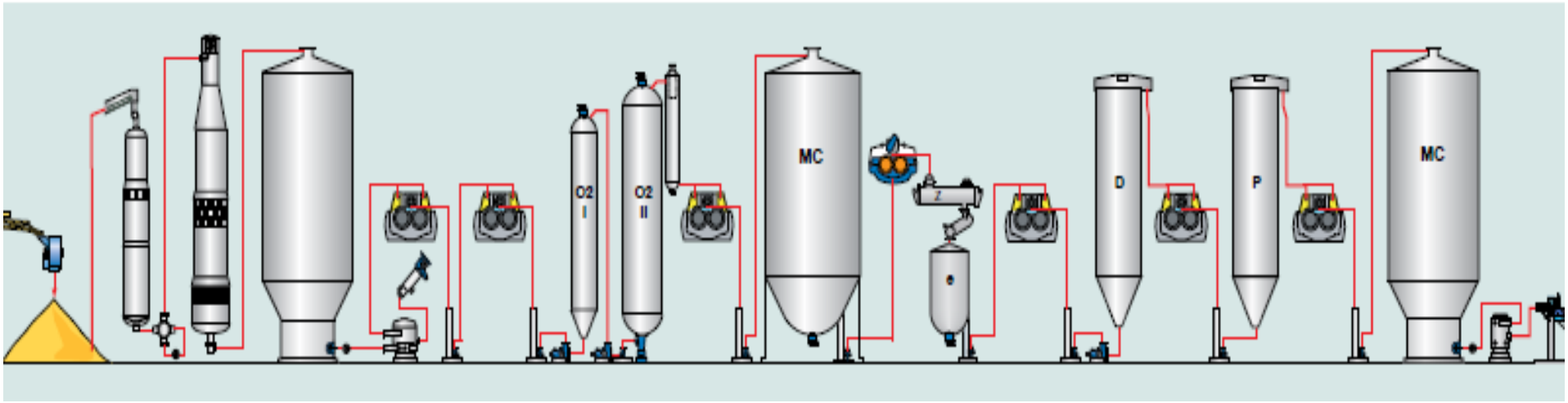
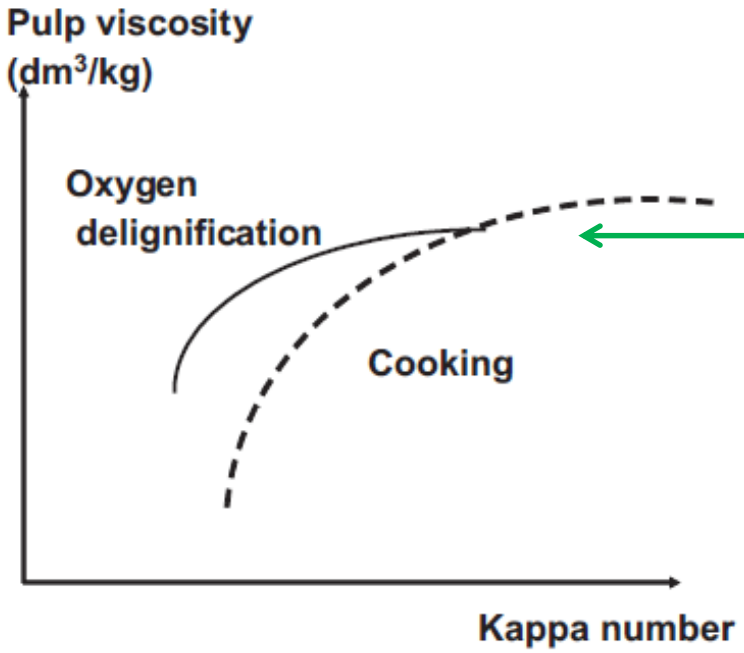
Sequências industriais de branqueamento



