New quinone-based pulping catalysts

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ABSTRACT

2,6/7-Dimethylanthraquinone (or DiMAQ) and its precursor, octahydro-DiMAQ (or ODiMAQ), have been synthesized from benzoquinone in high yield and at potentially low cost. Both catalysts were twice as active as anthraquinone in soda, kraft, and polysulfide pulping systems. Pulps produced using these catalysts were as easy to bleach as the corresponding AQ pulps and had the same strength properties. Analysis of unbleached pulps indicated that ODiMAQ was converted to DiMAQ during pulping and that there was approximately four times as much DiMAQ in these cooks as there was residual anthraquinone in the AQ cooks. Consequently, the end-of-cook concentration of DiMAQ may be higher than that of anthraquinone.

Application:

Dimethylated anthraquinone catalysts can be synthesized by a simple preparation method that could lower the cost of using pulping catalysts.

THE ADDITION OF CATALYTIC amounts of anthraquinone to alkaline pulping processes offers several advantages. Pulping rates increase, pulp yields are higher, and the chemical recovery system is improved in terms of capacity (1). In recent years, the use of anthraquinone has increased, due in part to a substantial reduction in price (2). We have been investigating ways to prepare pulping catalysts at even lower costs and thus to encourage more widespread use of catalysts (3, 4).

We have prepared AQ-type catalysts by treating a hardwood lignin with an oxidizing agent to produce 2,6-dimethoxybenzoquinone, which is converted into 2,6/7-dimethylanthraquinone (DiMAQ) precursors and other structurally related compounds by treatment with isoprene (a Diels–Alder reaction). This pathway is shown in **Fig. 1**. Many of the precursors are converted to DiMAQ by the loss of methanol and hydrogen during the preparation of the catalyst; others are converted to DiMAQ during the cooking process.

This method of preparing catalysts has the advantage of utilizing an inexpensive starting material—lignin. However, the method is hampered by low synthetic yields. The first step (oxidation) is best accomplished by treating a hardwood lignin with nitrogen dioxide, but the yield is only about 10% (*4–9*). The addition of a diene, the second step, gives a mixture of components, the major one being DiMAQ in a yield of about 40%.

Here, we first outline a new, efficient, and potentially low-cost synthesis of DiMAQ from benzoquinone. Second, the pulping activities of DiMAQ and related structures are compared to that of anthraquinone. Third, we examine the bleachability and strength of DiMAQ pulps relative to that of AQ pulps.

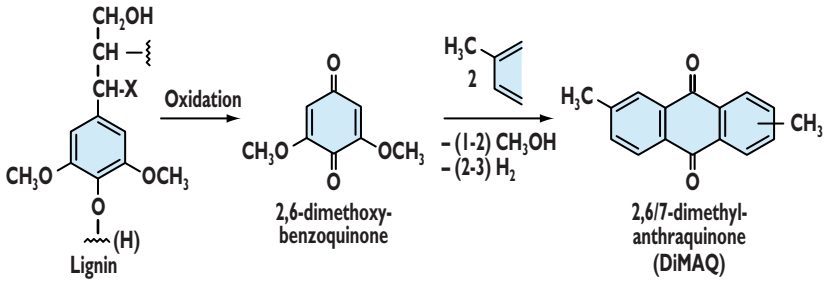
Of particular interest is the preparation and pulping activity of octahydro-DiMAQ, or ODiMAQ, the synthetic precursor of DiMAQ. In addition, data are presented on the pulping activity of the Diels–Alder reaction product (referred to as the "catalyst mixture") obtained from dimethoxybenzoquinone and isoprene (Fig. 1).

CATALYST PREPARATION FROM BENZOQUINONE

The Diels–Alder reaction of benzoquinone with isoprene is an alternative way to prepare DiMAQ. We optimized yields by varying the time and temperature, the reaction solvent, and the reactant ratios.

With ethanol as the solvent, a mixture of bis-adduct isomers, ODiMAQ, can be obtained in high yields (**Fig. 2**). With toluene as the solvent, ODiMAQ is obtained in 68% yield, along with a mono-adduct product in 30% yield. The best synthetic conditions involved thoroughly mixing a 2:1 ratio of isoprene to benzoquinone in absolute ethanol for 2 h at 165°C. Gas chromatography indicated a 93% yield of ODiMAQ; the isolated yield from 100-g runs was routinely about 85%. Treatment of the ODiMAQ with oxygen and KOH in an organic solvent gave DiMAQ in 93%-isolated yield (Fig. 2). However, this additional synthetic step is unnecessary because the pulping activity of ODiMAQ is the same as that of DiMAQ (next section).

