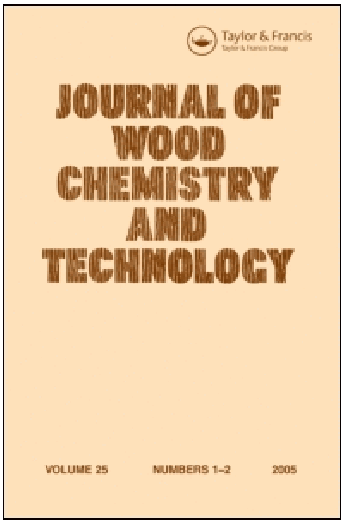

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QUINONES AS ADDITIVES DURING SODA COOKING

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ABSTRACT

Anthraquinone-1-acetic acid is a less effective delignification catalyst than anthraquinone but it gives an enhanced carbohydrate stabilization by converting reducing sugar end groups more effectively to aldonic acid end groups. This reaction produces the hydroquinone form of the additive which is then easily oxidized by oxygen at 80°C. Oxygen treatment favors the end group stabilization. Depolymerization of the cellulose is suppressed by the presence of magnesium hydroxide but cannot be avoided completely.

INTRODUCTION

Holton[1] made the important discovery that anthraquinone (AQ) and some derivatives containing nonpolar substituents were much more effective catalysts during alkaline pulping than anthraquinone-2--monosulfonate (AMS), earlier suggested by Bach and Fiehn[2]. Other derivatives than AMS, with a polar group linked directly to AQ, have also given inferior results compared to AQ[1,3] and it has even been proposed that a low solubility in water should be a prerequisite for a suitable catalyst for the delignification. The stabilization of the carbohydrates by oxidation of reducing sugar end groups to aldonic acid end groups[4] is, however, much more effective with AMS than with AQ[5]. Initially, the purpose of this investigation was to study the behaviour of quinone derivatives with a polar substituent separated from the aromatic ring in AQ by a methylene group. The methyl ester of anthraquinone-1-acetic acid was used in the present work. The ester is easily saponified in alkaline solution which means that the anionic form of anthraquinone-1-acetic acid is formed. The additive will be denoted AMA.

The possibilities of increasing the yield of pulp by pretreating the wood with oxygen and alkali in the presence of the quinone compounds were also studied[6].

EXPERIMENTAL

Synthesis and Identification of AMA

1-Aminoanthraquinone was converted to the corresponding diazonium compound[7]. The isolated intermediate was treated with 1,1-dichloroethylene and methanol[8]. The ester was recrystallized from methanol. The melting point was 187°C.

The mass spectrum (70 eV) of the compound confirmed the structure. The molecular ion was recorded at m/e 280. The four most prominent peaks were at m/e 249 and m/e 221, typical for methyl esters (M-31 and M-59), at m/e 248 consistent with the loss of methanol and at m/e 220. An additional loss of carbon monoxide explains the occurrence of this peak which was the base peak. Elementary analysis gave 72.93% C (calc. 72.85), 4.33% H (calc. 4.32) and 22.69% O (calc. 22.83).

The additions of AMA and other chemicals are calculated per 100 g of dry wood or hydrocellulose. AMA was determined by adsorption on XAD-2 and chromatography on ODS-Hypersil in aqueous methanol in the presence of tetrabutylammonium hydroxide.

Alkali Treatment of Hydrocellulose

Hydrocellulose (2 g) obtained by hydrolysis of purified cotton linters in 0.1 M sulfuric acid for 100 min at 100°C, was charged into autoclaves (130 ml) together with equimolar amounts of the quinone compounds and 100 ml 1 M NaOH. The autoclaves were closed and rotated in a polyglycol bath preheated to 100°C. The autoclaves were cooled rapidly after 30 or 140 min and the cellulose was washed on a glass filter (G 3) at 80°C with 0.2 M NaOH containing 15 g of sodium dithionate per liter until the filtrate was colorless. The cellulose was then washed carefully with water and dried in circulating air at 35°C.

