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

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

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ABSTRACT

Reactions of 1-(4-guaiacyl)-2-(O-guaiacyl)-1,5-pentanediol (1) provide relative rates of pulping reactions that involve quinone methides (QMs). Model 1 was reacted under soda, kraft, soda/anthrahydroquinone (AHQ), and sulfite conditions in the presence of various water/alcohol media. All alkaline reactions displayed the same lignin model disappearance rate, verifying that QM formation was the rate-determining step. Alcohol addition had the following effect on increasing the β-aryl ether cleavage of model 1: no increase for methanol addition to soda, kraft, and alkaline SO_3^{-2} systems; small increase for isopropanol addition to neutral sulfite and acid bisulfite systems; large increase for methanol addition to the soda/AHQ system. In the latter case, the amount of enhancement correlated with the level of methanol present; other solvent/water media exhibited a similar response as methanol. Several hypotheses relating to electron transfer (radical) chemistry are postulated for the observed synergism between the solvent and AHQ.

INTRODUCTION

Pulping in organic solvents and organic/water mixtures is a way to lower odoriferous emissions, improve selectivity, and lower the effluent load associated with bleached pulps. Of particular interest are

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two processes that add small amounts of methanol (< 20%) to pulping liquors: alkaline sulfite/anthraquinone/methanol (ASAM)[1,2] and soda/anthraquinone/methanol (organocell).[1,3] In comparison to their aqueous counterparts, the alcohol-reinforced pulping processes show increased delignification rates without negatively impacting the pulp's mechanical properties.[1-4]

The use of organic solvents during alkaline pulping may aid lignin dissolution and/or facilitate the delignification chemistry. The principal delignification mechanisms of solvent-reinforced pulping processes are generally believed to be similar to their aqueous counterparts.[5] However, little 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 β-aryl ether fragmentation was observed by Sakai, et al.[6] during bisulfite pulping of simple lignin models when isopropyl alcohol (IPA) was used. While bisulfite ions in aqueous solution show little ability to transfer electrons to quinone methides (QMs), the presence of IPA promotes such reactions.[7] Electron transfer reactions have been observed during the electrolysis of anthraquinone (AQ) and lignin model QMs in various solvents.[8]

Our objective in this paper is to use the reactions of 1-(4-guaiacyl)-2-(O-guaiacyl)-1,5-pentanediol (1) to examine the effect of alcohol/water solutions on the β-aryl ether fragmentation efficiency of typical pulping systems. The cleavage of β-aryl ether bonds is considered to be a major pathway for delignification of lignocellulosics.[9] Our previous studies have used 1 to measure fragmentation efficiencies of pulping additives[10] and select combinations[11] thereof in aqueous solutions; these studies will serve as controls to determine the effects of alcohol addition.

Model 1 provides QM 2 when heated in alkali. [Quinone methides are key intermediates in pulping chemistry.[9]] The intermediate 2 cyclizes at a specific rate; fragmentation reactions that give guaiacol (4) can be "timed" relative to the rate of cyclization (Figure 1).[10-12] If conditions are such that fragmentation is enhanced, then the yield of guaiacol will increase and the yield of cyclized product 3 will decrease.
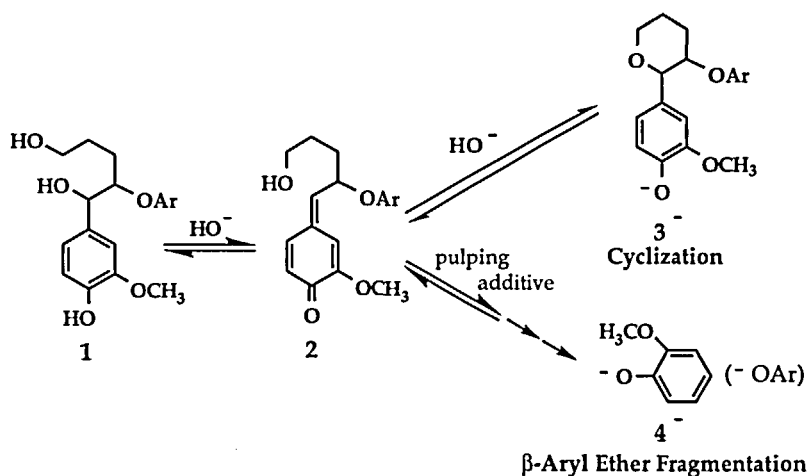
Figure 1. Competing parallel reactions for QM 2: cyclization and fragmentation reactions of model 1.[10-12]