In contrast to our earlier work, this process provides a direct route to a pure, effective pulping catalyst (ODiMAQ) in high overall yield, and it uses less isoprene than the catalyst-from-lignin route. The process requires a more expensive starting material in benzoquinone as opposed to lignin. Preliminary cost estimates indicate that the cost of ODiMAQ will be similar to that of AQ. However, since ODiMAQ is twice as active as AQ (next section), its effective cost would be substantially lower than that of anthraquinone.



1. Chemical steps in the conversion of a hardwood lignin to DiMAQ.

Catalyst type	Catalyst applied, %	H-factor	Kappa no.	Screened yield, %	Viscosity, mPa s	Recovered catalyst,[a] %
			Soda			
AQ	0.10	2090	33.7	45.0	…	…
	0.10	2097	33.1	43.7	…	…
	0.10	2089	33.1	45.1	…	…
	0.10	2111	31.2	45.4	…	…
	0.10	2114	32.3	44.1	17.3	0.3
ODiMAQ	0.05	2124	33.6	45.6	18.2	0.9
	0.05	2106	30.8	43.5	16.0	…
DiMAQ	0.05	2106	33.7	45.4	18.5	1.8
	0.05	2108	35.2	45.6	18.1	…
Cat. mixture[b]	0.05	2099	34.0	43.9	16.0	2.0
			Kraft			
AQ	0.10	1214	30.3	46.8	36.7	…
	0.10	1192	31.6	47.3	38.2	0.5
ODiMAQ	0.05	1195	31.8	46.1	40.2	1.9
	0.05	1200	30.8	47.0	36.8	…
DiMAQ	0.05	1197	32.7	47.2	36.4	…
	0.05	1197	31.3	46.5	37.7	2.3
Cat. mixture[b]	0.05	1197	30.8	40.6	33.1	2.5
None	0.00	1196	37.5	44.1	39.1	…
None[c]	0.00	1389	28.1	45.8	…	…
None[c]	0.00	1346	33.5	45.6	37.9	0.0
			Polysulfide[d]			
AQ	0.05	1053	32.2	46.4	29.6	0.3
	0.05	1040	33.0	46.7	31.4	0.1
DiMAQ	0.025	1045	33.0	45.2	31.2	0.3
	0.017	1031	35.9	46.3	31.0	0.4

Unless stated otherwise, the cooks were performed with 18% active alkali, a sulfidity of 25% for kraft cases, and a final cook temperature of 170°C.
[a]Percent of applied catalyst. The residual catalyst in the pulp was recovered by solvent extraction.
[b]The dose was based on the amount of DiMAQ in the mixture.
[c]The H-factor was modified in an attempt to get a pulp of kappa no. 31. Pulps were combined for viscosity measurements and further studies.
[d]Polysulfide = 1.22%. Active alkali = 19%. Sulfidity = 12%.

I. Detailed pulping results for 1-kg pine cooks

PULPING STUDIES

We conducted about 50 small-scale pulping studies involving 50 g of southern pine chips. The results indicate that DiMAQ and ODiMAQ are twice as effective as AQ in catalyzing delignification in soda-, kraft-, and polysulfide-catalyst cooks. This two-fold increase in reactivity was observed at AQ–DiMAQ ratios of 0.1% to 0.05% on wood and 0.05% to 0.025% on wood. For larger cooks (1 kg) of southern pine, a comparison was made only at the ratio of 0.1% to 0.05%.

Table I presents the results of the large-scale cook. The reproducibility of the cooks was quite good, as can be seen by the results of the five soda–AQ cooks conducted. As in the small-scale runs, the new catalysts at half the doses performed as well as full doses of anthraquinone for producing pulps of kappa no. 30 for each of the three pulping systems. Also, as expected, the presence of a catalyst improved the yield in the kraft case (*10*).

