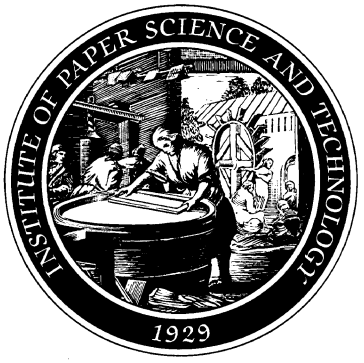

Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 677

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A. Leyva, D.R. Dimmel, and G.S. Pullman

August 1997

Submitted to
Tappi Journal

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Teak Extract as a Catalyst for the Pulping of Loblolly Pine

Argentina Leyva, Donald R. Dimmel, and Gerald S. Pullman
Institute of Paper Science and Technology
500 10th Street, N.W., Atlanta, GA 30318

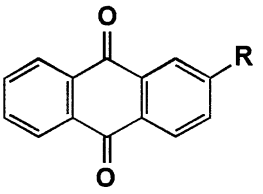
ABSTRACT

Commercial teak was extracted with toluene to give a 6.7% extractable residue yield. Analysis of the extract indicated the presence of a variety of naptha- and anthraquinones (AQs), of which 2-methyl anthraquinone was the major component (0.33% of the weight of the teak). When used as a catalyst in the pulping of loblolly pine, the extract was approximately twice as active as predicted, based on its 2-methyl AQ content. At low doses, the order of catalytic delignification effectiveness was extract > 2-methyl AQ > AQ. Pulp yields also paralleled this order. The other quinones present in the extract, while not expected to be as effective as 2-methyl AQ, collectively provide a pulping catalytic activity approximately equal to the content of 2-methyl AQ.

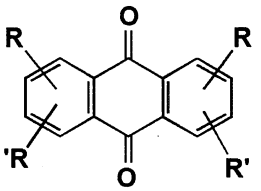
INTRODUCTION

Anthraquinone (**1**, AQ) is an effective catalyst for pulping lignocellulosics.[1] Levels of <0.1% on wood accelerate pulping, increase pulp yields, and lower the alkali requirements. However, widespread use of anthraquinone has been hindered by its cost, which in past years has ranged from $1.50-4.50/lb and is currently selling for about $2.50/lb (formulated) to pulp mills. The AQ cost would virtually disappear if pulpwood naturally contained AQ. Our long-term research goal is to genetically modify trees to produce AQ components that would catalyze their own pulping (or that of a mixture of woods).

Anthraquinones structures are present in a variety of higher plants, fungi, arthropods, and echinoderms, sometimes in quite high levels.[2] In plants, they have been found in leaves, flowers, wood, bark, roots, and fruit. About 30% of the dried mycelium of *Pyrenophora graminea* consists of two oxygenated anthraquinones; 17% of the dry weight of the bark of *Coprosma australis* is comprised of various anthraquinones. In most cases, the AQ components are highly oxygenated (**3**). Unfortunately, such structures are poor pulping catalysts.[3]



1, R = H (AQ)
2, R = CH_3



3, R = H, alkyl, CH_3
R' = OH, OCH_3

Teakwood (*Tectona grandis*) contains ~0.3% 2-methyl AQ (tectoquinone, **2**), along with several other quinones.[4] Teak is an exceptional wood and one of the oldest species sold commercially. It is resistant to insects, fungi, chemicals, mechanical wear, and possesses favorable swelling properties. There is a report of a wood sample from a Buddhist temple dating back 2000 years that showed neither fungal nor insect attack and had a tectoquinone content of 2%.[5] Tectoquinone, a termite repellent, undoubtedly contributes to the durability of teak. The level of 2-methyl AQ in teak is several times the concentration needed for pulping; 2-methyl AQ is reported to have a catalytic pulping activity similar to unsubstituted AQ.[3] The goals of the research described here were to isolate and quantify 2-methyl AQ from teak and to compare the pulping effectiveness of the teak extract to that of commercial AQ. If the results were promising, we would initiate a study to modify trees to produce AQ compounds.

RESULTS AND DISCUSSION

Isolation and Composition Studies

About 40 compounds have been isolated from teak extracts.[3] Analysis of several teak species from India and Indonesia gave 2-methyl AQ contents of 0.3 to 1.3%.[6] To confirm these levels, we exhaustively extracted the sawdust from a piece of commercial teak lumber with toluene and toluene-ethanol mixtures until the extract had no color. The combined extracts were evaporated to yield an oil in 6.7 weight % yield. Analysis of the extract residue by gas chromatography (GC) indicated the presence of 5.0 weight % 2-methyl AQ, along with several other quinones. Thus, the 2-methyl AQ content of the purchased teak was 0.33%; six different extractions were conducted, and the yields were consistent.

