HEXENURONIC ACID IN PULP BLEACHING AND HYDROLYSIS HEXENURONIC ACID

OUTLINE

- Hexenuronic acid (HexA)
- Hydrolysis of HexA
- HexA in chlorine dioxide stages
- HexA in ozone bleaching
- Impact of HexA on peroxide bleaching
- HexA in peracetic acid bleaching

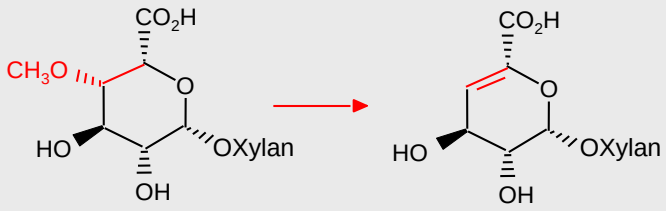
REACTIVE COMPONENTS OF OXYGEN DELIGNIFIED KRAFT PULPS

	Softwood pulp	Hardwood pulp
Lignin Phenolic Non-phenolic Chromophoric	~ 2 %	~ 1 %
HexA	< 0.5 %	< 1 %
Transition metals	< 0.01 %	< 0.01 %
Polysaccharides	~ 97 %	~ 98 %

CHEMICAL NATURE OF BLEACHING STAGES

Electrophilic: Lignin, HexA	D (Cl_2, HOCl), Z, Paa, A
Nucleophilic: Chromophores, carbonyl structures	O (HOO^-), D (ClO^-), P, Paa
Radical: Phenolic lignin	O, D
Other: Transition metals…	X, Q

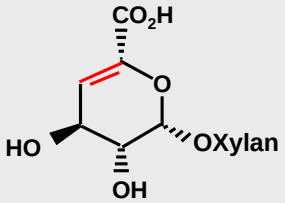
FORMATION OF HEXENURONIC ACID



Factors affecting:

Wood species (xylan content)
Cooking conditions (alkalinity, ion concentration)

PROPERTIES OF HEXENURONIC ACID

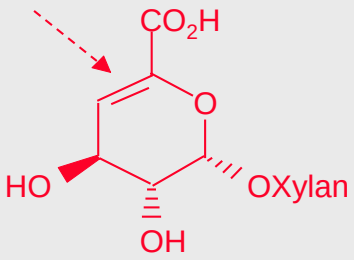


Heat → Brightness reversion

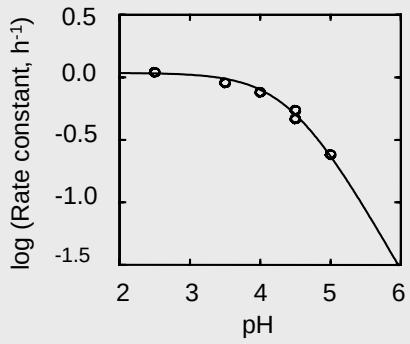
uncoloured
Oxidized by permanganate
Cation binding capacity

CHEMICAL REACTIVITY OF HEXENURONIC ACID

- Chlorine
- Hypochlorous acid
- Chlorine dioxide
- Ozone
- Peracids
- Oxygen
- Alkaline peroxide

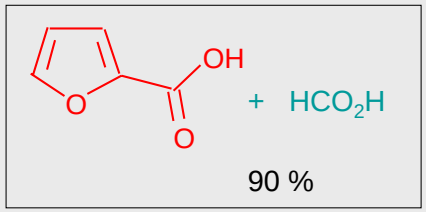


HYDROLYSIS OF HEXENURONIC ACID

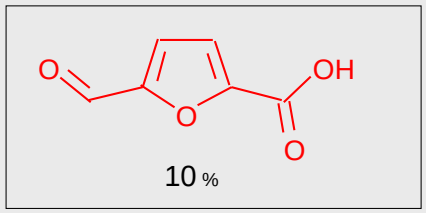


HYDROLYSIS OF HEXENURONIC ACID

- Furancarboxylic acids
  - Consume $KMnO_4$
  - Soluble in water
- Autocatalysis
- Autobuffering (pH 3-4)
- Removal of metal ions (binding sites)
  - A/Q very efficient for removal of Mn