The value of the catalyst in kraft systems can be seen from the higher kappa number (37.5) of the standard control kraft cook that has no catalyst but that was performed under the same conditions as the kraft cooks with catalyst. A 1-kg soda control was not performed; however, based on previous small-scale experiments, we expect the kappa number would have been about 60. Two kraft cooks were performed at elevated H-factors to get a 31-kappa pulp for comparison to the kraft–catalyst pulps; the resulting kraft pulps of kappa nos. 28.1 and 33.5 were combined to give the desired pulp of kappa no. 31.

The pulps were extracted, and the level of catalyst was determined by gas chromatography. The data obtained (Table I) indicate that (a) ODiMAQ was aromatized to DiMAQ during cooking and (b) except in the polysulfide cooks, the level of recov-

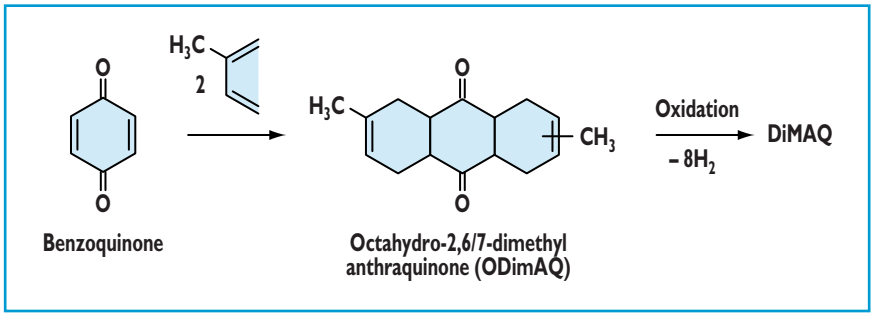
ered catalyst was about four times higher for DiMAQ and ODiMAQ than for AQ. The latter result may explain the superior effectiveness of the new catalysts. The DiMAQ concentration may be higher throughout the cook than the concentration of anthraquinone in AQ pulping.

The "catalyst mixture" led to delignification levels similar to those of the other DiMAQ (or ODiMAQ) cooks. However, the pulp yield and viscosity were somewhat lower in the catalyst mixture cases. Because of limited availability of the catalyst mixture, we were unable to perform multiple cooks to confirm these trends.

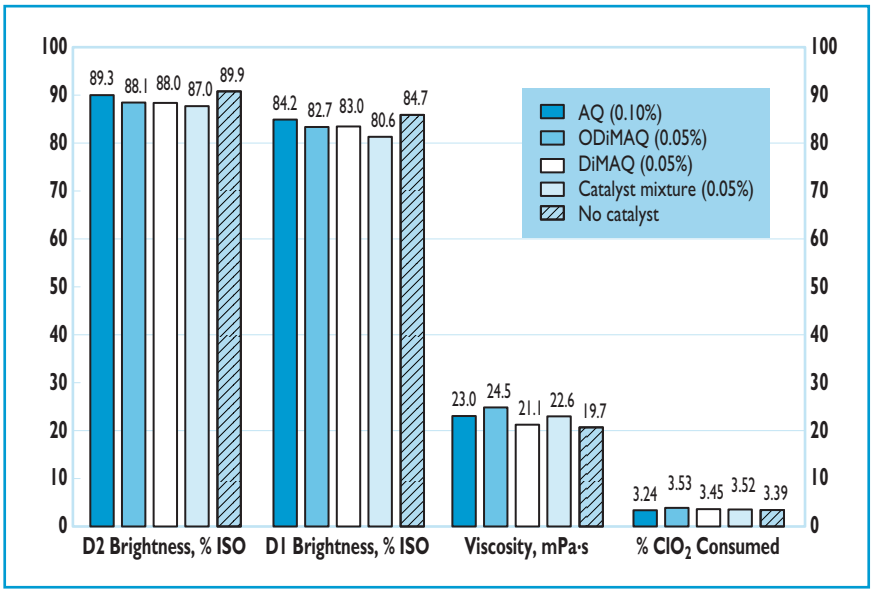
BLEACHING STUDIES

The DiMAQ pulps were compared to the corresponding AQ pulps for bleachability. Bleachability refers to the amount of bleaching chemicals consumed to reach a certain brightness for a set of pulps. This brightness can be the final brightness or some intermediate brightness. By going to fully bleached pulps, we were able to compare brightness values at many points and generate pulps for which strength could also be measured. The bleachability of each pulp was determined using a D(EOP)DED bleaching sequence, in which D = chlorine dioxide (ClO_2), E = extraction with dilute NaOH, and EOP = extraction with dilute NaOH in the presence of oxygen and hydrogen peroxide (H_2O_2).

