

Sodium Hydroxide and Calcium Hydroxide Hybrid Oxygen Bleaching with System

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Abstract. This study investigates the replacement of sodium hydroxide in the oxygen bleaching stage using a hybrid system consisting of sodium hydroxide calcium hydroxide. Commercial Kraft pulping was studied using yellow pine Kraft pulp obtained from a company in the US. The impact of sodium hydroxide, calcium hydroxide hybrid system in regard to concentration, reaction time and temperature for Kraft pulp was evaluated. The sodium hydroxide and calcium hydroxide dosage was varied between 0% and 15% based on oven dry fiber content. The bleaching reaction time was varied between 0 and 180 minutes whereas the bleaching temperature ranged between 70 °C and 110 °C. The ability to bleach pulp was measured by determining the Kappa number. Optimum bleaching results for the hybrid system were achieved with 4% sodium hydroxide and 2% calcium hydroxide content. Beyond this, the ability to bleach pulp decreased.

1. Introduction

Wood is the major raw material used for the chemical Kraft pulping process that was developed 1879 by Carl Ferdinand Dahl in Danzig Prussia Germany and US patent 296,935 was issued April 15, 1884, [2]. Kraft pulping was first commercially used in Sweden in 1885. The word “Kraft” is German, and translated it means strong [2]. Kraft pulping produces a high-strength pulp compared to the sulfite process. The sulfite process is an acid process for making pulp from wood in which chips are cooked at high temperature and pressure in a solution of bisulfite of calcium, magnesium, sodium, or ammonium [2]. However, there are some advantages of using the Kraft instead of the sulfite process such as the recovery of chemicals and continuous digester which helps to reduce cost of the pulping operation. Further Kraft pulping can be used for all wood species compared to the sulfite process [2].

Wood fiber is mainly composed of cellulose, hemicelluloses, lignin and extractives. The general chemical composition of hardwood and softwood are presented in Table 1.

Table 1. Chemical composition of hardwood and softwood [3]

Composition	hardwood	softwood
Cellulose	40-44%	40-44%
Hemicellulose	15-35%	30-32%
Lignin	18-25%	25-32%
Extractives	2%	5%



One drawback of Kraft pulping is the darker color in the pulp compared to the sulfite process. This means, more chemicals are needed in the bleaching operation, to brighten the pulp.

Bleaching is to increase brightness of pulp with chemical agents. Bleaching of chemical pulps is achieved by delignification [4]. Cellulose and hemicellulose are white and do not contribute to the pulp color. Lignin is the component in wood which absorbs visible light. Further, lignin is slightly colored in wood; however, it is darker colored after Kraft process. Increasing of lignin darkness is also caused by aging of wood [5]. Lignin removal improves the fiber-fiber bonding in paper. However, a degradation of cellulose through bleaching chemicals negatively impacts paper strength [4]. Besides lignin, unbleached pulp contains other materials; extractives such as resin compounds, dirt from wood, cooking process residues, and external sources [6].

The development of oxygen bleaching was driven by environmental regulation for bleached plant effluents. In particular, the amount of residual chlorine compounds in the waste water of pulp mills has a major negative impact on the environment [7]. This resulted that oxygen bleaching replaced the use of the chlorine bleaching stage of Kraft pulp [8, 4, 6, 8, 9]. Since 1970, chlorine bleaching has been replaced by chlorine dioxide and oxygen delignification, which allows that fifty to sixty percent of the residual lignin in Kraft pulp is removed without degrading the cellulose chain [10]. The effluent from the oxygen stage can be recovered in the recovery boiler. This reduces the environmental impact of waste water [11]. In addition, oxygen bleaching is more cost-efficient than chlorine dioxide and hydrogen peroxide bleaching [11].

A limitation to oxygen bleaching is the lower reactivity and selectivity compared to a chlorine dioxide [11]. Hemicellulose degrades during the oxygen bleaching process. The loss of hemicellulose negatively impacts the paper strength [6]. Carbon monoxide and volatile organic compounds such as methanol, acetaldehyde, and terpenes are released to the environment after the blow tank and the post-oxygen washer filtrate tanks [11].