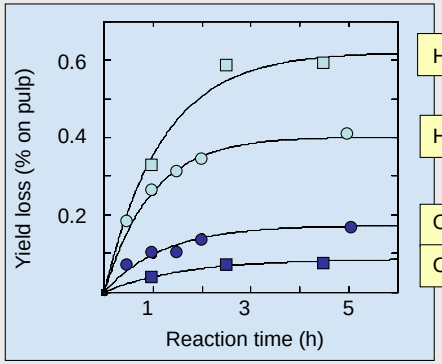


90 %



10 %

HYDROLYSIS OF HEXENURONIC ACID



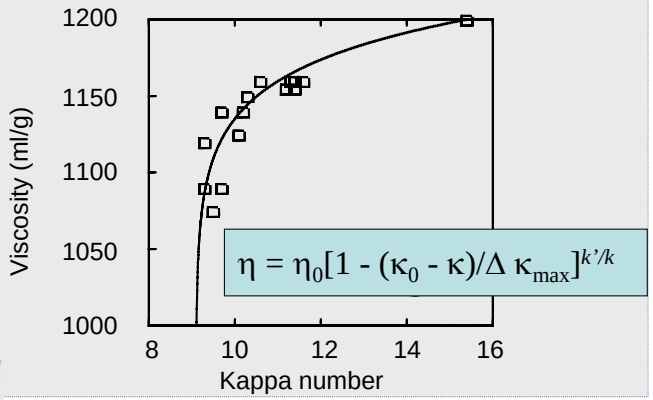
HexA (hardwood kraft)

HexA (softwood kraft)

Other (softwood kraft)

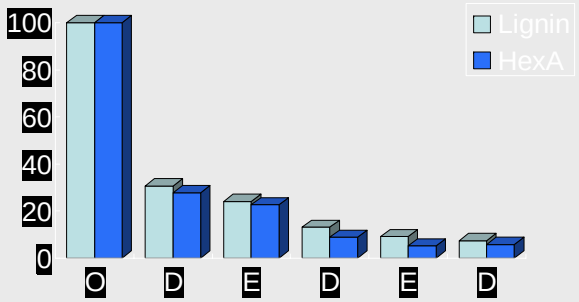
Other (hardwood kraft)

HYDROLYSIS OF HEXENURONIC ACID

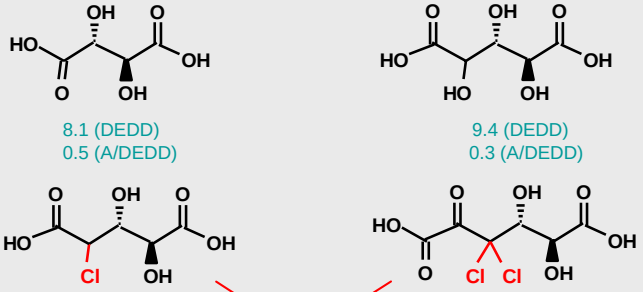


$$\eta = \eta_0[1 - (\kappa_0 - \kappa)/\Delta\kappa_{max}]^{k'/k}$$

REMOVAL OF LIGNIN AND HEXENURONIC ACID IN AN ECF BLEACHING STAGE

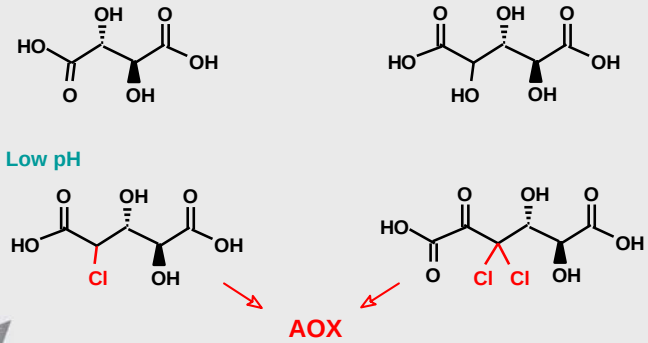


PRODUCTS OF HEXENURONIC ACID IN ECF BLEACHING STAGES (mmol/kg pulp)