Cooking of Spruce Meal without Pretreatment

The same autoclaves were instead charged with spruce meal (0.13-0.36 mm) corresponding to 10 g dry wood obtained by grinding chips of *Picea abies* (L.) Karst. in a Wiley mill. The meal was mixed with quinone compounds and 70 ml 1 M sodium hydroxide. The temperature of the polyglycol bath was 170°C. After 30-180 min the autoclaves were cooled and the pulp treated as described above.

Pretreatment and Cooking of Chips

Chips from spruce with average dimensions 23 x 13 x 2 mm prepared in a laboratory chipper and one batch of industrial spruce chips (31 x 13 x 4 mm) but subjected to screening in the laboratory were supplied by Mo och Domsjö AB, Örnsköldsvik. The air dried chips were impregnated for 3 days at room temperature with a 0.03 M solution of magnesium sulfate. After draining the chips were dried in circulating air at 35°C. The magnesium content determined by atomic absorption was 0.1%.

The laboratory chips (corresponding to 100 g dry wood), the quinone additive and 450 ml sodium hydroxide solution were introduced into autoclaves (1500 ml). The air was displaced by nitrogen or oxygen under pressure (116 mmol per 100 g wood). Eight autoclaves in each series were inserted in a preheated polyglycol bath and rotated at 80°C for 120 min. After this pretreatment the autoclaves were cooled rapidly and the gas was displaced by nitrogen. The autoclaves were again inserted in the polyglycol bath and the temperature was raised from 80°C to 170°C in 135 min. The chips were finally treated at 170°C for varying lengths of time. After rapid cooling the pulps were fiberized (Ultra-Turrax) for 2 min and treated at 80°C with 0.1 M NaOH containing 5 g sodium dithionate per liter. The pulp was then washed at room temperature with water, 1% acetic acid and finally with water and dried at 35°C.

In the experiments with the industrial chips the weight of the chips and the volume of the sodium hydroxide solution were doubled. This means that the gas volume in the autoclave decreased. The volume of oxygen corresponded to 40 mmol per 100 g wood. Pretreatment, displacement of the gas and heating was then carried out according to the same schedule as that used in the cooks of laboratory chips.

Cooking of Wood Meal with Pretreatment

Spruce meal of the same particle size was prepared from the industrial spruce chips. The meal was slurried in 0.02 M magnesium sulfate for 1 hour. After draining and drying at 35°C the meal contained 0.1% Mg.

The impregnated meal (corresponding to 100 g dry wood) was pretreated for 120 min at 80°C under nitrogen or oxygen (40 mmol per 100 g wood) in the 1500 ml autoclaves in the presence of quinone additive and 700 ml 1 M sodium hydroxide. The gas was then displaced by nitrogen and the cooking continued as described for the experiments with chips except for the fiberization which was omitted.

RESULTS AND DISCUSSION

Hydrocellulose

In agreement with previously reported results[5] AQ gave rise to a slight but significant stabilization of hydrocellulose towards endwise degradation (peeling) during hot alkali treatment while a very large effect was obtained with an equimolar addition of AMS (Table 1). As shown in the table AMA takes an intermediate position. The reduced quinone compound formed in these experiments exhibited a blood red color similar to that of anthrahydroquinone. The color disappeared in the presence of air but was stable for several days when the solution was protected by a layer of paraffin oil.

In the experiment with AMS the yield decreased only by 1% when the duration of the alkali treatment was increased from 30 min to 140 min. Evidently, the reducing sugar end groups were oxidized to aldonic acid groups so rapidly that only a minor proportion remained after 30 min. The superior result with AMA compared to AQ is explained by a rapid saponification of the ester group leading to the ionized carboxylate form of anthraquinone-1-acetic acid, which is much more soluble than AQ. At pH 11 and room temperature the saponification was complete within less than one min. In the experiments with hydrocellulose the additions of quinones were very large (24 mmol corresponding

TABLE 1

Yield of Hydrocellulose after Treatment at 100^{o}C for 30 and 140 min without and with Addition of Quinones (4.8 mmol per litre).

Additive	Yield (5) after treatment for 30 min	 140 min
—	77.7	66.0
AQ	79.4	69.1
AMS	92.3	91.3
AMA	85.0	79.0

to 5 g AQ per 100 g of the hydrocellulose) while the volume of air corresponded to 12 mmol of O_2 per 100 g hydrocellulose.