To make the oxygen bleaching process more environmentally friendlier work has been performed on replacing sodium hydroxide with calcium hydroxide for peroxide bleaching of Kraft pulp. Calcium hydroxide is less expensive chemical to use, and allows the use of existing equipment. In addition oxygen bleaching results in a lower chemical oxygen demand (COD) in effluent water [12, 13], but might cause scaling in the reactors interior surface [14]. A recent study suggested a calcium hydroxide content of 2 % to 3 % for the Kraft pulp oxygen bleaching [15]. However, no additional research work has been reported about the use of calcium hydroxide as an alternative bleaching chemical.

The focus of this study is to expand and explore oxygen bleaching with calcium hydroxide and sodium hydroxide as a hybrid additive system.

2. Methodology

The methodology section describes the equipment, procedures and materials used for this study. As part of this study several test methods were applied. These are described in detail in the following subsections. All tests were performed and reported according to TAPPI standards or as noted otherwise. Repeatability of the results stayed in between the allowable margins of the TAPPI testing standards.

2.1. Material and Methods

For this study commercial yellow pine Kraft pulp after the washing stage of the digester was used. The pulp was washed in the laboratory due to high residual black liquor content in the pulp. This resulted in an initial Kappa number of 11 or 12. The Kappa number expresses the bleach ability of pulp where as a high Kappa number indicates a higher lignin content and better bleach ability whereas a low initial Kappa number indicates low lignin content and lower bleach ability [16]. Kappa number of the recycled pulp was measured in accordance with T 236 om-06 [17].

2.2. Oxygen Bleaching

A Quantum Reactor was used to perform the bleaching experiments. The Quantum reactors three liter reaction vessel can be pressurized and heated. It has a large agitator, which can mix a pulp fiber suspension with of up to 10 % consistency. The agitation is automated which allows to individually

adjust the mixing speed, running and pause time. Through a valve in the lid the oxygen gas is injected into the Quantum reactor vessel [15]

2.3. Washing of Pulp, Kappa Number

A washing procedure described by Doelle and Bajrami [15] uses a 15 cm Büchner funnel for washing the bleached pulp. The Büchner funnel is attached to a 20-liter filter flask which is connected to a vacuum system. A paper machine former fabric is added to the Büchner funnel instead of a filter paper, to maximize dewatering and prevent clogging of the funnel pores. Bleached pulp is placed in the Büchner funnel and washed with 15 liters of deionized water. By applying a vacuum to the 20-liter flask, deionized water is forced to move through the pulp cake. After washing is completed, the pulp is wrapped in a larger paper machine former fabric. With a small press, the wrapped pulp cake is additionally dewatered. After this, the pressed pulp cake is chopped into homogenous small pieces by a crumbling machine. From the homogenized pulp, a pulp pad is made using an 8 cm Büchner funnel. The pulp pad is air dried for Kappa number measurement. The Kappa number and viscosity were measured according to the TAPPI test method T 236 om-06 and T 254 cm-00 [9, 10].

3. Results and Discussion

3.1. Hybrid of Sodium Hydroxide and Calcium Hydroxide

A hybrid of sodium hydroxide and calcium hydroxide was evaluated. Because sodium hydroxide has a higher solubility, combination with calcium hydroxide might improve the diffusion of the alkali in the fiber wall. Further, the combination of sodium hydroxide and calcium hydroxide should help reduce scale, which forms on reactor wall when calcium hydroxide alone is used.