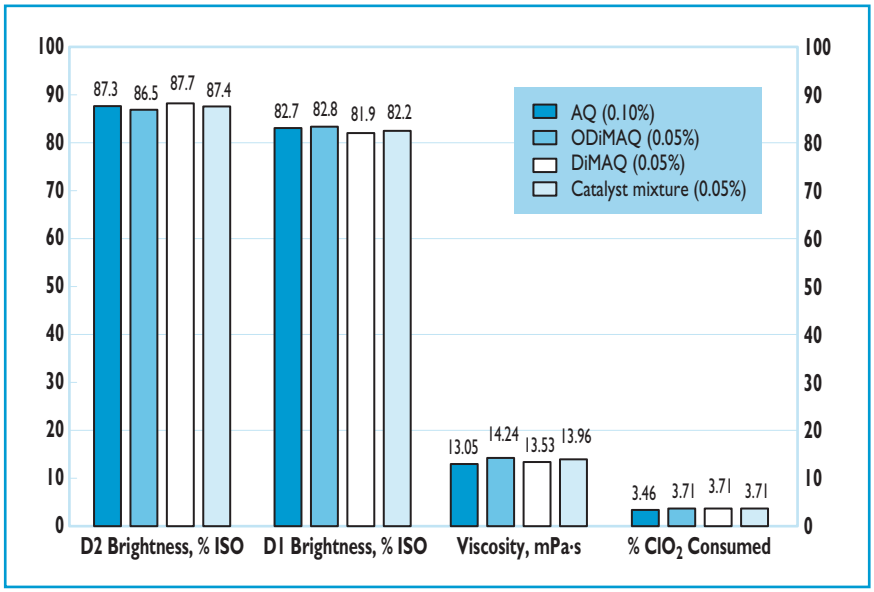
The bleaching results are shown graphically in **Figs. 3** and **4**. Data showed good reproducibility for duplicate bleaching runs on the same pulp and on two pulps produced by the same catalyst. Small differences were observed in brightness and viscosity between pulps produced with different catalysts, but these differences were within the experimental error for duplicate runs performed on the same pulp. On this basis, we concluded that the



2. Preparation of DiMAQ from benzoquinone.



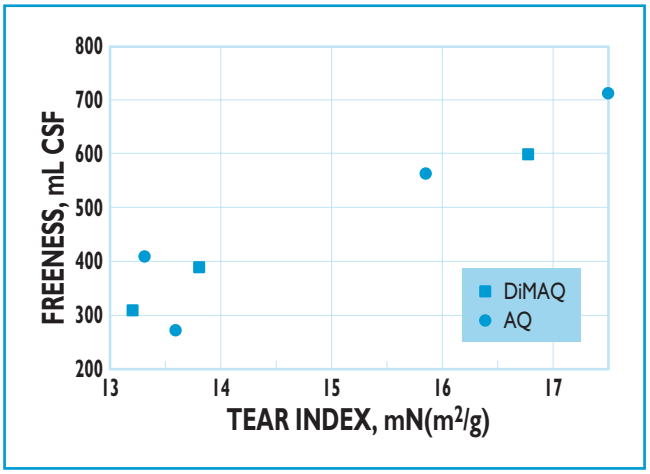
3. Kraft bleaching comparisons.



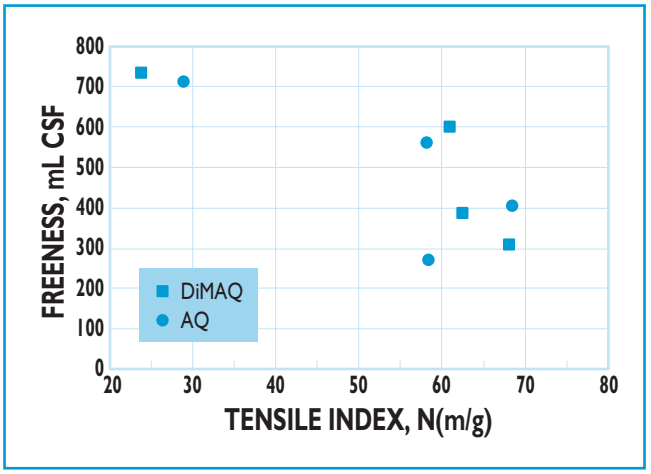
4. Soda bleaching comparisons.

