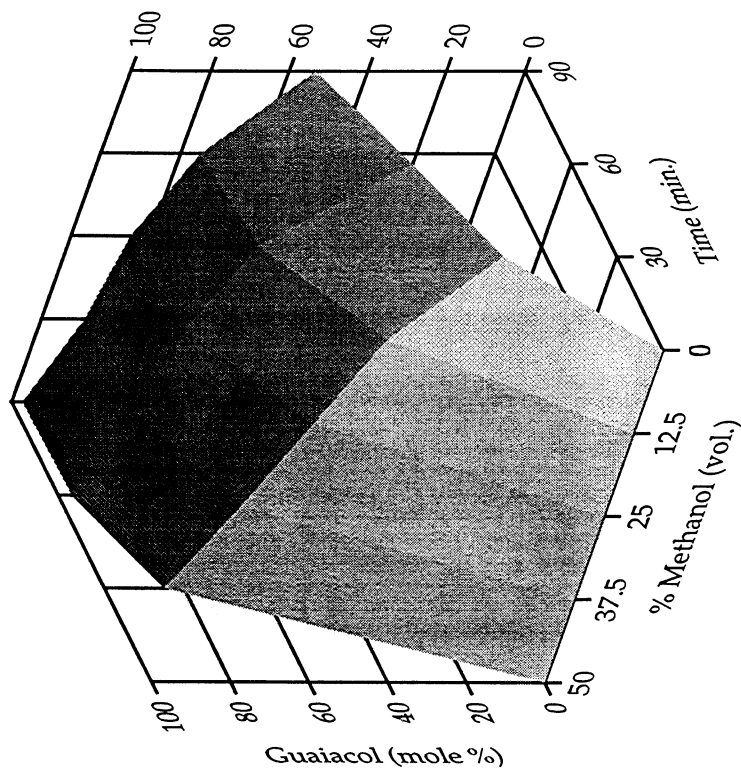


Figure 7. Effect of methanol content on the product distribution during soda/AHQ/methanol degradation of model 1. Left graph: Yields of guaiacol (....), cpd. 1 (---), and cpd. 3 (---) for various methanol substitution levels at 60 min. Right graph: Guaiacol formation from 1 as a function of methanol substitution and time. [Cooks performed at 25 equiv. NaOH, 2 equiv. AHQ, and 150°C.]

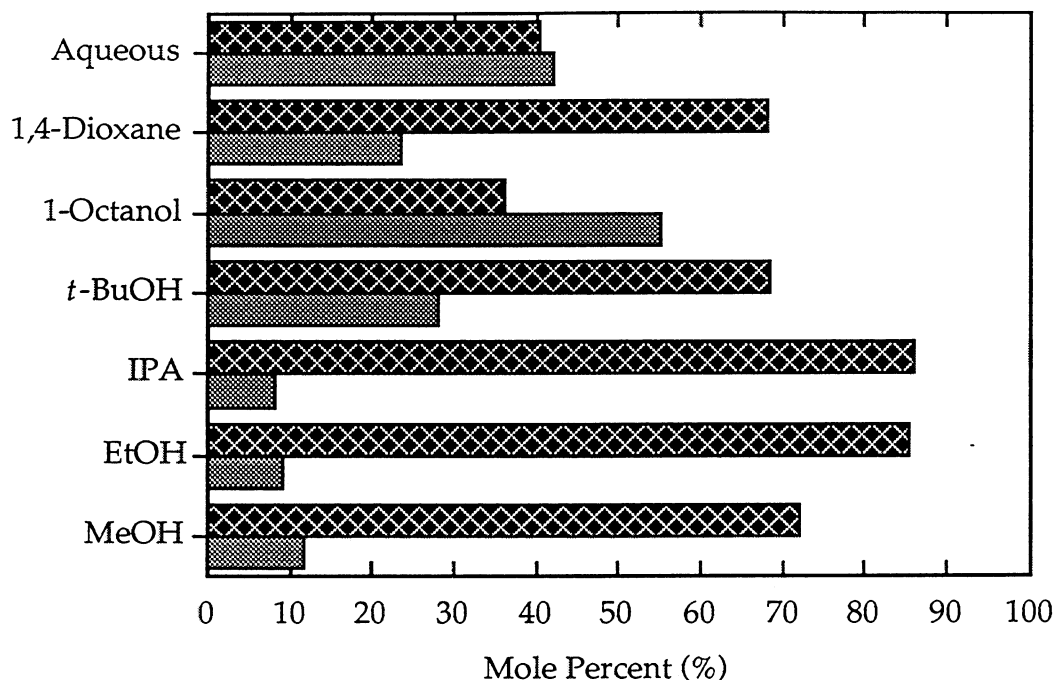


Figure 8. Yields of guaiacol 3 (▣) and cyclized compound 2 (▤) after 60 minutes for soda/AHQ degradation of 1 with various organic solvents at a 12.5%-volume substitution level at 150°C.

weight alcohols: ethanol, IPA, *t*-butanol, and methanol. 1-Octanol did not improve  $\beta$ -aryl ether fragmentation over an aqueous system; this result may be attributed to immiscibility of 1-octanol and water. The 1,4-dioxane addition enhanced guaiacol production compared to the aqueous control and a fragmentation efficiency about equal to that of methanol. Substituting deuterated methanol ( $\text{CD}_3\text{OH}$ ) for regular methanol (at the 12.5% level) had little effect on the 1-hour yield of guaiacol (66 vs. 73%, respectively).

