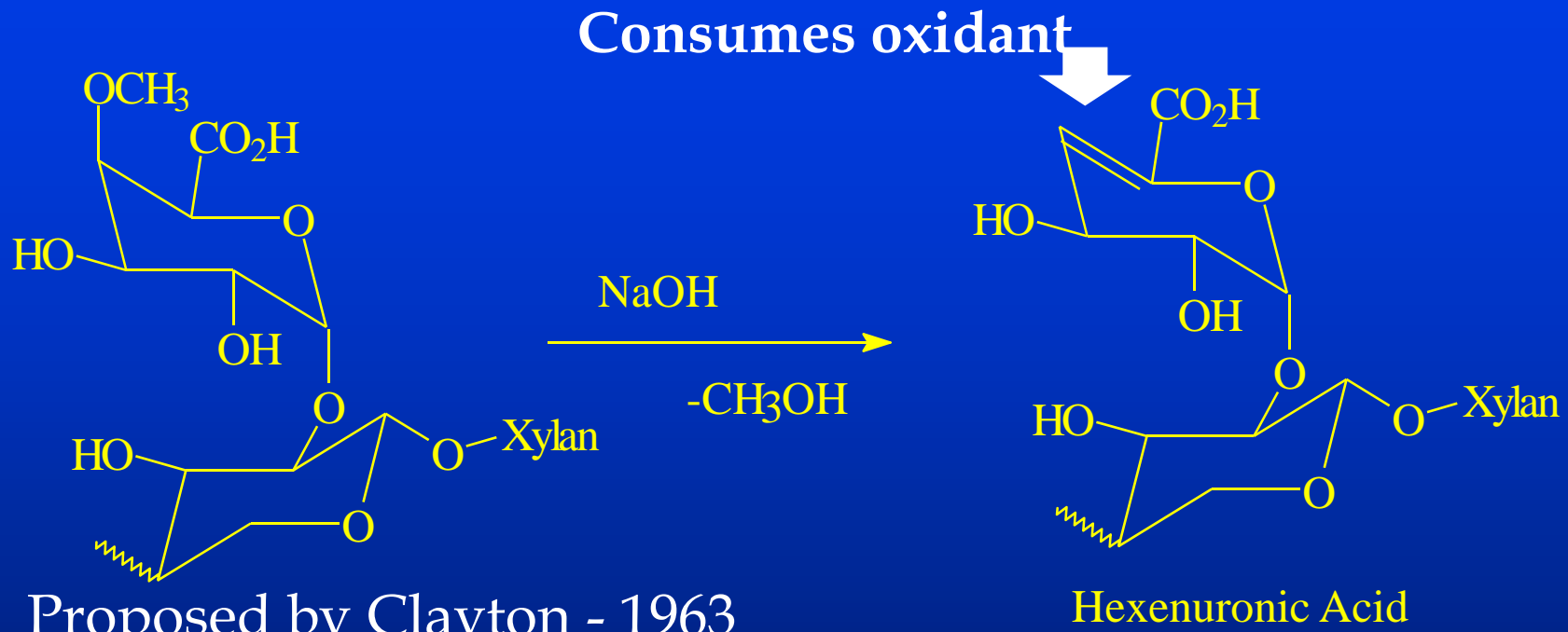


**Fundamentals of Bleaching
Chemistry
Hexenuronic Acids – HW Kraft**

Art J. Ragauskas

Hexenuronic Acids: Background



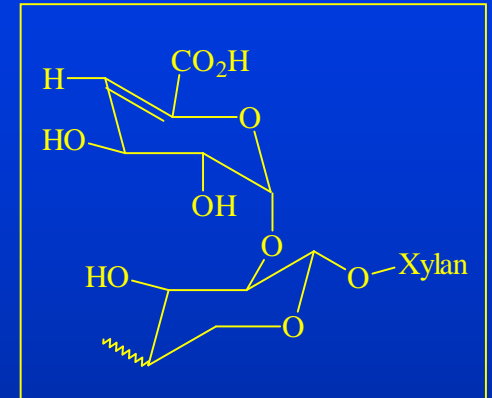
Proposed by Clayton - 1963

Studied:

