THE EFFECT OF OZONE CONCENTRATION ON THE BLEACHED PULP PROPERTIES

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Abstrak

Totally chlorine free (TCF) bleaching has been widely applied as a response to the environmental restrictions and the increase of market demand on chlorine-free chemical-bleached pulp. Ozone is highly reactive and reacts readily with most organic materials; therefore ozone is an attractive bleaching agent. The advantage of utilize ozone technology in the bleaching sequence is that the effluent from this process can be recycled, unlike the effluent from the chlorine-based system. The problem with ozone delignification or bleaching is the non-selectivity of ozone, which also attack cellulose and cause deterioration of pulp mechanical properties. The aim of this study was to examine the effect of ozone concentration on the bleaching to the optical and mechanical properties of the pulp. The experiment was conducted by react the acidified pulp with ozone in a rotating reactor. Caustic extraction was also added after bleaching to dissolve more lignin. From the experiments, it was found that the optical properties of pulp were improved by reaction with ozone in the bleaching. Theoretically, the lack of selectivity of ozone reaction will reduce the pulp strength after bleaching. However, in this study the tensile strength improved by the rise of ozone concentration.

Kata Kunci : ozone bleaching, pulping, chemical

INTRODUCTION

Prosiding Totally chlorine free (TCF) bleaching has been widely applied as a response to the environmental restrictions and the increase of market demand on chlorine-free chemical-bleached pulp. Oxygen-based bleaching agents such as molecular oxygen, ozone, and hydrogen peroxide, are employed in the TCF technology to replace chlorine.

The chlorine bleaching sequences became less favourable as formation of chlorinated organics in the bleach effluent. These chlorinated organics takes years to degrade in water therefore pollute the environment. Besides that, the increase use of mechanical fibres has also causes the chlorine bleaching is uneconomical since the high lignin content in the mechanical pulp consumes more chemicals that also result in yield loss [1].

There are two ways of fibres bleaching, oxidation of the lignin, and colour stripping. Oxidation is aimed to modify the lignin therefore it becomes more soluble in water (e.g. chlorine and ozone bleaching) or colour less (e.g. peroxide bleaching) [1]. The effectiveness of oxidation bleaching is measured by brightness. The colour stripping bleaching is achieved by reduction of lignin. The reducing agents such as sodium dithionite and hypochlorite modify the structure of the coloured dyes therefore it appears colourless [1]. The effectiveness of colour stripping is determined by the change of pulp colour that can be measured by L*, a* and b*. The increase of L* will result on whiter appearance of the sheet. Ozone is a very attractive bleaching agent since it can both react with coloured dyes to make it colourless and oxidises chromophoric lignin groups in the pulp to make it more soluble in water [1].

Ozone is highly reactive and reacts readily with most organic materials. Therefore ozone is a very efficient bleaching agent. However, its application is limited, since ozone is generated in low concentration. Another restriction is that ozone has low solubility in water, as consequence it limits its reactivity in aqueous systems as ozone has to transfer from gas phase to liquid phase [2].

The advantage of utilize ozone technology in the bleaching sequence is that the effluent from this process can be recycled, unlike the effluent from the chlorine-based system [3]. As the effect, it is more suitable for the environmental demand on less water usage and less effluent released [2].

The problem with ozone delignification or bleaching is the non-selectivity of ozone, which also attack cellulose [4]. The side reaction with cellulose causes deterioration of pulp quality, particularly its mechanical properties. Attempts have been made to improve ozone selectivity, such as operation at low charge and also development of process conditions to minimize the reactions between ozone and cellulose [2].

The more ozone used for bleaching will give the better optical properties of the bleached pulp. On the other hand, when the ozone concentration is exceeded, it will reduce the pulp strength. Therefore, it is important to investigate the effect of ozone concentration on the bleaching to the property of bleached pulp to obtain the optimum concentration of ozone required.

The aim of this study was to examine the effect of ozone concentration on the bleaching to the optical and mechanical properties of the pulp. The properties being inspected were colour, brightness, opacity, and tensile.

FUNDAMENTAL ASPECTS OF OZONE BLEACHING

Ozone has an electrophilic character that promotes reaction with functional groups in the lignin. Aliphatic double bonds conjugated to the aromatic rings in stilbene, styrene, and enol ether structures will form epoxides or ozonides, or further form carbonyl groups and hydrogen peroxyde when reacts with ozone. The ozone reaction can also happen by insertion of an oxygen atom into carbon-hydrogen bonds in alcohol-, aldehyde-, and ether- type structures therefore disintegrate the lignin structure. In general the ozone reacts with structures in the lignin to form functional groups therefore change the macro molecular structure of the lignin. It was found that ozone appears to be more efficient than chlorine dioxide and hydrogen peroxide in inducing the formation of carboxylic acid from residual kraft lignin [2].