Analysis of the extract by GC-mass spectroscopy (MS) gave the data shown in Figure 1. The signal at 25.5 min was identified as 2-methyl AQ by comparison to the GC-MS of commercial 2-methyl AQ. Structures corresponding to the signals at 28.8 and 32.8 min were assigned based on a good match to the reported MS of the structures shown.[7] Other structures were tentatively assigned based on the apparent molecular ions in the MS and the known presence of these materials in teak; however, the spectral characteristics contained flaws that led to some uncertainties. Not shown in Figure 1, but noticeable in GC analyses of several extracts, were small signals that have retention times corresponding to authentic samples of 1-methyl and 2,3-dimethyl AQ.

While additional characterization studies are needed, it is apparent that the extract contains several potentially active AQ components, the major one being 2-methyl AQ. The efficacy of quinones as soda pulping catalysts is reported[3] to be: AQ, 1.00; 2-methyl AQ, 1.04; 1-methyl AQ, 0.90; 2,3-dimethyl AQ, 1.05; various dihydroxy AQs 0.4-0.7; 2-methyl-4,5-dihydroxy AQ, 0.56; 2-methylnaphthaquinone and 2-hydroxynaphthaquinone, 0.44. In general, napthaquinones and oxygenated AQs display poorer pulping activities. The reported effectiveness of the catalysts was determined at a relatively high level of material (1%). One of the catalysts, 2,6/7-dimethyl AQ, reported to have an efficacy of ~1 at 1% has a value of ~2 (twice as active as AQ) at typical pulping doses (0.025-0.1%);[7] this may be the case for several other studied compounds.

Pulping Studies

Pulping trials were carried out with loblolly pine to compare the kappa number and carbohydrate yield for pulps made with (a) the teak extract, (b) commercial AQ, and (c) commercial 2-methyl AQ. The amount of extract used was based on a target addition level of the 2-methyl AQ that was present in the extract. A random set of cooks was conducted that employed catalyst levels of 0.025, 0.05, and 0.10%; each condition was repeated four times. Kappa numbers, which reflect lignin content, were determined in each case. The data are provided in Table 1 and Figure 2.

The analysis of variance indicated that both catalyst type and addition level significantly affected the kappa number reduction. The order of delignification catalytic effectiveness was teak extract > 2-methyl AQ > AQ. The effect is magnified at the low addition levels. Only half the level of

teak extract is needed to achieve the same kappa reduction as pure 2-methyl AQ. Obviously, there are components in the extract, other than 2-methyl AQ, that are pulping catalysts. These other components collectively are equivalent to the effectiveness of the 2-methyl AQ that is in the extract. Another factor accounting for the effectiveness of the extract is the high activity of 2-methyl AQ in comparison to AQ. At low levels, pure 2-methyl AQ is considerably more effective than AQ; however, the differences are minor at a 0.1% addition level.

Data on pulp and carbohydrate yields, determined by subtracting the lignin content from the pulp yield, are given in Table 2 and Figure 3. There were no significant differences in either yield for 2-methyl AQ and the extract; both showed higher yields than AQ. It should be noted, however, that yield data for small cooks are difficult to determine accurately, and thus, conclusions are suspect.

CONCLUSIONS

Teak extract, when used as a pulping catalyst, gives significantly lower kappa numbers than industrial 2-methyl AQ and industrial anthraquinone. The extract is approximately twice as active as predicted, based on its 2-methyl AQ content; an extract from teak that contained 0.05% (weight basis) 2-methyl AQ had the same delignification efficiency as 0.1% 2-methyl AQ. Likewise, at 0.025% addition, teak extract gave the same kappa number as industrial 2-methyl AQ at 0.05% addition. Pulping with the extract provided as good, if not better, yields than comparable pulping runs done with AQ or 2-methyl AQ.

Our analysis of the teak extract shows that 2-methyl AQ is the main component of the extract. However, there are several other naptha- and anthraquinones present, and while not expected to be as effective as 2-methyl AQ, collectively provide a pulping catalytic activity equal to the content of 2-methyl AQ.

EXPERIMENTAL

Isolation and Characterization. A piece of commercial teak timber, purchased locally, was chipped and converted into sawdust. A 5-g sawdust sample was exhaustively extracted with 250

