

Vapor Phase ClO₂ Delignification of Hardwood and Softwood Kraft Pulps

Introduction

- “Vapor Phase” ClO_2 treatment has been proposed as an efficient, low-AOX alternative to low and medium consistency D_0 stages
- We have begun an investigation of this process to learn more about the reasons for its high efficiency, in an effort to achieve similar efficiency by other means

Experimental

- Passed gaseous mixture of N_2 , ClO_2 into rotating spherical flask containing fluffed pulp at $60^\circ C$ over a period of 10 min
- Excess ClO_2 was trapped and titrated
- Emphasized conventional and RDH hardwood pulps, with a smaller amount of work on softwood pulps

Experimental (2)

- Filtrates collected and analyzed for AOX, ClO_3^- , ClO_2^- , and Cl^-
- Lignin was isolated from some of the pulps before and after bleaching and characterized by ^{31}P NMR analysis

Conventional and Vapor Phase D₀: Conventional Hardwood Pulps

Process	Unbl. Kappa	D ₀ Stage		(EO) Stage	
		Kappa	$\Delta\kappa/\text{TAC}$	Kappa	$\Delta\kappa/\text{TAC}$
Conv.	11.4	6.2	2.3	4.2	3.2
	15.2	7.9	2.4	5.2	3.3
Vapor	11.4	4.2	3.5	2.3	4.4
	15.2	5.3	3.8	2.5	4.9

Conventional and Vapor Phase D₀: RDH Hardwood Pulps

Process	Unbl. Kappa	D ₀ Stage		(EO) Stage	
		Kappa	$\Delta\kappa/\text{TAC}$	Kappa	$\Delta\kappa/\text{TAC}$
Conv.	7.8	5.6	1.4	3.1	3.0
	13.4	10.0	1.3	5.2	3.1
	22.9	13.9	2.0	5.2	3.9
Vapor	7.8	3.3	3.7	1.5	5.2
	13.4	5.4	3.5	2.8	4.6
	22.9	8.2	3.8	2.6	5.3

Vapor Phase D₀: Hardwood Conventional and RDH Pulps

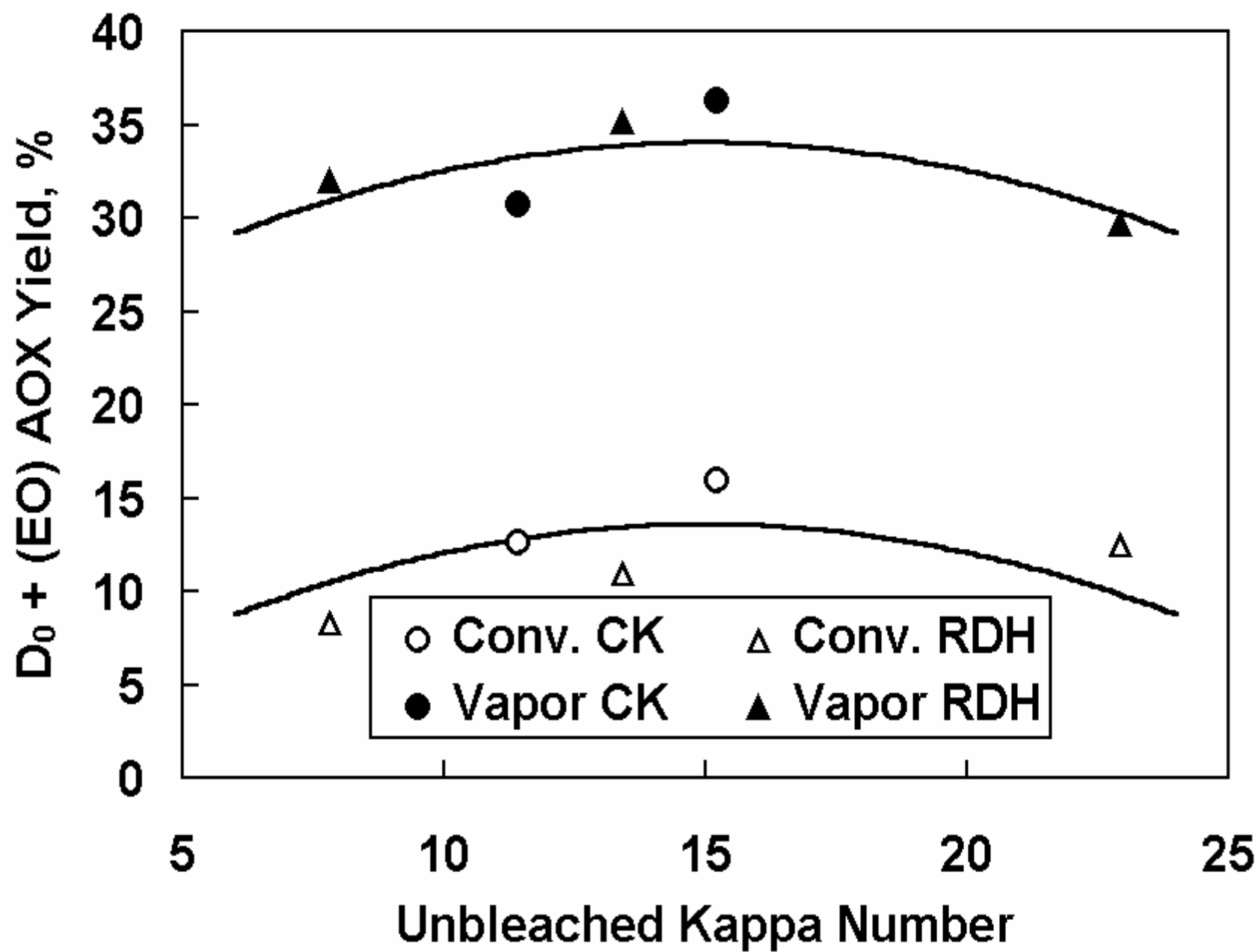
Pulp Type	Unbl. Kappa	D ₀ Stage		(EO) Stage	
		Kappa	$\Delta\kappa/\text{TAC}$	Kappa	$\Delta\kappa/\text{TAC}$
Conv.	11.4	4.2	3.5	2.3	4.4
	15.2	5.3	3.8	2.5	4.9
	22.9	8.2	3.8	2.6	5.3
RDH	7.8	3.3	3.7	1.5	5.2
	13.4	5.4	3.5	2.8	4.6
	22.9	8.2	3.8	2.6	5.3

