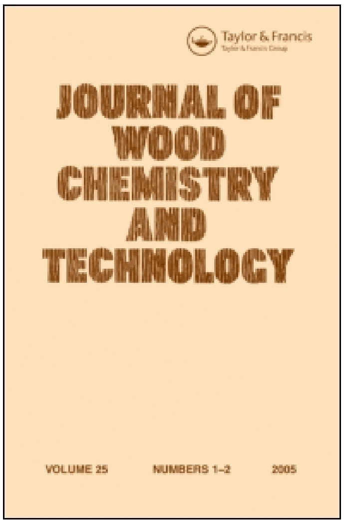

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FUNDAMENTAL STUDY OF RELATIVE DELIGNIFICATION EFFICIENCIES (II): COMBINATIONS OF PULPING ADDITIVES

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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 (QMs). Model 1 was reacted with sulfite/anthrahydroquinone (AHQ), sulfide (kraft)/AHQ, and sulfide/sulfite reagent combinations at pH ~13. Both sulfite/AHQ and sulfide/AHQ systems enhanced β-aryl ether cleavage when compared to their individual component systems; the greatest fragmentation was observed for the sulfide/AHQ system. Several hypotheses are proposed for the observed synergism. β-Aryl ether scission was not affected when sulfite was added to the sulfide (kraft) system. This paper is the second in a three-part study designed to examine β-aryl ether cleavage in multi-reagent pulping systems (e.g., alkaline sulfite/AQ/methanol [ASAM]).

INTRODUCTION

Research efforts have intensified over the past several years to find alternatives and to make improvements to alkaline pulping. There are primarily two factors driving this research: (a) to improve chemical pulping selectivity, and (b) to extend delignification during pulping in order to reduce bleaching discharges.[1]

In recent years, several pulping modifications have used combinations of different reagents, such as sulfide (kraft)/anthraquinone (AQ),[2] sulfide/polysulfide,[3] sulfide/polysulfide/AQ,[4] alkaline sulfide/sulfite[5a] and alkaline sulfite/AQ (ASAQ).[5b,5c] Several fundamental studies have examined the ASAQ system and have postulated various mechanisms for the observed synergistic effect (i.e., increased β-aryl ether cleavage) between sulfite and AQ.[6,7] Similar synergistic interactions could be occurring with other multi-reagent pulping systems. We sought to better understand the lignin chemistry involved with systems utilizing combinations of sulfide, sulfite, and AHQ.

Modified processes still have a common feature with conventional alkaline pulping systems: the first step in the initial phase of delignification is dominated by quinone methide (QM) formation. [QMs are key intermediates in delignification chemistry.[8,9]] The rates of subsequent 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).[8]

Our objective of this paper is to investigate β-aryl ether fragmentation efficiencies of sulfite/anthrahydroquinone (AHQ, the reduced form of AQ), sulfide/AHQ, and sulfide/sulfite systems under alkaline conditions. We have developed a qualitative method for evaluating fragmentation efficiencies of individual reagents by using the reactions of 1-(4-guaiacyl)-2-(O-guaiacyl)-1,5-pentanediol (**1**, Fig. 1).[10,11] This model has a built-in "clock" reaction (i.e., cyclization to **3**) which occurs at a specific rate. Reagent-induced cleavage reactions, resulting in guaiacol (**4**), can be timed relative to the cyclization event. A high proportion of fragmentation product versus cyclization signifies an efficient set of conditions for delignification. Previously, we have examined the reactions of **1** under sulfide, sulfite, and soda/AHQ pulping conditions;[11a] the results provide the base cases with which to assess reagent-reagent interactions for the multi-reagent systems considered here. The accompanying paper will consider the influence of alcohol on β-aryl ether cleavage reactions of **1** with pulping reagents in alcohol/water mixtures.[11b,11c,12]

