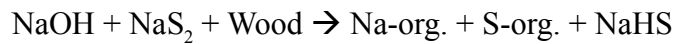


1 CHEMICAL REACTIONS IN KRAFT PULPING

1.1 IN COOKING

The main objective is to facilitate the disintegration of wood into fibrous product. This is achieved by breaking the bonds in the lignin macromolecule. The main chemical reactions in the cooking process can be described as:



Where the wood represents many different organic compounds such as:

Lignin, Cellulose, Hemi-cellulose, and Resins. Hemi-cellulose can be divided into three major organic group: Glucomannan, Xylan and other hydrocarbon groups. These are present in following proportions in wood(1):

Cellulose:	38- 42 %
Glucomannan:	2-20 %
Xylan:	7-30 %
Other hydrocarbons	< 5 %
Lignin	20-30 %
Resins	2- 6 %

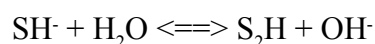
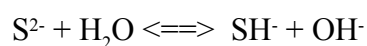
The chemical composition of the pulp final product is(1):

Cellulose:	72-73 %
Glucomannan:	2-10 %
Xylan:	10-30 %
Other hydrocarbons.	<1 %
Lignin	2-5 %
Resins:	<1 %

Cellulosa is basically a long molecule chains formed by the monomer of glucose. Any reaction with the cellulose molecule is not wanted in the pulp production (1).

1.1.1 Consumption of Alkali

The solution of Sodium sulphite and Sodium hydroxide in water is generating a equilibrium as follows (3):



Alkali in the cooking liquor is basically consumed in three different reactions(3): 1. With lignin, 2. Neutralisation of organic acids, 3. With resins in the wood.

REACTIONS WITH LIGNIN

As the carbon to carbon bond are stable in alkaline conditions, the cleavage of oxygen - carbon bonds are the most significant reaction in the cooking process. This reaction will take place and is producing phenolic hydroxyl groups from the cleavage of the aryl-alkyl-ether bounds. (12.) One of the main products being the phenyl coumaran. The phenolic carbons are in the following reaction mainly converted to stilbene. See also the reaction description in appendix 1.

NEUTRALISATION OF ORGANIC ACIDS

Most of the alkaline is consumed in the cooking process by the saccharine acids formed in the degradation of hemicelluloses. Hemicellulose is a polysacchridic substance which includes galactoglucomannan, arabinoglucoronxylan, arabinos, arabinogalactane, glucoronxylan, glucomannan, and acids from glucorans and galactorons. The saccharinic acids formed by the degradation contains ; isosaccharidic acids, milk acid, formic acid and acetic acid.

REACTIONS WITH RESINS OF WOOD

In the cooking reaction many of the resins forms sodium salts of fatty and harts resins this are occurring a soap. And are usually skimmed of from the black liquor in the evaporation area. They are also processed to produce tall oil. See below.

1.1.2 Sulphidity in Kraft pulping

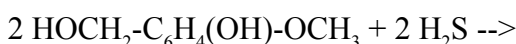
Sulphidity is defined as : $100 \frac{[\text{Na}_2\text{S}]}{([\text{NaOH}]+[\text{Na}_2\text{S}])}$ where the concentrations are expressed as equivalents of Na_2O or NaOH , respectively.

The function of sulphide in the kraft process is two-fold; it promotes and accelerates the cleavage of the ether links in phenolic units and is reduces the extent of undesirable condensation.

CLEAVAGE OF ETHER LINKS

Only the arylglycerol-ether are direct reactive of all the non-phenolic units in lignin. Under influence of a high temperature they are converted to free glycerol side-chains and new phenolic groups.

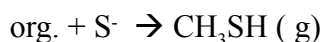
THE UNDESIRABLE CONDENSATION



The condensation of dissolved material is larger in the case of pine kraft pulp then in the case of Birch Kraft pulp. This may be due to the different contents of hemicellulose , as Birch has mostly xylan hemicellulose while Pine contain both xylan and glucoman hemicellulose (4).

REACTIONS PRODUCING MALODOUROUS GASES

Unwanted reactions are the once producing:



These are all gases which is limited dissolved in the black liquor exiting the cooking process.

BY-PRODUCTS

Also turpentine and methanol is a by-product of the cooking reaction , this is usually about: 0,1 - 0,5 kg / ADt,

1.2 IN BLEACHING

Bleaching of Kraft pulp is essentially degrading of the few per cent of aromatic products, originated from lignin, which could not be dissolved during cooking. This is called residual lignin and is of a phenolic type. Many phenolic groups have a conjugated double bond on side chain forming stilbene, styrene and enol-groups (5).

