

**U.S. DEPARTMENT OF ENERGY**  
**FEDERAL ASSISTANCE PROGRAM/PROJECT STATUS REPORT**

**OMB Burden Disclosure Statement**

Public reporting for this collection of information is estimated to average 47.5 hours per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Office of Information Resources Management, AD-241.2 - GTN, Paperwork Reduction Project (1910-0400), U.S. Department of Energy, 1000 Independence Avenue, S.W., Washington, DC 20585; and to the Office of Management and Budget (OMB), Paperwork Reduction Project (1910-0400), Washington, DC 20503

1. Program/Project Identification No.  DE-FC07-96ID13442	2. Program/Project Title  High-Efficiency Chlorine Dioxide Delignification	3. Reporting Period  4/1/98 through 6/30/98
4. Name and Address  Thomas J. McDonough 500 10th Street, NW, Atlanta, GA 30318 (404) 894 - 97017, thomas.mcdonough@ipst.edu		5. Program/Project Start Date  8/9/96
		6. Completion Date  Extended 1 yr to 7/9/99

## 7. Approach Changes

*DOE/ID/13442-71*

None

## 8. Performance Variances, Accomplishments, or Problems

- Comparative conventional D<sub>0</sub>(EO) bleaching of pulps from conventional and modified processes showed slightly improved bleachability for the latter and confirmed high efficiencies and low chlorate yields at low kappa factor
- Effectiveness of ultralow-AOX ClO<sub>2</sub> delignification process demonstrated
- Process for high-efficiency delignification identified
- Completed experiments to study mechanism by which low kappa factors give high efficiency
- Determined relationship between hexeneuronic acid content and unbleached kappa number of hardwood pulps
- Presented paper at 1998 International Pulp Bleaching Conference

None

## 9. Open Items

- Molecular weight analysis of softwood kraft continues
- Isolation and analysis of conventional and vapor phase bleached, unbleached hardwood pulp residual lignins continuing
- Analysis of data from low-kappa-factor efficiency study underway
- Further development of high-efficiency delignification process in progress

None

## 10. Status Assessment and Forecast

- Project behind schedule by 6+ months due to Olympics related startup delay and loss of postdoctoral research fellow. Replacement PDF now fully productive and current progress in NMR and molecular weight studies is good. One co-p.i. (AJR) currently on 6-month sabbatical in Sweden. One-year no-cost extension was requested and has been granted.

No Deviation from Plan is Expected

## 11. Description of Attachments

- Brief summary of results obtained during the second quarter of 1998 is attached.

None

## 12. Signature of Recipient and Date

*Thomas J. McDonough* July 31, 1998

Thomas J. McDonough, July 31, 1998

## 13. Signature of U.S. Department of Energy (DOE) Reviewing Representative and Date

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## **DISCLAIMER**

**Portions of this document may be illegible  
electronic image products. Images are  
produced from the best available original  
document.**

## High-Efficiency Chlorine Dioxide Delignification

U.S. Dept. of Energy Project DE-FC07-96ID13442

### Summary of Progress

April 1 - June 30, 1998

Arthur J. Ragauskas and Thomas J. McDonough  
Institute of Paper Science and Technology

We have been pursuing strategies for improving the efficiency of utilization and environmental performance of ClO<sub>2</sub> in the delignification of kraft pulps. These strategies will apply several of the findings of this project. These strategies combine a pretreatment followed by ClO<sub>2</sub> treatment under conditions selected to result in high efficiency, and a suitably altered alkaline extraction stage. The potential for patentability of these strategies is currently being investigated. Detailed results will be presented after we have made a determination of their patentability.

In addition, a series of experiments was completed in which we compared the response to conventional D(EO) delignification of conventional kraft pulps and pulps from a laboratory simulation of Ahlstrom's Lo-Solids<sup>®</sup> extended delignification (modified) process. These experiments were conducted over a range of kappa numbers for both pulping processes, and at high and low kappa factors. The results (Table 1) showed that the modified pulps were slightly easier to bleach in the conventional process, an observation which parallels the corresponding observation made earlier, when the same pulps were bleached with the "Rapid D<sub>0</sub>" short-retention process. As in previous work, there was a slight deterioration in bleachability as the unbleached kappa number was decreased. The bleachabilities of these pulps will be correlated with the structural features of the residual lignins they contain, to add to our database of lignin structure-bleachability relationships.

In other experiments, two sets of hardwood pulps of varied unbleached kappa number were subjected to determinations of their hexeneuronic acid contents. Pulps representing both conventional batch and extended (RDH) kraft pulping processes were included. Hexeneuronic acids are carbohydrate-derived components formed during kraft pulping by demethoxylation of a hemicellulose, 4-O-methyl-D-glucuronoxylan ("xylan"). Their presence in bleachable grade pulps is significant for two reasons: (1) they falsely inflate the unbleached kappa number, and (2) they consume electrophilic bleaching chemicals, such as chlorine dioxide. The analyses we performed consisted of acid hydrolysis under standard conditions, followed by spectrophotometric determination of the hydrolysis product (2-furoic acid) in the hydrolyzates. An alternate method is to determine the kappa number reduction that accompanies hydrolysis. The results we obtained are shown in Figure 1. It is apparent from the figure that, at a given kappa number, the two pulp types did not differ with respect to their hexeneuronic acid contents. On the other hand, there was a significant effect of unbleached kappa number. As the kappa number was decreased below 30 by extending the kraft cook, the hexeneuronic acid content first increased, then passed through a maximum, following which it decreased sharply. This finding will have considerable practical implication in the manufacture of hardwood kraft pulps for bleachable grades.