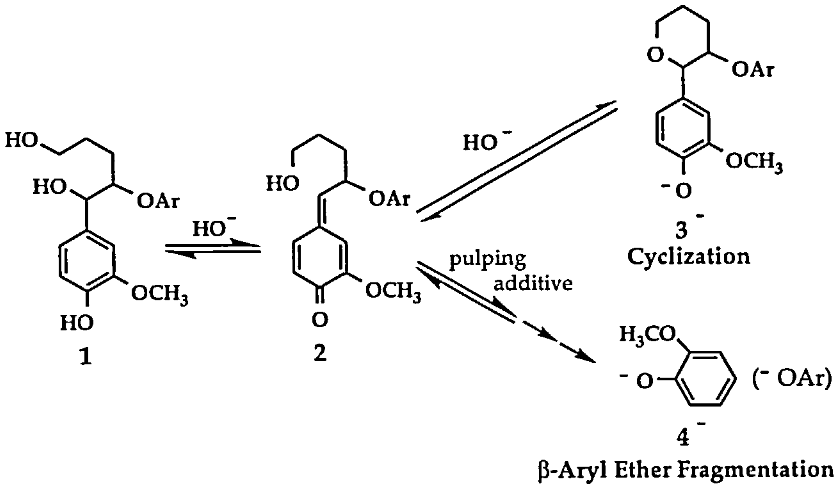

Figure 1. Competing parallel reactions for QM **2**: cyclization and fragmentation of model **1**.[10,11]

RESULTS

Soda/AHQ and Alkaline Sulfite/AHQ (ASAQ) Reactions of Model 1

Prior to examining mixtures of sulfite and AHQ, we conducted several soda/AHQ experiments to arrive at conditions that would allow some cyclization to occur in the presence of AHQ. Our previous study showed that very little cyclization occurred when 5 equiv. of AHQ was reacted with **1**.[11a] We have found that 2 equiv. of AHQ (Fig. 2) will give a product distribution similar to the kraft case,[11] roughly equal amounts of fragmentation and cyclization in the first 60 min. of reaction.

We conducted experiments using the alkaline sulfite/AHQ (ASAQ) system with model **1** employing 2 equiv. of AHQ, 5 equiv. of Na_2SO_3, and 25 equiv. of NaOH. The addition of AHQ restored the predominance of β-aryl ether cleavage of model **1** compared to the alkaline sulfite system[11] (Fig. 3). The 60 minute-yields for soda/AHQ, alkaline sulfite, and ASAQ runs are presented in Table 1. The ASAQ system afforded more guaiacol than the soda/AHQ system at the same AHQ level; however, the ASAQ system was not as efficient as the soda/AHQ system with 5 equiv. of AHQ.[11]

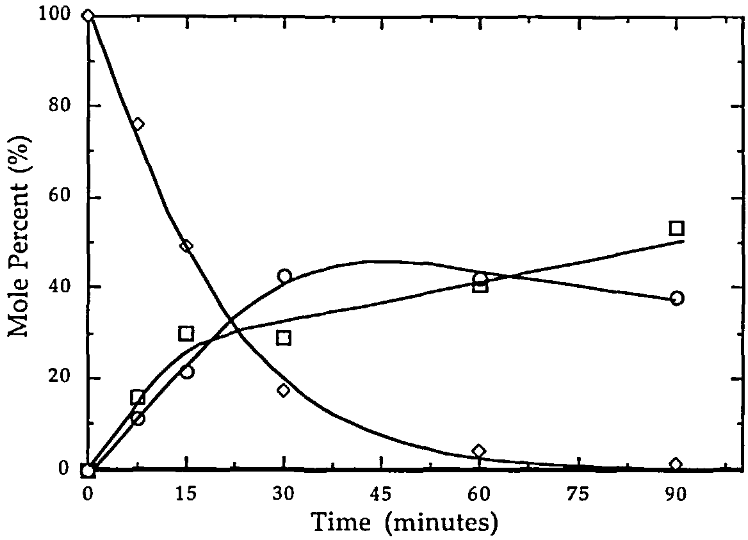

Figure 2. Yields of guaiacol 4 (□) and cyclized cpd. 3 (○) for the soda/AHQ degradation of model 1 (◇) at 150°C. [AHQ level at 2 equiv.]