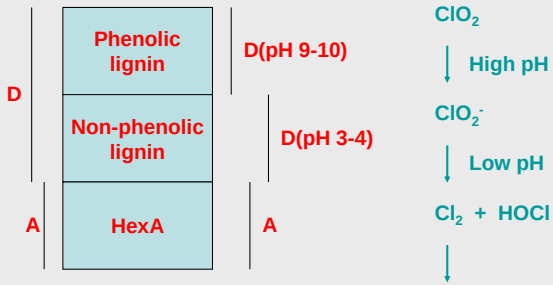


PRODUCTS OF HEXENURONIC ACID IN ECF BLEACHING STAGES

High pH

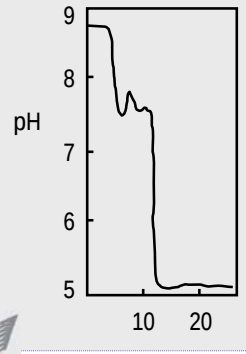


PRINCIPLE OF A/D AND D/A/D PREBLEACHING



ClO_2
↓ High pH
ClO_2^-
↓ Low pH
Cl_2 + HOCl
↓
Cl^-

REACTION RATE OF CHLORINE DIOXIDE WITH A HARDWOOD KRAFT PULP AT 95 °C



$ClO_2 \Rightarrow H^+ + ClO_2^-$

After the fast reaction:
- colour of ClO_2 disappeared
- 60 % of active chlorine left

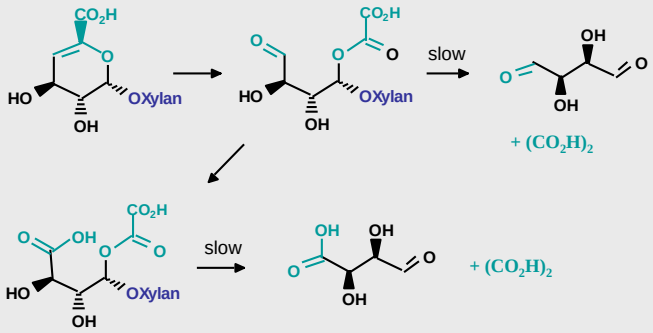
EFFECTS OF TEMPERATURE AND TIME ON A/D PREBLEACHING (pH 3.5 => 2.5)

Temperature (°C)	75	75	85	85	95	95
Time (min)	5	60	3	60	2	60
Kappa number	4.1	4.0	3.8	3.7	4.0	3.4
Brightness (%)	60.9	61.0	63.7	62.2	63.3	62.3
Viscosity (kg/m^3)	950	960	970	930	950	900
Residual ClO_2 (%)	0.1	0.0	0.0	0.0	0.0	0.0

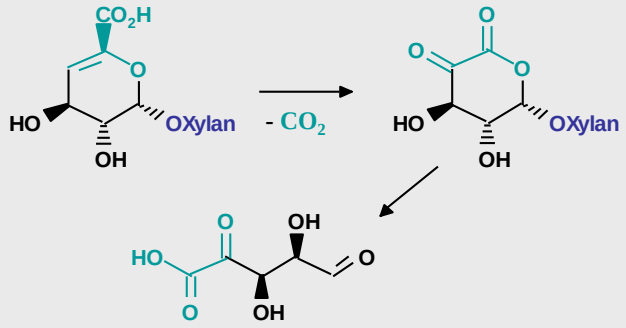
HEXENURONIC ACID AND CHLORINE DIOXIDE BLEACHING