Cooking of Spruce Meal without Pretreatment

In the experiments with wood meal the additions of quinones were 4.8 mmol or 1.2 mmol per 100 g wood corresponding to 1% or 0.25% AQ, respectively. The autoclaves were inserted in a polyglycol bath preheated to 170°C. The volume of air corresponded to 4.6 mmol of O_2 per 100 g of wood meal. Fig. 1 illustrates the influence of AQ and AMA on the relationship between kappa number and cooking time. These curves, as well as plots of the product of

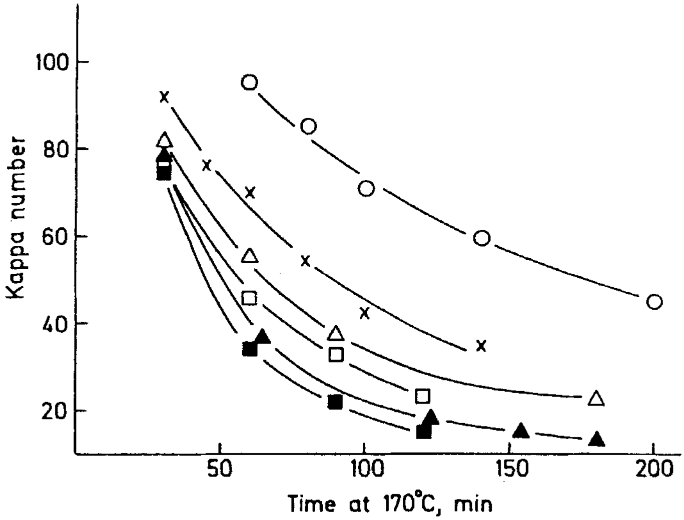

FIGURE 1. Influence of AMA and AQ on the relationship between kappa number and cooking time for pulps prepared from spruce meal without pretreatment.

△ AMA 1.2 mmol/100 g	▲ AMA 4.8 mmol/100 g
□ AQ 1.2 mmol/100 g	■ AQ 4.8 mmol/100 g
X AMS 1.6 mmol/100 g, from (3)	○ No addition, from (3)

kappa number and yield versus time, show that AMA exerted a large catalytic effect on the delignification. The effect increased with an increasing addition. At the highest addition the effect was only slightly lower than that of an equimolar addition of AQ. With the lower addition the difference in favor of AQ was larger. A very large effect of the additives on the kappa number was observed already after a short duration of the cook but an effect was obtained also during prolonged cooking. The results from analogous experiments with wood meal from the same chips with addition of AMS (1.6 mmol/100 g) included in Fig. 1 show that AMA was much more effective than AMS.

The depolymerization of the carbohydrates, studied by determination of the intrinsic viscosity, was more rapid at the highest amounts of AQ and AMA than at the lower additions and in the blank. The difference between additives was small. The increase in viscosity compared at a given kappa number (Fig. 2) with increasing additions can therefore be ascribed to the enhanced delignification rate. Accordingly, a higher viscosity at any given kappa number was observed with AQ than with AMA.

During alkaline pulping the reducing sugar end groups present in the wood are attacked by endwise degradation (peeling). In addition the depolymerization of the carbohydrates is followed by a consecutive endwise degradation which starts at reducing sugar moieties formed during the depolymerization[9]. Although the viscosity compared at any given kappa number was lower in the experiments with AMA than in comparable cooks with AQ, the yield obtained with the largest addition was slightly higher in the experiments with AMA (Fig. 3). Since a longer cooking time was required with AMA compared to AQ and the viscosities of the pulps were lower, it is evident that also with wood meal AMA gave a more effective stabilization against endwise attack on the carbohydrates than AQ. In the experiments with the lower additions of the quinones the observed difference in yield at a given kappa

