



A KINETIC MATHEMATICAL MODEL OF KRAFT PULPING PROCESS FOR CONTROL AND OPTIMIZATION APPLICATIONS

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Abstract: Kraft wood pulping is the predominant process used in the pulp and paper industry for its versatility and insensitivity to variations of wood supply. In this work, a deterministic model has been developed for a Kraft Pulping Process of Eucalyptus by combining intrinsic kinetic equations (Lignin, Carbohydrates) and it is used to investigate the effects of process conditions on the extent of delignification. The aim of this work is to develop a mathematical model which at some time is able to represent the main phenomena taking place in the process and suitable to be used in control and optimization applications.

Keywords: Kraft pulping, kinetic equation, deterministic model and mass transfer equation.

1. INTRODUCTION

Chemical pulping includes all methods of pulp manufacture in which materials containing cellulose fibers are treated with aqueous alkaline or acidic solutions. The aim of chemical pulping is to remove enough lignin so that the fibers are free and give then the required characteristics at the lowest possible cost.

Two processes dominate chemical pulping: the Sulfate and the Sulfite process (Lemmetti et al., 1998). The Sulfate process is also known as Kraft Pulping where it is complex process which involves mass transfer of cooking chemical into wood structure, complex heterogeneous chemical reactions between wood components and the cooking chemicals. The Sulfite pulping derives its name from the use of a bisulfite solution as the delignifying medium. The cation used is usually calcium, magnesium, sodium, or ammonium. Sulfite pulping has also advantages over the Kraft process: easier pulp bleaching, higher carbohydrate yields, and the possibility of producing specialty pulps with high cellulose contents (Gullichsen, J.; Fogelbolm, C. J., 2000).

This work concentrates only on the Kraft process in which pulping liquor, mainly solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), are used at controlled conditions to remove wood lignin. Wood chips are subjected to digestion

in the pulping liquor at an elevated pressure and temperature (about 170°C) in a pressure vessel (digester) to release cellulose fibers (Zhu et al., 2002).

The digestion process can be either batch or continuous. In batch cooking a pressured reactor is filled with chips and cooking liquor. The contents are heated under pressure according to a specified temperature-time program (H- Factor) and after that the digester is emptied.

Basically, there are two types of batch digesters to examine: those with direct steam heating and those with indirect steam heating. The second type is equipped with forced liquor circulation and a heat exchange in the circulation line (Yliniemi et al. (1995). In continuous cooking chips and cooking liquor are fed into the top of the digester in a co-current flow. The digester is a large, vertical pressurized tube. The chip column is heated up by various circulation systems as it moves downwards.

The cooked and partly washed pulp is fed out at the bottom in a uniform flow. In both cases, the cooking process is basically the same. The chips are impregnated with cooking liquor, heated under pressure and held at the certain temperature for some time. Then pressure and temperature are lowered and the cooked chips are blown or washed out of the digester. The chemical reactions which dissolve the

lignin take place mainly when the digester is at maximum pressure and fibers are released. The pulp is then washed, screened, cleaned and dried or pumped over to the paper mill (Lemmetti et al., 1998). The product of the digesting process is cellulose fibers, or pulp, which is used to make paper products (Al-Awami et al., 1999). Several different types of pressure vessel have been used for batch cooking over the years, including stationary horizontal and spherical configurations and rotating vertical digesters. Some factors favoring batch digesters may be pointed out: more reliable operation, greater operating flexibility (ability to change grades), ability to cook softwood and hardwood concurrently, easy to start-up and shut-down; and more efficient turpentine recovery. A simplified scheme is shown in Figure 01.