- Johansson & Samuelson - 1977
- Simkovic - 1986
- Teleman ... - 1995

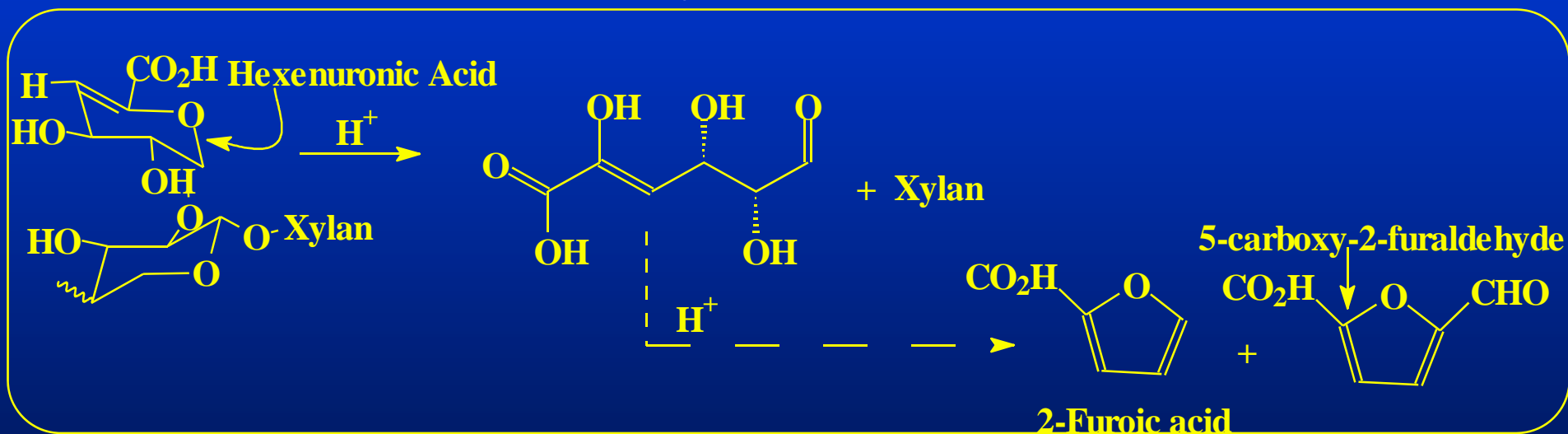
Hexenuronic Acids: Background

- Consumes D & Z
- Inert to P & O
- Sensitive to acid
- **Related to % xylan in pulp**
- **HW kraft: 30-55% of apparent kappa #**
- **SW kraft: 0 - 18%**
- **Binds metals**
- **AQ influences % HexA**
- **PS does not influence % HexA**