Ozone itself found to be 106 times more reactive to lignin than to carbohydrates. However, the by-products from those reactions of are easier to react with carbohydrates. The nature of this reaction lead to a hypothesis that pulp with high lignin will sustain more on viscosity loss than low lignin pulp.

The critical parameters to determine the amount of ozone added to remove lignin are lignin removal (measured by kappa number or optical properties) and carbohydrate degradation (measured by pulp strength or by viscosity). Those two parameters will be used to express the effectiveness of ozone delignification and its selectivity.

The main process variables that influence the effectiveness and selectivity of ozone delignification are pulp consistency, ozone charge, pH, time, temperature, chemical additives, effects of metal ions, residual organic matters and pulp treatment before an ozone stage. A rapid and efficient transfer of ozone into appropriate fibre constituents is very important to enhance ozone-lignin reaction instead of cellulose decomposition [2].

One of studies of utilisation of ozone in a bleaching sequence involving xylanase enzyme found that at certain extent of kappa number, the addition of ozone into the reaction would lower the viscosity while the kappa number remained constant. Therefore, it is undesirable to increase the concentration of ozone while the lignin removal reaches a limit which means that the remained lignin is inaccessible [5].

Much of early ozone bleaching works on low (0.5-3%) and high (30-40%) stock consistency. Low consistency allows optimum mixing. In the high consistency maximum exposure of fiber surface to ozone is achieved by fluffing to separate fiber aggregates to the greatest extent possible. The most efficient delignification for ozone bleaching occurs near pH 2. In high consistency ozone bleaching, acid treatment prior to bleaching can remove metal ions from pulp, while acid brings H+ that replace M+ in the pulp [2]. Alkali extraction stage after ozone bleaching is purposed to reduce kappa number of ozone-delignified pulp. Alkali has an important role to remove lignin from pulp.

EXPERIMENTAL PROCEDURES

The raw material used in this experiment was Eucalyptus kraft pulp with initial kappa number of 25 and pulp consistency of 24.2%.

The first stage of the experiment was pulp preparation to meet the ozone bleaching conditions.

Pulp preparation

Initially, 170 g o.d. (oven-dried) pulp was acidified for about 10 minutes using 2.5 M sulphuric acid. Water was added to the slurry to obtain pulp consistency of 11% and pH ~4. After the acidification, the pulp was dewatered to improve its consistency using a mechanical hand press. The pulp consistency was then determined by Infrared Moisture Determination Balance. The pulp entered the reactor at stock consistency of 44.1%. And the pulp needs to be fluffed prior to ozone delignification reaction to improve surface area of reaction. Pulp was fluffed for about 30 s using a household food processor.

Ozone delignification

Ozone was generated by passing an electrical discharge through air. The high ozone concentration can be obtained by adding pure oxygen to the feed stream of ozone generator or by applying higher currents. The non-ozone components in the gas leaving the ozone generator are called carrier gas. This stream contains a large amount of unconverted oxygen, which can be collected and recycled back to the ozone generator. This recycle process could minimize the oxygen costs and allowed higher ozone concentration to be

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produced. Before the recycled carrier gasses was returned to the generator, all residual ozone and hydrocarbons have to be destroyed.

The ozone delignification reaction was conducted in 5 different ozone/pulp ratios, which were 0.2, 0.4, 0.6, 0.8 and 1.0%, based on oven-dried mass of pulp. For those different ozone concentrations, the reaction times were adjusted to 29, 59, 88, 118 and 147 s, respectively. The electrical current to the reactor was constant. The amount of fluffed pulp added to the reaction was 25 g o.d. in each run. To maintain a good mixing in the reactor, the rotation was set at 30 revs/min. The setting of the ozone generator is as follows:

- Pressure 1.65 bar
- Oxygen flowrate 55 % or 0.18 m3 / h
- Current 0.8 amp
- Ozone Concentration 34 g/m3

The diagram of the ozone delignification and ozone generator reactor is presented in Figure 1.

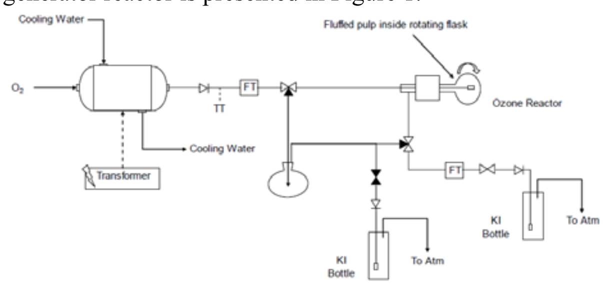

Figure 1. Schematic diagram of the ozone delignification reactor

Caustic extraction and washing

Following the ozone delignification, the bleached pulp samples (25g o.d.) from each run was extracted using caustic at 11% consistency. Caustic and water were added to reach slurry pH of 10.5 to 11. The extraction was conducted in a steam bath at 60°C for 30 minutes. The pulp samples then was washed using distilled water until the pH is approximately neutral.