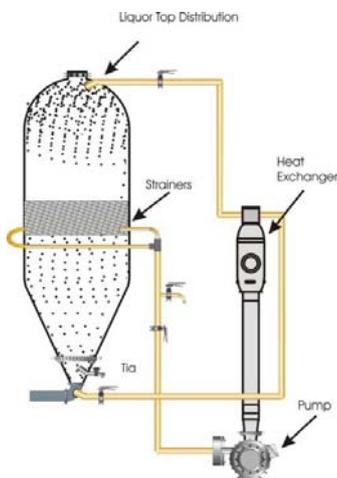


Figure 01: Batch Digester with Indirect Heating

The objective of this work is to present a deterministic model for batch pulp digester taking into account the main phenomena taking place in the process. It is considered that the reactions occur for lignin, hemicellulose, cellulose and extractive reactions with time.

An additional contribution of this paper is to develop a deterministic model for the *Eucalyptus* as a feedstock of cellulose. Most of papers in open literature deal with chips of pines but there exists an enormous advantage to use *Eucalyptus* since it grows up very much quicker and it is cheaper. Both woods have quite different structure in terms of fiber length so that an extensive analysis has to be made for the *Eucalyptus* in this work.

2. MODEL DESCRIPTION

In the digester, reaction start when chips are at the cooking temperature. The active chemicals in the cooking liquor react with lignin in chips and convert it chemically into compound that dissolves in the cooking liquor.

Lignin is the bonding material in chips that holds individual fibers together. Lignin is the “glue” of wood and it is a very complex three dimensional network polymer with hydroxyl phenyl propane groups as the basic units (Gullichsen et al., 2000). After dissolving the lignin, fibers are easily separated into the mass that is leaving the digester as pulp. Unfortunately the chemicals also react with fibrous material and break down the molecular bonds of them. These reactions have to be avoided as much as possible because they lead to losses in fiber yield and decrease the strength of pulp. Therefore cooking conditions that prefer lignin removal with the lower effect in the fibers should be preferred. Cooking models, with different approaches, can be found in literature.

One of the earliest kinetic models was developed by Vroom (1957), who used an Arrhenius type expression for the reaction rate temperature dependence to derive the “H-factor”. H- Factor is regularly used in controlling the reaction end-point in batch digesting. It describes the combined effect of reaction temperature and reaction time. In practice it means that when longer reaction time is available the same cooking result can be obtained with a lower temperature. Equation (1) describes the delignification of Kraft pulping:

$$\frac{dL}{dt} = kCL \quad (1)$$

where L is the lignin content of chips, C is the effective alkali concentration of the liquor in the chips, k is the temperature dependent rate constant and t is the cooking time. The temperature dependency of the reaction rate constant k is usually presented by the means of Arrhenius equation

$$k = k_0 e^{B-E/RT} \quad (2),$$

where E is the activation energy, R is the universal gas constant, T is the absolute temperature and k_0 and B are constant. The parameters depend on wood species, cooking stage, etc. H-factor describes the joint effect of time and temperature and it is usually given as following

$$\text{integral: } H = \int_{t_0}^t k_r dt \quad (3),$$

where t_0 is the initial time for calculation, t is the actual time and k_r is the relative reaction rate coefficient as defined bay the following equation: $k_r = e^{43,2-16113/T}$ (4), where T is the absolute temperature.

For the dissolution of high-reactivity lignin, cellulose, hemicelluloses and extractives the following kinetic equation will be used for each:

$$-\frac{dW}{dt} = [(k1[OH]^a + k2[OH]^b [HS]^c)(W - W_\infty)]$$

(5), where W is the wood component concentration; $k1$, $k2$ are rate constants that are correlated as a function of temperature using the Arrhenius equation; W_∞ is the wood component after infinite time; a,b,c are the kinetic orders; $[OH^-]$ and $[HS^-]$ are

the OH⁻ and HS⁻ concentrations, respectively and t is time.