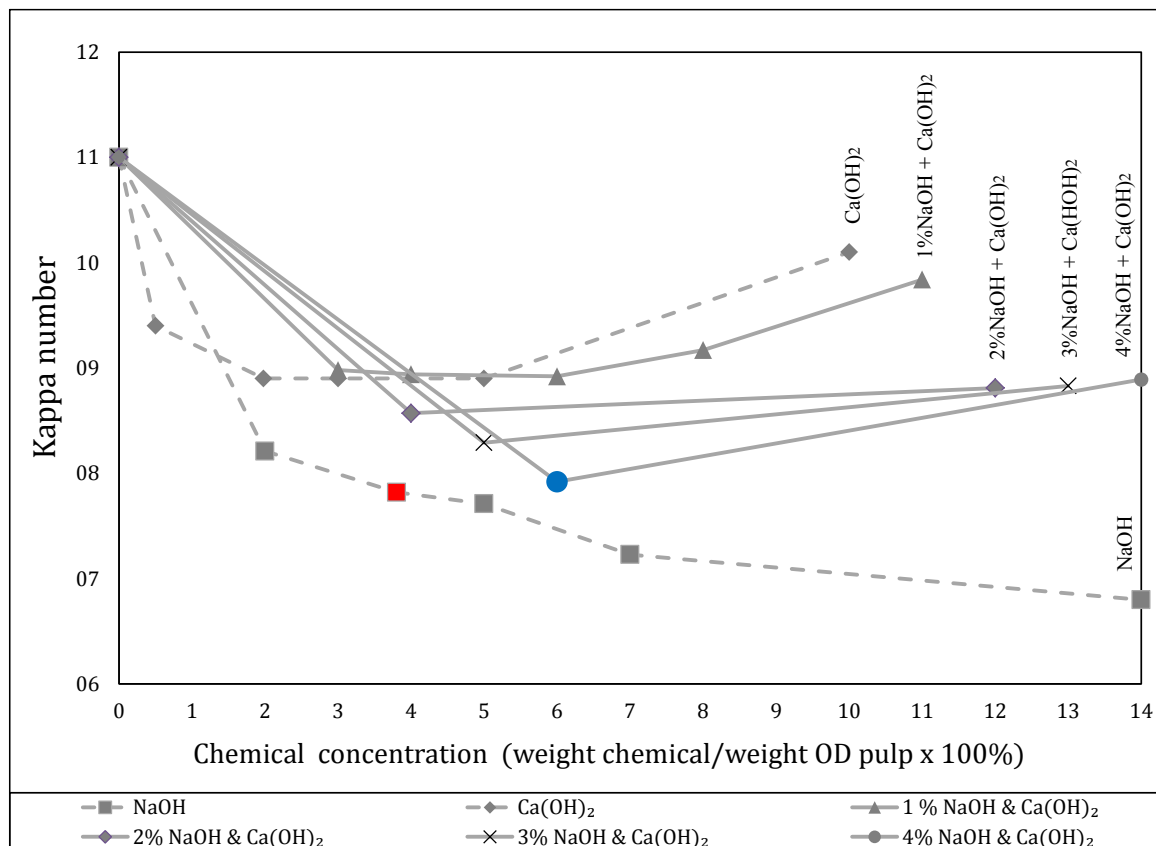


Figure 1. Effect of relation of sodium hydroxide and calcium hydroxide to Kappa number in O-stage, Quantum reactor (90 °C, 90 PSI, 60 min)

On Figure 1 the slashed lines represent only calcium hydroxide or sodium hydroxide. From an earlier study [15] the solid lines represent a mixture between calcium hydroxide and sodium hydroxide. Each point on the graph represents a bleaching experiment. With increasing sodium hydroxide concentration, a lower Kappa number can be achieved. However, the overall concentration of the chemical has to be increased to achieve the result.

Figure 2 presents the data of Figure 1 in a more detailed fashion. In the legend, the relation of sodium hydroxide and calcium hydroxide is given in percent. A hybrid of sodium hydroxide and calcium hydroxide helps to achieve a more efficient bleaching result than bleaching with calcium hydroxide alone. However, if the concentration of 4% sodium hydroxide is compared to the hybrid of 4% sodium hydroxide and 2% calcium hydroxide, it is observed that with 4% sodium hydroxide alone, a better bleaching result is achieved. Using 4% sodium hydroxide instead of the hybrid (total chemical concentration 6%) would save in bleaching chemicals.