mL of toluene for 14 hr in a small Soxlet. A second extraction was carried out using 250 mL of 50% toluene-ethanol for another 14 hr. After the second extraction, the solvent had no color, indicating the probable absence of soluble extractives. The solutions from both extractions were combined and evaporated to near dryness using a rotary evaporator. The residue, containing a small amount of solvent, was transferred onto a glass plate dried to yield 0.334 g of oil (6.7 wt. %). The sample was analyzed by GC, using AQ as the internal standard; AQ was shown not to be naturally present in the extract. A response factor for AQ vs. commercial 2-methyl AQ was developed. The GC conditions consisted of: chloroform as the solvent; DB-17 (J&W Scientific) column, with a film thickness of 1 μm of (50% phenyl)methyl polysiloxane, inside diameter of 0.53 mm, and 15 m in length, a temperature program of 100°C (1 min), 10°C/min to a final temperature of 250°C (10 min); an injection temperature of 250°C and a detector temperature of 280°C. The results of the GC/MS analysis are presented in Figure 1; the equipment consisted of a 5890 Series II Hewlett-Packard GC, containing a DB-17 capillary column, with a film thickness of 0.18 micron, inside diameter of 0.18 mm, and 10 m in length, connected to a Hewlett-Packard 5971-A mass selective detector. The GC conditions were similar to those described above.

Pulping Studies. Eight small batch digesters (bombs), rotating in an automated heat-controlled oil bath, were used to carry out the soda cooks. Each bomb contained loblolly pine (*Pinus taeda*) chips which, if oven dried (o.d.), would weigh 50 g. The cooking liquor contained, on an o.d. wood basis: 18% NaOH; AQ at levels of 0.05 and 0.1%; industrial 2-methyl AQ at 0.025, 0.05, and 0.1%; and teak extract that contains 0.025, 0.05, and 0.1% 2-methyl AQ. The liquor-to-wood ratio was 4:1 mL/g. Pulping was carried out for 3.5 hr by: heating from 80 to 100°C over 15 min; holding at 100°C for 15 min; heating from 100 to 175°C over 90 min; and holding at 175°C for 90 min. The bombs were then removed from the bath, cooled, and opened. The contents were put inside a cloth mess, washed with water, emptied into a blender, and disintegrated for ~30 sec. The pulp was then placed back in the cloth mess, washed, filtered, and pressed several times until the wash water was clear. The pulp yield was determined by weighing the collected pulp and determining the moisture content by drying small duplicate weighed samples of pulp in a 105°C oven overnight and reweighing. The kappa numbers were determined according to TAPPI Method T 235 cm-85, keeping the reaction time fixed but using half the

amount of specified chemicals. Several preliminary cooks were performed to define conditions that would produce a 30-kappa pulp at 0.1% catalyst addition levels. An analysis of variance was carried out using a completely randomized, two-factor experiment with four replications.

ACKNOWLEDGMENTS

Portions of this work were used by A. L. as partial fulfillment of the requirements for the M.S. degree at the Institute of Paper Science and Technology. We would like to thank Mr. Chuck Courchene for his help in guiding the pulping studies.

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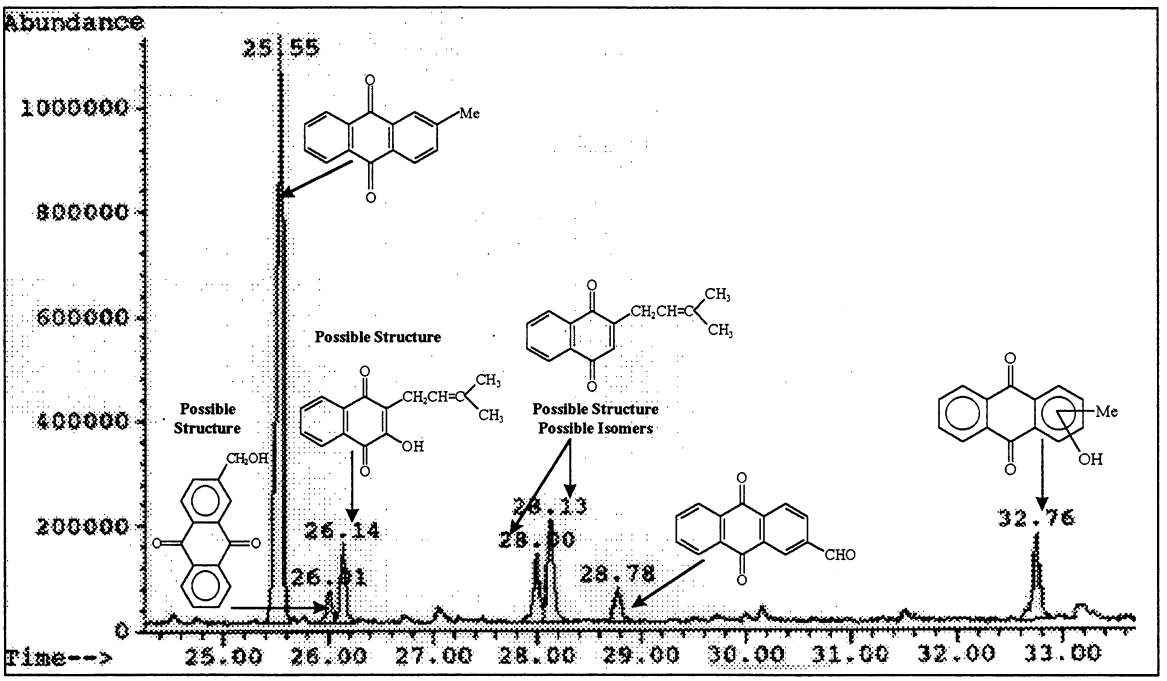

Figure 1. Chromatogram of teak extract showing the most abundant compounds and their structures (or possible structures).