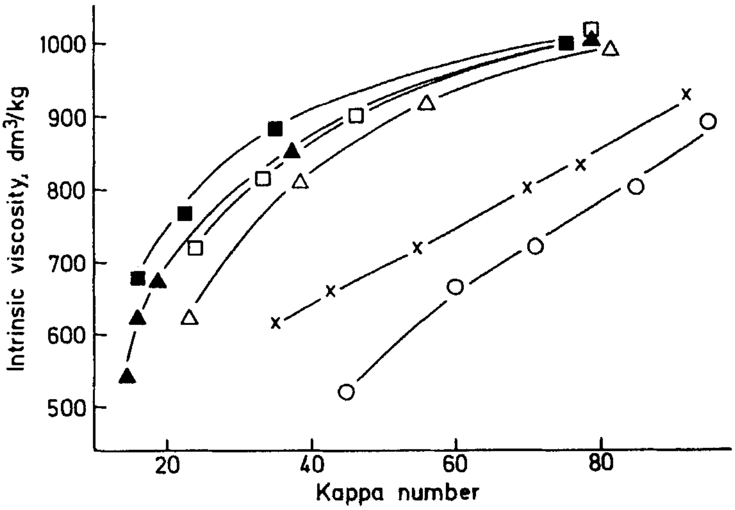

FIGURE 2. Relationship between viscosity and kappa number for pulps referred to in Fig. 1.

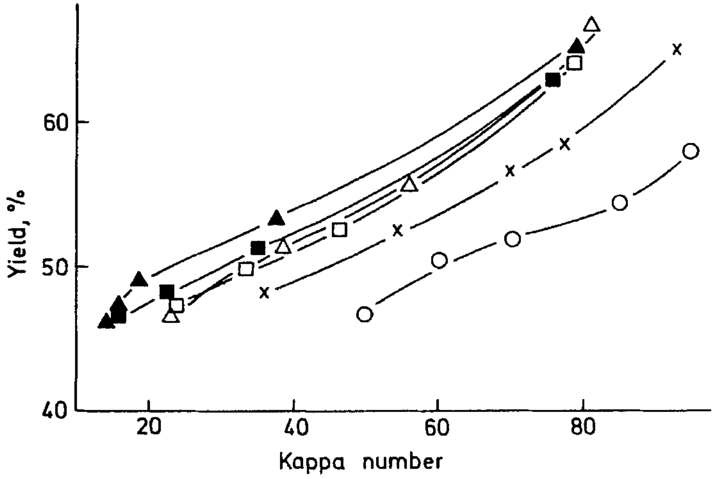

FIGURE 3. Relationship between yield and kappa number for pulps referred to in Fig. 1.

number was small. This can be mainly explained by the lower viscosity obtained when AMA was used instead of AQ which is a result of the lower catalytic effect of AMA on the delignification. Hence, it is obvious that both with large and with small quinone additions the stabilization of the carbohydrates was more effective with AMA than with an equimolar amount of AQ.

Delignification in Cooks with Pretreatment

The purpose of the pretreatment with oxygen was to increase the carbohydrate yield by reoxidation of the hydroquinone form of the additive produced during an early stage of the cook and in this way promote the conversion of reducing sugar end groups to terminal aldonic acid groups. The wood was impregnated with magnesium sulfate to suppress the depolymerization of the carbohydrates by oxygen during the pretreatment. The pretreatment was made for 120 min at 80°C. After this treatment the oxygen was replaced by nitrogen and the cooking finished at 170°C.

In the blanks with pretreatment under nitrogen at 80°C the delignification was much slower in cooks with AMA (1.2 mmol) as catalyst than in those with an equimolar addition of AQ. This holds true for wood meal (Fig. 4), laboratory chips (Fig. 5) and industrial chips (Table 2). The results are consistent with those obtained with wood meal without pretreatment and show that although AQ is less soluble than AMA it is a superior catalyst for the delignification. A mixture of AMA (0.6 mmol) and AQ (0.6 mmol) resulted in a catalytic effect which was much larger than that of AMA but lower than that of AQ.