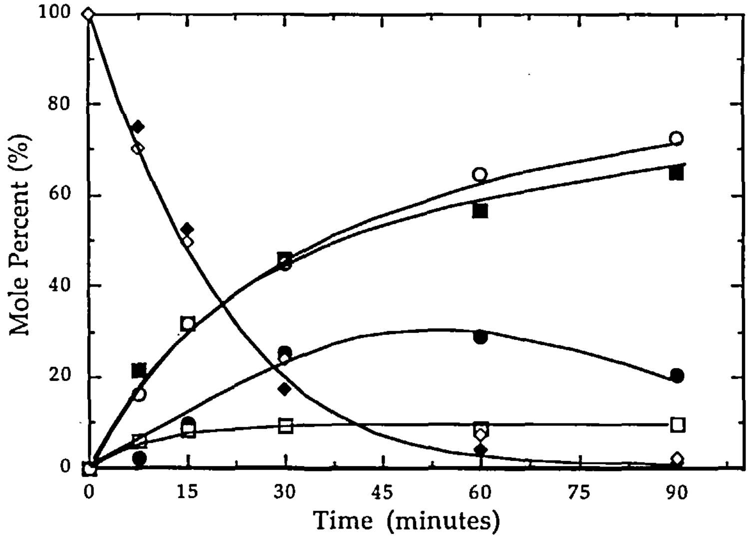

Figure 3. Yields of guaiacol 4 (■;□) and cyclized cpd. 3 (●;○) for the alkaline sulfite (□;○;◇) and alkaline sulfite/AHQ (■;●;◆) degradation of model 1 (◆;◇) at 150°C. [AHQ level at 2 equiv.]

Table 1. Yield comparison for AHQ, sulfite, soda, and combinations, all with 25 equiv. of NaOH.

AHQ^{-2} (equiv.)	SO_3^{-2} (equiv.)	% Yield after 60 min. at 150°C Model 1	 Guaiacol (4)	 Cyc. Cpd. 3
5	-	0	99	0
2	-	4	41	42
-	5	8	9	65
2	5	4	57	30
-	-	4	20	70

Experiments were also conducted to determine the influence of alkali on the ASAQ system.[6,7] The addition of 2 equiv. of AHQ to a sulfite system with no added alkali (pH 8.5-9) did not promote cleavage reactions; instead, sulfonation of **1** occurred, similar to our previous neutral sulfite cooks.[11a,11c] These results agree with a prior study by Suckling.[6]

The ASAQ product mixtures contained a component not previously observed in runs that contained the individual pulping additives. The fast eluting unknown (1.9 min.) increased in intensity as the reaction time increased. Its intensity paralleled that of the guaiacol being produced; the LC signal areas were nearly identical. In addition, the UV spectrum of the unknown lacked strong absorptions at 280 and 310 nm which would indicate an unsaturated, conjugated system (i.e., vinyl ethers and styrenes).[11a,11c,13] The spectrum and elution time of the unknown were similar to previous α-sulfonates characterized by us.[11a] However, attempts to isolate the component from the ASAQ reaction mixture and characterize it by ^1H- and ^{13}C-NMR were unsuccessful.

Reactions of Model 1 with Sulfide (Kraft)/Sulfite and Sulfide/AHQ

Experiments were performed with **1** to examine the possible enhancement of β-aryl ether cleavage with sulfide/sulfite system under alkaline conditions (pH ~13). In Table 2 the product distribution at selected times and at 150°C are compared with distributions from each individual component.[11a] Little change was noted at 30 or 60 min. in the product distribution of the sulfide/sulfite system compared to the sul-

Table 2. Yield comparisons for kraft, alkaline sulfite, 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 (**4**)	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

Table 3. Yield comparisons for sulfide (kraft), and kraft/AHQ with model **1**, all with 25 equiv. of NaOH at 150°C.