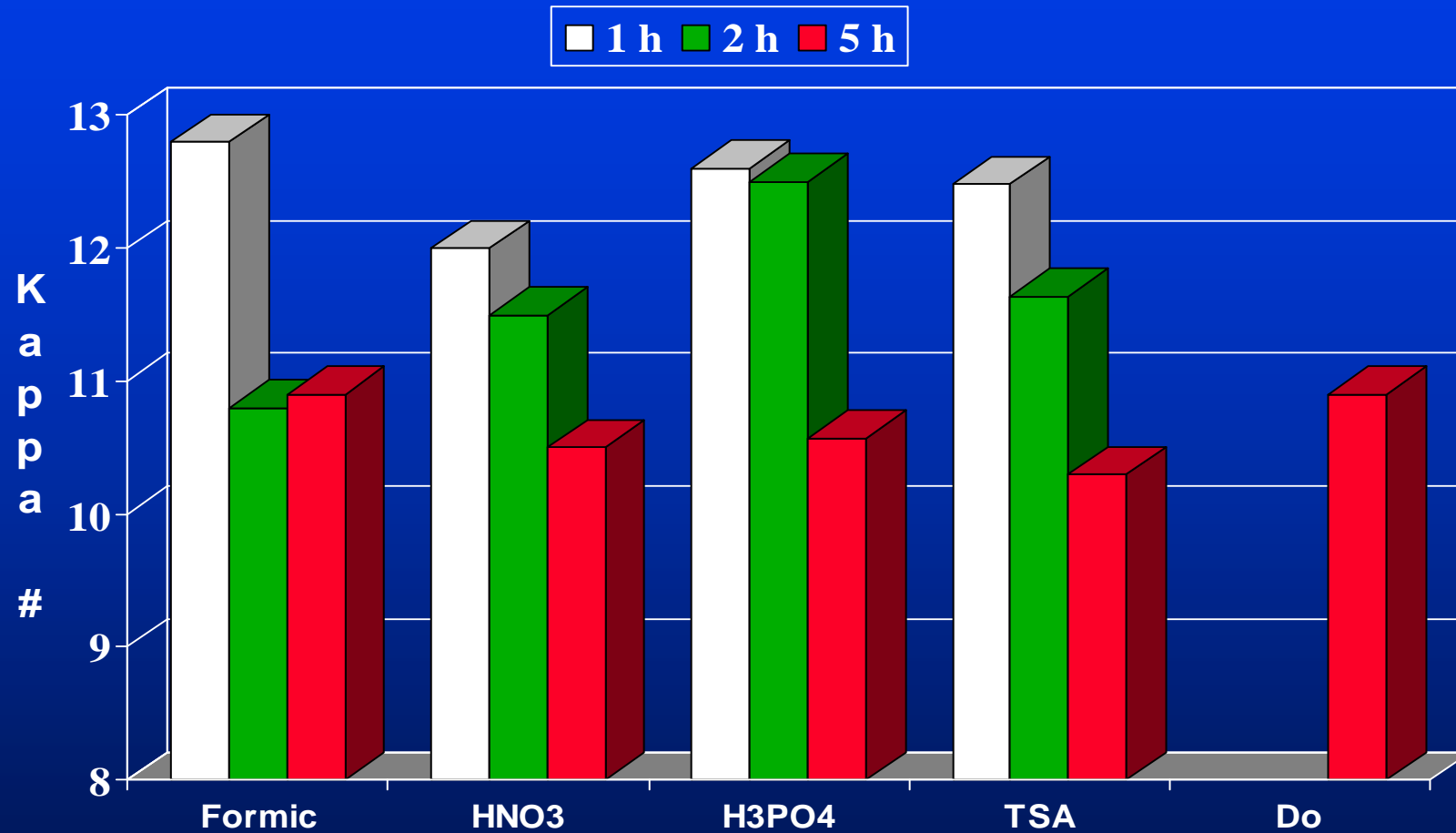


Hexenuronic Acids: Background

Acid treatment chemistry



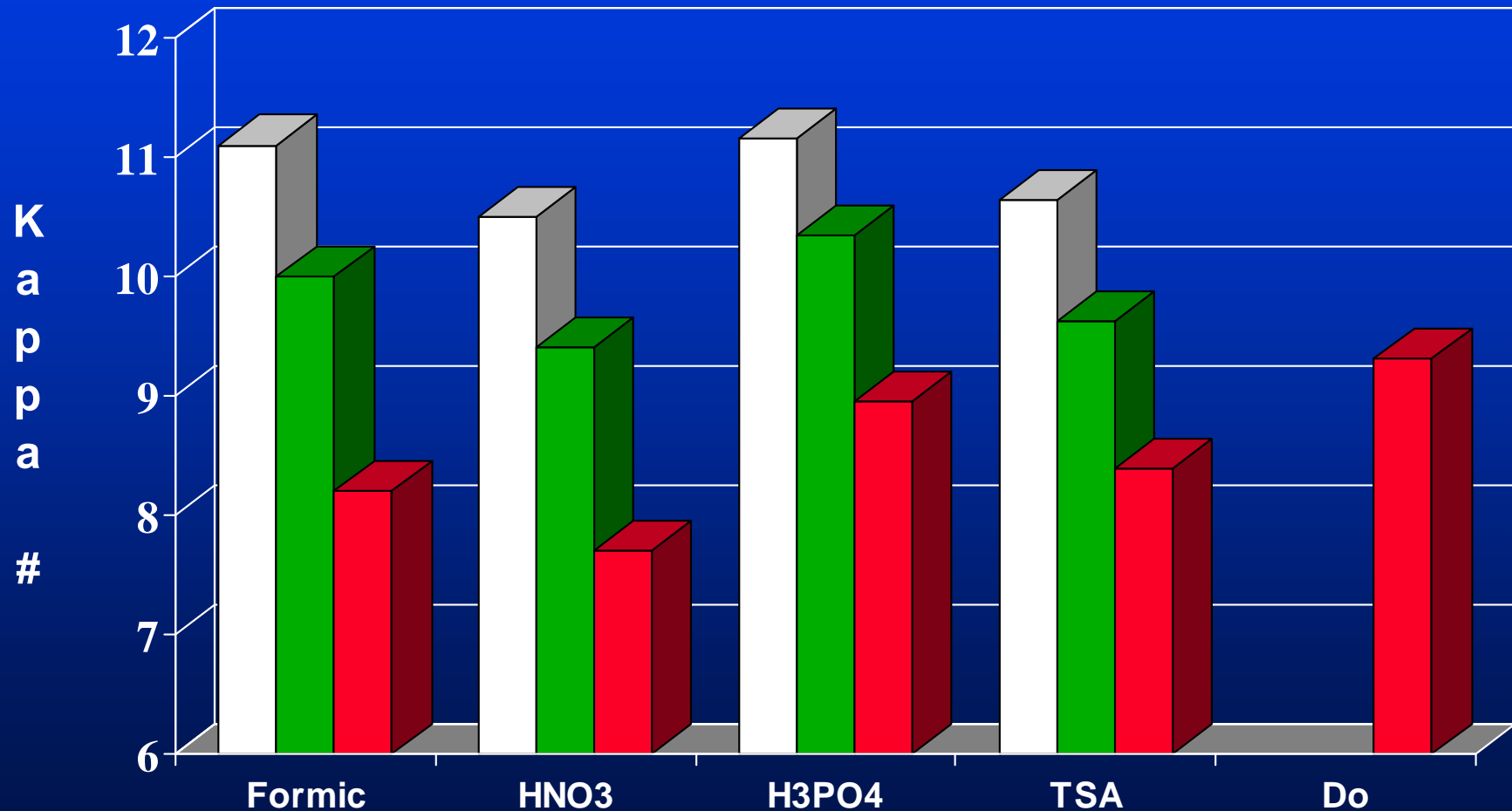
HexA: Acid Hydrolysis at 80° C



Brownstock kappa #: 13.5

HexA: Acid Hydrolysis at 95° C

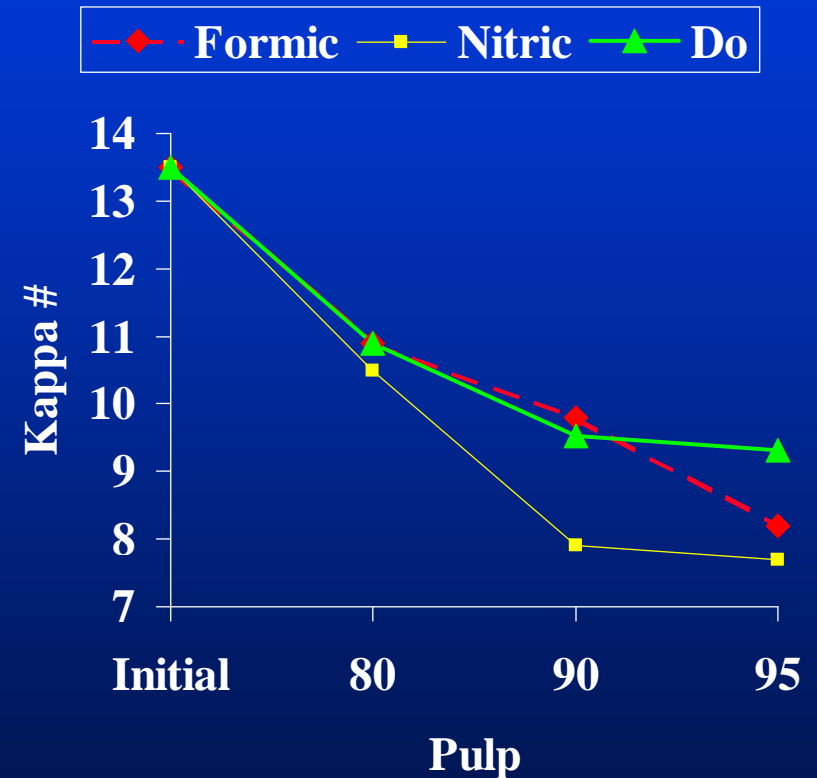
