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# ANTHRAQUINONE INDUCED SCISSION OF POLYSACCHARIDE CHAINS

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Note to the editor

Anthraquinone induced scission of polysaccharide chains

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    random chain cleavage, yield

Since the great potential of soda-anthraquinone (AQ) pulping was first

demonstrated (1), it has been verified repeatedly and research related

to this area has mushroomed.  Most published research tends to support

the basic hypothesis that AQ functions as a redox catalyst, essentially

transferring electrons from the wood carbohydrates to intermediate radi-

cal sites in partially degraded lignin (2).  The net result is higher

yield and lower kappa number relative to AQ-free conditions.

Detrimental side effects from the addition of AQ are small, although

decreases in viscosity (3,4) and tear strength are often observed.  The

present note gives evidence that AQ under certain conditions is able to

attack a polysaccharide chain and induce cleavage.

Experimental

In this work, purified potato amylose (1% w/v on alkali) was degraded in

1.0M NaOH in a Teflon lined reactor.  To avoid any influence from a heating-

up period, the reagents were kept isolated from each other within the re-

actor until the desired temperature (normally 100°C) had been reached.

Pressurization of the reactor mixed the reagents and initiated the re-

action.  Digested liquor samples were withdrawn periodically for analysis.

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Measurements of amylose yield loss and molecular weight distribution were used to characterize the modes of depolymerization during the reactions. Complete experimental details will be published elsewhere (5).

## Results

The addition of 5% AQ (w/w on amylose) drastically changed the anaerobic degradation of amylose. The yield and number average degree of polymerization ($\overline{DP}_n$), expressed as percent of original values, are shown in Fig. 1A and 1B. In the absence of AQ, the two curves follow each other closely, indicating that the degradation was purely a "peeling-type" process without any random cleavage of amylose chains. The average chain length lost in peeling was about 400 glucose units. When AQ was present (Fig. 1B) the yield loss due to peeling was much smaller, while the $\overline{DP}_n$ decreased rapidly. This shows that depolymerization via random chain cleavage had become important with addition of AQ.

The reactions were repeated with oxygen instead of nitrogen atmospheres. Both yield curves (with and without AQ) were essentially the same as that in Fig. 1B. The $\overline{DP}_n$ curve for the AQ-free oxygen cook was also similar to that in Fig. 1B. However, when AQ was present under oxygen, the $\overline{DP}_n$ was consistently about one-half of the corresponding AQ-free $\overline{DP}_n$. Thus, the combination of AQ and oxygen reduced the $\overline{DP}_n$ to about 30% in only 30 minutes.

## Discussion

The generally accepted mechanism for AQ catalytic activity assumes that oxidation of polysaccharide end-groups to aldonic acids is a key part of a redox cycle between AQ and anthrahydroquinone (AHQ). However

most end group stabilization must take place in the early part of a cook at low temperature to be effective in improving yield, while the major part of the delignification occurs only after the final, higher temperature has been reached. Thus, since the two halves of the postulated redox cycle would not occur at the same time and temperature, the mechanism does not explain how the amount of anthrahydroquinone (AHQ) necessary to prevent lignin condensation reactions is kept sufficiently high at the cooking temperature. Our results suggest a likely pathway for high temperature generation of AHQ. AQ can react with dissolved polysaccharides in chain cleavage reactions, and in subsequent stabilization of new reducing ends ("secondary stopping"), thereby providing the needed AHQ.

Considerable controversy remains regarding the influence of oxygen on AQ activity (6-9). In the case of amylose with 5% AQ, there was no significant difference in yield losses when the reactor was pressurized with oxygen versus nitrogen. Neither was there any appreciable difference between the amylose yield losses for AQ and AQ-free degradations under oxygen atmospheres. The AQ addition did, however, increase random chain cleavage. Thus, the average chain length lost via peeling must be much shorter when AQ is present to account for the similar yield losses. We estimate that an average of 50-65 glucose units were peeled in oxygen-alkali (5) while about half as many units were peeled when 5% AQ was added.

