Tertiary Amines in Catalytic Pulp Bleaching

Ghazaleh Afsahi
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Aalto University
School of Chemical Engineering
Bioproducts and Biosystems
Wood Chemistry
Supervising professor
Professor Tapani Vuorinen, Aalto University, Finland

Thesis advisor
Professor Tapani Vuorinen, Aalto University, Finland

Preliminary examiners
1- Professor. M. Lachenal Dominique, Grenoble Institute of Technology, France.
2- Professor Raimo Alén, University of Jyväskylä, Finland.

Opponent
Professor Gerard M. Mortha, Grenoble Institute of Technology, France.
Abstract

The motif of the current study arises from the importance of the paper in Finland as one of the core industries. The latest released statistics reported by the Confederation of European Paper Industries (CEPI) confirms that Finland, by producing 28.5% of pulp production, possesses the second rank in terms of the production of pulp among all members of the CEPI. Pulp bleaching as one of the subcategories of the tremendous paper industries aim at producing high quality paper with three fundamental goals. Environmental concerns prompted this industry to opt the Elemental Chlorine Free (ECF) and the Totally Chlorine Free (TCF) bleaching processes, which alleviate the concerns about the release of organochlorine compounds. Nowadays, the ECF with chlorine dioxide is the dominant technology worldwide. Consequently, in this thesis we present a couple of catalysts which introduce a significant reduction in the retention time and chemical consumption of the ECF bleaching processes.

In modern ECF hardwood pulp mills the bleaching sequences (A/D-E_{op}P-D-P or D/A-E_{op}P-D-P) initiate with a long, hot acidic stage which a primary target is to remove most of hexenuronic acid in the pulp. After discovering a catalyst, triethylenediamine that is both an industrially used and stable enough chemical, catalytic bleaching (H_{cat}), utilizing hypochlorite (H), triethylenediamine (DABCO) and its derivative N-carboxymethyltriethylenediamine (CM-DABCO), has the potential to improve the chemical and energetic efficiency of bleaching processes in chemical pulp mills, e.g., through reducing the reaction time of the bleaching processes. Indeed, this thesis studied to clarify if new kraft pulp bleaching sequences with not only H_{cat} as the first stage (H_{cat}ZP and H_{cat}Z/DP) but also as an initial stage of chlorine dioxide (D) and an intermediate stage of H_{cat} (D_{0}EH_{cat}P) could provide fully bleached pulps.

The bleaching sequences of the studied eucalyptus pulps include H_{cat}ZP, H_{cat}Z/DP and D_{0}EH_{cat}P which attained a final brightness of 88, 89, and 88% ISO, respectively. In this thesis, it was shown that the H_{cat}ZP bleached pulps had low carbonyl group content. Interestingly it was shown that cellulose is not damaged at all in the ozone stage that typically depolymerizes cellulose. In the last part of the thesis, the efficiency and stability of the applied catalysts were studied which made the CM-DABCO as the supreme catalyst. Thus, it can already be claimed that production of almost fully bleached pulp with an exceptionally efficient system is feasible.

Softwood pulp bleaching technology has not undertaken major developments in comparison with hardwood pulp bleaching during the last generation. The reason is the content of hexenuronic acid in softwood pulps is relatively low which makes the use of the long, hot acid treatment uneconomic. The catalytic bleaching offers here a solution which extracts hexenuronic acid fast without depolymerizing cellulose.

Keywords Pulp bleaching, Tertiary amines, Kinetic model, Hexenuronic acid, Lignin, Brightness reversion, Chemometry.
Acknowledgements

This study was carried out under the supervision of Professor Tapani Vuorinen, taken place at the Department of Bioproducts and Biosystems (Bio2), Aalto University School of Chemical Engineering. Kemira, Andritz, Stora Enso, UPM, and Metsä fiber mainly funded this work, as a major part of my PhD studies, for the whole duration of my PhD studies and by TEKES for the first year.

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The last but not least is my husband and also my closest and best friend whose presence is the air I breathe. I would like to thank you, Mohammad, for being unconditionally supportive and patient during my studies. Whenever, my experiments were failing or any kind of disappointments were happening in my studies, you always were listening to my nagging and soothing me. I would like to say, I just love you.