1 h 2 h 5 h



See report for 90°C results

HexA: Summary of Acid Work

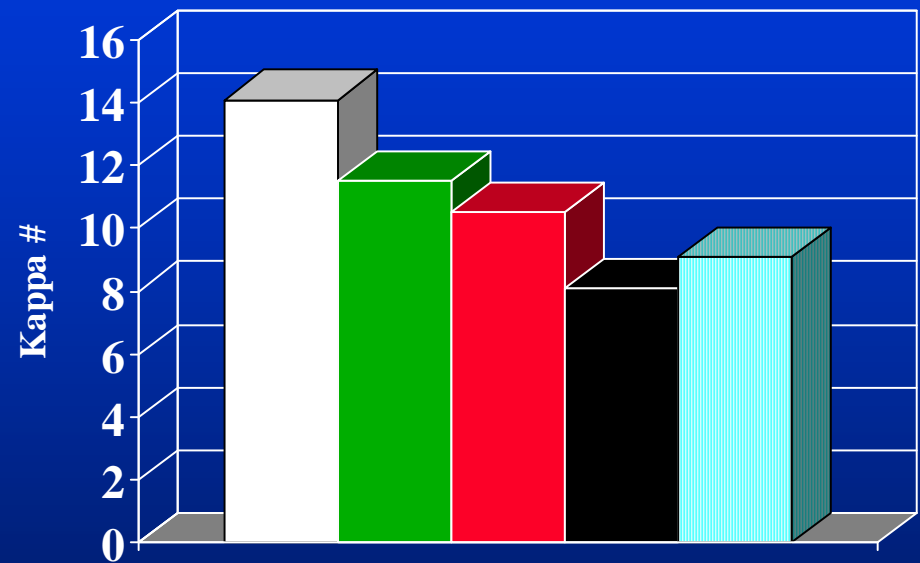
- D₀ wash is an effective treatment for HexA
- At 95°C need 5 h for max. effect >> For this pulp!
- 20 - 28% loss in viscosity (95 C)