Previous investigations of AQ cooking of wood meal in the presence of magnesium hydroxide showed that oxygen, present during the pretreatment only, had little effect on the kappa number of the final pulp[6] while in the absence of magnesium hydroxide an appreciable oxygen delignification was obtained. Under the conditions used in the present work, the presence of oxygen during the

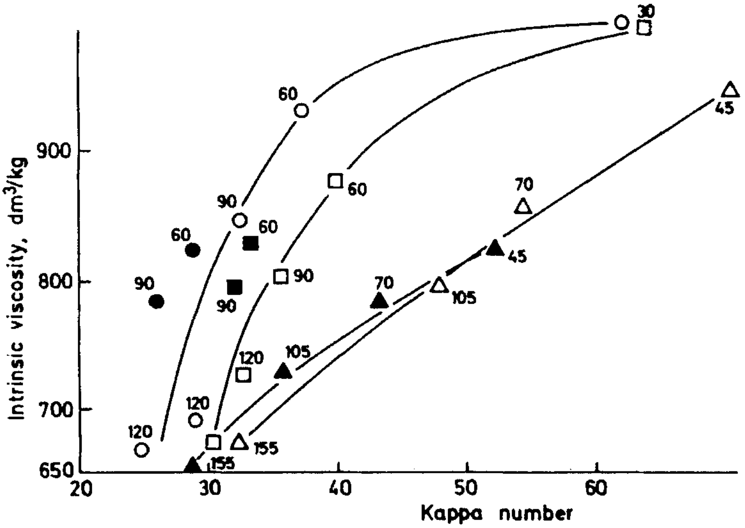

FIGURE 4. Influence of AMA and AQ on the relationship between viscosity and kappa number for pulps prepared from spruce meal pretreated for 120 min at 80°C under nitrogen (open symbols) or oxygen (filled symbols). The values given in the diagram refer to the cooking time (min).

△ ▲ 1.2 mmol AMA/100 g ○ ● 1.2 mmol AQ/100 g
□ ■ 0.6 mmol AMA/100 g + 0.6 mmol AQ/100 g

pretreatment of wood meal resulted in a lowered kappa number although magnesium hydroxide was present. The same effect was observed when a mixture of AQ and AMA was applied. The largest influence of oxygen was found in the cooks with AMA, especially those carried out with a fairly short cooking time.

For the laboratory chips a markedly increased delignification resulting from the presence of oxygen during the pretreatment was obtained only in the experiments with AMA. For the industrial chips slightly lowered kappa numbers were obtained in the experiments with AMA under these conditions while in some experiments with AQ the final pulps exhibited higher kappa numbers when oxygen was

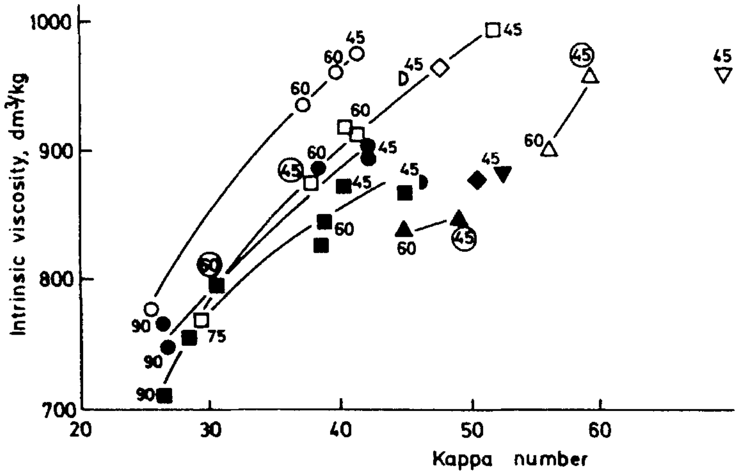

FIGURE 5. Influence of AMA and AQ on the relationship between viscosity and kappa number for pulps prepared from laboratory chips pretreated for 120 min at 80°C under nitrogen (open symbols) or oxygen (filled symbols). The values given in the diagram refer to the cooking time at 170°C (min). Values within circles refer to experiments with slower heating between 80°C and 170°C.

△ ▲ 1.2 mmol AMA/100 g; 26% NaOH
▽ ▼ 1.2 mmol AMA/100 g; 24% NaOH
○ ● 1.2 mmol AQ/100 g ; 26% NaOH
D ◗ 1.2 mmol AQ/100 g ; 24% NaOH
□ ■ 0.6 mmol AMA/100 g + 0.6 mmol AQ/100 g; 26% NaOH
◇ ◆ 0.6 mmol AMA/100 g + 0.6 mmol AQ/100 g; 24% NaOH

present in the pretreatment stage. A precipitation of AQ during the pretreatment by the reoxidation of soluble anthrahydroquinone to AQ can explain the difference.

