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KINETIC OF PULP BLEACHING BY HYDROGEN PEROXIDE

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ABSTRACT

As the result of increasing environmental concern, new technologies for bleaching pulps have been developed. Chlorine containing bleaching agents have been replaced by more environmentally benign chemical, and the importance of hydrogen peroxide in pulp bleaching has rapidly increased. This paper reports the results of experimental and kinetics studies of pulp bleaching. About 20 g of dry pulp was treated by using sulfuric acid and ethylene diamine tetra acetate (EDTA) at chelating stage. The treatment was carried out in plastic bags placed in a pre-heated water bath. The bleaching was performed with addition of H_2O_2 and NaOH at 70°C and 90°C. After the bleaching, the pulp was dewatered and washed carefully. The filtrate obtained from the initial dewatering was used to determine the pH and residual H_2O_2. The pulp was analyzed its lignin content. Two kinetics models were proposed. Both models assume that the process consist of two consecutive reactions, which are decomposition of H_2O_2 producing HOO^- and reaction of lignin with HOO^-. Further, the first model assumes that decomposition of H_2O_2 producing H_2O and O_2 does not occur, while the second model does. The results of the two models were verified by the experimental data. It turns out that the first model works well at the temperature up to 70°C, while the second model work well until 90°C.

Key words: mathematical modeling, kinetics, bleaching, hydrogen peroxide

I. INTRODUCTION

The world's paper consumption has increased by 50 % during the last decade. Consequently, the consumption of bleaching agent for pulp bleaching has increased as well [1]. Pulp and paper has long been recognized as a significant source of pollution. Especially the use of chlorine based bleaching agent has had a negative impact on the environment. When gaseous Cl_2 is used in bleaching, considerable amount of organ chlorine compounds are formed. Gaseous Cl_2 has largely been replaced by chlorine dioxide (ClO_2) in bleaching in recent year, to reduce the formation of lipophilic organ chlorine and volatile molecular chlorinated compounds. However, the use of ClO_2 in bleaching does not totally eliminate the formation of some harmful material, so from an environmental point of view, it could be advantageous if the use of ClO_2 was decreased [7]. Society awareness of the environment has urged the use of environmentally friendly compounds in bleaching sequences. Such a bleaching concept is usually referred to as totally chlorine free (TCF) bleaching. The use of bleaching chemical must be considered in the context of the health and safety of workers and inhabitant of the neighboring environment and in the context of responsible environmental management. Hydrogen peroxide is one of the key chemicals in TCF bleaching [4].

The principle of pulp bleaching is to achieve a high brightness, with secondary objective, for particular end uses, being high brightness stability, high pulp cleanliness and high cellulose content. These objectives must be achieved with out cellulose degradation, because it can lead to significant loss of strength in product paper sheet. The strength of paper is due in part to the strength of individual cellulose chains and in part to hydrogen bound formed between adjacent cellulose molecule, within fiber, and between fibers, which are responsible for the strength of paper sheet. Cellulose has a great capacity to form hydrogen bounds and, as a result, has a great affinity for water. Cellulose is essentially colorless and does not require bleaching. However, during the bleaching of pulp fibers, to decolorize other component, cellulose degradation can occur. This can lead to cellulose fragments being dissolved. Further, if cellulose degradation is sufficiently suffered, pulp strength will decrease [6].

Lignin is material which gives a great contribution in darkener pulp. Pulping process can not remove all lignin in wood, and the residual lignin is often darker than the original lignin. Lignin content must be measured during chemical pulping and bleaching. Because of its complex structure and relatively low concentration, lignin is difficult to measure directly and therefore relative lignin content is measured by standardized reaction of potassium permanganate with pulp. There are several types of this test; one of them is termed kappa number. There is linier relationship between kappa number and lignin content. Lignin content (in weight percent) is approximated by multiplying the kappa number by 0.15 [3].