HexA: Effect of Consistency

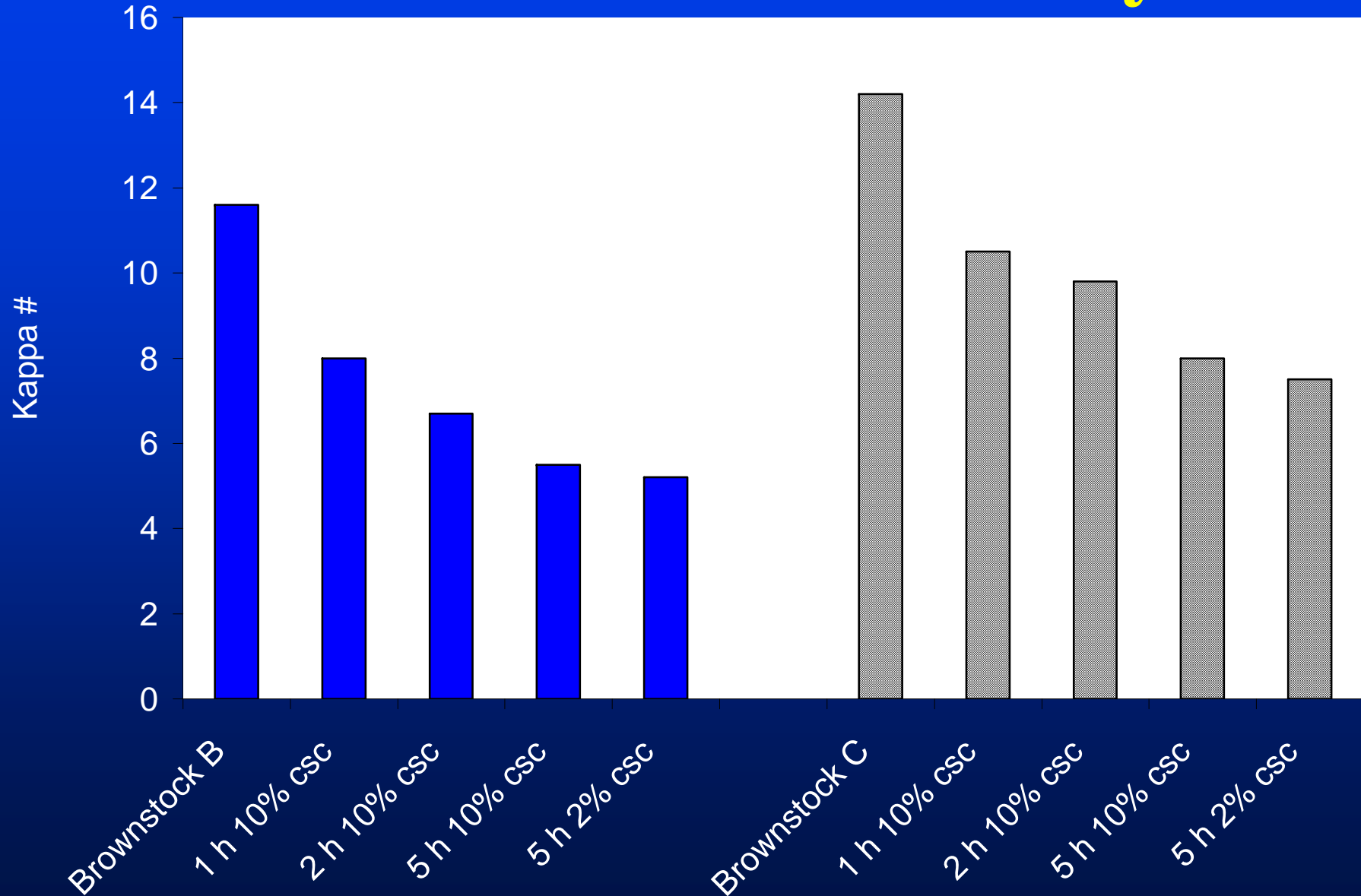
- **Exp. Conditions**

- Employed mill HW kraft pulp
- 2 & 10% csc
- Initial pH: 3 (H_2SO_4)
- measure kappa, viscosity, Klason, COD, & color



■ Brownstock ■ 1 h 10% csc ■ 2 h 10% csc
■ 5 h 10% csc ■ 5 h 2% csc

HexA: Effect of Consistency



HexA: Effect of Consistency

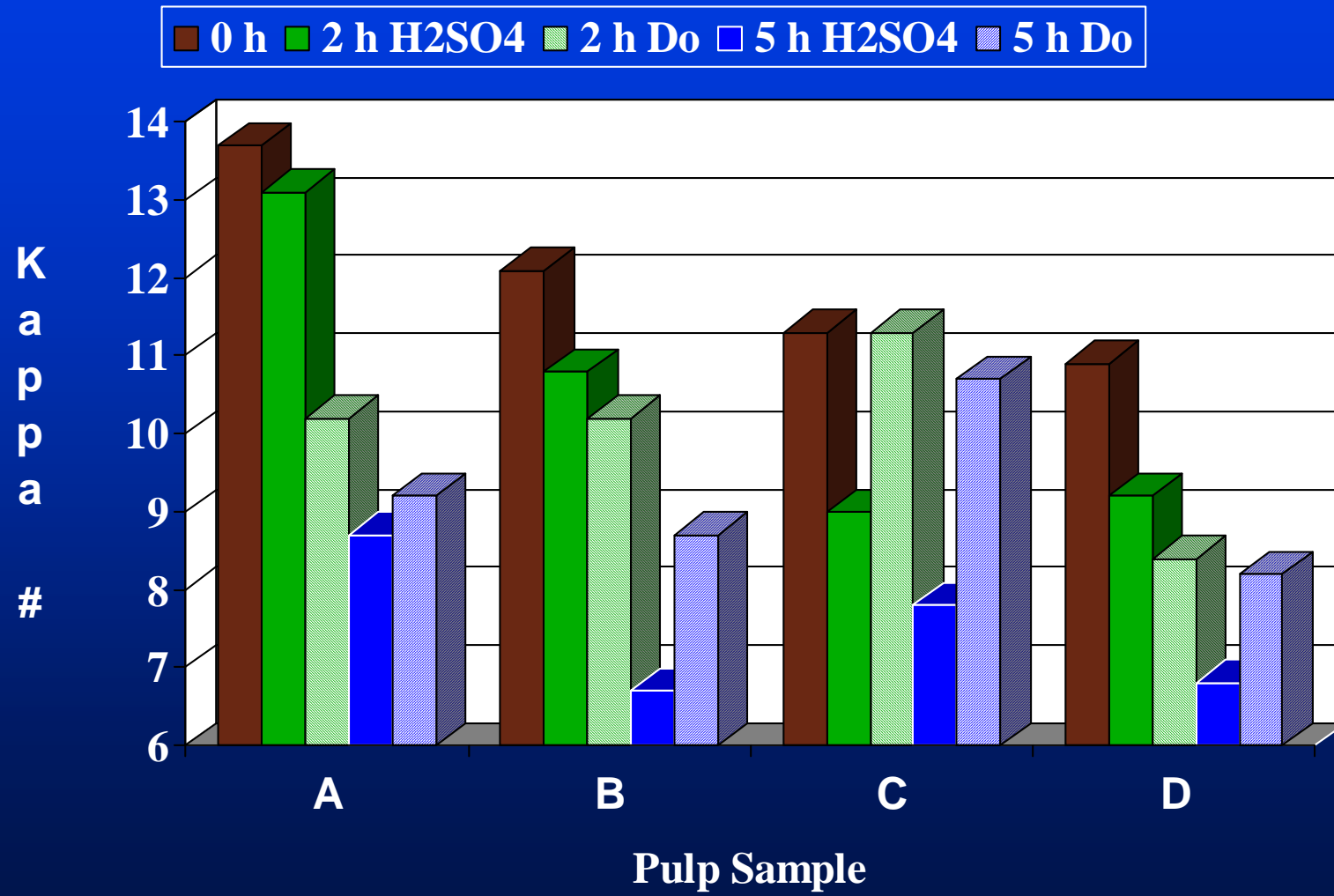
		Brownst.	1 h H ⁺ 10% csc	2 h H ⁺ 10% csc	5 h H ⁺ 10% csc	5 h H ⁺ 2% csc
Viscosity	(A)	29.6	27.6	26.8	26.1	29.4
	(B)	36.6	35.6	33.7	32.9	32.5
Klason	(A)	2.10	1.76	1.75	1.47	1.28
	(B)	1.63	1.62	1.41	1.42	1.20
COD	(A)	===	620	950	1,200	270
	(B)	===	1,200	1,400	1,500	380
Brownstock Kappa #			A: 14.1			
			B: 14.2			