	Density, g/cm³ (± 0.03)		Burst index kPa m³/g (± 0.5)		Zero-span index, N m/g (± 10)		Viscosity, mPa s
	350	500	350	500	350	500	
Kraft (no catalyst)	0.69	0.66	7.2	6.2	132	125	19.7
Kraft AQ	0.70	0.69	8.5	7.8	117	124	23.0
Kraft DiMAQ	0.67	0.67	8.4	7.8	118	122	21.1
Kraft DiMAQ(II)	0.73	0.71	7.6	7.1	128	117	22.7
Kraft ODiMAQ	0.70	0.69	7.3	6.3	116	110	24.5
Kraft and catalyst mixture	0.74	0.64	6.6	6.2	126	133	22.6
Soda AQ (II)	0.70	0.69	6.7	6.0	123	118	14.2
Soda DiMAQ	0.71	0.69	6.5	6.1	125	122	13.5
Soda DiMAQ (II)	0.70	0.68	6.7	6.2	127	116	12.7
Soda ODiMAQ	0.69	0.65	6.8	7.0	108	118	14.2
Soda and catalyst mixture	0.69	0.68	6.5	5.5	112	111	14.0

II. Comparison of selected strength parameters for kraft–catalyst and soda–catalyst bleached pulps at freenesses of 300 mL and 500 mL CSF



5. Average tear indexes for soda–AQ and soda–DMAQ pulps at several freenesses.



6. Average tensile indexes for two soda–catalyst pulps at four freenesses.

kraft and kraft–catalyst pulps were equally bleachable; the same held true for the soda–catalyst pulps.

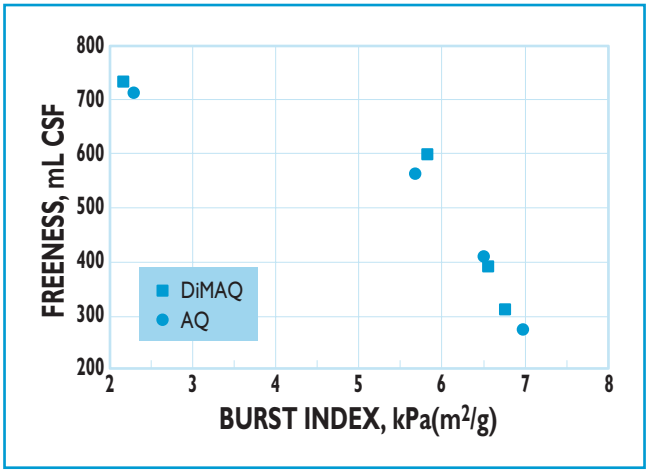
The slightly lower amount of chlorine dioxide consumed in the soda–AQ and kraft–AQ cases hints that DiMAQ pulps may be slightly harder to bleach. The lower viscosity of the kraft control may reflect the longer cooking times that were required to reach the targeted kappa number. A longer cook would likely exhibit more carbohydrate damage.

The kraft pulps produced from the catalyst mixture were a little more difficult to bleach. However, the soda pulps produced using the catalyst mixture showed no differences from the other pulps in brightness, viscosity, and chlorine dioxide consumed.

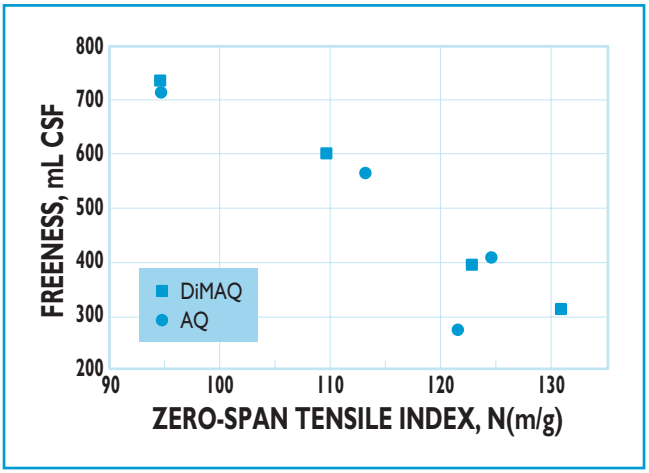
PULP STRENGTH COMPARISONS

The fully bleached pulps (starting freeness of ≈750 mL CSF) were refined in a PFI mill at 10% consistency to provide pulps at roughly three different levels of freeness: 300, 400, and 600 mL CSF. Handsheets made from the beaten and unbeaten pulps were evaluated for specific strength parameters. **Table II** compares the average density, burst, and zero-span values for the nine pulps at 350 mL and 500 mL CSF. Viscosity values for the unbeaten pulps are also provided in the table.