Handsheet forming

Handsheets were prepared using Tappi Test Method T205 sp-95. Handsheets was prepared at 60 and 80 gsm using a British Handsheet Former for each pulp sample as follows:

- Acid treated pulp
- Ozone bleached pulp 0.2% charge
- Ozone bleached pulp 0.4% charge
- Ozone bleached pulp 0.6% charge
- Ozone bleached pulp 0.8% charge
- Ozone bleached pulp 1.0% charge

The handsheets need to be dried in a conditioned room (25ºC and 50% relative humidity) for at least 24 hours prior to the measurement.

Testing of optical and mechanical properties

An Elrepho spectrophotometer was used to test colour (L*, a* and b*), brightness (R457) and opacity. All samples needed to be conditioned for at least 24 hours prior to testing. The tensile strength of the pulp was determined as well.

RESULTS AND DISCUSSIONS

Effect of delignification on colour and brightness

The effect of ozone consumption on colour, as can be seen on Figure 2,3, and 4, was that as ozone consumption increased it enhanced L* while a* and b* tend to decrease.

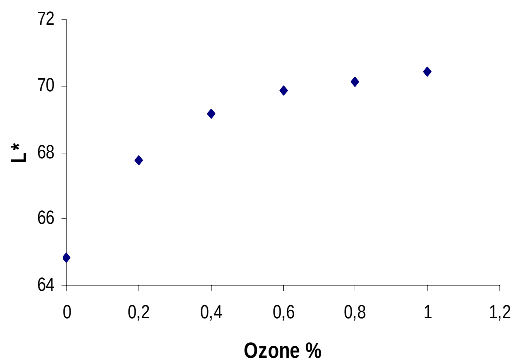

Figure 2. Effect of ozone charge on colour (L*)

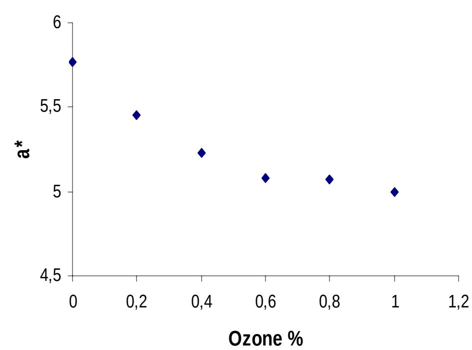

Figure 3. Effect of ozone charge on colour (a*)

L*, a*, and b* represent the amount of colour of the paper where L* is the value of lightness, the range of black to white colour, a* identifies the green to red axis, and b* characterizes blue to yellow axis [6]. As pulp was bleached, and lignin was removed, the pulp became more white or light, therefore the L* increased. The decline of a* and b* was consistent with the improvement of pulp brightness. As a* and b* decreased, the colour of the sample tended to be more greenish and bluish, respectively. The enhancement of those two colours indicated brighter appearance of sample measured. The measurement of L*, a* and b* determines the colour removal by ozone bleaching.

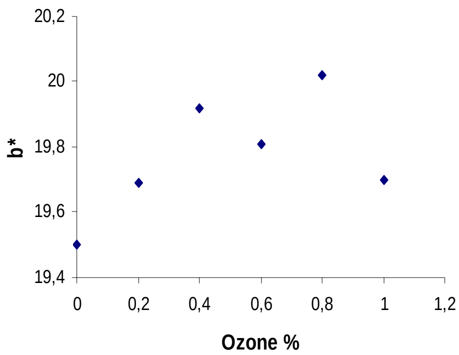

Figure 4. Effect of ozone charge on colour (b*)

The ISO brightness measured by R457 increased with the extent of ozone charge indicates more lignin removed by ozone reaction as presented in Figure 5. The improvement of ISO brightness indicates the more lignin removed in the bleaching process as there is more oxidized lignin dissolved in water.

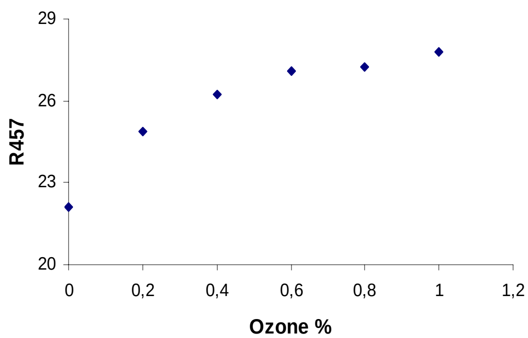

Figure 5. Effect of ozone charge on ISO brightness (R457)

As ozone reacted with lignin during bleaching reaction to form water-soluble compounds, lignin could be removed from the pulp resulting brighter pulp. Role of caustic extraction after bleaching was for lignin removal. Beside that, caustic could react with lignin and produced water-soluble compounds as well. By washing bleached and extracted pulp after bleaching and caustic extraction, lignin content of pulp that has been compared to water-soluble compound was removed and resulting brighter pulp.