HexA: Effect of D₀ Hydrolysis

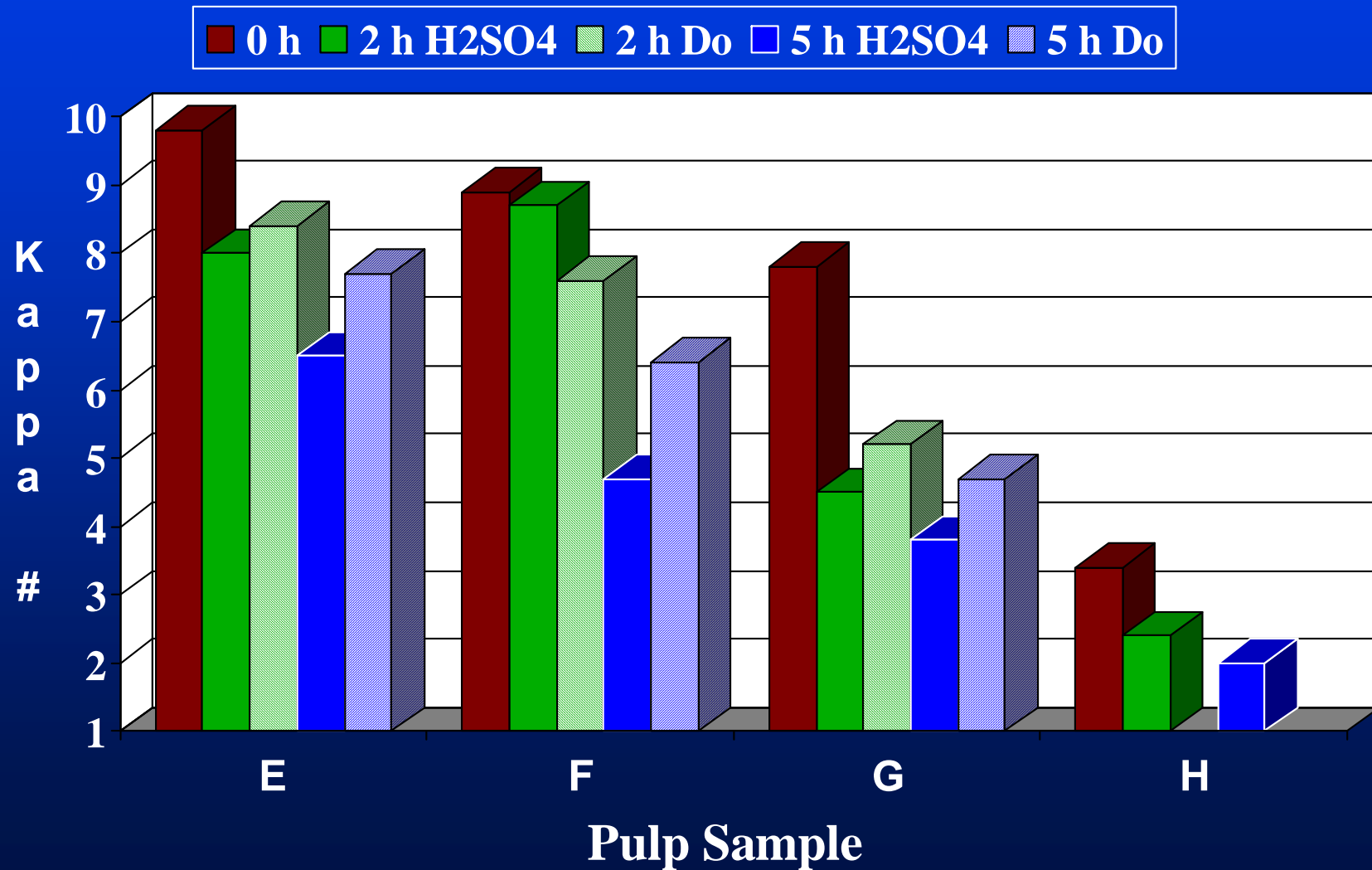
Exp. Protocol: Hydrolyze mill pulps with mill bleach effluents

Mill	HW Kraft Pulp Kappa #	1st Bleach Effluent
A	13.7	C/D pH: 2.5
B	12.1	Do pH: 3.4
C	11.3	Do pH: 2.8
D	10.9	Do pH: 2.3
E	9.8	Do pH: 2.3
F	post O ₂ 8.9	Do pH: 2.6
G	post O ₂ 7.8	Do pH: 2.6
H	3.4	{H ₂ SO ₄ }