RESULTS

Alcohol-Reinforced Soda, Kraft, and Alkaline Sulfite Reactions

Compound 1 was heated in water[10] 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_2SO_3. 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 β-aryl ether fragmentation efficiencies of sulfide,

Table 1. Yield comparisons for aqueous[10] 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$_2$O		50% IPA/ 50% H$_2$O		Aqueous		50% MeOH/ 50% H$_2$O	
	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)
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[10] and alcohol-reinforced neutral and alkaline sulfite cooks with model 1 at 150°C. [5 equiv. Na$_2$SO$_3$; 25 equiv. NaOH for alkaline sulfite.]

Reaction Time (min.)	Neutral Sulfite						Alkaline Sulfite			
	Aqueous			50% IPA/ 50% H$_2$O			Aqueous		50% IPA/ 50% H$_2$O	
	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)	Adduct 5 (%)	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)	Adduct 5 (%)	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)	Guaiacol 4 (%)	Cyc. Cpd. 3 (%)
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

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_2SO_3, were performed with model 1 using aqueous[10] and IPA/water solutions. A 50% IPA neutral sulfite cook 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).

(1)
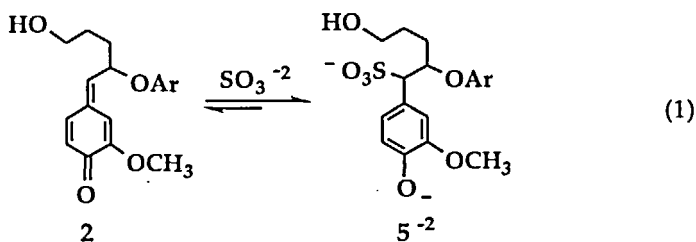
Alkaline Sulfite/AHQ/Methanol and AHQ/Alcohol Reactions

Model 1 was subjected to methanol-reinforced alkaline sulfite/AHQ (ASAM) conditions using 25 equiv. of NaOH, 5 equiv of. Na_2SO_3, and 2 equiv. of AHQ. [Anthrahydroquinone (AHQ) is the reduced form of AQ.] The results are compared to previous experiments with aqueous alkaline sulfite/AHQ[10,11] (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.
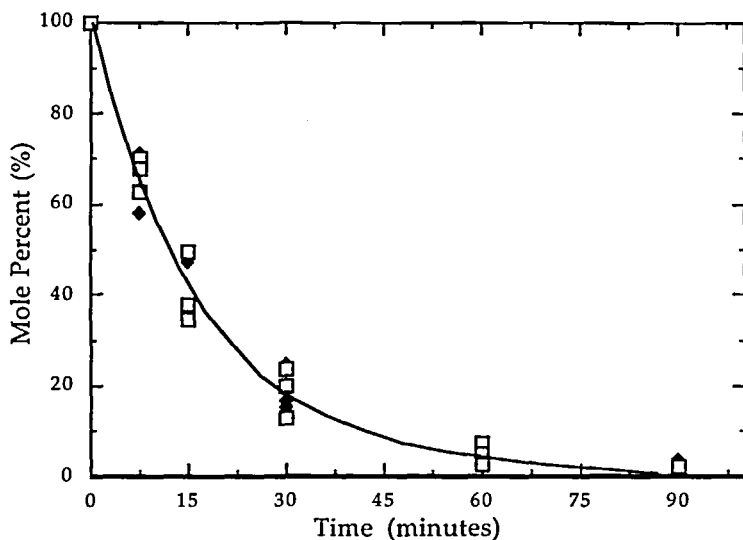
Figure 2. Disappearance of 1 as a function of time at 150°C for aqueous[10] (□) and alcohol-reinforced (◆) cooks under soda, kraft, and alkaline sulfite conditions. [Corresponds to Tables 1 and 2.]
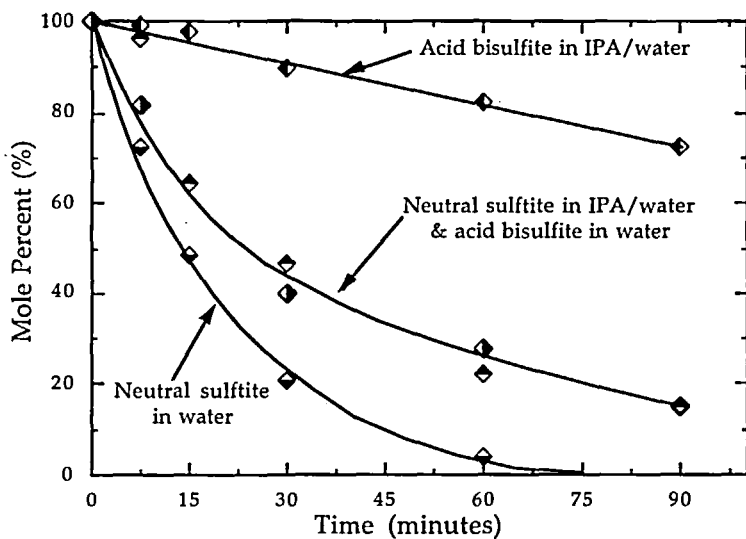

