RESIDUAL ACID EFFECT ON OXYGEN DELIGNIFICATION

Authors*: Rafael dos Santos¹ ²
Gustavo Ventorim ²
José Cláudio Caraschi ²

ABSTRACT
This work has aimed to evaluate the effect of usage of residual acid from the chemical plant of chlorine dioxide production as a flowing part of oxidized white liquor (OWL). Delignification processes were accomplished using as alkali OWL already dosed with residual acid and with NaOH, comparing, thus, the results. Brown stock kraft pulp of eucalyptus industrially produced was used for oxygen delignification accomplishment, being this bleaching stage studied in its particularities according to raw material supplying industry. The oxygen delignification, also named “pre-O2”, consists of executing previously the bleaching sequence an oxidation of lignin through the oxygen, and subsequently proceeding with these oxidized compounds removal by alkaline media, looking for larger improvements of pulp bleaching this way. The oxygen delignification stages were performed in a Regmed laboratorial reactor provided with four electrically heated capsules. Conditions kept constants were: alkali charge (19 kg/adt), consistency (11%), oxygen pressure (5.8 kgf/cm²), retention time (90 min), initial COD stage (8 kg/adt) and MgSO₄ charge (1.5%). The temperature was varied in four different levels (95, 100, 105 and 112°C), and the presence of residual acid in reaction media was also varied. For delignification accomplished at 112°C with NaOH was obtained brightness 62.2%ISO, selectivity 21.7% and delignification efficiency 41.7%. For delignification also at 112°C accomplished with OWL dosed with residual acid was obtained brightness 59.7%ISO, selectivity 20.3% and efficiency 38.6%. The results have evidenced the negative effect of residual acid presence on delignification process, once brightness, selectivity and delignification efficiency were inferior in residual acid presence.

INTRODUCTION
The effluent reuse in factories comes in handy to the increasing and constant market requirements that currently demand, not only a quality product, but a product developed in an ecological and social correct way.

The oxygen delignification is an excellent alternative to the bleaching processes that aim both: decreasing the effluent load destined to the treatment pond (which decreases environmental impacts), as well as getting high quality of the bleached pulp regarding its chemical and physic-mechanical qualities.

The influences of temperature and alkali charge on bleaching are parameters from the process frequently studied in both industry and academic research institutions looking for improvements. There is, though, a blank in researches regarding the residual effluents addiction to the process, intending, this way, propitiating environmental earnings to the whole system.

According to Maia and Colodette (2003), the oxygen delignification is currently one of the best technologies to the bleached pulp production by ECF and TCF processes. The ECF bleaching process has been adjusting very well to oxygen-delignified pulp, evidencing very efficient, however, it’s still possible getting improvements (Ventorim, Eiras, Colodette, 2002).

The oxygen delignification, also named pre-O₂, demonstrates environmental earnings once it possibilities reduction in bleaching reagents usage, decreasing the effluent toxicity and gaseous emissions during bleaching process (Milanez, 1981; Salvador et al., 2001).

The significant increasing in pulp delignification rate with the temperature enlargement can be justified by the increasing in activating energy, because the removal of free phenolic structures condensed as biphenyl is hard, once these structures present low reactivity with oxygen (Argyropoulos and Liu, 2000).

The complexity of the reactions that occur in the pre-O₂ includes a variety of organic compound derived from lignin and carbohydrates, once the alkaline conditions activate the reactions with the pulp where free phenolic hydroxyls groups from lignin are ionized generating, this way, anionic sites full of electrons and vulnerable to the oxygen attack (McDonough, 1996).

Keywords: oxidized white liquor, oxygen delignification.

*Authors references:
1. IFSP – Instituto Federal de Educação, Ciência e Tecnologia de São Paulo. Brazil
2. UNESP – Universidade Estadual Paulista “Júlio de Mesquita Filho”. Brazil

Corresponding author: Rafael dos Santos. UNESP – Universidade Estadual Paulista “Júlio de Mesquita Filho”. Rua Geraldo Alckmin, 519. Itapeva. 18409-010. Brazil. Phone: +55-14-99777-3672. E-mail: rafasantos01@hotmail.com
The alkaline charge sources that can be used during the oxygen delignification are: sodium hydroxide, white liquor partially oxidized and/or white liquor totally oxidized (Ventorim, 2004). According to Gevert and Lohmander (1997), oxidized white liquor has been used as an alkali source in oxygen delignification for years, being the chemical balance of the factory kept once the residual liquor from this bleaching stage is destined to chemical recovery system.