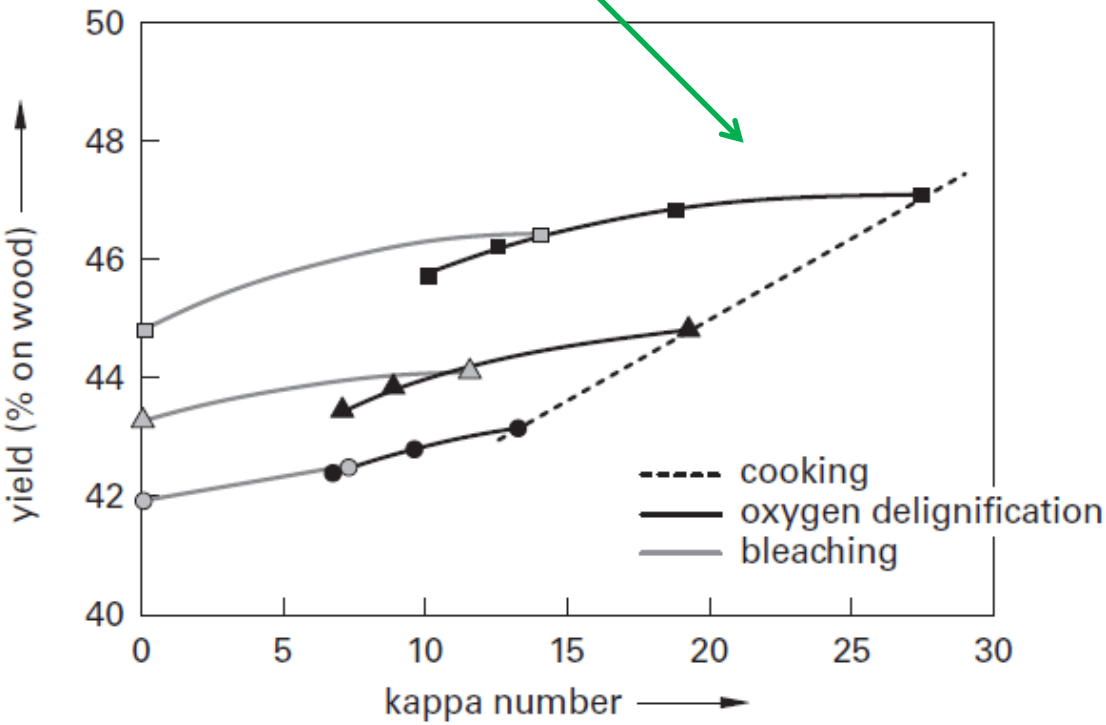
Aqui começa, efetivamente, o branqueamento

O_2 é considerado etapa de deslignificação ou pré-branqueamento

Sequências industriais que incluem a etapa de pré-deslignificação com O_2 em meio alcalino