The deterministic model equations can be written as follows:

- Lignin

$$\frac{dL_1}{dt} = k_{L_1} \exp\left(\frac{E_{L_1}}{RT}\right) [OH]^a [HS]^b L_1 \quad (6)$$

$$\frac{dL_2}{dt} = k_{L_2} \exp\left(\frac{E_{L_2}}{RT}\right) [OH]^a [HS]^b L_2 \quad (7)$$

$$\frac{dL}{dt} = \frac{dL_1}{dt} + \frac{dL_2}{dt} \quad (8)$$

- Cellulose

$$\frac{dC_1}{dt} = k_{C_1} \exp\left(\frac{E_{C_1}}{RT}\right) [OH]^a C_1 \quad (9)$$

$$\frac{dC_2}{dt} = k_{C_2} \exp\left(\frac{E_{C_2}}{RT}\right) [OH]^a C_2 \quad (10)$$

$$\frac{dC}{dt} = \frac{dC_1}{dt} + \frac{dC_2}{dt} \quad (11)$$

- Hemicelluloses

$$\frac{dH_1}{dt} = k_{H_1} \exp\left(\frac{E_{H_1}}{RT}\right) [OH]^a H_1 \quad (12)$$

$$\frac{dH_2}{dt} = k_{H_2} \exp\left(\frac{E_{H_2}}{RT}\right) [OH]^a H_2 \quad (13)$$

$$\frac{dH}{dt} = \frac{dH_1}{dt} + \frac{dH_2}{dt} \quad (14)$$

- Extractives

$$\frac{dE}{dt} = -0.6E \quad (15)$$

- Carbohydrates

$$\frac{dCT}{dt} = \left[\left(\frac{dC_1}{dt} + \frac{dC_2}{dt} \right) + \left(\frac{dH_1}{dt} + \frac{dH_2}{dt} \right) \right] \quad (16)$$

- Diffusion Coefficient

$$D = 60 \times 10^{-4} \sqrt{T} \exp\left(\frac{-223 \times 10^3}{RT}\right) \times (1.24 \times 10^{-2} - 1.12 \times 10^{-4} \times [L+H+C+E]) \quad (17)$$

- Hydroxide

$$\frac{\partial OH}{\partial t} = \frac{1}{X^2} \frac{\partial}{\partial x} \left(D \frac{\partial OH}{\partial x} \right) + \frac{\rho}{0.1\varepsilon} \left[3.2 \times 10^{-3} \frac{dL}{dt} + 6.1 \times 10^{-3} \left(\frac{dH}{dt} + \frac{dC}{dt} \right) + 7.0 \times 10^{-3} \frac{dE}{dt} \right] \quad (18)$$

$$\frac{\partial HS}{\partial t} = \frac{1}{X^2} \frac{\partial}{\partial x} \left(D \frac{\partial HS}{\partial x} \right) \quad (19)$$

In the deterministic model the following considerations are made:

- The wood chips are treated as symmetrical plane sheets with only one important direction - the chip thickness (the chips are cut in such way that the thickness is the representative direction);
- The chips are fully impregnated with liquor before the heating period starts. This is a reasonable assumption, since the chips are exposed to the liquor for a long period prior to cooking;
- Heat transfer to and inside the wood chip is instantaneous and the heats of reaction are negligible;
- Mass transfer resistance between the bulk liquor and wood chip is negligible (no film theory is considered which is also reasonable due to agitation caused by the liquor forced flow along the vessel);
- The reactions are irreversible and the reaction products do not interfere in the pulping reactions.
- The concentration of hydroxide ions is equal to the effective alkali, the sum of the sodium hydroxide and half the sodium sulfide;
- The rate of sulfide ions diffusion is the same as for hydroxide ions.

The model has the following boundary conditions:

- The concentration gradient of each compound is zero at the center of the wood chip (symmetry condition);
- The concentrations of each compound at edge of the chip are equal to the concentrations in the bulk liquor surrounding the chip; the concentrations of hydroxide and hydrogen sulfide in bulk liquor are obtained by mass balances on the bulk liquor;

Some alternative models may be developed using hybrid approach, combining deterministic model and neural networks models as proposed by Aguiar and Maciel Filho (1998), but in any case they require a good deterministic description to be valid over a large operational range.