NaOH utilization in kraft pulp factories to the alkali charge composition, either in cooking or in oxygen delignification, is the least, because, besides expensive, its continuous utilization can promote an unbalance on the Na/S relation, resulting in a factory’s sulfidity problem.

An important limiting matter regarding white liquor (NaOH+Na₂S) usage in bleaching stages consist of sodium sulfide (Na₂S) presence, which consumes the main bleaching reagents (including active reagents in the pre-O₂), decreasing the pulp quality and increasing the reagent consumption costs. Additionally, another possible problem starting from the white liquor utilization is the hydrogen sulfite (H₂S) formation in the case of liquor’s pH is lower than 10. For these reasons, sodium sulfide must be oxidized to sodium sulfate before the white liquor can be used as alkali source in the several chemical processes involving pulp bleaching (Parpala et al., 2001).

It has been studied the possibility of inserting residual effluents in bleaching processes regarding to reduce the organic charge destined to the effluents treatment pond. Dioxide chlorine is a chemical reagent widely used in cellulosic pulp bleaching, mainly in Elementary Chlorine Free (ECF) sequences, however, its industrial production can generate, as a subproduct, sodium hydrogen sulfate (NaHSO₄) as a residual effluent.

The sodium hydrogen sulfate (NaHSO₄) – industrially named residual acid – is a high value subproduct in pH adjustments - when acid stages are utilized as part of the bleaching sequence -, once it matches low cost and its utilization in industrial processes decreases the quantity of residual effluents to be treated, besides collaborating to the Na/S relation adjustment (factory’s chemical balance) when added in oxygen delignification, as it can be observed in the scheme showed in Figure 1.

This work aimed to develop the oxygen delignification process studying the possibility of using residual acid (sodium hydrogen sulfate), generated as a subproduct in dioxide chlorine production, as a fluid part of the oxidized white liquor in oxygen delignification, seeking to verify its effects on the productive process of oxygen-delignified pulp.

METHODS

Industrial brown stock pulp

In this work it was used as a raw material Eucalyptus spp. brown stock pulp industrially produced by a pulp and paper company, which supplied this work with pulp, chemical products, as well as information from company’s conditions applied (information that supported this study).

The pulp utilized in this work was collected right after the first alkaline washing stage, and presented the following initial characteristics: kappa number 16.0; brightness 45.5%ISO and viscosity 51.0 cP.

Figure 1. Representative flowchart of the kraft recovery system cycle
Oxidized white liquor and residual acid

For this study accomplishment, it was used a typical pulp factory chemical reagent: oxidized white liquor, industrially named OWL. Specifically for this study, the OWL utilized had, as a particularity, being composed not even by oxidized white liquor (NaOH+Na₂SO₄), but also, in a rate about 10% (in volume), of residual acid.

The residual acid that makes part of the oxidized white liquor is a subproduct from the dioxide chloride production, and for the present study as much raw material as chemical products utilized are from a pulp factory. The industrial dioxide chloride production in the partner company, taken as base for this study, occurs by an adapted chemical plant, which generates as a subproduct sodium hydrogen sulfate (NaHSO₄) instead of sodium sulfate (Na₂SO₄).

The oxidized white liquor used was obtained jointly to an industrial pulp producer of short fiber pulp of eucalyptus, a company that performs its activities in São Paulo central west state, Brazil. The materials were collected and stored in the industry, being later transported to Itapeva (SP), where it had been utilized in UNESP’s Pulp and Paper Laboratory, realization site of the present work.

Oxygen delignification processes

Brown stock pulp was submitted to different oxygen delignification conditions in a way to explore the usage of oxidized white liquor dosed with residual acid and sodium hydroxide, looking for best yield, lower reagent consumption and pulp (after pre-O₂ stage) at kappa number 10±1. The delignification stages were performed in a Regmed laboratorial reactor provided with four electrically heated capsules, with 1.5 liters capacity each one.

Delignification processes were accomplished utilizing 4 different temperature levels (95, 100, 105 and 112°C) and 2 different alkali sources: NaOH and OWL.

Delignification processes were conducted in a way to simulate double-stages (O/O), regarding the industrial condition taken as base of this study this way. Others parameters used in the process are presented in Table 1, which were maintained constant to every bleaching.