Figure 3. Disappearance of 1 as a function of time at 150°C for aqueous[10] (◈;◆) and IPA-reinforced (◇;◆) cooks under neutral sulfite (◈; ◇) and acid bisufite (◈;◆) conditions.
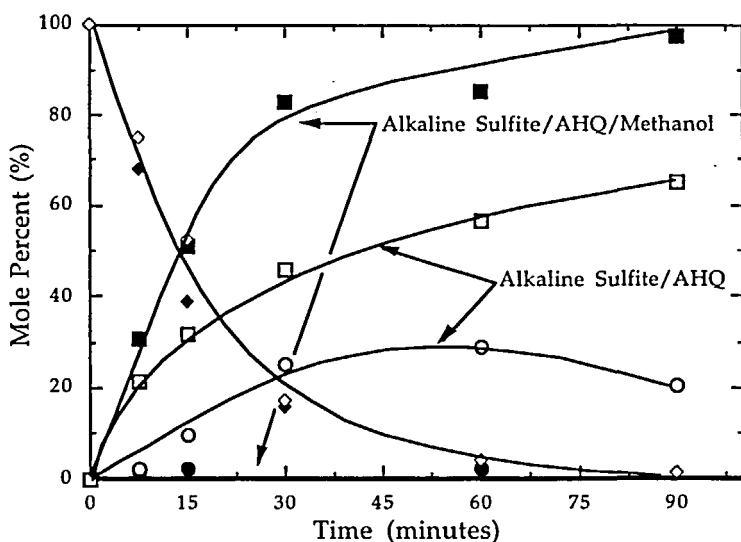
Figure 4. Yields of guaiacol 4 (□;■), and cyclized cpd. 3 (O;●) for aque-
ous[10,11] (□;O;◇) and methanol-reinforced (■;●;◆) alkaline sul-
fite/AHQ degradations of model cpd. 1 (◇;◆) at 150°C.

Several methanol-reinforced soda/AHQ experiments were per-
formed as controls to ASAM cooks (Fig. 5). The soda/AHQ/methanol
cooks showed identical appearance of guaiacol and dis-appearance of
model 1 when compared to ASAM. The results indicated that the in-
creased 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 β-aryl
ether cleavage as 5 equiv. of AHQ in a 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%; cor-
respondingly, the level of cyclization decreased (Fig. 7).