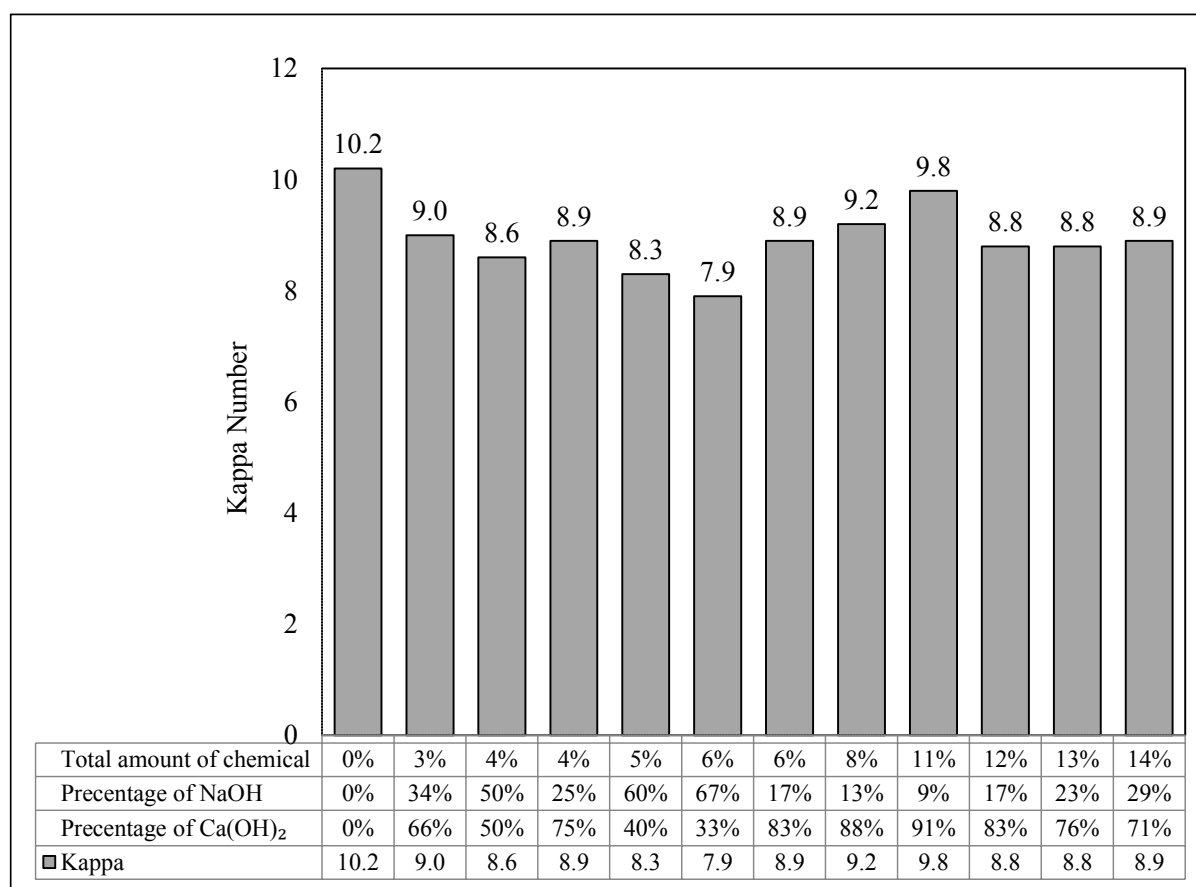


Figure 2. Effect of relation of sodium hydroxide and calcium hydroxide and changes in Kappa number in O-stage, Quantum reactor (90 °C, 90 PSI, 60 min) (2)

3.2. Promising Hybrids

This section summarizes the best performing hybrids: Three sequential runs with calcium hydroxide achieve the best bleaching result compared to all hybrids (Figure 3). However, running the O-stage three times increases the process cost. Acid washing of pulp is a good alternative, because it improves the bleaching efficiency. However, it will degrade the cellulose which causes weaker paper strength.

Next, bleaching pulp for three hours, instead of bleaching it for one hour, reduces Kappa number by 0.8. A similar bleaching result is achieved by running the bleaching stage twice with 2% calcium hydroxide. By increasing the pulp temperature from 90 °C to 110 °C a positive effect on bleaching is observed. Further, for the 110 °C run, 1.6% calcium hydroxide is needed instead of 2.5%. Therefore, a lower amount of bleaching chemicals is used, leading to cost savings. The combination of calcium

hydroxide and sodium bicarbonate reduces the Kappa number by 0.7 points. One of the important advantages of using sodium bicarbonate is that scale does not form on the reactor. All hybrids are in a level where they can compete with sodium hydroxide. However, some of the hybrids with calcium hydroxide might not be as cost efficient as sodium hydroxide alone.