**Table 1.** General conditions of oxygen delignification (O/O) applied to the different processes

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp mass per capsule (o.d. g)</td>
<td>100</td>
</tr>
<tr>
<td>Consistency (%)</td>
<td>11</td>
</tr>
<tr>
<td>Retention time (min)</td>
<td>90</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>Variable</td>
</tr>
<tr>
<td>Alkaline charge (kg/adt)</td>
<td>19</td>
</tr>
<tr>
<td>O₂ charge (kg/adt)</td>
<td>19</td>
</tr>
<tr>
<td>O₂ pressure (kgf/cm²)</td>
<td>5.8</td>
</tr>
<tr>
<td>Stage’s initial COD (kg/adt)</td>
<td>8</td>
</tr>
<tr>
<td>Magnesium sulfate (%)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

During oxygen delignification were controlled/observed yield, reject content and residual liquor pH, besides, it had been analyzed kappa number (TAPPI T 236 om-99), brightness (TAPPI T 452 om-98) and viscosity (TAPPI T 230 om-99). It was also analyzed selectivity and efficiency of the process according to the Equations 1 and 2, respectively.

\[ S = \frac{\Delta k}{\Delta v} \times 100 = \frac{k_i - k_f}{v_i - v_f} \times 100 \]  

where:
\[ S \] - selectivity (%);
\[ k_i \] - kappa number before pre-O₂ (brown stock pulp);
\[ k_f \] - kappa number after pre-O₂;
\[ v_i \] - pulp viscosity before pre-O₂ (brown stock pulp);
\[ v_f \] - pulp viscosity after pre-O₂;

\[ \varepsilon = \frac{\Delta k}{k_i} \times 100 = \frac{k_i - k_f}{k_i} \times 100 \]  

where:
\[ \varepsilon \] – delignification efficiency.

Viscosity, brightness and kappa analysis were accomplished twice for each one of the 3 condition replicates.

Degradation and consumption analysis of hydrogen peroxide

The simultaneous behavior of hydrogen peroxide (H₂O₂) generation and degradation during the oxygen delignification stage was indirectly analyzed by pre-O₂ stage simulations through reagents, which make part of the bleaching liquor.

To accomplish these simulations, it has been used titration techniques of residual solution according what Kraft (1967) describes. The oxygen delignification simulation was conducted in a thermostatic bath at temperature 95°C.

Initially, reagents were added (in different Erlenmeyers) in a way that compose the typical oxygen delignification reaction media utilizing NaOH and OWL, which were increased in volume with deionized water regarding an adequate volume to the titration. The erlenmeyers with the solution content were taken to the thermostatic bath and maintained under heating to achieve temperature 95°C. Once the temperature 95°C was reached, 5 mL of a high pure hydrogen peroxide solution (solution of known concentration) were added to every Erlenmeyer, and the reaction time had been initiated.

Once the titration process was accomplished in “ideal” condition (NaOH condition) and in “critical” condition – high residual acid presence in the reaction media – (OWL condition), it was decided to name as hydroxide degradation the curve obtained under “ideal” conditions and, otherwise, it was named as hydrogen peroxide consumption the curve obtained through the “critical” condition simulation.

The residual hydrogen peroxide concentrations were used to establish consumption (“critical” condition) and degradation (“ideal” condition) curves according to the Equation 3.
Peroxide consumption (%) = \frac{\Delta[H_2O_2]}{[H_2O_2]_i} \times 100 = \frac{[H_2O_2]_i - [H_2O_2]_f}{[H_2O_2]_i} \times 100 \quad (3)

where:

- \([H_2O_2]_i\) - Initial hydrogen peroxide concentration (g/L);
- \([H_2O_2]_f\) - Final hydrogen peroxide concentration (g/L).

Statistical analysis

To accomplish the statistical analysis, every oxygen delignification was accomplished with three replicates, where each chemical analysis (kappa number, viscosity and brightness) were done twice for each delignification, once the result dispersion regarding the average was expressed through standard deviation.

It was initially used the Shapiro-Wilk normal test. It was also used the F test from ANOVA 1 Factor (Fixed effects) and the Tukey multiple mean comparison test. To evidence the differences between the treatments it was adopted the letters principle associated to the result means, where means followed by the same letters are not statistically different regarding the significance level. The significance level adopted to every statistical analysis was 5%.