Residual lignin and effluent structural analyses by NMR and gel permeation chromatography are continuing to generate data for the development of structure-bleachability relationships. Analysis of this data is in progress.

Table 1. Conventional D(EO) Bleaching Parameters

Pulp Type	D <sub>n</sub> Stage						(EO) Stage				Total								
	Kappa No.		Kappa Factor		Delta Kappa	AOX	Cl <sup>-</sup>	ClO <sub>3</sub> <sup>-</sup>	Kappa No.		AOX		Cl <sup>-</sup>	ClO <sub>3</sub> <sup>-</sup>	Delta Kappa/ TAC	AOX Yield, %	Cl <sup>-</sup> Yield, %	ClO <sub>3</sub> <sup>-</sup> Yield, %	Cl Recovery, %
		Brightness			Kappa/ TAC	%	%	%		Brightness		%	%						
Conv.	29.6	26.0	0.05	25.0	3.1	5.4	(13)	1	15.3	36.1	3.5	12	9.7	8.9	25	1	35		
			0.20	14.8	2.5	8.8	48	15	5.7	49.2	2.6	10	4.0	11.5	58	15	84		
	21.3	28.9	0.20	10.5	2.5	8.3	51	16	4.1	52.1	2.6	10	4.0	10.9	61	16	89		
	14.9	29.1	0.20	7.6	2.4	7.0	55	15	3.2	54.3	2.4	9	3.9	9.4	64	15	89		
	28.7	25.2	0.05	24.9	2.6	4.9	54	5	14.3	35.1	3.5	13	10.0	15.3	67	5	81		
			0.20	14.5	2.5	8.5	52	17	4.7	49.2	0.9	8	4.2	9.3	60	17	87		
Lo-Solids	18.8	28.1	0.20	9.4	2.5	8.5	52	15	3.2	54.3	2.7	10	4.1	11.2	62	15	89		
	15.6	28.8	0.20	7.9	2.5	7.2	52	14	3	55.5	2.3	10	4.0	9.5	62	14	86		

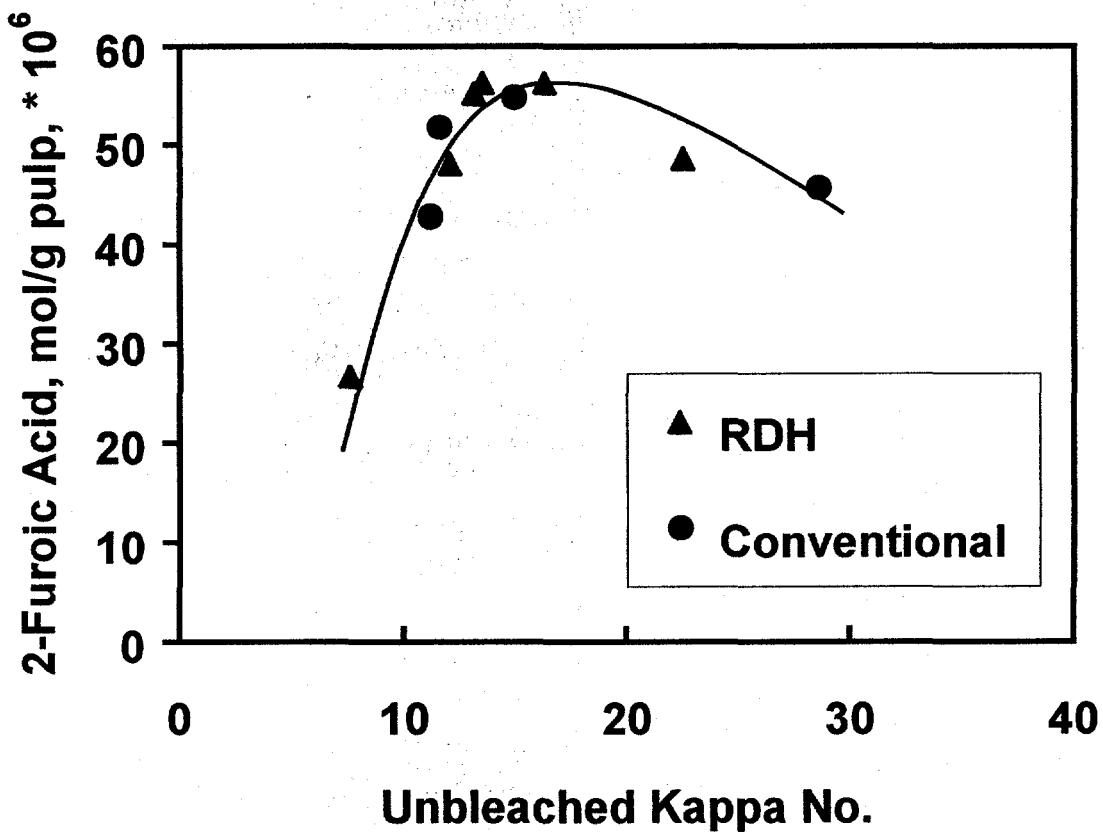


Figure 1. Hexeneuronic acid content of unbleached RDH and conventional kraft pulps from sweetgum.