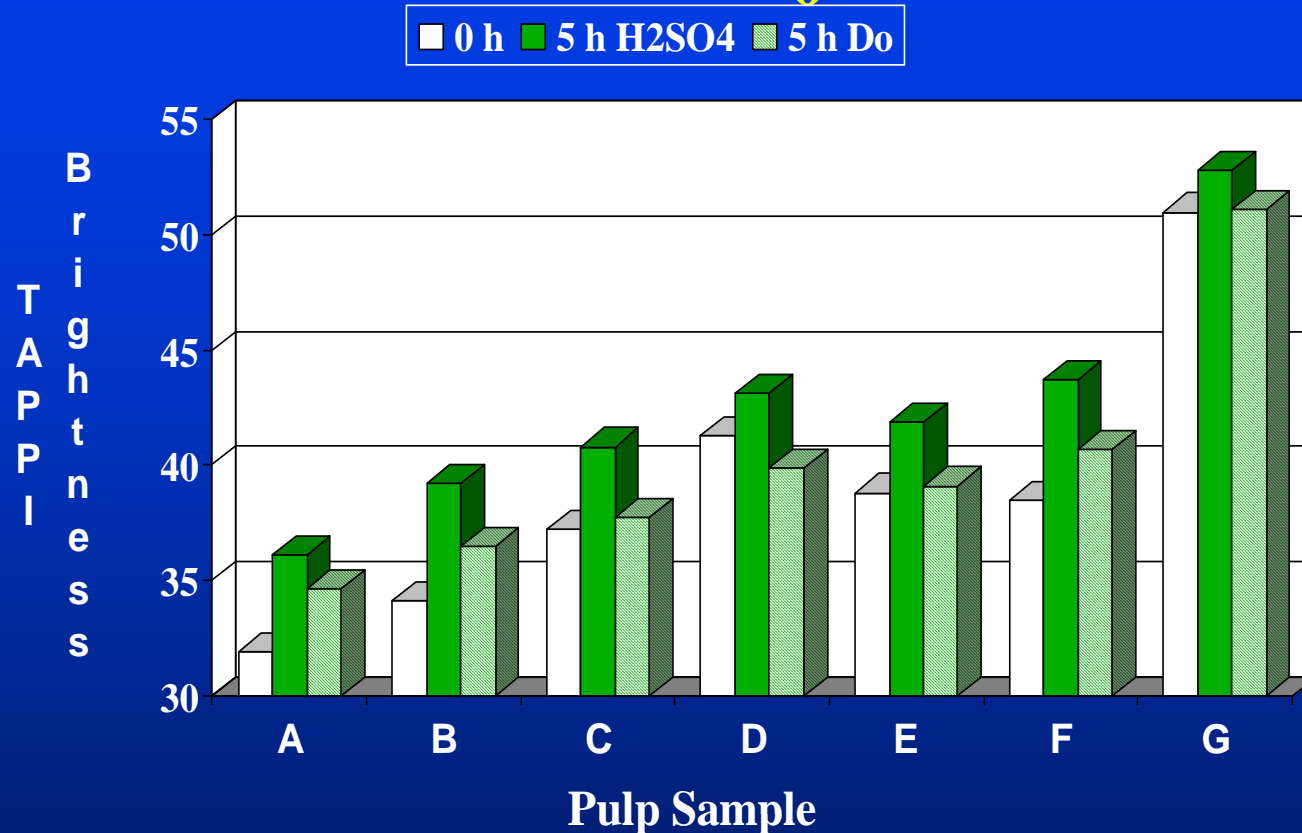
HexA: Effect of D₀ Hydrolysis



HexA: Effect of D₀ Hydrolysis



HexA: Effect of D₀ Hydrolysis



- D₀ heat treatment of HW pulp reduces apparent kappa #
- D₀ heated treated pulps do not detrimentally impact pulp brightness
- D₀ treatment slightly less effective as H₂SO₄