Every data was organized in spreadsheet through the Microsoft Excel software, which was also utilized to the graphic generation. Every statistical analysis was performed through the open statistical software Action, 2.4 version, which was utilized as a supplement to the Microsoft Excel software.

RESULTS AND DISCUSSION

Seeking for evaluating the effects from residual acid presence on the oxygen delignification, it has been studied this reagent application, specifically, by varying the alkaline charge source that was composed with sodium hydroxide and oxidized white liquor (being the OWL dosed with residual acid).

The residual acid utilization is industrially an interesting alternative regarding to reduce the effluent destined to treatment, however, this chemical reagent application on pre-O₂ has negatively affected the stage, which has been conducted at high temperatures in order to keep a certain delignification level, demonstrating the necessity of improving the process this way.

Hydrogen peroxide degradation and consumption analysis on pre-O₂ stage

Essentially characterized as sodium hydrogen sulfate (NaHSO₄), it has been tried to understand the effect of the residual acid originated from the dioxide chlorine production on oxygen bleaching. Observing this objective, it has been performed a \(H_2O_2\) consumption/degradation analysis in a way to simulate the residual acid action on oxygen delignification processes.

Figure 2 shows the results of hydrogen peroxide consumption simulating extreme reaction media that may have according to the processes: aqueous media and ions charged media (according to described on methods).

Aqueous media represented by the exponential curve simulates an ideal situation of delignification. In this situation the alkaline charge is provided rightly according to oxygen delignification particularities, and the reaction media is free of impurities (solution in deionized water).

Ions charged media (represented by logarithmic curve), on the other hand, is a simulation according to the aqueous media simulation before described, however, the ions presence has been provided by neutralized residual acid to compose the solution (instead of deionized water).

Based on \(H_2O_2\) consumption analysis, it can be seen that accentuated residual acid presence promotes a high and fast hydrogen peroxide degradation that is generated during the oxygen stage.

![Figure 2. Hydrogen peroxide behavior according to the reaction media along time (95°C)](image-url)
Hydrogen peroxide degradation generates ions as hydroxyl, perhydroxyl and superoxide that indistinctly attack the pulp (Bouchard, Wang and Berry, 2011; Brasileiro, Colodette and Piló-Veloso, 2001; McDonough, 1996). One of the phenomena that occur starting from H₂O₂ decomposition is the ions attack (ions generated from hydrogen peroxide) on carbohydrates, justifying possible viscosity loss this way. However, results obtained in this work demonstrate that residual acid quantities added were not enough to promote viscosity loss in a pronounced way (Figure 3).

Other phenomenon that can happen by the hydrogen peroxide decomposition consists of the ions generated from this degradation also attack the lignin. This effect can be observed through efficiency improvements (Figure 4), where, through these reactions, it can be increased the lignin removal even with impurities in reaction media.

When simultaneously considering the effects caused on lignin and carbohydrates, the presence of residual acid from dioxide chlorine chemical plant can promote stability in selectivity analysis. Once selectivity is a quotient between kappa number (which is an indirect measure of pulp’s lignin content) and viscosity (indirect measure of carbohydrates’ degree polymerization) according to Equation 1, it could be expected that the reactions propitiated from hydrogen peroxide degradation could answer as a little alteration on process selectivity (what in fact had been observed along this work – Figure 4) in function of these reactions juxtaposition effects, which simultaneously attack lignin and carbohydrates.

Analyzing Figure 2 regarding pulp brightness effect, it can be expected that smaller brightness values would be reached once the residual acid were applied in the oxygen delignification, because the most hydrogen peroxide consumption during this stage, the least amount of this strong bleaching agent will react directly on the pulp (fact that was also observed along this study – Figure 5).

CONCLUSIONS

Through oxygen delignification stage simulation in aqueous mean and enriched of ions originated from the residual acid mean, it can be concluded that during this process under high ions concentration conditions, there is a very fast hydrogen peroxide degradation in the stage;

In spite of negative effect has been evidenced on delignification process, residual acid usage in factories’ bleaching processes is an interesting alternative, mainly to reduce the effluent destined to the treatment.

Seeking for chemical balance control, residual acid insertion in the weak black liquor prior to sending the black liquor to the evaporators is a way to increase the factory’s sulfidity due to the effluent destination to the chemical recovery system without impacting the oxygen delignification stage.

According to the overall results, it can also be concluded that the temperature has a higher influence on oxygen delignification results than the amount of residual acid originated from the chemical plant of dioxide chlorine production.
REFERENCES