- HexA increases chemical consumption
- HexA increases AOX
- HexA and lignin react at ~ equal rates
- Generally A/D prebleaching is most cost-efficient
  - kappa factor must be low and optimized
  - little reaction with furancarboxylic acids
  - no additional washing needed
  - short retention time (D)

OZONATION OF HEXENURONIC ACID



OZONATION OF HEXENURONIC ACID – ALTERNATIVE ROUTE



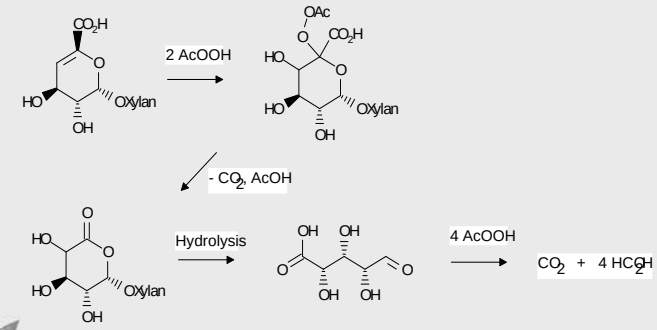
HEXENURONIC ACID AND OZONE BLEACHING

- HexA increases chemical consumption
- HexA forms oxalic acid
  - calcium oxalate scalings
- HexA forms reducing sugars
  - additional chemical consumption in a subsequent P-stage
- Chemical reaction rates are diffusion controlled
  - HexA and lignin react at ~ equal rates
  - furancarboxylic acids react rapidly
  - washing is needed between A- and Z-stages

HEXENURONIC ACID AND PEROXIDE BLEACHING

- Hydrogen peroxide does not react with HexA
- Reducing sugars from Z-stage increase chemical consumption and decrease viscosity

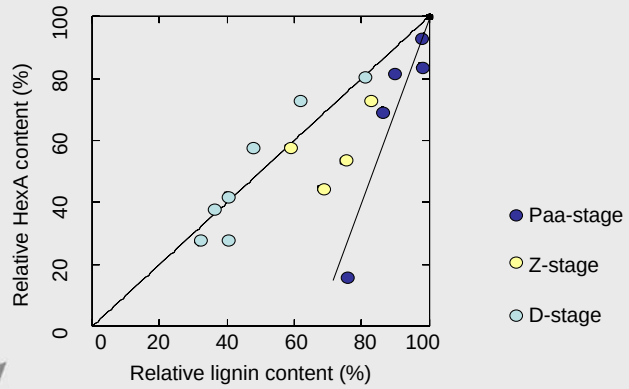
REACTIONS OF PERACETIC ACID WITH HEXENURONIC ACID



COMBINATION OF A- AND PAA-STAGES IN BLEACHING OF BIRCH KRAFT PULP

Stage	-	PAA	A	(A)-PAA
PAA (%) (mmol/kg)	-	2.0 263	-	1.35 178
Kappa number	11.8	6.1	8.2	3.7
HexA (meq/kg)	49.2	7.9	22.2	3.1
Brightness (% ISO)	42.9	58.0	45.8	62.7
Formic acid (mmol/kg)	-	47	22	33

REMOVAL OF LIGNIN AND HEXENURONIC ACID IN ELECTROPHILIC BLEACHING



HEXENURONIC ACID AND PERACETIC ACID BLEACHING

- HexA consumes huge amounts of chemical
- HexA reacts faster than lignin
- Peracetic acid bleaching is uneconomic if HexA content is high

SUMMARY

- Effects of hexenuronic acid
  - brightness reversion
  - consumption of bleaching chemicals
    - chlorine dioxide
    - ozone
    - peroxide (when combined with ozone bleaching)
    - peracetic acid
  - calcium oxalate scalings
    - ozone
- Selective hydrolysis of hexenuronic acid
  - A-Z-
  - A-D-, A/D-
  - others possible