The goals when using hydrogen peroxide in bleaching are to maximize delignification, brightness and selectivity toward lignin, and to minimize the consumption of hydrogen peroxide. Hydrogen peroxide is very stable under acidic conditions, but under alkaline conditions, it has a propensity for decomposition. The decomposition of hydrogen peroxide is also accelerated by temperature. The active bleaching species in alkaline hydrogen peroxide systems is the perhydroxyl anion, HOO^-, which is formed under alkaline conditions [3]. The dissociation of hydrogen peroxide (the formation of the perhydroxyl anion) is shown in equation (1).

$$HOOH + HO^- \leftrightarrow HOO^- + H_2O \qquad (1)$$

This anion is a strong nucleophile and is primarily responsible for the bleaching effect of alkaline hydrogen peroxide. There are two competing reactions in hydrogen peroxide bleaching: the first leads to delignification and a brightness increase while the second parallel reaction leads to the decomposition of hydrogen peroxide into water and oxygen. The decomposition of hydrogen peroxide into water and oxygen is catalyzed by transition metal ions and is usually claimed to involve the formation of reactive intermediates ($HO\cdot$, and $O_2^{-}\cdot$). The overall reaction can be written as in equation (2).

$$H_2O_2 + HO_2^- \longrightarrow H_2O + O_2 + HO^- \qquad (2)$$

Kinetic management in using hydrogen peroxide as bleaching agent is very important. The decomposition should be directed to equation 1. For this purpose, the metal ions in a pulp which catalyze to decompose of hydrogen peroxide (equation 2) must be removed from pulp; it can be done by chelating stage [5].

Hydrogen peroxide bleaching is usually performed at pH 10-11.5. Under these conditions transition metals can hardly exist as free ions. Collodete [2] has studied the solubility of Fe^{3+}, Cu^{2+} and Mn^{2+} in the pH range of 9.8 to 11.8. After aging at 50°C for 120 minutes, the solutions were subjected to ultra filtration (cut off >1000 MW) and analysis of the filtrates showed that no amounts of iron, copper or manganese above the detection limit (10 ppb) could be found in the solution. The rate of peroxide decomposition was shown to be considerably lower in the filtrates than in the original solution, which implies that the decomposition is surface-catalyzed by colloidal transition metal-oxides/hydroxides [2].

II. THEORETICAL DEVELOPMENT

Cellulose has a great capacity to form hydrogen bounds, so it has a great affinity for water. Based on this characteristic, the concentration of system in the solution is assumed homogenous. Bleaching mechanism is started by formation of HOO^-. This anion is believed to be the principal active species involved in the elimination of chromophores in lignin structure. This anion then reacts with lignin:

$$HOO^- + \text{lignin} \longrightarrow \text{lignin=O} + OH^- \qquad (3)$$

This paper proposes 2 kinds of model in bleaching process by using hydrogen peroxide. The first model assumed that no side reaction producing H_2O and oxygen, and the second model considers that the side reaction producing H_2O and oxygen is occurred as an equation (4).

$$H_2O_2 \longrightarrow H_2O + O_2 \qquad (4)$$

A. Development of the first model

At the first model, we assume that no side reaction (4). The concentration of H_2O_2 changes as equation (1), so the rate of $[H_2O_2]$ depletion is:

$$\frac{d[H_2O_2]}{dt} = -k_1[H_2O_2][OH^-] + k_2[HOO^-] \qquad (5)$$

Anion of HOO^- produced from equation (1) reacts with lignin, so the increase HOO^- is equal to $[HOO^-]$ produced from equation (1) minus $[HOO^-]$ reacting with lignin.

$$\frac{d[HOO^-]}{dt} = -\frac{d[H_2O_2]}{dt} - k_3[HOO^-][lignin]\varphi \qquad (6)$$

The lignin content in pulp will decrease as equation (3), and the content of lignin can be calculated by:

$$\frac{d[lignin]}{dt} = -k_3[HOO^-][lignin]\varphi \qquad (7)$$

The values of H_2O_2, HOO^- and lignin at t = 0 are:

$$[H_2O_2] = [H_2O_2]_0$$
$$[HOO^-] = 0$$
$$[lignin] = [lignin]_0$$

Equations (5), (6) and (7) are calculated by Runge-Kutta method, while the values of reaction parameters (k_1, k_2 and k_3) are optimized using Hooke–Jeeves minimization method. In this case, the sum of squares of errors (SSE) between the calculated and experimental results of residual of H_2O_2 and lignin content is being minimized.

B. Development of the second model

The second model assumes that side reaction is occured as a reaction (4). The rate of change of $[H_2O_2]$ is then:

$$\frac{d[H_2O_2]}{dt} = -k_1[H_2O_2][OH^-] + k_2[HOO^-] - k_4[H_2O_2] \qquad (8)$$

Anion of HOO^- produced from equation (1) reacts with lignin, so the rate of increase of HOO^- is equal to $[HOO^-]$ produced from equation (1) minus $[HOO^-]$ reacting with lignin.

$$\frac{d[HOO^-]}{dt} = k_1[H_2O_2][OH^-] - k_2[HOO^-] - k_3[HOO^-][lignin]\varphi \qquad (9)$$

The initial conditions, and the methods of solving the equations and of evaluating the values of kinetic parameters are the same as for the first model.