3. SOLUTION PROCEDURE

The model is a system of differential partial equations with the concentration of hydroxide varying with time. Note that the concentrations of lignin, hemicelluloses and cellulose impact the amount of hydroxide.

For lignin, it was assumed that the kinetic expression was the same as found by Mortha et al. (1992) and there are three types of lignin in proportions of 25.0, 73.8, 1.2 per cent. The third type

of lignin was estimated from the extended delignification results of Irvine et al. (1996), which showed that there was a small fraction of lignin that was no reactive. The rate of reaction of this lignin fraction was effectively zero. The proportions of the two types of hemicelluloses were calculated to be 36 and 64 per cent. For cellulose, the two reactions probably correspond to the different types of reaction - peeling and cleavage, and the proportions were calculated to be 17 and 83 per cent. In most models, the extractives are assumed to react instantaneously but the inclusion of a rate equation is more realistic and does not make the model much more difficult to solve. Available data on the rate of removal of extractives has been used in this study to calculate the rate constant, assuming that the reaction is first order. It was not possible to determine if the reaction rate depends on temperature or chemical concentration because it is a fast reaction compared to the reactions of other wood components. Only alkali diffusion was considered, and the same diffusivity coefficient is assumed for both sodium hydroxide and sulfide. In this model a proper energy balance was not developed. Flow characteristics, channeling, different wood compositions and other phenomena were not considered.

The equations describing the diffusion phenomena lead to a system of nonlinear partial differential equations, which are conveniently transformed by the orthogonal collocation method into a system of ordinary differential equation through the discretization of the spatial variable through the concept of the method of lines. The equations are integrated in respect to time by a LSODE integrator since stiffness may occur.

To solve the model equations, the pulping conditions need to be specified along with various properties of wood. Some inputs terms are specified in Table 1:

Table 1: Pulping Conditions

Process Variable	Input Values
Thickness of Wood Chip (m)	0.003
Liquor to Wood Ratio (l/kg)	4.0
Initial Temperature ($^{\circ}$ C)	80
Cooking Temperature ($^{\circ}$ C)	170
Density (kg/dm ³)	0.6
Porosity	0.59
Heating time (min)	90
Cooking time (min)	180

4. RESULTS AND DISCUSSION

Wood chemistry and reaction mechanisms are not fully understood. In these studies the curves of lignin content and the carbohydrate (cellulose and hemicelluloses) content vs. time are presented in Figures 02 and 03. All the curves are simulated. The mathematical model was validated with experimental

data from an industrial paper mill using *Eucalyptus* as feedstock. It use three different initials temperature (Tfo), in $^{\circ}$ C.

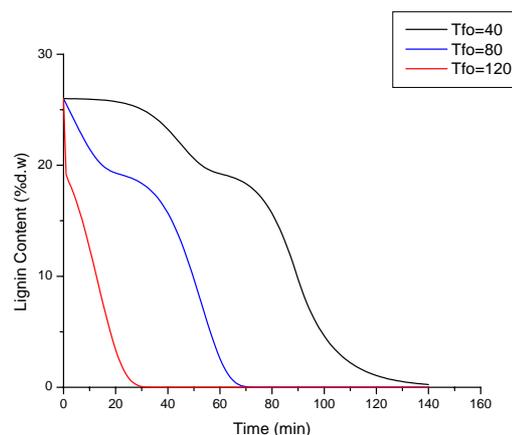


Figure 02: Lignin content vs. time

Lignin reactions in Kraft pulping can be divided in three phases: initial, bulk and residual delignification. Initial delignification occurs during the impregnation phase. About 20% of the total amount of lignin is dissolved in this stage. Another 70% of lignin is removed during bulk delignification when the cooking temperature is raised above 140 $^{\circ}$ C. The rate of bulk delignification depends on the alkali and hydrosulfide concentration as well as on the temperature in the digester. The final residual delignification proceeds very slowly.