Time (min.)	HS^- (equiv.)	AHQ (equiv.)	% Yield at 150°C Model **1**	Guaiacol (**4**)	Cyc. Cpd. **3**
15	-	2	43	27	29
15	5	-	33	17	43
15	5	2	40	40	19
30	-	2	17	32	43
30	5	-	16	25	49
30	5	2	15	56	19

fide (kraft) system. [The material balance for the 30 min. sulfide/sulfite data was >100%; however, the product distribution is the same as the kraft data, namely 2:3:6 for cpd. **1**/guaiacol **4**/cpd. **3**.]

Model **1** was also used to evaluate the sulfide/AHQ system; cooks were conducted at 15 and 30 min. with 2 equiv. of AHQ, 5 equiv. of NaSH and 25 equiv. of NaOH at 150°C. The observed results were compared to sulfide[11a] and soda/AHQ cooks of **1** at similar reagent levels (Table 3). Unlike the sulfide/sulfite system, the sulfide (kraft)/AHQ combination augmented β-aryl ether fragmentation; the cyclization reaction was also reduced in this multi-reagent system. Guaiacol production was enhanced ~50% over the soda/AHQ case and was almost doubled the amount observed in the kraft case. Obviously, there is some interaction occurring between sulfide and AHQ that is efficiently causing scission.

Table 4. Guaiacol (4) yield comparisons at 30 min. for various pulping systems for model 1, all with 25 equiv. of NaOH at 150°C.

Additive (equiv.)	Guaiacol (%)			
	Observed	NaOH[a]	Additive[b]	Predicted[c]
1. Control [Soda]	10			
2. Alk. sulfite (5)	9	10	0	
3. Sulfide [Kraft] (5)	25	10	15	
4. Soda/AHQ (5)	75	10	65	
5. Soda/AHQ (2)	32	10	22	
6. Alk. sulfite (5)/AHQ (2)	46	10	0 + 22	32
7. Sulfide (5)/AHQ (2)	56	10	15 + 22	47
8. Sulfide (5)/Sulfite (5)	26[d]	10	15 + 0	25

[a]Assumed yield due to NaOH in the system (entry 1); [b]Guaiacol due to additive(s); [c]Predicted values for entries 6-8 by summing NaOH and additive columns; [d]Value has been normalized from Table 2.

DISCUSSION

The sulfide/AHQ and alkaline sulfite/AHQ (ASAQ) combinations substantially improved 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 4 into two categories: (a) guaiacol from alkali reactions (column 2), and (b) guaiacol from additive reactions (column 3). The values are based on our previous study with 1.[11a] For additive combinations (entries 6-8), a predicted guaiacol yield is estimated from each additive alone (column 4). The data analysis indicates that both sulfide/AHQ and sulfite/AHQ (ASAQ) systems synergistically enhance β-aryl ether fragmentation. This enhancement appears to be related to the unique chemistry by which AHQ cleaves β-aryl ether structures.[10-13] The question is: what mechanism accounts for this synergism when AHQ is combined with other additives? Some possible explanations are postulated below; however, our results do not specifically provide an answer.

An earlier AQ solubility study[14] indicated that sulfide ions slowly reduce AQ to $\mathrm{AHQ}^{\dot{-}}$ or AHQ^{-2}. Sulfide ions could have reduced some of

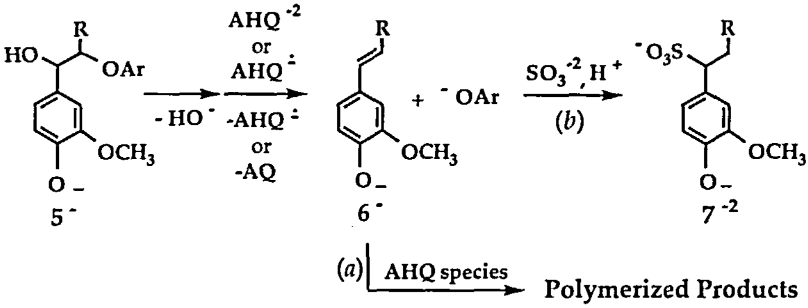

Figure 4. Possible lignin model reactions with AHQ and AHQ/sulfite.

the AQ to AHQ anions during the kraft/AHQ cooks of 1; however, the reduction was not complete, since only 56% fragmentation was observed after 30 min. For efficient conversion, the amount of fragmentation should have resembled the 5 equiv. soda/AHQ case.