Several other organic solvents were tested with the soda/AHQ sys-
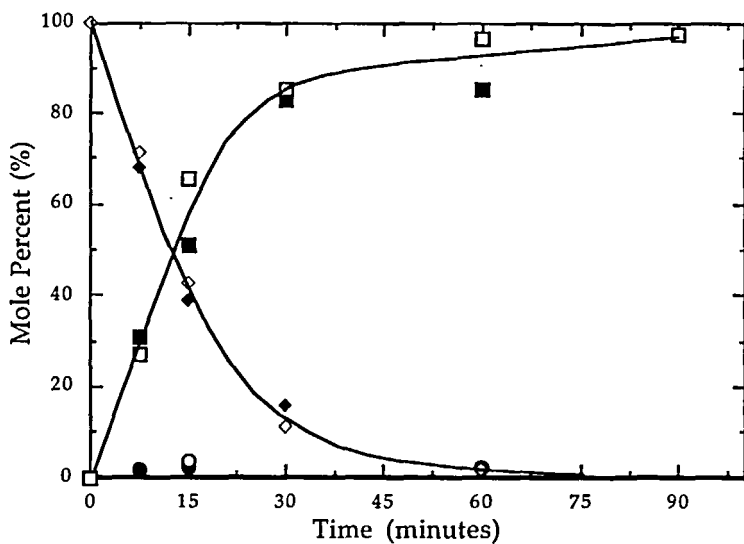tem at 12.5% organic solvent substitution level and 60 min. for model 1

Figure 5. Yields of guaiacol 4 (■;□) and cyclized cpd. 3 (●;○) for methan-
ol-reinforced alkaline sulfite/AHQ (■;●;◆) and soda/AHQ[10]
(□;○;◇) degradations of model cpd. 1 (◆;◇)at 150°C.
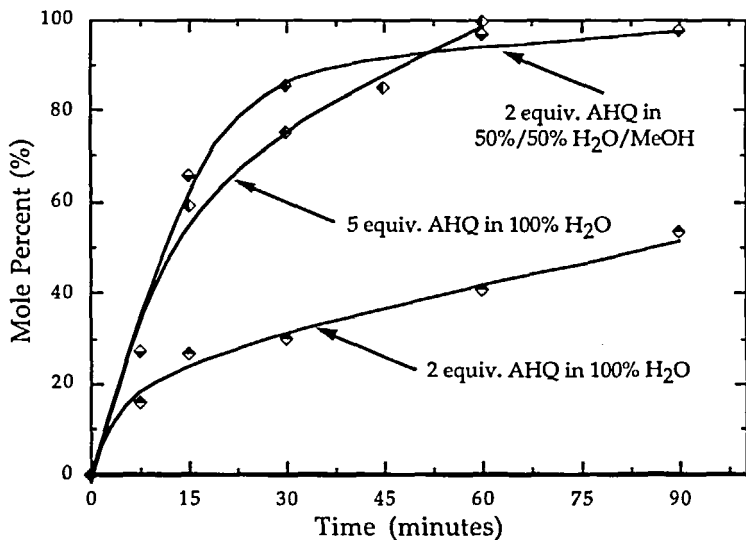
Figure 6. Yields of guaiacol with time for aqueous[10] and alcohol-rein-
forced soda/AHQ cooks of model compound 1 at 150°C.

Figure 7. Effect of methanol content on the product distribution during soda/AHQ/methanol degradation of model 1. Left graph: Yields of guaiacol 4 (□), cpd. 3 (○), and cpd. 1 (◇) 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.]

