HW High Efficiency ClO_2 Delignification: Process Studies

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Pro's and Con's of Vapor Phase ClO_2 Delignification

- Vapor phase delignification (VPD) with ClO_2 is much more efficient in terms of kappa number reduction per unit of total active chlorine consumed and yields much lower extracted kappa no.
- VPD generates more AOX and would require expensive capital equipment

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Conventional and Vapor Phase D_0: Conventional Hardwood Pulps

Pro-cess	Unbl. Kappa	D_0 Stage Kappa	D_0 Stage $\Delta\kappa$/TAC	(EO) Stage Kappa	(EO) Stage $\Delta\kappa$/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

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Having the Pro's Without the Con's

- **The essential differences between VPD and conventional delignification are the consistency and rate of ClO_2 addition**
- **We have done experiments to independently examine the effects of these changes**

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Rate of ClO_2 Addn. at 3% Final Consistency, 0.2 KF Applied

Addn. Time, min	Total Time, min	React-or	(EO) Kappa No.	ClO_3^- Yield, %	AOX Yield, %
0.1	30	Quant.	5.2	n.d.	n.d.
0.1	30	Rotov.	5.2	23	17.5
30	30	Rotov.	5.4	19	16.7
30	60	Rotov.	5.2	n.d	n.d.

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Rate of ClO_2 Addn. at 20% Final Consistency, 0.2 KF Applied

Addn. Time, min	Total Time, min	React-or	(EO) Kappa No.	ClO_3^- Yield, %	AOX Yield, %
0.1	30	Bag	2.7	15	34
0.1	30	Rotov.	2.5	15	37
30	30	Rotov.	3.4	n.d.	n.d.

Effect of Consistency

Consis-tency, %	Kappa Factor	Addn. Time, min	(EO) Kappa No.	ClO_3^- Yield, %	AOX Yield, %
3	0.1	0.1	7.0	12	17
3	0.2	0.1	5.2	23	18
3	0.2	30	5.4	19	17
24	0.11	0.1	5.6	11	32
20	0.2	0.1	2.5	15	37
20	0.2	30	3.4	n.d.	n.d.

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Conclusions

- Slow addition of aqueous ClO_2 does not reproduce the high efficiency of VPD
- Addition of aqueous ClO_2 to high consistency pulp reproduces both the high efficiency and high AOX generation rate of VPD
- The characteristics of VPD are not due to vapor phase ClO_2 addition, but are rather due to the high consistency of VPD

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HexA Removal by D_0 Filtrate and H_2SO_4, 5h at 95C, pH 2.7-3.1

Unbl. Kappa	Acid $\Delta\kappa$	Filtrate $\Delta\kappa$	Acid $\Delta\eta$, cp.	Filtrate $\Delta\eta$, cp.
11.8	5.1	5.1	10.1	0.0
12.9	5.5	5.7	3.3	4.7
17.3	5.0	5.2	12.3	16.7
29.1	4.2	6.0	21.7	20.2

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Bleaching After Hydrolysis With Filtrate (Af Stage)

Unbl. Kappa	Af Kappa	AfD(EO) Kappa	D(EO) Kappa
16.1	9.5	2.2	5.2
11.6	7.0	2.0	4.2
24.1	15.4	3.0	5.2
14.2	8.8	2.3	5.2
7.8	5.6	1.8	3.1

Seeking Practical Ways to Remove Hexeneuronic Acids (HexA)

- Investigated effects of
  - Temperature
  - Time
  - Acid source
  - Consistency

Temp., Time Effects in Hydrolysis of Kappa 16.7 Gum RDH Pulp

Temp., °C	Time, h	Acid Source	Final Kappa No.	Viscos-ity, mPa.s
90	1	$D_0+H_2SO_4$	14.7	47.7
	2	"	13.5	44.1
	5	"	12.1	34.6
95	5	"	11.2	35.1
100	2	HCOOH	11.4	39.5