Interrupção prematura do cozimento é vantajoso



Reações com lignina e polissacarídeos

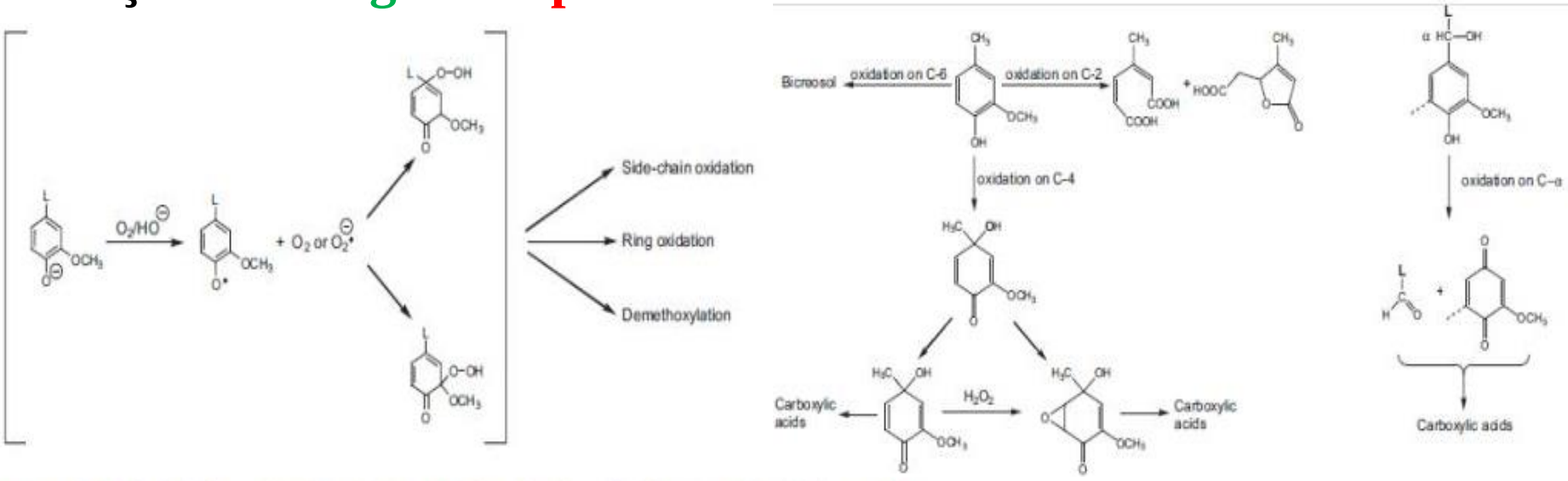


Figure 9.9. The initial reaction step in the oxidation of a phenol with oxygen in alkaline media.

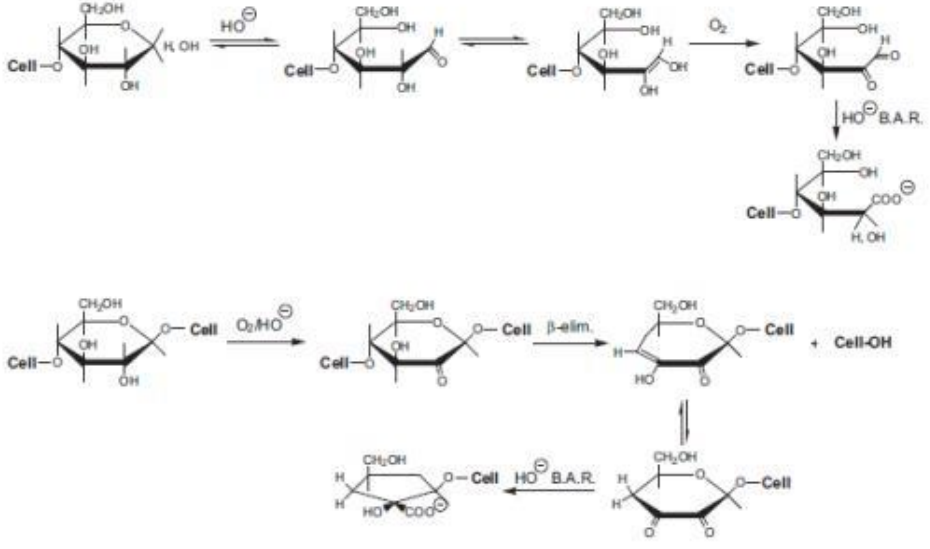


Figure 9.14. Major carbohydrate reactions in the O-stage. Oxidative stabilization of a reducing end group (upper reaction), oxidative cleavage of a polysaccharide chain (lower reaction). B.A.R. = benzilic acid rearrangement.

Reação com lignina residual predomina
Reação com polissacarídeos pode ser evitada

Composição química dos produtos detectados nos licores de reação de branqueamento de polpas com O2 em meio alcalino

Table 9.2. Composition of the bleaching effluent obtained after oxygen delignification of a pine kraft pulp (Pfister and Sjöström 1979).