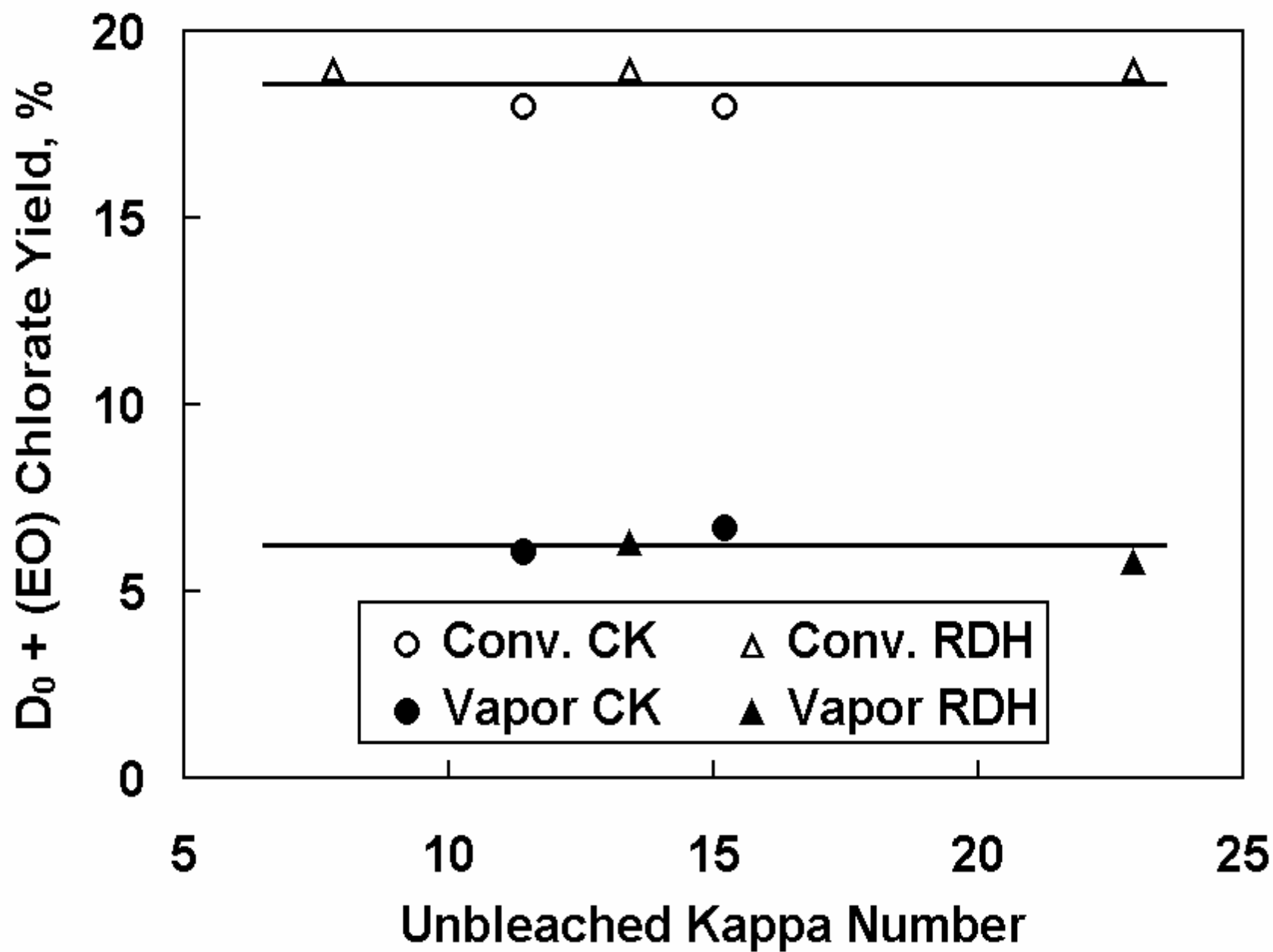
Conventional and Vapor Phase D₀: Softwood Pulps

