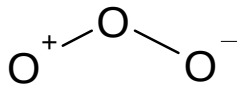
Ozone bleaching

Ozone, O_3

- Ozone is a powerful oxidizing agent
- A strong electrophile



Ozone bleaching

- Ozone reacts extremely fast with unsaturated structures, such as lignin, HexA and unsaturated extractive structures.
- The reactions in the cell wall are diffusion limited.

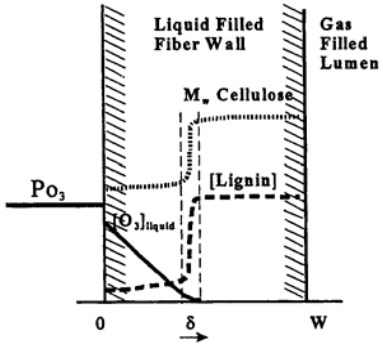
The reaction front

Propagation of the reaction front in the cell wall. Microscopy pictures of fibre cross-sections at two degrees of reactivity.

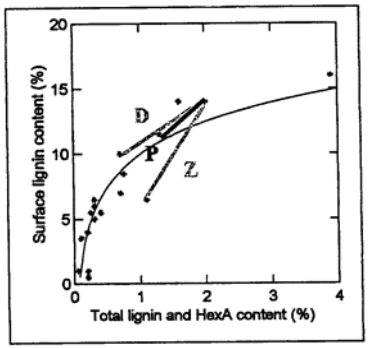
Shrinking core model

- Molecular diffusion is extremely fast over short distances (i.e. thickness of a cell wall) therefore ozone is used up approximately in 1 second.
- The molecular diffusion is slow, if the distance increases (>1 mm). And it is nonexistent if distance is more than 1 cm.
- “Shrinking core” –model illustrates the progress of the reaction front

Shrinking core model



O_3 – a surface selective bleaching agent



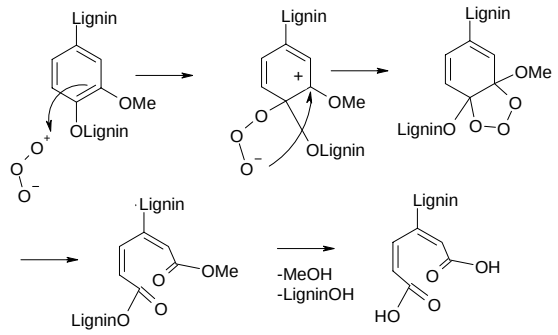
Ozone and lignin

- Reactions of ozone toward lignin are electrophilic.
- However the primary reaction product of ozone (i.e. ozonide) is a strong nucleophile.
- The net reaction is the cleavage of a carbon-carbon double bond and formation of a carbonyl group in the both sp2-hybridized carbon atoms.

Ozone and lignin

- Muconic acids are formed in the course of the reaction.
- Carbon-carbon double bonds of these acids may be further oxidized and glyoxylic acid (COOHCHO) can be liberated from the residual lignin.
- Glyoxylic acid can be further oxidized forming oxalic acid (COOHCOOH)

Ozone and lignin



Ozone and carbohydrates

- Ozone is 10^6 times more reactive toward lignin than toward carbohydrates
- However by-products from lignin reactions (and decomposition of O_3) react more easily with carbohydrates:
  - Hydroxyl radical (HO·)
  - Perhydroxyl radical (HOO·)

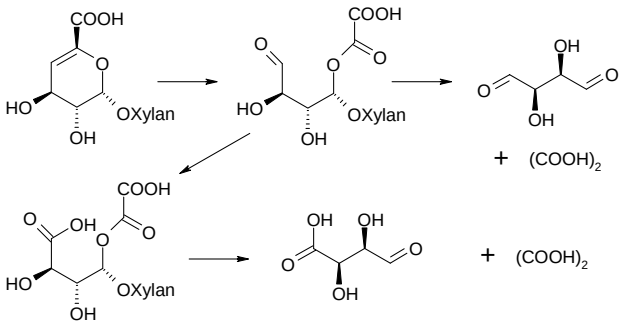
Ozone and HexA - reaction path 1

- Ozone is able to partly oxidize HexA (approx. 50 %).
- The first oxidation stage is followed by a partial oxidation of an aldehyde to a corresponding carboxylic acid.
- One of the oxidation products is an ester of oxalic acid.

Ozone and HexA - reaction path 1

- Usually the ozone stage is followed by some kind of an alkaline treatment, such as a peroxide bleaching stage.
- The oxidation products of HexA are released in alkaline media.
- Formation of calcium oxalate is probable if calcium ions are present. Poorly soluble calcium oxalate precipitates can be found for example in the washers.

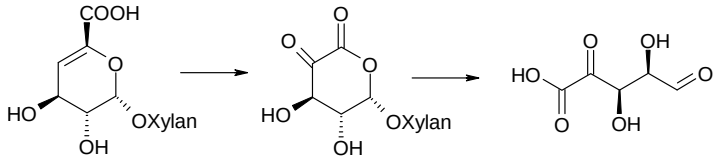
Ozone and HexA - reaction path 1



Ozone and HexA - reaction path 2

- HexA can be oxidised in another way. The reaction leads to decarboxylation and formation of a hexacyclic lactone.
- Lactone is an ester and it is released from the pulp by hydrolysis during the next alkaline stage.
- The product of hydrolysis, 4-ketopenturonic acid, is a reducing sugar and therefore it catalyses the degradation of peroxides and increases the consumption of peroxides due to the cleavage of carbon-carbon double bonds.

Ozone and HexA - reaction path 2



Ozone and extractives

- As mentioned earlier ozone is able to react with unsaturated resin components.
- For example in the case of hardwood birch pulp the amount of unsaturated fatty acids, squalene, betulaprenols and sitosterol is reduced in ozone bleaching.