Effect of delignification on opacity

The opacity of the handsheets was determined by measuring the light absorption (k) and light scattering (s). When light pass through a pad of paper there are three possibilities of the path of the light. First, it can be reflected on random direction or scattered, second is that the light can be absorbed by the paper, and the last is that the light pass through the sheet [2]. The lower light absorption and scattering means the less opaque the paper. The effect of the ozone charge on the absorption and light scattering can be seen in Figure 6 and Figure 7, respectively.

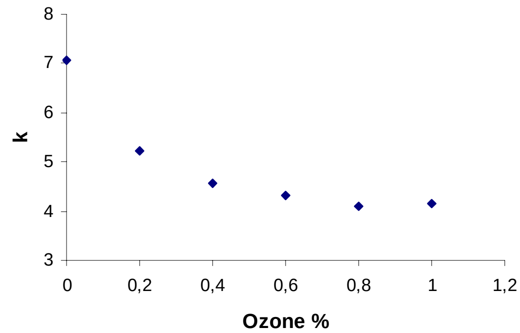

Figure 6. Effect of ozone charge light absorption (k)

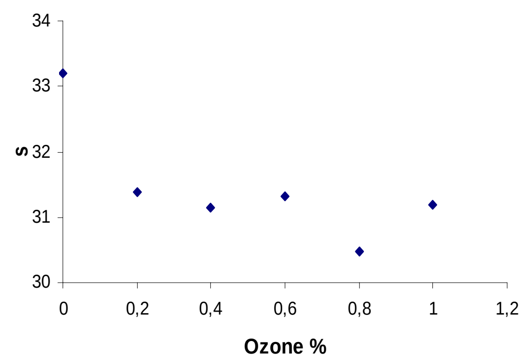

Figure 7. Effect of ozone charge light scattering (s)

The light absorption decreased with the improvement of ozone concentration. As there was more ozone added to the delignification reaction, there was more lignin removed. One of the functions of the lignin content in the pulp is to absorb light pass through the paper, where the cellulose tends more to let the light pass through. As consequence, less lignin content in the pulp results on less light absorption as indicated by lower k value.

The light scattering also reduced with higher ozone concentration as can be seen in Figure 7. While the lignin removed, the wall of the pulp fibres became thinner. Therefore the fibres were easier to collapse when a sheet is formed. As the effect, the sheet formed will be thinner. When there is a light come to the thin sheet, it will pass through it instead of be reflected. The low lignin content will flatten the sheet surface, therefore less light scattered resulting on the brighter appearance of the sheet.

The lower k and s values show the lower opacity of the paper. The less lignin content compared by cellulose in the pulp will lower the opacity since cellulose is more transparent. As consequence, the paper produced absorbed and scattered less light compared to the amount of light pass through it.

Effect of delignification on mechanical properties

Theoretically the higher ozone concentration ends on a lower tensile strength. However, in this experiment the tensile strength improved by the addition of ozone concentration as described in Figure 8.

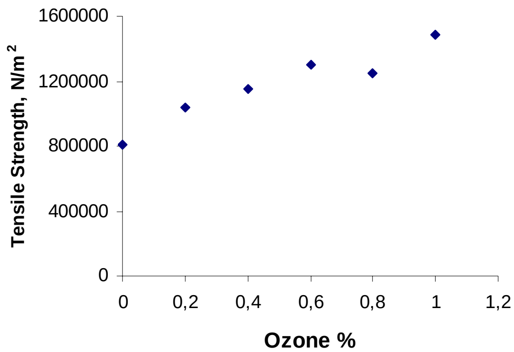

Figure 8. Effect of ozone charge on tensile strength

From the previous studies, it was found that when the ozone concentration in high, side reactions will occur, where the by-products attack cellulose cause degradation of pulp strength.

In this study, the tensile strength of the pulp developed by improvement of ozone concentration. One of the factors that lead to this phenomenon is the fibre wall thickness. The removal of lignin results on thinner fibre wall. The fibre with thinner wall is easier to collapse and the bond between fibres in the web or paper is stronger. As consequence, the paper formed from this pulp is stronger, as can be shown by higher tensile strength.

CONCLUSIONS

From the experiments, numbers of conclusion is drawn as follow:

3. The extent of ozone concentration improved L* while a* and b* declined as indication of more colour removed with more ozone.
4. The higher ozone concentration resulted on elevated ISO brightness of the pulp.
5. The level of ozone concentration reduced light absorption (k) and light scattering (s) of the sheet therefore decreased the opacity.
6. The tensile strength levelled up with extension of ozone concentration.

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