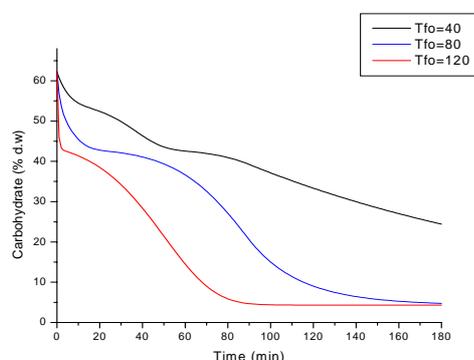


Figure 03: Carbohydrates vs. Time

Figure 03 shows the Carbohydrate reactions in Kraft pulping for the three phases (initial, bulk and residual) in three initials temperature (Tfo) in $^{\circ}$ C. During Kraft pulping not only delignification reactions occur but carbohydrate degradation also takes place. Carbohydrate degradation is not wanted because it results in pulp yield decrease and fiber strength loss during the pulping process.

In Figure 04, carbohydrate concentration is plotted against the lignin concentration.

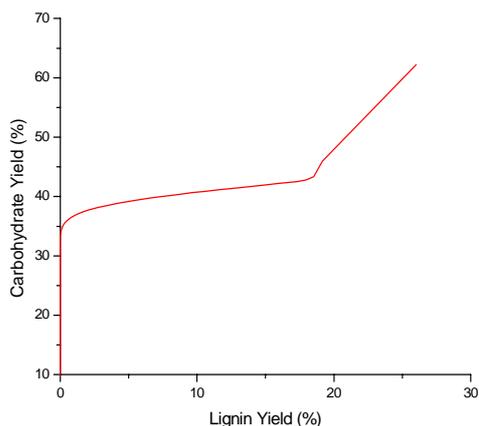


Figure 04: Yield of Carbohydrate material as a function of lignin yield for different parts of Eucalyptus wood

The carbohydrate removal is proportional to the rate of lignin removal. This is supported by the type of behavior shown in Figure 04. The three phases can be identified using plots of carbohydrate as a function of lignin. The initial phase lasts until the lignin concentration has decreased to about 18 per cent. The bulk phase continues until the lignin concentration has been reduced to about 3 per cent and this is followed by the residual phase. Similar behavior for carbohydrate concentration can be found in Virkola (1983), in Figure 05.

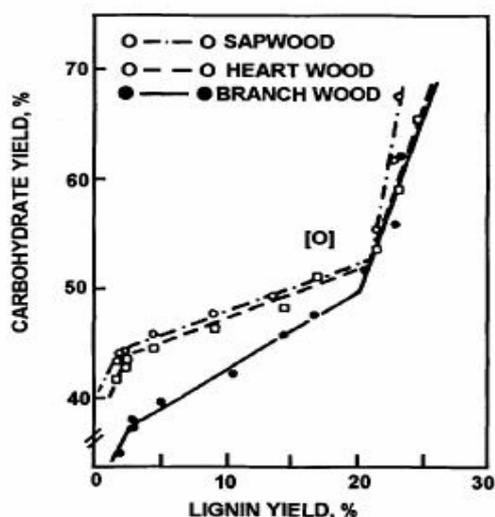


Figure 05: Yield of Carbohydrate as a function of lignin yield for different part of Pine wood (Virkola, 1983)

5. CONCLUSION

A deterministic model to describe Kraft pulping of Eucalypts has been developed. Most of the published papers deal with Kraft pulping of *Pines*, but the economic advantage in using *Eucalyptus* and the

changes in digester behavior for both cellulose feedstocks has to be accounted for. The developed model was able to represent well the process theory. The model is used to investigate the effects of process conditions on the extent of delignification and it is a valuable tool to investigate the performance of control and optimization strategies...

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