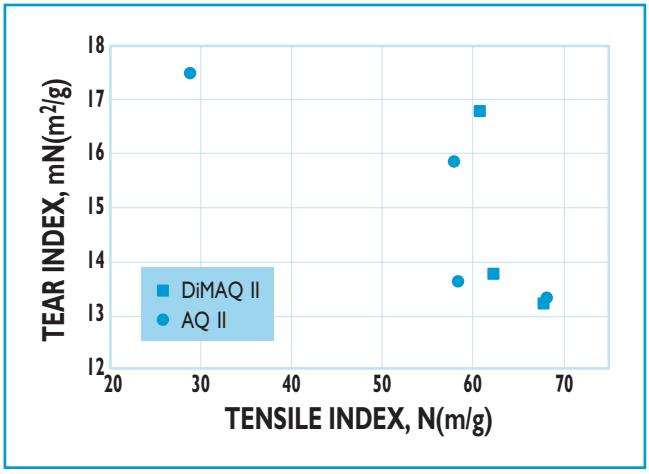
As expected, lower freeness values normally led to increased values of density, burst strength, and zero-span tensile index. The zero-span index, which is a measure of individual fiber strength, should correlate with the viscosity, a measure of average polymer chain length. Except for an anomalously low viscosity for the kraft control, the data in the table indicate no real differences in viscosities and zero-span indexes. In general, the strength values for the two series are all within the standard



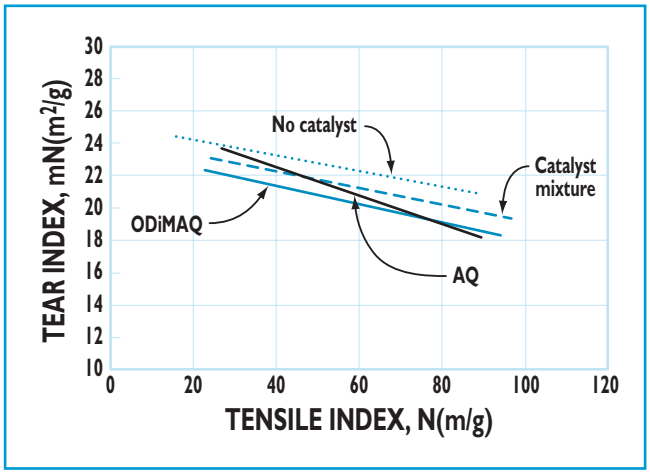
7. Average burst indexes for two soda–catalyst pulps at four freenesses.



8. Average zero-span tensile indexes for two soda–catalyst pulps at four freenesses.



9. Tear vs. tensile indexes for two soda–catalyst pulps.



10. Trend lines for tear and tensile indexes for kraft and kraft–catalyst bleached pulps.

deviation (± values in the table) of one another.

Figures 5–8 compare the strength properties of two carefully prepared soda-AQ and DiMAQ pulp handsheets. Property trends are nearly identical for the two pulps for each of the strength parameters examined. Another frequently used measure of comparative strength properties involves comparing plots of tear index vs. tensile index for each pulp. Here again, as shown in **Fig. 9**, there were no basic differences between the soda–AQ and DiMAQ pulps. Since ODiMAQ converts to DiMAQ during cooking, extensive testing of ODiMAQ pulps was not performed. However, a limited number of handsheets showed properties nearly identical to those of the AQ and DiMAQ pulps.

Within the experimental error of our measurements, the kraft and kraft–catalyst pulps were similar with regard to the trend lines of tear index vs. tensile index over the span of freenesses examined. The trend lines shown in **Fig. 10** are based on 80 data points. The expected downward slope in the lines is apparent. (Data for tear vs. tensile for the kraft–DiMAQ pulp are not included here because of a problem with the preparation of some of the handsheets. Limited results suggest no difference from the other data.) The addition of DiMAQ, ODiMAQ, or AQ to a kraft pulping system had no adverse effects on tear vs. tensile strength parameters; this outcome was expected for the kraft–AQ case (*10*).