Compound	Amount, kg/tonne of pulp
Lignin	29
Low M_w lignin products	3.7
Polysaccharides[1)]	4.5
Methanol	1.5
Carbon dioxide	7.5
Formic acid	3.0
Oxalic acid	1.1
Acetic acid	1.0
Glycolic acid	1.0
3,4-Dihydroxybutanoic acid	0.9
Minor acids, total	2.5

[1)] xylose as predominant sugar moiety

Branqueamento com peróxido de hidrogênio (aplicável em polpas químicas e também em polpas mecânicas)

Peroxide bleaching Metso

Typical process conditions in a (PO)- and P-stage

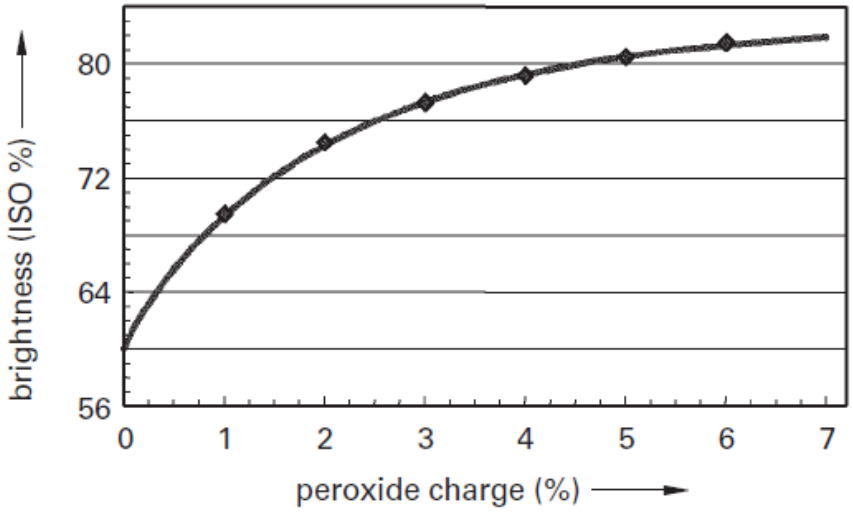
	(PO)	P
Final pH value	9.5-11	9.5-10.5
Temperature	80-100 °C	80-85 °C
Pulp consistency	≥ 11%	≥ 11%
Time	60-120 min	60-180 min
Pressure (top)	3-5 bar	atmospheric

Table 9.5. Changes in brightness, viscosity and kappa number for an industrial birch kraft pulp after an O-stage and subsequent bleaching in a peroxide-based sequence. Contributions to the kappa number from lignin, hexenuronic acid and other oxidizable structures are also shown.

Pulp sample	Brightness, % ISO	Viscosity, dm^3/kg	Kappa Number	Lignin[1)]	HexA[1, 2)]	Non-lignin[1, 3)]
after O-stage	59.1	920	9.6	3.2	4.3	2.1
after OQ(OP)	73.3	850	7.3	2.2	3.7	1.4
after OQ(OP)Q(PO)	89.0	710	4.6	0.8	3.0	0.8

[1)] calculated in Kappa number units
[2)] HexA = hexenuronic acid
[3)] Non-lignin = unspecified but oxidizable structures

Peróxido de hidrogênio sobre polpas químicas



Peróxido de hidrogênio sobre polpas mecânicas

Figure 10.32. The brightness of a TMP pulp versus the peroxide charge. Bleaching conditions used: 3 hours, 70 °C, 3 % silicate, 25% consistency, Spruce TMP, 60% ISO (Metso Paper).

Reações da lignina com peróxido de hidrogênio (aplicável em polpas químicas e também em polpas mecânicas)