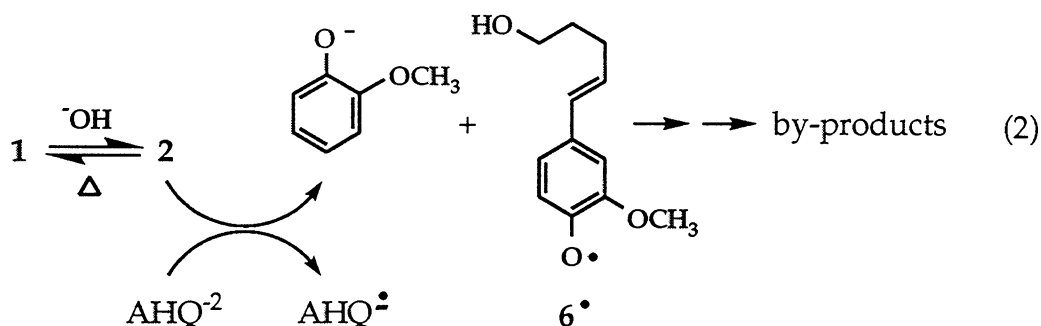
## DISCUSSION

Relative delignification efficiencies of different pulping systems are reflected in the degree of fragmentation (guaiacol production) from model 1 versus the amount of cyclization that occurs. Our results demonstrate that addition of several types of organic solvents increases

the guaiacol production, at the expense of cyclization from model **1** for reactions that *involve* AHQ. Alcohol addition to alkaline pulping reactions of **1** appear not to affect the rate-determining step -- QM formation.<sup>9,10</sup> The fact that methanol addition had little effect on soda, sulfite, and kraft reactions of **1** suggests a unique chemistry for the AHQ system. There is an abundance of evidence that AHQ reacts via electron transfer reactions,<sup>8,11-13</sup> while soda and kraft chemistry involves nucleophilic addition and displacement chemistry.<sup>14</sup> The question is: what is the mechanism that accounts for the promotion of electron transfer fragmentation reactions of **1** by organic solvents? Our research results do not provide a specific answer, but some explanations are offered below.

Ethanol and isopropanol (IPA) increased guaiacol production almost by a factor of two (compared to the control) and were 10% higher than a methanol cook. Examination of the bombs after reaction with 2 equiv. of AHQ showed a deep red color in ethanol and IPA bombs, a light red color in methanol and *t*-butanol bombs, and no color in pure water runs. The red color is associated with the presence of anthrahydroquinone dianion (AHQ<sup>-2</sup>) and radical anion (AHQ<sup>•-</sup>).<sup>15</sup> Thus, the more efficient solvent systems retain more of the active reactants.

An organic solvent might act as a free radical scavenger, deactivating reactive radicals that consume AHQ species. A radical reaction of concern is the possible coupling of the anthrahydroquinone radical anion, AHQ<sup>•-</sup>, with the styrene radical **6**<sup>•</sup> (Eq. 2). The two radicals are expected products of the electron transfer reaction between AHQ<sup>-2</sup> and quinone methide **2**.<sup>9,12</sup> Very little styrene product **6** is observed (in comparison to guaiacol);<sup>12,16</sup> this is probably because the radical **6**<sup>•</sup> undergoes polymerization-type reactions, leading to undetectable products, rather than reduction to **6**. There is evidence that some liberated guaiacol is incorporated into secondary reactions of styrenes, *when AHQ is present*;<sup>15</sup> possibly AHQ<sup>•-</sup> can be lost in a similar manner. [AHQ condensation products with lignin have been isolated from soda/AQ pulping liquors.<sup>17</sup>] If so, the effective concentration of AHQ drops, and less fragmentation of model **1** would occur.