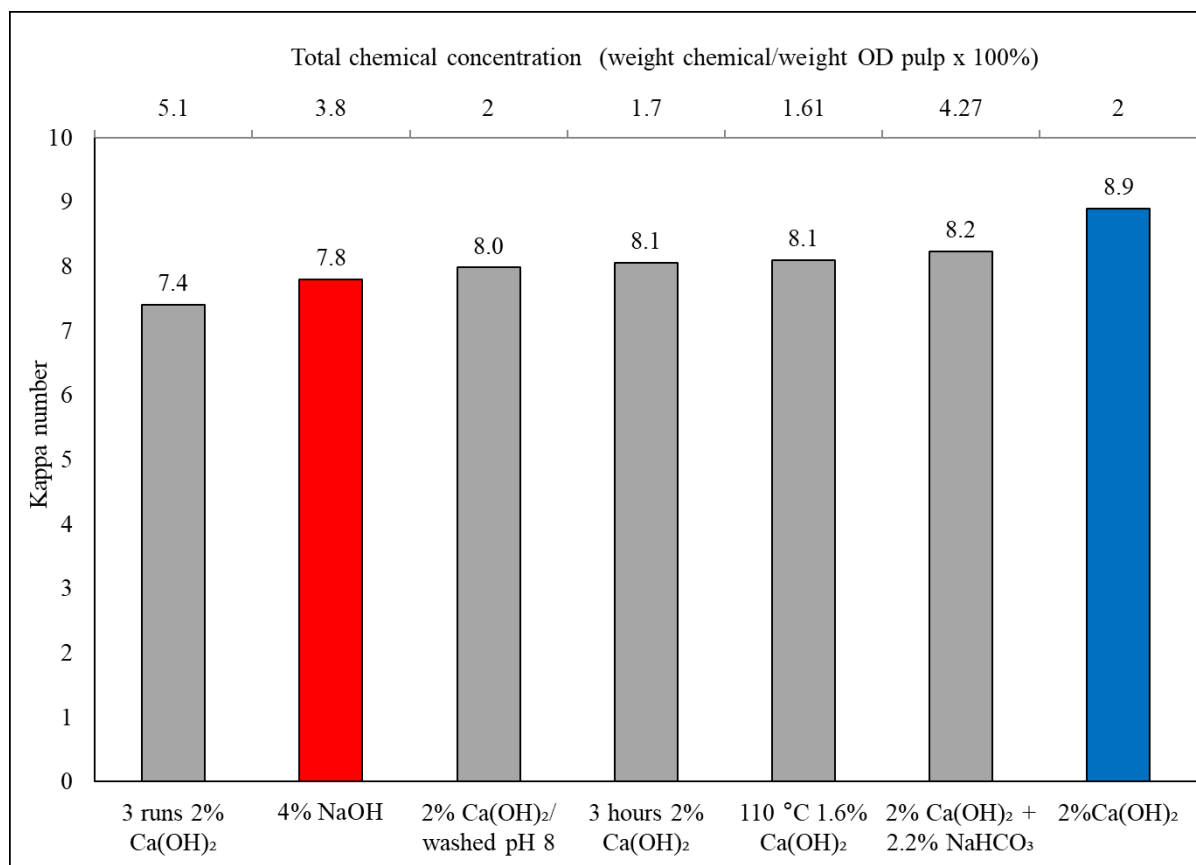


Figure 3. Effect of promising hybrids on Kappa number in O-stage, Quantum reactor (90 °C, 90 PSI, 60 min)

4. Conclusion

In this study, replacement of sodium hydroxide with calcium hydroxide in the oxygen bleaching stage of commercial Kraft pulps was studied. It was observed that calcium hydroxide concentration reached maximum bleaching efficiency at 2% and 3% calcium hydroxide dosage for yellow pine and eucalyptus/pine Kraft pulps, respectively. Beyond this level the bleaching result was negatively impacted.

Increasing bleaching time, bleaching temperature, number of bleaching sequences and sodium hydroxide concentration in combination with calcium hydroxide achieved positive impacts on bleaching efficiency.

5. Recommendations

Further studies of the oxygen bleaching stage should be carried out with the hybrid system alone and with the addition of sodium bicarbonate using Kraft pulp material with a higher initial Kappa numbers. In addition, it is suggested to evaluate the hybrid system using recycled pulp.

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