HexA: Full Sequence HW Kraft Bleaching Studies

Experimental Design

I. Study DEDED vs ADEDED

A-stage: Formic Acid/Sodium Formate 3 h

D₀ 0.20 kf, 3.5% csc, 45 min, 50°C

D1: 0.6% Charge, 10% csc, 3h , 75°C

D2: 0.1, 0.2, 0.4, 0.6% charge

II. Study ODED vs OADED

D₀ 0.20 kf, 3.5% csc

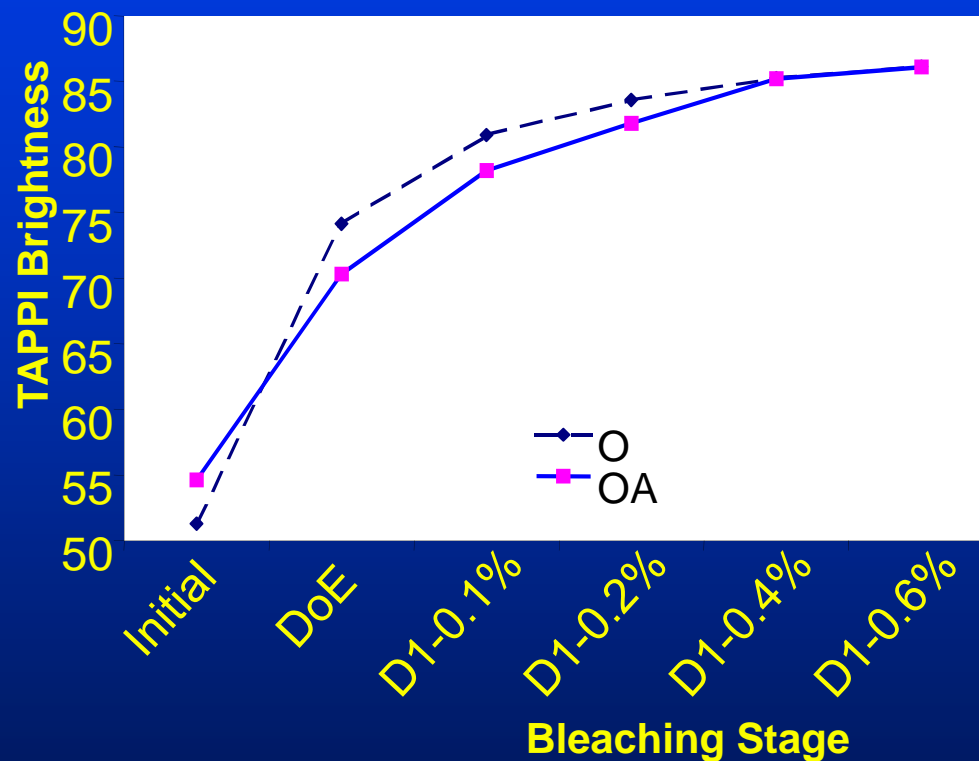
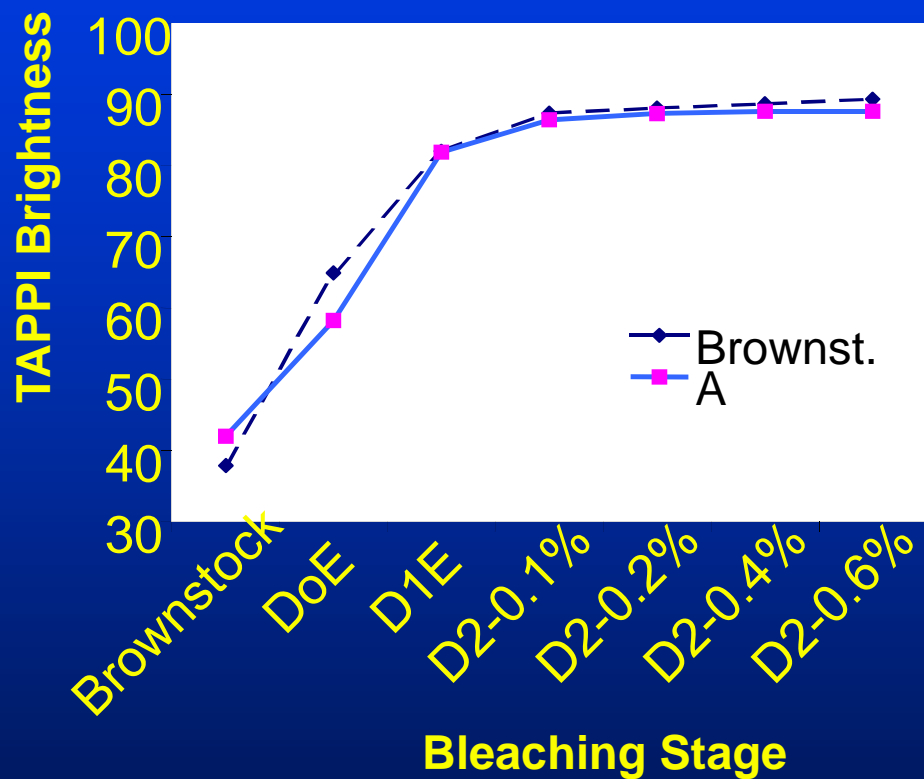
D1: 0.1, 0.2, 0.4, 0.6% charge

HexA: Full Sequence HW Kraft Bleaching Studies

Experimental Results

	<u>Kappa #</u>	<u>Viscosity/cP</u>	<u>Yield %</u>
<u>Pulp</u>			
Brownstock	11.4	24.4	
Brownstock(A)	5.6	22.8	98.2
O	8.5	21.8	
OA	2.8	19.9	98.0

HexA: Full Sequence HW Kraft Bleaching Studies



HexA: Yield Studies

Pulp	Kappa #	Viscosity/cP	% Yield
<u>HW kraft</u>	11.6	24.9	
$A_{(H_2SO_4)}$	6.2	24.3	97.8
<u>HW kraft</u>	14.1	29.6	
$A_{(H_2SO_4)}$	12.7	--	98.4
$A_{(D_0)}$	10.2	--	98.0
<u>Post O2 HW</u>			
	8.5	22.8	
$A_{(H_2SO_4)}$	3.7	20.2	98.1

HexA: Conclusions

- Exact acid not overly important for HexA removal
- Temp. is important for HexA removal
- HexA acid stage is not impacted by csc
- HexA removal can be accomplished by Do effluents
- HexA removal is beneficial for Do and subsequent stages
- HexA removal has yields of ca 98%
- Removal of HexA has small benefits wrt pulp brightness
- A-stage removes HexA and lignin

HexA: Benefits & Future Goals

Benefits

- A stage can potentially reduce HW kraft bleaching cost by 30 - 50%
- Simplify closed mill operations

Goals

- Optimal of D_0 kappa reduction with minimal yield loss
- Wood species variation in HexA precursors
- Minimization of HexA by kraft cooking