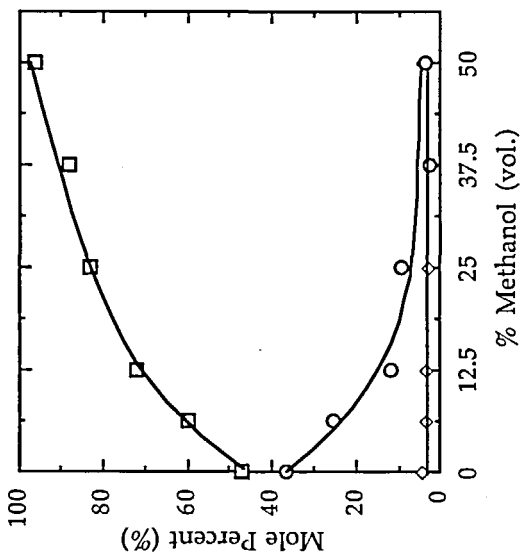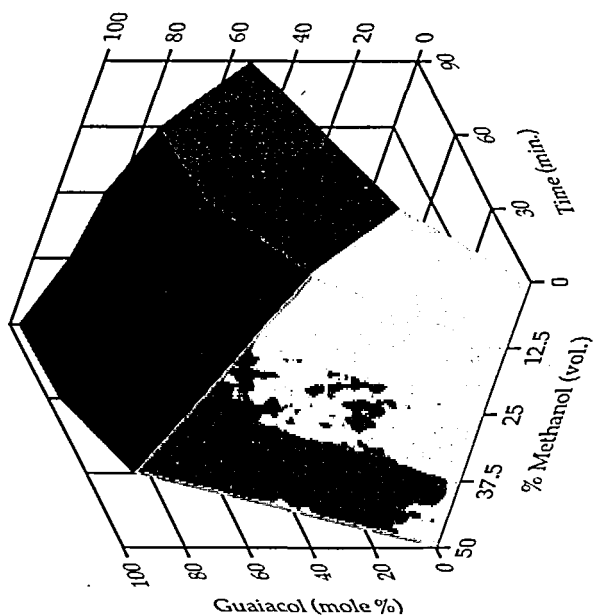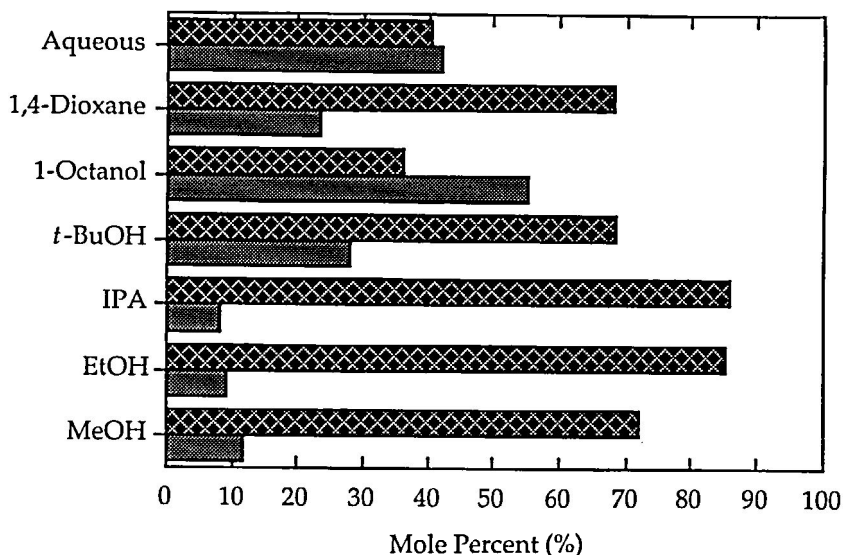Figure 8. Yields of guaiacol 3 (⬚) and cyclized compound 2 (⬚) after 60 minutes for soda/AHQ degradation of 1 with various organic solvents at a 12.5%-volume substitution level at 150°C.

(Fig. 8). A similar product distribution was observed for the lower molecular weight alcohols: ethanol, IPA, *t*-butanol, and methanol. 1-Octanol did not improve β-aryl ether fragmentation over an aqueous system; this result may be attributed to immiscibility of 1-octanol in water. Dioxane was similar to methanol in its effectiveness to enhance guaiacol production. Substituting deuterated methanol (CD_3OH) for regular methanol (at the 12.5% level) had little affect on the 1-hour yield of guaiacol (66 vs. 73%, respectively).