No appreciable amount of AMA was present in the spent liquors after the final cooking at 170°C. In the experiment with wood meal pretreated under oxygen with the mixture of AMA and AQ 30% of the added AQ was present after 30 min at 170°C, while 20% remained when the pretreatment was made under nitrogen. In the corresponding experiments with AQ as the only additive the remaining AQ amounted to 35 and 22%. The larger loss of AQ under nitrogen, observed also

TABLE 2

Soda (NaOH) Cooking of Magnesium Impregnated Industrial Chips at 170^{o}C after Pretreatment at 80^{o}C.

Additive mmol/100 g		NaOH	Time	Pretreatment under nitrogen			Pretreatment under oxygen		
		% on	min	Yield	Kappa	Viscosity	Yield	Kappa	Viscosity
AQ	AMA	wood	at 170^{o}	%	number	dm^{3}/kg	%	number	dm^{3}/kg
1.2		26	60	49.5	30.6	872	50.6	32.3	833
1.2		26	90	47.9	27.4	856	49.8	26.5	806
1.2		28	40	49.2	41.0	939	49.9	40.9	881
1.2		28	70	47.6	27.7	811	48.0	30.3	769
0.6	0.6	26	60	50.2	35.8	888	52.2	40.2	859
0.6	0.6	26	90	49.0	29.3	-	50.6	26.0	801
	1.2	28	40	50.9	63.9	938	51.8	56.6	907
	1.2	28	70	48.6	47.8	810	49.0	44.5	798

in previously reported experiments[10], and the lowered recovery at a low liquor to wood ratio suggest that reactions between reduced AQ and the wood are mainly responsible for the destruction of AQ.

Attack on the Carbohydrates in Cooks with Pretreatment

In the experiments with pretreatment under nitrogen the differences in viscosity of the final pulps after a given duration of the cook were small when either AQ, AMA or the equimolar mixture was used. This is true both for experiments with wood meal and chips (Figs. 4-5).

Independent of the catalyst and the wood specimen the presence of oxygen during the pretreatment resulted in a lower viscosity of the final pulp although the wood was impregnated with magnesium salt. Much lower viscosities were obtained in experiments in which the magnesium salt was added to the cooking liquor instead of being impregnated into the wood before the addition of the alkaline cooking liquor. The results indicate that magnesium hydroxide precipitated in the wood served as a protector against oxidation with oxygen and with peroxide which is formed during the reaction between reduced quinone compounds and oxygen.

In the absence of oxygen during the pretreatment the yield of pulp compared at any given kappa number was much lower in the cooks with AMA than in those with AQ. This is true both for wood meal (Fig. 6) and chips (Fig. 7) and is explained by the longer duration of the cook required to obtain a desired kappa number when AMA is used. The observation that approximately the same yield was obtained with 1.2 mmol of AQ and AMA in the experiments referred to in Fig. 3 may be explained by presence of air in the autoclaves in these cooks. In the experiments with pretreatment under nitrogen referred to in Fig. 6 the delignification was slower with the equimolar mixture of the two quinone compounds than with AQ. A higher yield compared at a given kappa

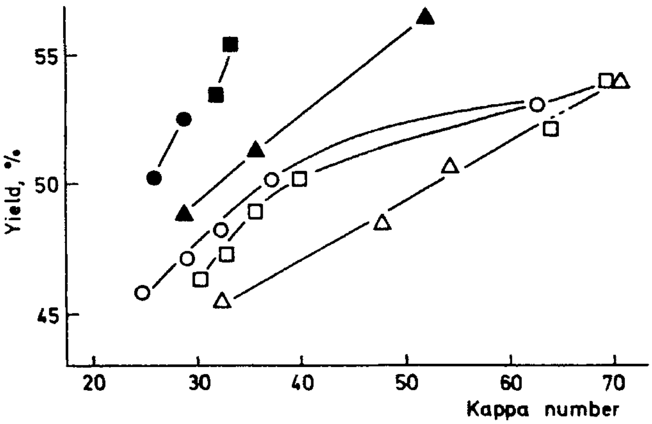

FIGURE 6. Relationship between yield and kappa number for pulps referred to in Fig. 4.