III. EXPERIMENTAL METHODOLOGY

The raw material used in this research was oxygen–delignified eucalyptus kraft pulp (*Eucalyptus globulus*) with kappa number of 10.8 and brightness of 56.6 % ISO. This experimental research was divided into two sections, which are chelating section and bleaching section.

A. Chelating stage

About 20 g of dry pulp was treated by using sulfuric acid and ethylene diamine tetra acetate (EDTA). The treatments were carried out at 10 % consistency in plastic bag placed in a pre-heated water bath for 1 hour at 70°C. After that, the pulps were dewatered and washed carefully.

B. Bleaching stage

After the treatment in the chelating stage, pulps were subjected to hydrogen peroxide bleaching immediately. The bleaching was performed for various times, at 10 % consistency in plastic bag placed in water bath pre-heated to 70°C and 90°C, with addition of 2.5 % H_2O_2. After the bleaching, the pulps were dewatered and washed carefully. The filtrate obtained from the initial dewatering was used for determination of pH and residual of H_2O_2. The pulps were subjected to analyses of brightness, kappa number and intrinsic viscosity.

B1. Determination of residual H_2O_2

Distilled water (30 ml) is put into an Erlenmeyer flask together with 10 ml H_2SO_4 (20 %), 10 ml of sample, 10 ml of KI solution (50 g/L)and some drops of saturated ammonium molybdate solution(catalyst). If H_2O_2 is present in the sample, a formation of iodine will take place. The amount of iodine in the solution was determined by titration with $Na_2S_2O_3$ solution. The concentration of H_2O_2 in the sample can then be calculated by the formula:

$$H_2O_2(g/L) = [S_2O_3]^2 * \frac{b*34}{a*2} \tag{10}$$

B2. Determination of lignin content

Pulp (between 0.5 g to 3 g, depending on the predicted kappa number) was put into a glass beaker together with 230 ml distilled water. This mixture was mixed using a blender to disintegrate the pulp. Then 25 ml of $KMnO_4$ solution (0.1 N) and 25 ml of H_2SO_4 (2M) was added. The reaction was carried out at 25°C. After 10 minutes, the reaction was terminated by the addition 6 ml of 1 M KI solution. The iodine formed was then titrated with 0.1 M of $Na_2S_2O_3$ solution. The kappa number can be calculated by:

$$kappa = \frac{(x-y)*d}{m} \tag{11}$$

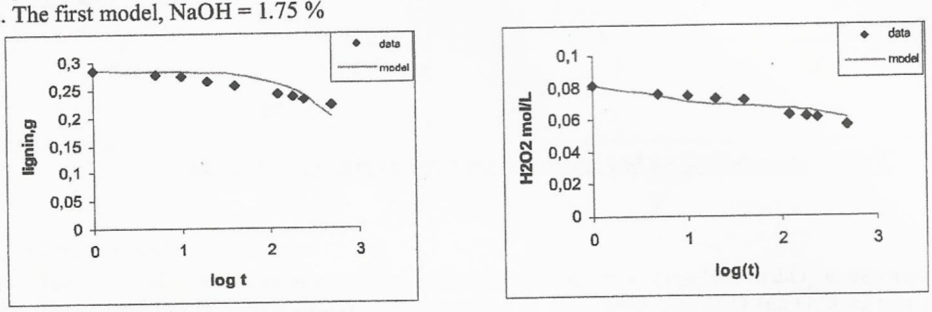
$$d = 10^{0.00093\left[\frac{x-y}{0.3}-50\right]}$$

The lignin content can be then calculated by multiplying the kappa number by 0.15 [3].

IV. RESULT and DISCUSSION

The accuracy of this model is examined by comparison between the residual of H_2O_2 and lignin content of experimental data and calculation using the models proposed. The results are presented in figure 1 and 2.