At the end, I like to thank my son, Mehrad, who was giving me energy while I was revising my manuscripts and dissertation by his beautiful smiles. I am so happy for having him.

Espoo, 21 April 2019
Ghazaleh Afsahi
Contents

Acknowledgements ................................................................................... 1
List of Abbreviations and symbols .......................................................... 5
List of publications .................................................................................. 7
Author’s contribution .............................................................................. 8
1. Introduction .................................................................................. 9
2. Background .................................................................................. 11
   2.1 Principles of bleaching ............................................................. 11
   2.2 Chemical pulp bleaching sequences ........................................ 11
      2.2.1 Oxygen delignification ....................................................... 12
      2.2.2 Catalytic bleaching (H_{cat}) ............................................ 13
      2.2.3 Hypochlorite bleaching ..................................................... 15
      2.2.4 Chlorine dioxide bleaching (D) ....................................... 15
      2.2.5 Ozone bleaching (Z) ......................................................... 17
      2.2.6 Alkali extraction (E or EOP) ........................................... 18
      2.2.7 Peroxide bleaching (P) ...................................................... 18
   2.3 Brightness stability .................................................................. 19
   2.4 Catalyst stability ...................................................................... 20
3. Materials and methods ............................................................... 22
   3.1 Raw materials ......................................................................... 22
   3.2 Pulp bleaching experiments .................................................... 23
   3.3 Pulp analyses .......................................................................... 24
      3.3.1 UV resonance raman Spectroscopy ................................ 24
      3.3.2 Kappa number .................................................................. 24
      3.3.3 Viscosity .......................................................................... 24
      3.3.4 Production of sheets ........................................................ 25
      3.3.5 Brightness ...................................................................... 25
      3.3.6 Carbonyl group content and molar mass distribution ...... 25
      3.3.7 Organically bound chlorine in pulp (OX) ......................... 25
      3.3.8 Brightness reversion test ................................................ 25
3.3.9 Time-gated Raman spectroscopy.................................26
3.4 Stability of catalyst ........................................................26
3.4.1 Kinetic measurements .................................................26
3.4.2 Chemometric modelling and computational aspects ....26
4. Results and discussion ......................................................28
  4.1 Bleaching studies............................................................28
    4.1.1 Intensified and short catalytic bleaching of eucalyptus Kraft pulp (paper 1) .................................................................28
  4.2 Analyses of bleached pulp from short catalytic investigation 30
    4.2.1 Wet chemical analyses (Paper 2).................................30
  4.3 Modification of catalytic bleaching studies .....................32
    4.3.1 Optimized catalytic bleaching sequences (Paper 3) ....32
  4.4 Analyses of two tertiary amine catalysts .......................34
    4.4.1 Reactivity and stability of tertiary amine catalysts (Paper 4)34
5. Conclusions ......................................................................37
# List of abbreviations and symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Acid extraction</td>
</tr>
<tr>
<td>Act.Cl</td>
<td>Active chlorine</td>
</tr>
<tr>
<td>AOX</td>
<td>Adsorbable organic halogen</td>
</tr>
<tr>
<td>CCOA</td>
<td>Carbazole-9-carboxylic acid 2-(2-aminoethoxy) etoxy amide</td>
</tr>
<tr>
<td>CM-DABCO</td>
<td>N-Carboxymethyl-1,4-diazabicyclo[2.2.2]octane</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal-oxide semiconductor</td>
</tr>
<tr>
<td>D</td>
<td>Chlorine dioxide stage</td>
</tr>
<tr>
<td>D₀</td>
<td>Chlorine dioxide prebleaching</td>
</tr>
<tr>
<td>D₁</td>
<td>Chlorine dioxide bleaching</td>
</tr>
<tr>
<td>D_{cat}</td>
<td>Catalytic bleaching with added chlorine dioxide</td>
</tr>
<tr>
<td>DABCO</td>
<td>1,4-Diazabicyclo[2.2.2]octane</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>E</td>
<td>Alkali extraction</td>
</tr>
<tr>
<td>ECF</td>
<td>Elemental chlorine free</td>
</tr>
<tr>
<td>E_{OP}</td>
<td>Peroxide and oxygen reinforced alkali extraction</td>
</tr>
<tr>
<td>gpc</td>
<td>Gel permeation chromatograph</td>
</tr>
<tr>
<td>H</td>
<td>Hypochlorite</td>
</tr>
<tr>
<td>H_{cat}</td>
<td>Catalytic hypochlorous acid bleaching</td>
</tr>
<tr>
<td>HexA</td>
<td>Hexenuronic acid</td>
</tr>
<tr>
<td>HMF</td>
<td>5-hydroxymethyl-2-furaldehyde</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>κ</td>
<td>Kappa number</td>
</tr>
<tr>
<td>MALLS</td>
<td>Multiple-angel laser light scattering</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>MC</td>
<td>Medium consistency</td>
</tr>
<tr>
<td>MCR-ALS</td>
<td>Multivariate curve resolution–Alternating least squares</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>$n$</td>
<td>Molarity</td>
</tr>
<tr>
<td>OD</td>
<td>Oxygen delignification</td>
</tr>
<tr>
<td>ODT</td>
<td>Oven dry ton</td>
</tr>
<tr>
<td>OX</td>
<td>Organic halogen bound to fibers</td>
</tr>
<tr>
<td>P</td>
<td>Hydrogen peroxide bleaching stage</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal component analysis</td>
</tr>
<tr>
<td>PCN</td>
<td>Post color number</td>
</tr>
<tr>
<td>R.H.</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SFM</td>
<td>Stopped flow mixer</td>
</tr>
<tr>
<td>SFS</td>
<td>Stopped flow spectrometry</td>
</tr>
<tr>
<td>SPAD</td>
<td>Single-photon avalanche diode</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TCF</td>
<td>Total chlorine free</td>
</tr>
<tr>
<td>UK</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>UVRR</td>
<td>Ultraviolet resonance Raman</td>
</tr>
<tr>
<td>VWR</td>
<td>Van Waters &amp; Rogers chemical company</td>
</tr>
<tr>
<td>$v$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>Z</td>
<td>Ozone bleaching stage</td>
</tr>
</tbody>
</table>
List of publications