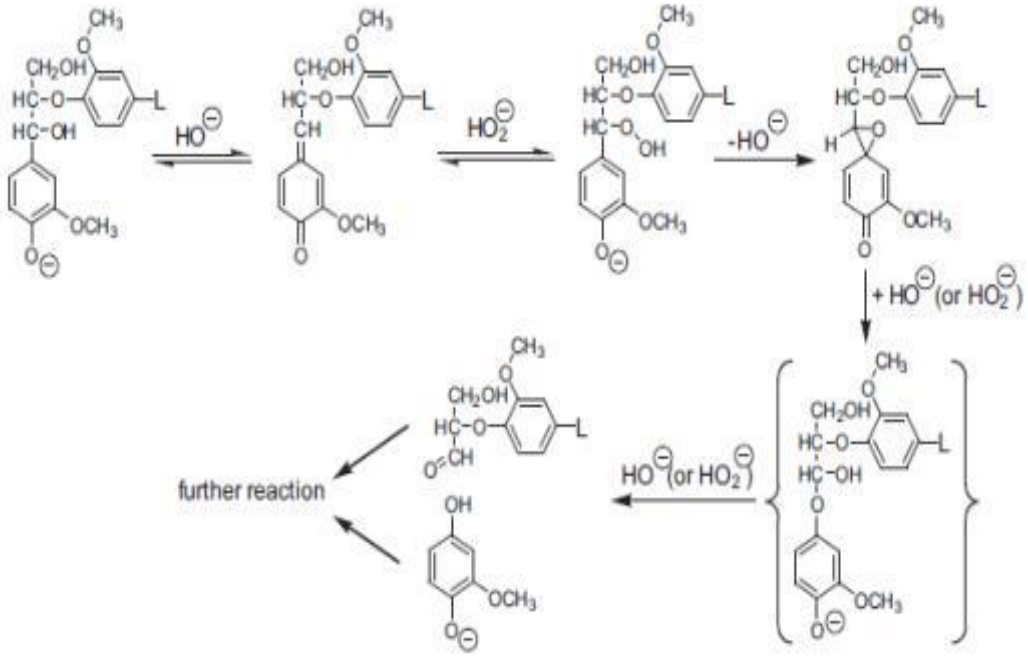


Figure 9.20. Side chain cleavage of a phenolic β-O-4 structure in lignin on oxidation with alkaline hydrogen peroxide. Reaction conditions for L (lignin)=H: 90 °C, 180 min (Heuts 1998).

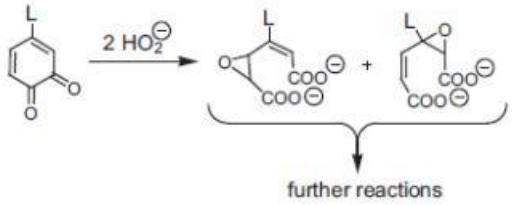


Figure 9.22. Oxidation of a quinone structure by alkaline hydrogen peroxide.

Branqueamento com dióxido de cloro

Chlorine dioxide bleaching

Conditions used in an industrial D0-stage

	Do	Dht
Final pH value	2-3	2.5-3.5
Pressure	atmospheric	atmospheric
Pulp consistency	≥ 11%	≥ 11%
Temperature	45-85 °C	85-95 °C
Time	45-60 min	90-180 min

Conditions in D1-stage and D2-stage:

	D1-stage	D2-stage
Final pH value	3.5-4.2	3.5-4.5
Temperature	65-75 °C	65-80 °C
Pulp consistency	≥ 11%	≥ 11%
Time	60-180 min	120-180 min
Pressure	atmospheric	atmospheric

O ClO_2 é um gás produzido in situ devido a sua grande instabilidade.

Oxidação de clorato de sódio em meio ácido pela redução de metanol.

O gás ClO2 é dissolvido em água acidificada e usado como agente de branqueamento para a estação de tratamento de efluentes