Ethanol and isopropanol 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 anthrahydro-

quinone dianion (AHQ^{-2}) and radical anion ($AHQ^{\bullet -}$).[13] Thus, the more efficient solvent systems retain more of the active reactants.

DISCUSSION

Alcohol addition to alkaline pulping reactions of 1 did not affect the rate of the rate-determining QM formation step,[10,14] or the product distribution in the case of soda, sulfite, and kraft reactions. However, the alcohol addition increased guaiacol production, at the expense of cyclization, for reactions of model 1 that *involve AHQ*. These results further support the fact that AHQ operates by a unique chemistry. This chemistry involves electron transfer reactions,[8,12,15] while soda, sulfite, and kraft involve nucleophilic addition and displacement chemistry.[9] So, 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 for the observed synergism.

The alcohol (or dioxane) may be acting as a free radical scavenger, deactivating reactive radicals that consume AHQ species (e.g., $AHQ^{\bullet -}$) and thus, preserving more of the AHQ species for scission reactions with QMs. An analogy might be the alkaline oxygen oxidation reactions of creosol in ethanol.[16] Very little creosol reacts over a 5-hour period when treated with $O_2/NaOH$ in the presence of ethanol. However, in pure water, the creosol is nearly all converted to radical coupling products. The results suggest that ethanol stabilizes or deactivates the radical intermediates that are generated by the alkaline oxygen conditions.

Primary and secondary alcohols can scavenge radicals by donating α-protons ($-CH_\alpha O-$) to reactive radicals. Based on radical stabilities,[17] the performance of the alcohols should follow the order of IPA > ethanol > methanol > t-butanol. To some extent, this order was followed in our case. However, the scale was compressed; IPA was less effective and t-butanol was more effective than anticipated. In the case of dioxane, a C_α-radical is secondary and stabilized by an adjacent oxygen but inductively destabilized by the C_β-oxygen; therefore, dioxane might be expected to behave similarly to methanol.

One experiment was tried to test out the radical scavenging hypothesis and it failed to confirm the hypothesis. There was only a small difference in guaiacol yield between soda/AHQ reactions of 1 done in CD_3OD and CH_3OH. Because more energy is required to dissociate a C-D bond than a C-H bond,[18] the deuterated methanol should be poorer at donating an α-hydrogen atom and, therefore, should have been much less effective than methanol in promoting fragmentation.

A second hypothesis for the synergism between organic solvents and AHQ relates to possible changes in oxidation and reduction potentials of AHQ species and QMs. Several studies have shown a correlation between the redox potential of pulping liquor and the rate of delignification; as the redox potential of liquor decreases, the rate of delignification increases.[19] The effectiveness of various pulping additives appears related to reduction potential of the additive.[20] The reduction potentials for AQ and AHQ· are: -0.78 and -1.53 volts (vs. Ag/AgCl) in DMSO and -0.92 and -1.72 volts in acetonitrile.[8] The electron transfer reaction between an AHQ· and a QM is more rapid and complete in acetonitrile than in DMSO.[8] It is probable that organic solvents, mixed with water, can affect the redox behaviors of AHQ species and improve electron transfer rates with QMs. 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 to soda/AHQ treatments of lignin model 1 considerably enhanced the β-aryl ether fragmentation reaction. Similar additions to soda, kraft, and alkaline sulfite showed no effect. The alcohol/AHQ synergistic effect indicates that the chemistry of AHQ pulping systems is different than the typical nucleophilic addition/elimination chemistry of other alkaline pulping systems. Evidence continues to mount that β-aryl ether scission by AHQ involves electron transfer reactions between AHQ^{-2} and quinone methides. The delignification associated with the ASAM pulping process is likely being facilitated by both AHQ/sulfite[11] and AHQ/methanol synergistic interactions.

EXPERIMENTAL

The equipment, model 1 degradation procedure, product analysis by reverse phase liquid chromatography (LC), and compound characterization have been previously described.[10,21] 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. None of the inorganic additives used was observed to precipitate out during the degradation of model 1 for the organic solvent/water mixtures examined.

ACKNOWLEDGMENTS

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