An analogy for this proposal is found in the studies of the alkaline oxygen oxidation reactions of creosol in ethanol.<sup>19</sup> Very little creosol reacted over a 5-hour period when treated with O<sub>2</sub>/NaOH in the presence of ethanol. However, in pure water, the creosol was nearly all converted to coupling products. The results suggest that ethanol stabilizes or deactivates the radical intermediates.<sup>18</sup>

Primary and secondary alcohols (and dioxane) can scavenge radicals by donating  $\alpha$ -protons ( $-\text{CH}_\alpha\text{O}-$ ) to reactive radicals; such reactions may interfere with incorporation of AHQ into undesirable side reactions. [A similar argument was offered to explain the synergism between AHQ and sulfite; the latter may be reacting with styrene byproducts, rather than AHQ reacting with the styrene.<sup>9</sup>] Based on radical stabilities,<sup>19</sup> the performance of the alcohols should follow the order of IPA > ethanol > methanol > *t*-butanol. To some extent, this order was followed. However, the scale was compressed; IPA was less effective and *t*-butanol was more effective than anticipated.

In the case of dioxane, a C $\alpha$ -radical is secondary and stabilized by an adjacent oxygen but inductively destabilized by the C $\beta$ -oxygen. Therefore, dioxane might be expected to behave similarly to methanol. [It should be noted that dioxane substitution levels were kept low to avoid phase separations;<sup>20</sup> at dioxane levels of 25% or greater,  $\beta$ -aryl ether fragmentation can be retarded during a soda-AHQ cook.<sup>20-22</sup>]

There are, however, some flaws to the radical scavenging explanation: (a) simple reduction products of 6 were not observed, and (b) reactions were not significantly retarded in the presence of CD<sub>3</sub>OH. Deuterated methanol should be much less effective than methanol in

donating a hydrogen atom, since more energy is required to dissociate a C-D bond than a C-H bond.<sup>23</sup>

A second explanation for the synergism between organic solvents and AHQ relates to possible changes in oxidation and reduction potentials of AHQ species and quinone methides that could facilitate electron transfer reactions and  $\beta$ -aryl ether fragmentation. A correlation between the redox potential of pulping liquor and the rate of delignification has been observed; as the redox potential of liquor decreases, the rate of delignification increased.<sup>24</sup> Early pulping studies with AQ and related compounds suggested that the effectiveness of various pulping additives was related to reduction potential of the additive.<sup>25</sup>

The reduction potentials of AQ,  $\text{AHQ}^{\cdot-}$ , and QM change with solvent changes; for AQ and  $\text{AHQ}^{\cdot-}$  the values are -0.78 and -1.53 volts (vs. Ag/AgCl) in DMSO and -0.92 and -1.72 volts in acetonitrile.<sup>8</sup> The electron transfer between  $\text{AHQ}^{\cdot-}$  and a QM is more rapid and complete in acetonitrile than in DMSO.<sup>8</sup> It is probable that organic solvents, mixed with water, can affect the redox behaviors of AHQ species and improve electron transfer rates with quinone methides. Or, stating it in another way, key transition states may be more solvated (stabilized) by lowering the ionic strength of the reaction medium.

## CONCLUSIONS

The addition of low-molecular-weight alcohols did not effect  $\beta$ -aryl ether fragmentation efficiency for  $\text{HO}^-$ ,  $\text{HS}^-$ , and alkaline  $\text{SO}_3^{-2}$  additives. Isopropyl alcohol slowed the disappearance rate of **1** for neutral  $\text{SO}_3^{-2}$  and acid bisulfite additives;  $\beta$ -aryl ether fragmentation was marginally enhanced with neutral  $\text{SO}_3^{-2}$ .  $\beta$ -Aryl ether scission was improved by a factor of 2 when 50% methanol was added to an alkaline sulfite-AQ (ASAM) system. The enhancement of the ASAM process was attributed to an alcohol-AQ synergistic effect.

Experiments were performed to probe the synergism involved with an alcohol/soda/AQ system. The fragmentation of **1** with 50% methanol and 2 equiv. of AQ was just as effective as 5 equiv. of AQ in a

totally aqueous system. Methanol additions as low as 6.25% were seen to improve  $\beta$ -aryl ether fragmentation. Several different solvents were tested; ethanol and isopropyl alcohol best enhanced the fragmentation of **1**. Two theories were proposed to explain synergism between low molecular weight alcohols and AQ: 1) alcohols act as radical scavengers during pulping and deactivate reactive free radicals that interfere with AHQ species, and 2) the addition of alcohols alters the oxidation and reduction potentials of AHQ and QM species in a way that improves the rates of  $\beta$ -aryl ether fragmentation reaction.

### EXPERIMENTAL

The equipment, model reagent amounts, model **1** degradation procedure, product analysis by reverse phase liquid chromatography, and compound characterization have been previously described.<sup>9,22</sup> All pulping reactions used 0.015 mmoles (= 1 equiv.) of **1** and 25 equiv. of NaOH; all experiments involving AHQ used 2 equiv. each of glucose and AQ unless otherwise noted. The only differences from previously described experiments were that the reagent solutions for pulping reactions were made from the appropriate solvent/water mixture. All solvent substitution percentages are on a volume basis prior to mixing.

### ACKNOWLEDGMENTS

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