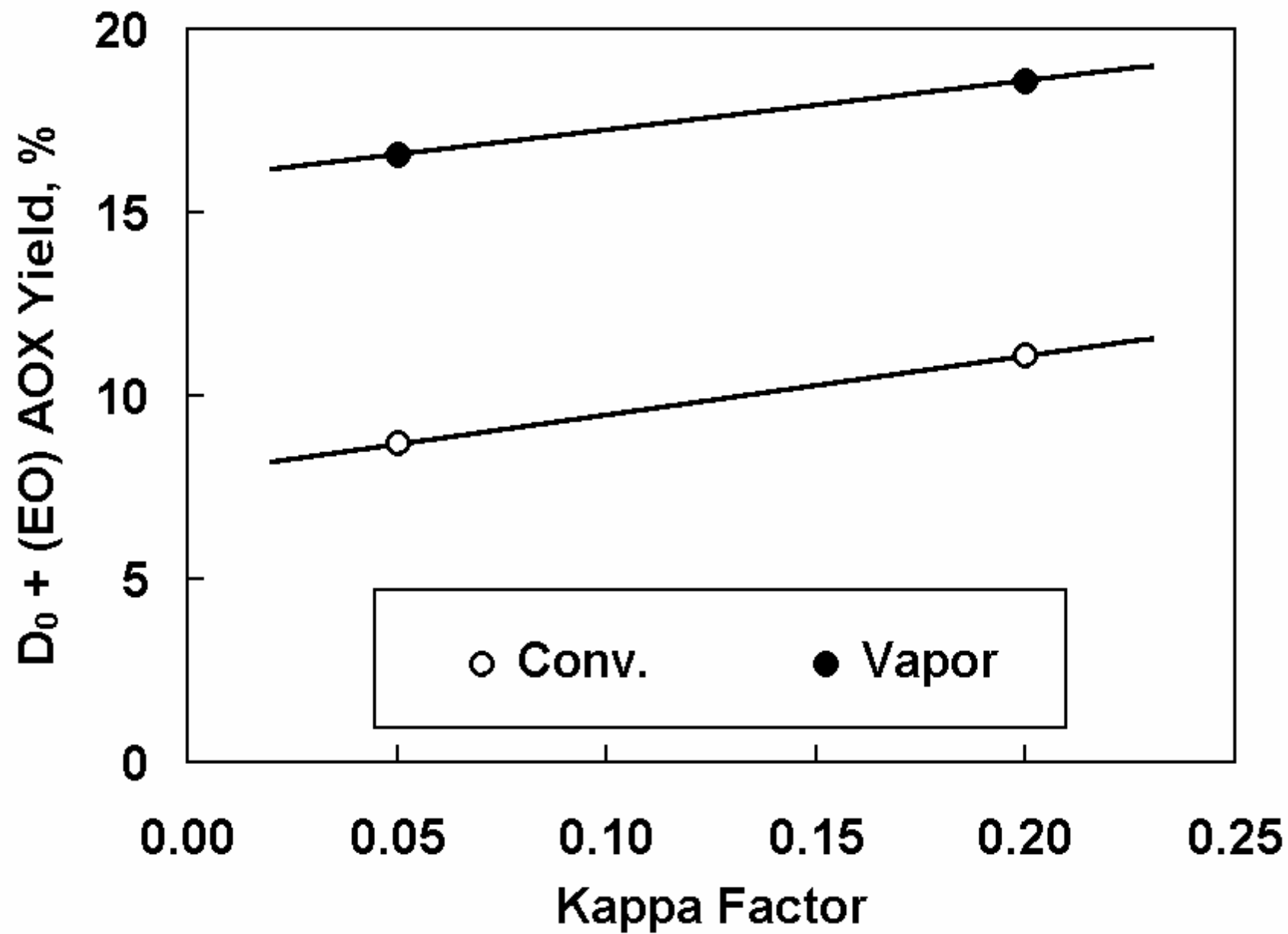
Pro- cess	Unbl. Kappa	D ₀ Stage		(EO) Stage	
		KF	$\Delta\kappa/\text{TAC}$	Kappa	$\Delta\kappa/\text{TAC}$
Conv.	18.7	0.05	4.8	10.2	9.1
		0.20	2.6	3.9	4.0
	30.4	0.20	2.6	4.2	4.3
Vapor	30.7	0.05	2.8	15.8	9.7
		0.18	2.7	4.5	4.6