SUMMARY

A new, simple, two-step, high-yield preparation of DiMAQ from benzoquinone has been developed. The product of the first-step octahydro-DiMAQ, is a very effective pulping catalyst, as good as DiMAQ itself, and twice as good as AQ. The pulps produced from the new catalysts are as easy to bleach as AQ pulps and are as strong. Consequently, we now have a one-step, high-yield, economical way to prepare a new, effective pulping catalyst. Steps are being taken to commercialize octahydro-DiMAQ.

EQUATIONS

$$\text{Yield, \%} = \frac{\text{Consistency of the pulp, \%} \times \text{Quantity of pulp, g}}{\text{Chips used in digester, g (o.d.)}} \times 100\% \quad (1)$$

$$\text{Residual, \%} = \frac{\text{Catalyst peak area} \times \text{Std. added, mg} \times \text{Response factor}}{\text{Std. peak area} \times \text{Catalyst used in cook, mg}} \times \frac{\text{Pulp yielded in cook, g (o.d.)}}{\text{Pulp extracted, g (o.d.)}} \times 100 \quad (2)$$

EXPERIMENTAL PROCEDURES

Preparation of ODiMAQ

A mixture of benzoquinone (0.45 mole) and isoprene (1.13 mole) in ethanol (100 mL) was sealed in a Parr 300-mL, stainless steel bomb and heated at 170°C for 7 h. The bomb produced a pressure of 170 psi. After cooling, the bomb contents were cooled, filtered, and washed with cold ethanol to afford a white solid. Successive concentrations and precipitations gave additional batches of solid. A yield of 80% was found in the first fraction. An additional 5% could be isolated from the filtrate when it was concentrated.

Analysis of the collected ODiMAQ by GC/MS indicated the presence of three compounds, eluting very near one another, with identical molecular weights *m/z*: 244 (M^+). Several isomers are possible, based on the geometry of the methyl groups and the nature of the ring conjunctures relative to each other. The structures of the ODiMAQ products were confirmed by ^{1}H NMR: ($CDCl_3$) d 5.37 (bs, 2H, =CH); 3.03 (apparent q, J = 6 Hz, 2H, CHC=O); 2.96 (apparent q, 6 Hz, 2H, CHC=O); 2.51–2.34 (m, 4H, CH_2–C=); 2.22– 2.08 (m, 4H, CH_2–C=); 177 (bs, 6H, CH_3).

Preparation of DiMAQ from ODiMAQ

Attempts to oxidize ODiMAQ to DiMAQ using basic hydrogen peroxide and chlorine dioxide failed. However, ODiMAQ was oxidized by two other methods. First, a suspension of ODiMAQ (10.5 mmol) in 100 mL of ethanol containing KOH (35.7 mmol, 3.40 equivalent) was heated at reflux under a stream of air. The mixture turned dark green and then dark red after heating for 1 h. After heating for an additional 3 h, the mixture was cooled, stirred at room temperature overnight, acidified to pH 1, and filtered. Partitioning between ether and water purified the collected crude product. Evaporation of the ether solvent under reduced pressure gave DiMAQ (8.52 mmol, 81%). The sample could be further purified by recrystallization (EtOAc/hexane).

Analysis by gas chromatography showed two DiMAQ isomers of nearly identical retention time. The presence of DiMAQ was confirmed when spectral properties were compared to those of previously prepared DiMAQ (*3*). ^{1}H NMR showed: ($CDCl_3$) d 8.19 (d, J = 8 Hz, 2H, H–4 + H–8 or H–5); 8.09 (d, J = 1 Hz, 2H, H–1 + H–5 or H–8); 7.58 (dd, J = 1 Hz, 8 Hz, 2H, H–3 + H–7 or H–6); 2.53 (s, 6H, $ArCH_3$). The mass spectrum displayed a strong molecular ion at *m/e* = 236.

The oxidation was also accomplished by stirring ODiMAQ (32.8 mmol) in 95% ethanol (400 mL) containing KOH (321 mmol) in a Parr 1000-mL, stainless steel bomb with a glass liner under an oxygen atmosphere (145 psi) at room temperature. As ODiMAQ was added to the colorless caustic solution, the solution changed to dark green. When the reaction was complete (no longer a green or red color, after 2 h), a heterogeneous mixture was obtained which had a tan solid suspended in a clear solution.