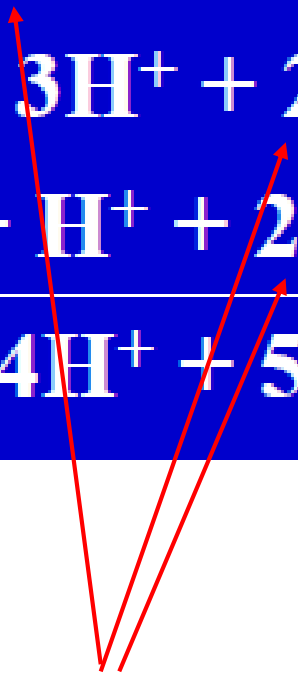
Chemistry

$$ClO_2 + e^- \Rightarrow ClO_2^-$$

$$ClO_2^- + 3H^+ + 2e^- \Rightarrow HClO + H_2O$$

$$HClO + H^+ + 2e^- \Rightarrow Cl^- + H_2O$$

$$ClO_2 + 4H^+ + 5e^- \Rightarrow Cl^- + 2H_2O$$



Componentes passíveis de oxidação na polpa é que doam o elétron

Sequências **típicas** do branqueamento

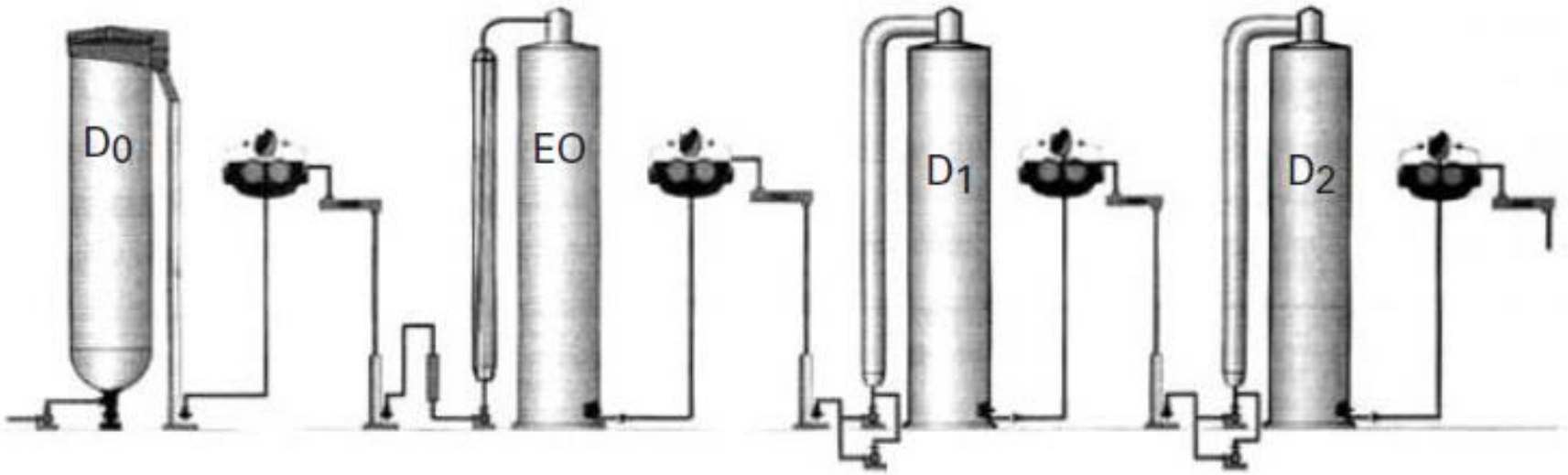


Figure 10.6. A bleaching sequence with four stages according to $D_0(EO)D_1D_2$. (Metso Paper).

Dióxido de cloro sobre polpas químicas

Table 9.6. Changes in brightness, viscosity and kappa number for an industrial softwood kraft pulp after an O-stage and subsequent ECF-bleaching. Contributions to the kappa number from lignin, hexenuronic acid and other oxidizable structures are also shown.

Pulp sample	Brightness, % ISO	Viscosity, dm^3/kg	Kappa Number	Lignin[1)]	HexA[1, 2)]	Non-lignin[1, 3)]
after O-stage	44.7	910	10.7	4.6	1.2	4.9
after ODE	73.3	850	3.3	1.6	0.8	0.9
after ODEQP	88.8	800	1.6	0.8	0.7	0.1