A similar type of mechanism could have occurred with AQ and sulfite; however, sulfite does not reduce *solid* AQ to $AHQ^{\dot{-}}$ or AHQ^{-2} in 1 M NaOH at 150°C.[14] Yet, sulfite might be capable of reducing *soluble* $AHQ^{\dot{-}}$ to AHQ^{-2}. Experimental proof for such a reduction would be difficult since $AHQ^{\dot{-}}$ tends to disproportionate to AQ and AHQ^{-2} in water.[15] Again, if this conversion was efficient, the amount of guaiacol should have resembled the 5 equiv. AHQ/soda case.

An alternative explanation for the sulfite/AHQ synergistic effect could be related to the new component found in our ASAQ reaction mixtures. Fragmentation of a β-aryl ether model (5, Fig. 4) with AHQ should afford equal amounts of guaiacol and a styrene product 6.[9,16] However, the latter is very reactive towards sulfite. Suckling observed the α-sulfonate 7 (R = H) from the reaction of a β-aryl ether model with sulfite and AHQ.[6] Suckling also synthesized and reacted styrene 6 (R = H) with sulfite; analysis of the product mixture showed a complete conversion of 6 to α-sulfonate 7.[6] Gellerstedt, et al. also produced α-sulfonates by reacting styrenes with sulfite.[17] The uncharacterized compound that we observed in levels similar to guaiacol during ASAQ runs with 1 probably is the α-sulfonate 7 (where R = $CH_2CH_2CH_2OH$).

Several model studies involving AHQ have shown that the two products of β-aryl ether cleavage, the styrene 6 and guaiacol, are not *observed* in equal amounts;[9-12,15] 6 apparently has a strong tendency to polymerize, resulting in lower observed amounts of 6. There is evidence that AHQ species, such as $AHQ^{\bullet -}$, can cause polymerization reactions of 6 (Fig. 4, path *a*);[15] in the process, some AHQ is probably lost. We did not detect the styrene 6 (R = $CH_2CH_2CH_2OH$) in the product mixtures of pulping runs of **1** with AHQ. The sulfite in the ASAQ runs may prevent these polymerization reactions by reacting with styrene **6** to give an α-sulfonate 7 (Fig. 4, path *b*). Consequently, sulfite may preserve AHQ species for fragmentation reactions. This reasoning could also help explain why 2 equiv. of AHQ (an excess of reagent) in a soda/AHQ run gave only a 40% guaiacol yield (Table 1); some of the excess AHQ may have been lost in unproductive reactions.

CONCLUSIONS

β-Aryl ether scission was synergistically enhanced when AHQ was added to kraft or sulfite cooks of **1**; a mixed sulfide/sulfite cook of **1** had the same product distribution as a sulfide (kraft) cook. The observed synergism when *AHQ was involved* could be due to a redox cycle between AQ (or AHQ species) and the additional reagent. For the sulfite/AHQ system, the synergism might involve SO_3^{-2} reacting with AHQ fragmentation products that otherwise consume AHQ species.

EXPERIMENTAL

The equipment, model reagent amounts, model **1** degradation procedure, product analysis by reverse phase liquid chromatography (LC), and most of the compound characterization have been previously described.[11,18] All pulping runs used 0.015 mmoles (= 1 equiv.) of **1** and 25 equiv. of NaOH and 5 equiv. of pulping additive(s) except were noted. Repeatability of product yields was within ±3% units for each of the main components analyzed (**1**, **3**, and **4**), except in the case of high amounts of the cyclized compound **3**, where it was ±6% units.

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