The mixture was diluted with water (400 mL) and acidified with concentrated HCl to pH 1. The mixture was filtered, and the yellow/purple solid was suspended in 400 mL of methanol and filtered again. The solid was then dried under high vacuum, which gave pure DiMAQ (30.5 mmol, 93%).

Attempts to carry out the same oxidation in water failed to give any reaction, presumably as a result of poor solubility of the adduct in water. Oxidations in 75% ethanol in water were slow, with mixtures of DiMAQ and ODiMAQ observed after 2 h.

Pulping procedure

Softwood pine chips, obtained from a Southeast pulp mill, were screened using a KMW screen with the +1/4-in. to –1-in. fractions retained and then separated by hand to remove any bark. Chips were stored frozen prior to use. The percent solids content of each chip bag was determined after the sample was dried for at least 24 h in a 105°C oven. Solutions of NaOH, Na_2S, and polysulfide were prepared to be approximately 110–120 g/L as Na_2O.

The NaOH and Na_2S concentrations were determined according to the ABC titration procedure (*11*). The polysulfide solutions were titrated according to procedures in TAPPI T 694. Large-scale cooks were performed at a 4:1 liquor-to-wood ratio. The digester charge of wet chips, on an oven-dried basis, was 1 kg. The H-factor values (*12*) of the large-scale cooks were determined using a cook programmer. The soda and kraft cooks employed 18% active

alkali, 25% sulfidity in the kraft case, and a temperature profile of 15 min. at 100°C, 60 min. (kraft) or 90 min. (soda) from 100°C to 170°C, with a hold at 170°C for the time required to get the desired H-factor. Polysulfide cooks employed 1.22% polysulfide, 19% active alkali, 12% sulfidity, and a temperature profile the same as that for the kraft cooks.

The product from each cook was disintegrated and then washed with water. The pulp was screened with a Sprout–Waldron, 0.01-in.-slot screen apparatus, centrifuged, weighed, and fluffed. The pulp was weighed before and after drying in a 105°C oven for at least 24 h. The ratio of dry to wet sample is the percent consistency. Percent yield was calculated from the Eq. 1. The pulp was analyzed for kappa number according to TAPPI procedure T 236 and for viscosity according to T 230.

Percent residual catalyst

Exactly 5.0 g of o.d. pulp was air dried and placed in approximately 250 mL $CHCl_3$ that contained 2.00 mL of 0.0642 mg/mL 2,3-DiMAQ standard solution. The mixture was evaporated to dryness in a rotary evaporator and was extracted with $CHCl_3$ for 24 h in a Soxhlet extraction apparatus. The resultant $CHCl_3$ solution was evaporated to a small volume, transferred to a 2-mL vial, and evaluated by gas chromatography for percent residual catalyst. Equation 2 was used for the calculation.

	Time, min	Temp., °C	Treatment	Notes
D_0	50	45	…	0.2 kappa factor
EOP	70	60	0.5% H_2O_2	% NaOH = TAC[a] × 0.6 60 psig O_2 pressure → 0 psig
D_1	70	90	1.0% ClO_2 0.25% caustic	…
E_2	70	60	0.5% caustic	…
D_2	70	180	0.2% ClO_2	…

[a]TAC = total active chlorine = kappa factor × kappa no.

III. Description of bleaching stages

Bleaching

All stages used different amounts of 10% consistency pulp. The stages are described in **Table III**. Each sample was evaluated for its kappa number after the EOP stage by TAPPI T 236. ISO brightness was measured after EOP, D_1, E_2, and D_2 stages according to TAPPI T 534. Filtrate percent residual ClO_2 was determined after each D stage by CPPA method J14P, and the filtrate pH was measured after each bleach stage.

Strength tests

The nine fully bleached pulp samples of interest were evaluated for viscosity using TAPPI T 230. These samples were also refined in a PFI mill to three different freeness points. Handsheets were prepared by TAPPI T 205 for each refined and unrefined bleached pulp. The following strength properties were determined by TAPPI T 220: basis weight, density, tensile index, tear index, zero-span index, and burst strength. **TJ**

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