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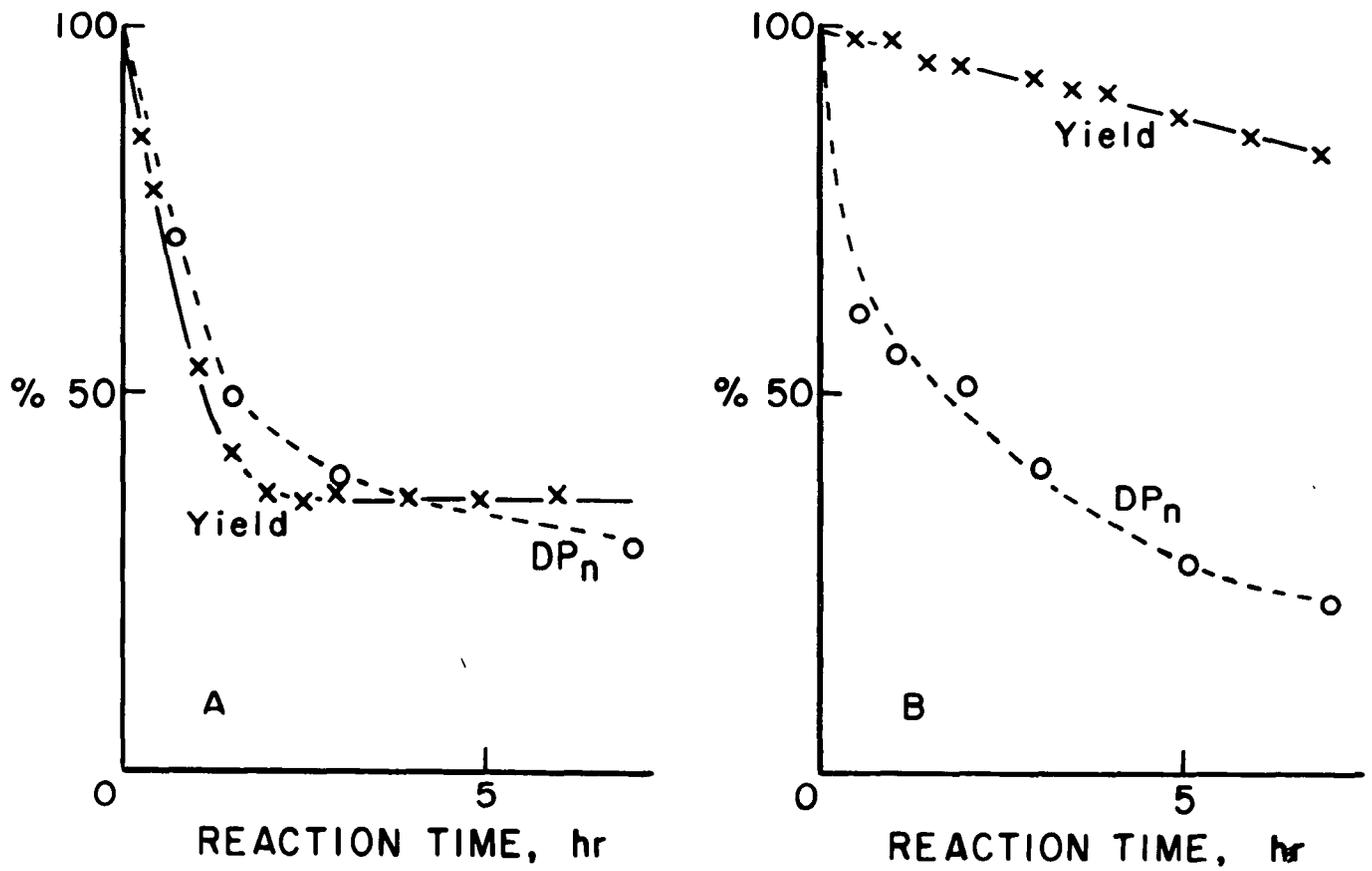9. Ruoho, K., Sjöström, E., _Tappi_ 61(7):87-8 (1978).

Figure 1.   Anaerobic degradation of amylose [1.0M NaOH, 1.0 MPa (150 psig)

nitrogen, 100°C, amylose concentration 10 g/L].   A.   Without AQ.

B.   With 5% AQ added.