This doctoral dissertation consists of the following publications which are referred to in the text by their numerals

1. Afsahi, Ghazaleh; Chenna, Naveen Kumar; Vuorinen, Tapani. 2015. Intensified and short catalytic bleaching of eucalyptus kraft Pulp. Published in Industrial and Engineering Chemistry Research, 54, 8417-8421. DOI: 10.1021/acs.iecr.5b01725.

2. Afsahi, Ghazaleh; Rojalin, Tatu; Vuorinen, Tapani. Chemical characteristics and stability of eucalyptus kraft pulps bleached with tertiary amine catalyzed hypochlorous acid. Published in Cellulose in the year 2019. DOI: 10.1007/s10570-018-2172-x.


Author’s contribution

**Publication 1:** Intensified and short catalytic bleaching of eucalyptus kraft pulp.

Prof. Tapani Vuorinen initiated the concept of catalytic bleaching studies. Ghazaleh Afsahi designed, did the experiments, analysed the results and wrote the manuscript under supervision of Prof. Tapani Vuorinen. Neveen Kumar Chenna assisted during the experiments.

**Publication 2:** Chemical characteristics and stability of eucalyptus kraft pulps bleached with tertiary amine catalyzed hypochlorous acid.

Ghazaleh Afsahi designed the experiments, did part of them including preparing the samples for the whole characterization, did the brightness reversion measurements and OX. The carbonyl group content measurement of the experiments was conducted in Boku University. Dr. Tatu Rojalin did the Raman spectroscopy in Helsinki University. Ghazaleh Afsahi analyzed the results and wrote the manuscript under supervision of Prof. Tapani Vuorinen.