a. The first model, NaOH = 1.75 %



b. The second model, NaOH = 1.75 %

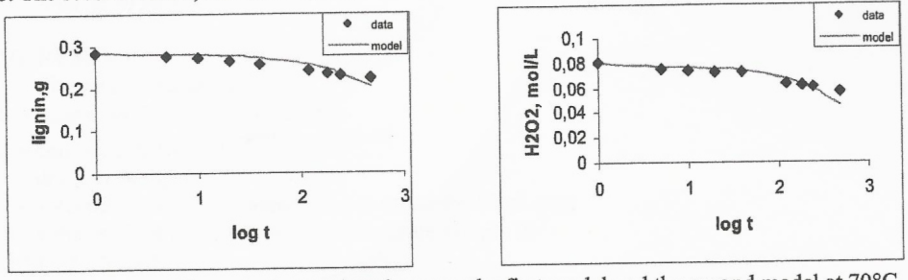
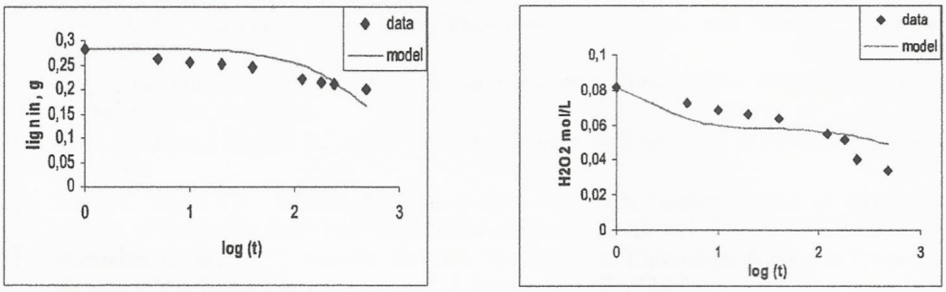


Figure 1. Comparison between the first model and the second model at 70°C

Figure 1 shows the residual of H_2O_2 and lignin content at various time of bleaching. It can be clearly observed that the results of calculation of both models not only have similar trend line but also the same values with the experimental data. The average error of the first model is 4.9%, while the second model is 5.3%. Based on this calculation, it can be concluded that both models work well up to 70°C. The two models were now tested at a higher temperature (90°C). The results are presented at figure 2.

Figure 2 shows that the second model still works well at 90°C. It is proved by the similarities of trend lines between the experimental data and the calculation results using the second model. The average error of the second model is 9.97%. Meanwhile, the first model looks poor at 90°C. The results imply that decomposition as in reaction (4) is not significant at 70°C, but significant at 90°C.

a. The first model, NaOH = 1.75 %



b. The second model, NaOH = 1.75 %

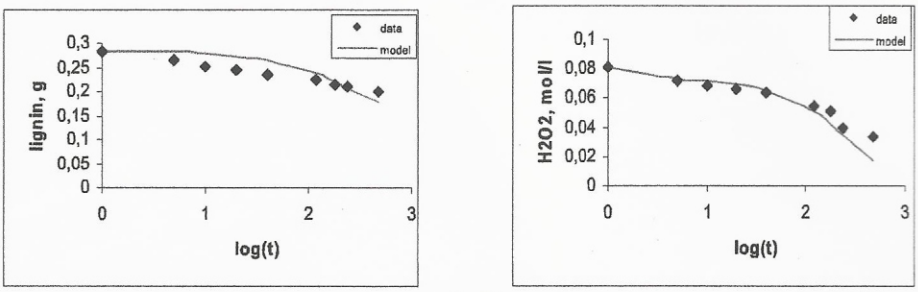


Figure 2. Comparison between the first model and the second model at 90 ^{0}C

V. CONCLUSION

1. The first model, which assumes no decomposition of H_2O_2 producing H_2O and O_2, works well up to 70°C.
2. The second model, which assumes decomposition of H_2O_2 producing H_2O and O_2 does take place, works well up to 90°C.

VI. SYMBOL

a = volume of sample (ml)
b = volume of $Na_2S_2O_3$ solution (ml)
d = corection factor, $10^{0,00093[(x-y)/0,3-50]}$
m= dry pulp weigh (g)
x = volume of $Na_2S_2O_3$ solution used to titrate the blank (ml)
y = volume of $Na_2S_2O_3$ solution used to titrate sample (ml)
t = time (minute)

$$\varphi = \frac{mass..of.fiber}{volume.ofsolution}$$

VII. ACKNOWLEDGMENT

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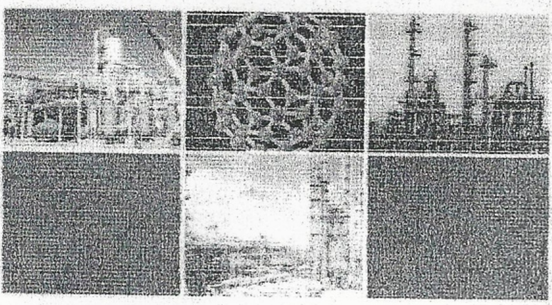

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