Note: All runs at 4% Consistency

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Cons'y., Time Effects in Hydrolysis of Kappa 12.6 Gum Kraft Pulp

Cons'y., %	Time, h	Acid Source	Final Kappa No.	Viscosity, mPa.s
4	5	D_0+H_2SO_4	6.6	24.4
12	1	"	8.7	28.8
"	3	"	7.3	26.6
"	5	D_0+H_2SO_4	6.8	23.3
12	"	H_2SO_4	6.8	24.1
20	"	D_0+H_2SO_4	7.7	19.5
30	"	"	7.1	15.4

Note: All runs at 95°C

Medium, Cons'y. Effects in Hydrolysis of Kappa 12.6 Gum Kraft

Cons'y., %	Acid Source	Final Kappa No.	Viscosity, mPa.s
12	D_0	6.6	24.4
"	$D_0+H_2SO_4$	6.8	23.3
"	H_2SO_4	6.4	24.9
30	D_0	6.9	16.3
"	$D_0+H_2SO_4$	7.1	15.4

Note: All runs 5 h at 95°C

High-Intensity Hydrolysis of Kappa 12.6 Gum Kraft Pulp

Temp., °C	Time, min	HexA Released, µmol/g	Final Kappa No.	Viscos-ity, mPa.s
123	15	42.5	7.4	29.1
122	60	71.1	6.1	24.4

Note: All runs at 12% consistency, pH 3, H_2SO_4

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Conclusions: Medium, Time and Temperature

- D_0 filtrate, H_2SO_4 and formic acid are equivalent in their abilities to decrease the kappa no. of gum kraft pulp
- Kappa number reduction is nearly complete in 5h @ 95^{o}C, 2h @ 100^{o}C, or 30 min @ 120^{o}C

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Conclusions: Consistency

- For given conditions of time, temp., & initial pH, kappa reduction is independent of consistency over the range 4-30%
- Pulp viscosity loss is greater at consistencies above 12%, but may be tolerable at 30%
- Further optimization of 30% consistency hydrolysis w.r.t. temperature and time would be desirable

Delignification Partial Sequences Incorporating Hydrolysis

Sequence	Kappa Before D_0	ClO_2 in D_0, % o.d. pulp	Kappa After (EO)	Viscos-ity, mPa.s
D_0(EO)	12.6	0.96	3.5	33.2
AD_0(EO)	6.1	0.46	1.5	n.d.
(A/D_0)(EO)	6.1	0.46	2.2	21.2

Note: A-stage conditions were 120^{o}C, 60 min.

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Short Sequences Incorporating Hydrolysis

Sequence	ClO_2 in D_0+D_1 , % o.d. pulp	Bright-ness	Viscos-ity, mPa.s
D_0(EO)D_1	1.76	84.0	>25
AD_0(EO)D_1	0.86	85.7	n.d.
(A/D_0)(EO)D_1	1.26	84.8	~18

Note: A-stage conditions were 120^{o}C, 60 min.

Full Sequences Incorporating Hydrolysis

Sequence	ClO_2 in $D_0+D_1+D_2$, % o.d. pulp	Bright-ness	Viscos-ity, mPa.s
$D_0(EO)D_1D_2$	2.16	88.4	25.1
$AD_0(EO)D_1D_2$	1.26	88.7	13.3
$(A/D_0)(EO)D_1D_2$	1.86	88.7	<18

Note: A-stage conditions were 120^{o}C, 60 min.

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Conclusions

- **Short sequences developed to date can achieve 85 brightness with ClO_2 savings of more than 50%, or 30% if the pulp is not washed between the A and D_0 stages**
- **Full sequences developed to date can achieve 88-89 brightness with ClO_2 savings of more than 40%, or 15% if the pulp is not washed between the A and D_0 stages**

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Conclusions (Cont'd)

- **Further optimization of the A stage may be desirable for increased viscosity retention**

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