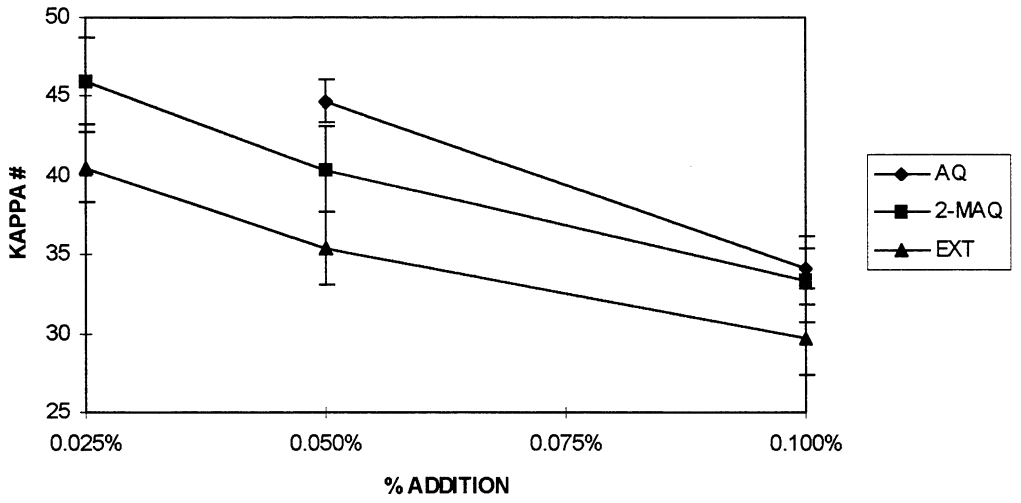

Figure 2. Kappa numbers for three addition levels of AQ, 2-methyl AQ, and teak extract in the soda pulping of loblolly pine.

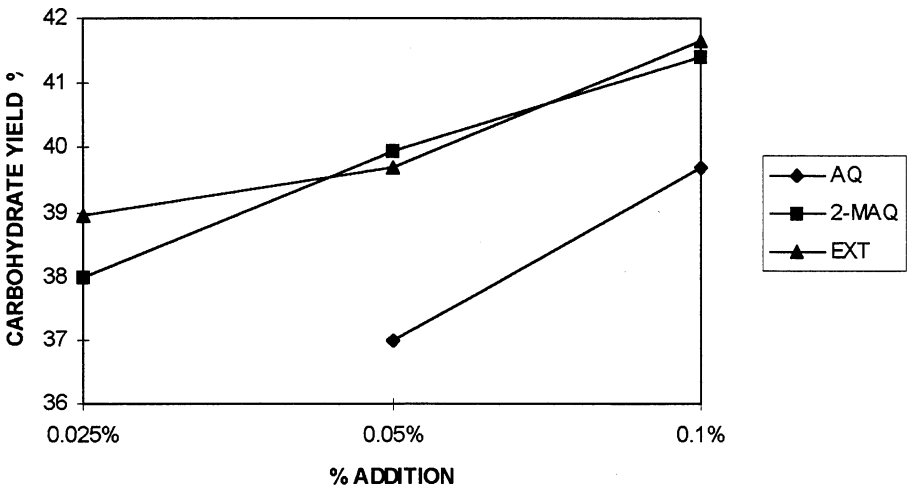

Figure 3. Carbohydrate yield for the three different catalysts at different levels of addition in the soda pulping of loblolly pine.

Table 1. Kappa number averages and standard deviations for four cooks, each of three addition levels of catalyst, in the soda pulping of loblolly pine.

	0.025%		0.05%		0.1%	
	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
AQ	N/A	N/A	44.7	1.7	34.2	0.4
2-Methyl AQ	46.0	2.1	40.4	2.8	33.4	1.9
Teak Extract (2-MeAQ Content)	40.5	3.2	35.4	3.6	29.7	1.3

Table 2. Averages and standard deviations of pulp yield at different catalyst charges.

	0.025%		0.05%		0.10%	
	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
AQ	N/A	N/A	43.7	2.7	44.8	0.7
2-MeAQ	44.9	1.5	46.0	2.4	46.4	0.7
Teak Ext.	45.0	2.8	45.0	1.6	46.1	0.7