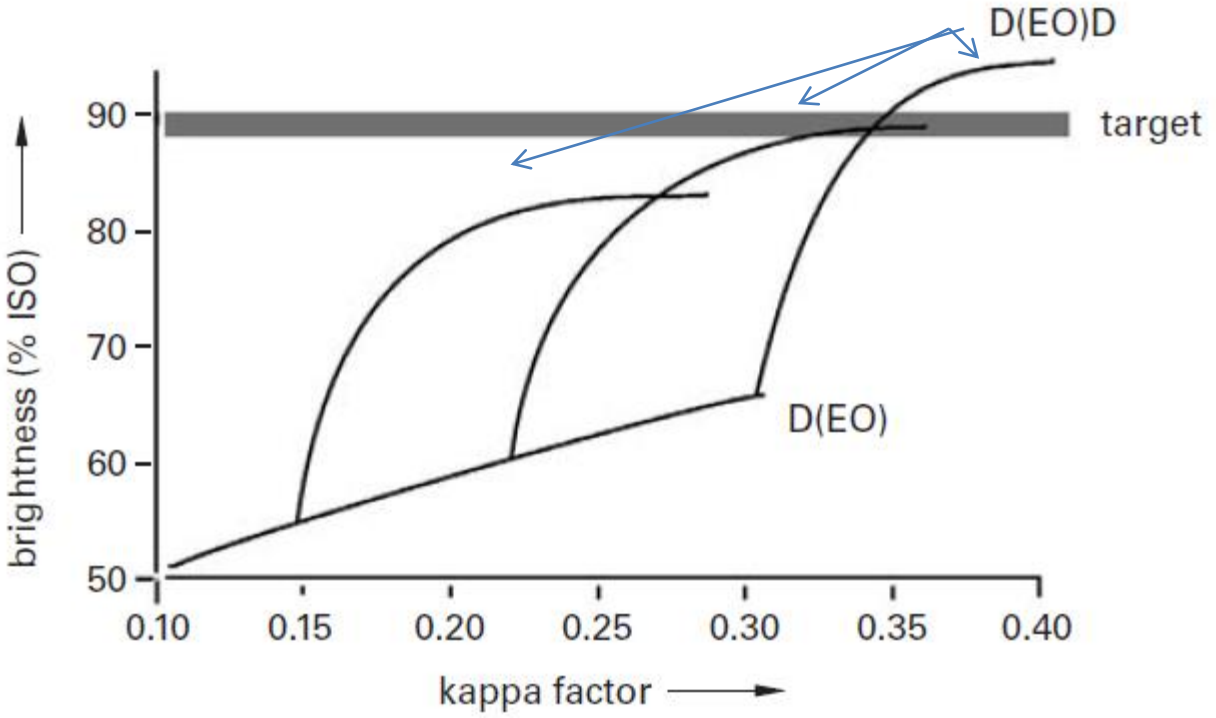
1) calculated in Kappa number units

2) HexA = hexenuronic acid

3) Non-lignin = unspecified but oxidizable structures

Adição do agente oxidante x eficiência

No caso da branqueamento com ClO_2, é usual que 2 etapas proporcionem melhor efeito do que uma única carga