The bleaching agents can be classified in three different groups :

Group I

Chlorine (Cl₂) (C)

Ozone (O₃) (Z)

Reacts: with any phenolic group + double bond

Group II

Chlorine dioxide (ClO₂) (D)

Oxygen (O₂) (O)

Reacts: with free phenolic groups (+ double bond)

Group III

Sodium hypochlorite (NaOCl) (H)

Hydrogen peroxide (H₂O₂) (P)

Group one reactions and reaction products:

The main reaction by chlorine and ozone is a electrophilic substitution on

aromatic rings, other reactions are cleavage of aryl-ether linkage i.e. demethoxylation and depolymerization (6) . These reactions take place on any phenolic group (5). The reaction products are mainly polychlorinated aromatic rings(with chlorine) or carboxylates (with ozone). Also formation of Muconic acid derivatives has been proposed in reactions between ozone and phenolic groups.

Group two reactions and reaction products:

These two agents have in common the fact that they are radicals. This again indicates that they primarily react with phenolic rings with free OH groups (of all residual lignin this is about 30 %) (7,8).

The reaction products in this case is carboxylic and carboxylate groups . These are soluble in alkaline medium.

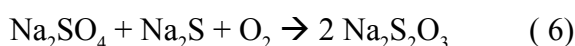
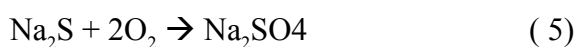
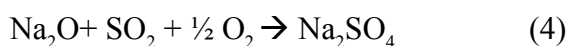
Group three reactions and reaction products

The active species are here anions $\cdot\text{OOH}$ and $\text{ClO}\cdot$. These anions reacts almost only with carbonyl groups (9,10)

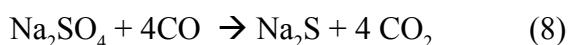
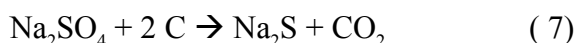
1.3 IN CHEMICAL RECOVERY

IN BLACK LIQUOR BURNING

The main reactions are (1-3 predominantly) :

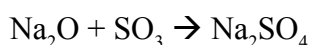


and other reactions:

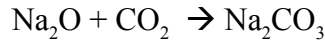


Fly ash :

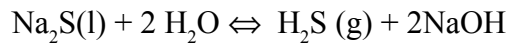
Fly ash is mainly consisting of:



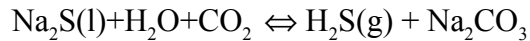
and



In the smelt there is equilibrium reactions:



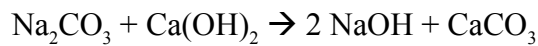
and



These reactions are **not wanted**.

Cooking liquor production

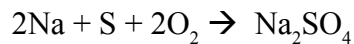
The green liquor produced in the recovery boiler smelter is then further reduced by the causticizing reaction:



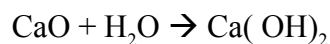
After separation of the solid CaCO_3 (lime mud), from the white liquor containing NaOH , the solid is burnt in a lime kiln.



There is usually also some sodium present in the lime mud, which reacts with any sulphur introduced in the lime kiln:



And the burnt lime is then reacted with water to produce:



Literature:

1. Puukemia, Waldemar Jensen, 1977, Suomen paperi-insinöörien Yhdistys Ry.
2. Chemie und Technologie der Zellstoff Herstellung, P. Lengyel & S. Morvay, 1973, Guntter-Stiab Verlag, Biberach/Riss.
3. Lignins , occurrence, formation, structure and reactions, K.V. Sarkanen & C.H. Ludwig, 1971, John Wiley & Sons, Inc.
4. The significance of glucomannan for the condensation of cellulose and lignin under kraft pulping conditions. O Karlsson, U Westermark, NP&P Research J. No. 3, vol. 12,1997
5. Degradation of Residual Lignin in Kraft Pulp with Ozone application to Bleaching. D. Lachenal, M. Mauguet. 6 th ISWPC, 1991.
6. A new mechanism for pulp delignification during Chlorination N.I.Y. ;

G.J. Kubes and A.R.P. Van Heiningen, Journal of Pulp and Paper Science, 16(1): J13-J19 (1990)

7. Structural changes in lignin during oxygen bleaching, G. Gellerstedt, K. Gustafsson and E.L. Lindfors, Nordic Pulp and Paper Journal (3) : 14-17 (1986)
8. Chlorine dioxide oxidation of lignin model phenols, G.B. Strumla and W.H. Rappson, Pulp and Paper Canada, 78 (12) , TR 119-126 (1977)
9. Delignification mechanism using oxygen and hydrogen peroxide, A Singh, Proc. Tappi oxygen Delignification Symposium : 53-59 (1990)
10. Chemistry of delignification . A general concept. Part II, J. Gierer, Holzforschung 36 (1) : 55-64 (1982)
11. SVP-HP CLO₂ Process , Eka Chemicals, Rev. 12, (1997)
12. Puumassan valmistus II, Part 2, N-E Virkola, Suomen paperi-insinöörien Yhdistys Ry, Turku, 1983.