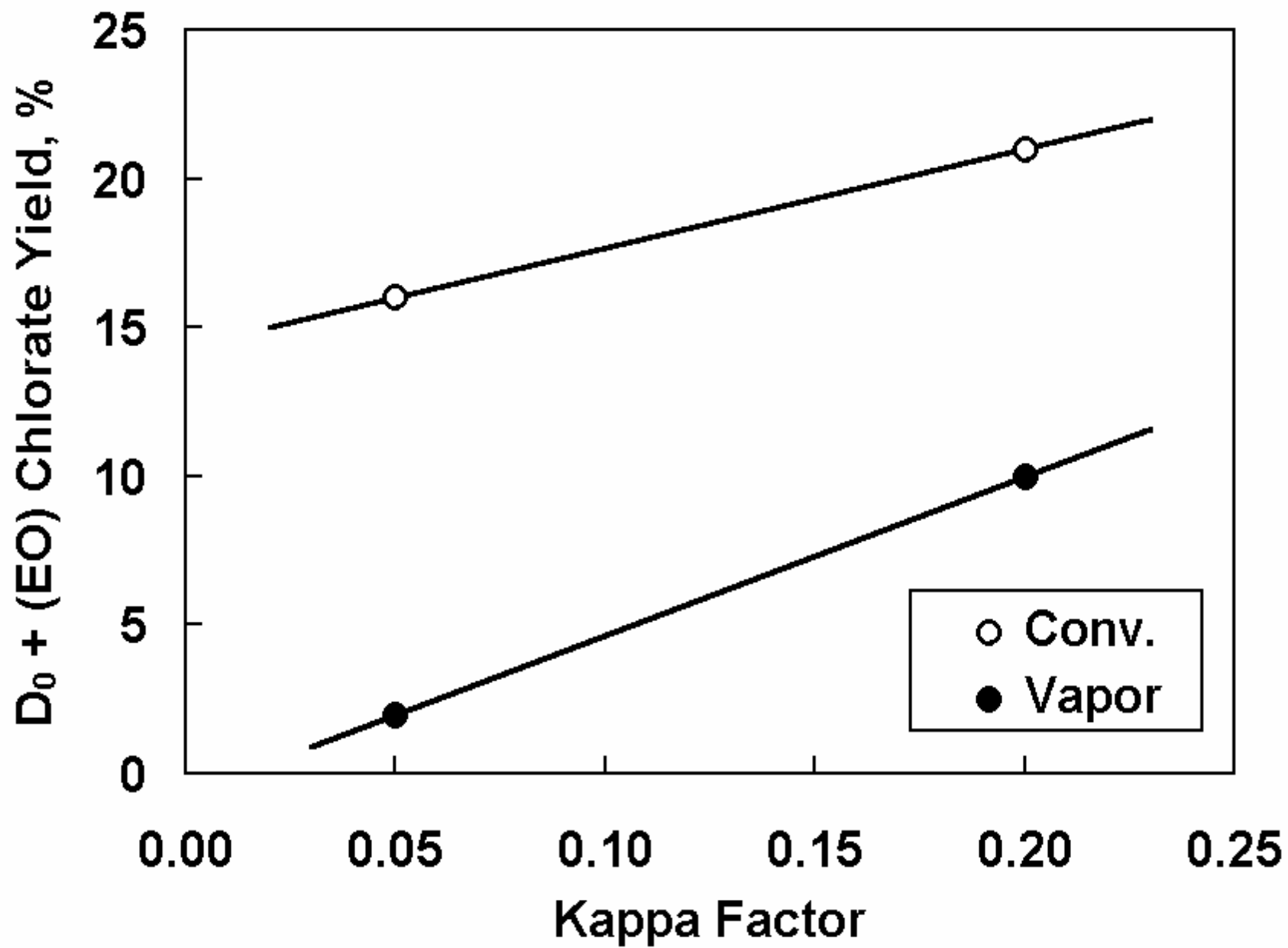
Summary of Bleaching Data

- For HW, VP much more efficient
- For SW, much less difference
- Efficiency decreases with unbl. kappa
- Efficiency much higher at low KF
- RDH slightly more bleachable









Summary of Filtrate Data

- Vapor phase delignification gave higher AOX yield and lower chlorate yield
- The effect on AOX was greater for hardwood pulp than for softwood
- Conventional and RDH pulps behaved similarly
- SW AOX and chlorate yields increased with KF

Conventional and Vapor Phase D₀: OH Groups in Lignin

Type of OH Group	Unbl.	D ₀ Stage		(EO) Stage	
		Conv.	Vapor	Conv.	Vapor
Aliphatic	1.58	1.17	1.25	1.47	1.53
Phenolic	1.64	0.71	0.75	0.63	0.62
Carboxylic	0.36	0.44	0.47	0.78	0.86

Conventional and Vapor Phase D₀: Phenolic Groups in Lignin

Type of Phenolic Group	Unbl.	D ₀ Stage		(EO) Stage	
		Conv.	Vapor	Conv.	Vapor
Syringyl	0.66	0.17	0.18	0.12	0.14
Guaiacyl	0.48	0.26	0.28	0.29	0.22
Condensed	0.51	0.27	0.30	0.24	0.27

Summary of Lignin Data

- Acid groups are introduced by both the D_0 and (EO) stages, especially in and after vapor phase delignification
- Aliphatic OH is lost in the D_0 stage and re-introduced in the (EO) stage
- Phenolic OH groups are extensively lost in the D_0 stage and, to a lesser extent, in the (EO) stage

Summary of Lignin Data (2)

- Syringyl units are more reactive than guaiacyl or condensed phenolic units
- Guaiacyl and condensed phenolics were removed to similar extents
- The smallness of the differences between residual lignin structures after vapor phase and conventional bleaching

Conclusions (1)

- Vapor phase ClO_2 delignification of hardwood kraft pulps made from sweetgum is remarkably more efficient than conventional ClO_2 delignification.

Conclusions (2)

- In the case of southern pine kraft pulps, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. This observation differs from those made earlier by others, indicating that vapor phase delignification efficiency is sensitive to operating conditions.

Conclusions (3)

- Vapor phase delignification of kraft pulps generated abnormally large quantities of AOX under the conditions employed in this study
- Vapor phase filtrates contained markedly less chlorate ion than filtrates from conventional ClO_2 delignification, in accord with the higher efficiency of vapor phase bleaching

Conclusions (4)

- Differences in the structure of residual lignin after conventional and vapor phase bleaching were slight. The superior bleaching efficiency of the vapor phase process may be due to the diminished importance of reactions that occur between active chlorine compounds and dissolved organic by-products.

Acknowledgments

- United States Department of Energy
- IPST Member Companies