number should therefore be expected with AQ than with the mixture. The experiments with both wood meal and chips showed, however,that the difference was small and hardly significant, although the viscosities were higher for the pulps prepared using AQ as catalyst. The results are consistent with the observation that under proper conditions AMA has a larger effect on the stabilization of the carbohydrates than AQ.

In the cooks of wood meal with AQ as catalyst the yield of pulp compared at any given kappa number increased markedly when oxygen was present during the pretreatment (Fig. 6). Similar results were obtained in a previous investigation[6]. A larger effect of oxygen was obtained in the experiments where both quinone additives were present. The results are consistent with the observation that AMA is superior compared to AQ as far the stabilization of carbohydrates at low temperature is concerned. Although the presence of oxygen resulted in a largely improved yield in the experiments with AMA alone, the yield compared at a given kappa number was significantly lower than obtained with AQ

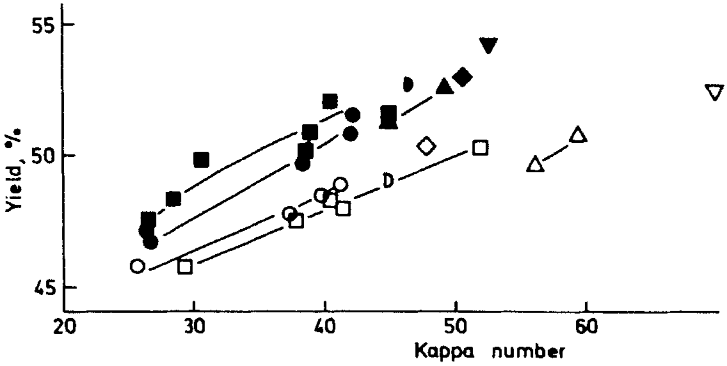

FIGURE 7. Relationship between yield and kappa number for pulps referred to in Fig. 5.

and AMA together and with AQ alone. The longer cooking time required with AMA to obtain a desired degree of delignification explains the difference.

Similarly, cooks with laboratory chips showed that the yield at any given kappa number increased when oxygen was present during the pretreatment (Fig. 7). An appreciable improvement was obtained with AQ but the influence of oxygen was larger when AMA was present. The effects were less than those obtained with wood meal indicating that mass transfer had an influence on the over-all reaction rates. The smaller effects of oxygen obtained with the industrial chips (Table 2) support the conclusion that mass transfer has a decisive influence on the carbohydrate stabilization when chips are used. The viscosities of the pulps obtained after pretreatment under oxygen were significantly lower than in comparable experiments under nitrogen (Table 2). Due to an increased consecutive peeling lower yields should have been obtained unless an improved end group stabilization had been obtained also with chips as a result of the presence of oxygen.

Conclusions

The results presented above show that during soda cooking in the absence of oxygen, AMA exerted a catalytic effect on the delignification which was less than that obtained with an equimolar addition of AQ but larger than that of AMS. The viscosity compared at any given kappa number was lower with AMA than with AQ while in cooks with large additions the yields were higher in the experiments with AMA. The results show that the stabilization of the carbohydrates due to conversion of reducing sugar end groups to aldonic acid groups was more effective with AMA.

The hydroquinone form of the additives produced during an early period of the cook in connection with the end group oxidation and other reactions can be reoxidized by oxygen at 80°C. This leads to an improved end group stabilization. The beneficial effect of this reaction on the final yield is suppressed more or less completely by the depolymerization of the cellulose and other polysaccharides which gives rise to new reducing end groups. Although magnesium compounds retard the depolymerization, more effective methods of protecting the carbohydrates have to be studied. One alternative technique is to oxidize the liquor continuously by oxygen treatment in a separate reactor and to remove oxygen and peroxide from the oxidized liquor before it is recirculated to the digester containing the wood. Promising results have been obtained.

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