Proporcional a carga de ClO_2

Reações do dióxido de cloro com lignina

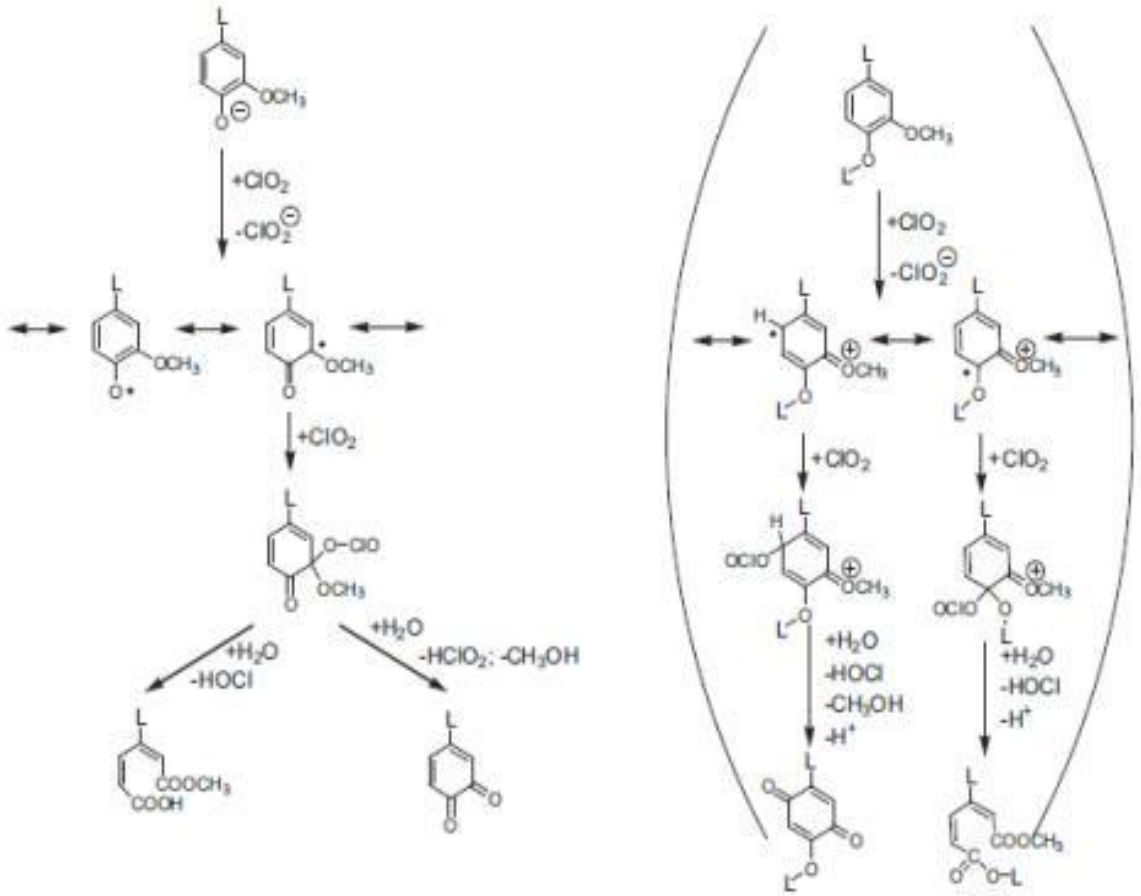


Figure 9.25. Reactions between a phenolic (left) and a non-phenolic (right) lignin structure respectively with chlorine dioxide under acidic conditions (Eriksson 1993). In benzylalcohol structures, a similar reaction will result in an oxidative elimination of the side chain. The reaction of non-phenolic lignin structures is less likely under technical pre-bleaching conditions.

Resumo com cargas e condições usuais em cada etapa de branqueamento

Conditions in the D_0-stage

- pH 2–3
- 40–70 °C
- 3–4 % or 9–13 % pulp concistency
- 0.5–1.0 hours
- atmospheric pressure
- 1.0–2.0 x kappa number (aCl/t)

Conditions in the Q-stage

– metal ion remover prior to P-bleaching

- pH 4–7 (9–10 in alkaline Q)
- pH 5–7
- 50–80 °C
- 9–13%
- 5 min–2h
- amospheric pressure
- 2–4 kg EDTA or DTPA/t

Conditions in the $D_{1,2}$ -stages

- pH 3.0–4.0 in D_1 and pH 3.5–4.5 in D_2
- 55–75 °C in D_1 and 60–85 °C in D_2
- 9–13% pulp concistency
- 1–3 h
- atmospheric pressure
- Σ 4–6 x kappa number (E_1) (a.Cl/t)
- D_1 /D_2-charge ratio usually 2/1–3/1

Conditions in the (PO)-stage

- pH 10.5–11.0
- 80–110 °C
- 9–13% pulp concistency
- 1–3 hours
- 3–8 bar
- 5–10 kg O_2/t and 5–40 kg H_2O_2/t

Ilustração fotográfica de uma indústria kraft

Duas linhas industriais de polpação Kraft

Evaporador de licor Kraft

Evaporador de licor Kraft

Torres de branqueamento

Tanques de reagentes de branqueamento

Visão geral da área de polpação e branqueamento (Kraft)

Controle operacional

Área de corte dos cartões de polpa e embalagem

Visão geral

Pátio de toras e cavacos

Caracterização de polpas celulósicas (*próxima aula*)

NORMAS USADAS INTERNACIONALMENTE

SCAN, Scandinavian Pulp, Paper, and Board Testing committee (Finland, Norway and Sweden)

• TAPPI, Technical Association of the Pulp and Paper Industry, USA

• CPPA-TS, Canadian Pulp and Paper Association, Technical Section

• APPITA, Australian Pulp and Paper Industry Technical Association

- ISO, envolve normas de ampla aplicação e também são usadas na indústria de celulose e papel