**Publication 3:** Optimized catalytic bleaching sequences for eucalyptus kraft pulp.

Prof. Tapani Vuorinen and Ghazaleh Afsahi initiated the concept of optimizing the bleaching sequences. Ghazaleh Afsahi designed the experiment, supervised the whole process, analysed the results and wrote the manuscript under supervision of Prof. Tapani Vuorinen. Estefania Isaza Ferro did the experiments as a part of her master studies. Dr. Kyösti Ruuttunen revised the manuscript.

**Publication 4:** Catalytic efficiency and stability of tertiary amines in oxidation of methyl 4-deoxy-β-L-threo-hex-4-enopyranosiduronic acid by hypochlorous acid.

Prof. Tapani Vuorinen initiated the concept of studying the stability and reactivity of different tertiary amine catalyst. Ghazaleh Afsahi designed and did the experiments. Dr. Carlo Bertinetto did the fitting part. Dr. Michael Hummel assisted with synthesizing one of the catalysts. Dr. Kavindra Kumar Kesari revised the manuscript. Ghazaleh Afsahi analyzed and wrote the manuscript under supervision of Prof. Tapani Vuorinen.
1. Introduction

Separating cellulosic fibers from wood or non-wood lignocellulose biomass is the object of chemical pulping processes. There are plenty of routes to convert wood into pulp suitable for paper production. The most popular one consists of three consecutive processes: kraft cooking of wood chips, oxygen delignification of the brown stock and bleaching of the pulp. During the cooking process, ca. 90% of the lignin present in the original wood is removed. This removal is conducted by applying so-called white liquor, an aqueous solution of sodium hydroxide and sodium hydrogen sulfide, at elevated temperatures from 130°C up to 170°C (Sixta 2006).

The cooking process consists of three phases, the initial, bulk, and residual delignification parts. During the initial cooking the phenolic lignin units degrade while the hemicelluloses undergo deacetylation and degradation from their reducing ends. In the bulk phase also the non-phenolic lignin units react and hexeneuronic acid (HexA) groups are formed via demethylation of the native 4-O-methylglucuronic acid groups attached to the wood xylan backbone. Pulping temperature and the alkali profile influence the residual lignin and HexA contents (Li and Ragauskas 2000; Sevastyanova 2005). In the residual phase delignification is slow while cellulose and the hemicelluloses continue to degrade by the action of alkali. Therefore, the process is ceased before entering the last phase (Chai et al. 2001). During the kraft process lignin-derived chromophores, which generate the brown color of pulp are formed (Teleman et al. 1995). Although HexA is colorless, it may enhance yellowing of bleached pulp with storage time (Rosenau et al. 2007; Sousa et al. 2014).

In the next step, oxygen is mixed with the brown pulp of the kraft cooking stage, in order to remove half of the residual lignin while maintaining high pulp yield, and minimizing the quantity of bleaching chemicals required in the bleaching process (Sousa et al. 2014).

Currently there are two types of bleaching sequences in use. The first and dominant group consists of elemental chlorine free (ECF) sequences where chlorine dioxide is the main oxidant (Sousa et al. 2014). However, chlorine dioxide is typically accompanied by some oxygen-based chemicals. On the other hand, totally chlorine free (TCF) sequences utilize oxygen-based chemicals only. The goal of the chemical multistage bleaching process, either ECF or TCF, is to increase the brightness or visible light reflectance of the pulp, mainly by eliminating the chromophores by oxidation (Sousa et al. 2014). Alternating acidic and alkaline stages enable achieving full brightness without loss of fiber
strength in a process that is cost effective and has a low environmental impact (Lindström and Österberg 1986). Both ECF and TCF bleaching processes involve three to five stages while the overall duration varies between four and eight hours. Moreover, each stage requires a large reactor or bleaching tower that can be several meters in diameter (Sixta 2006). As a result, operating this type of equipment for several hours at temperatures from 50°C to 90°C demands high energy input (Lapierre et al. 2000).

TCF bleaching technology was developed with the specific target to reduce the release of toxic chlorinated compounds in the environment (Reinstaller 2005). However, the pulp industry has not really shifted from ECF to TCF bleaching technology, because the ECF and TCF bleaching processes have been shown to produce effluents with similar toxicity (Tarkpea et al. 1999). Other factors, such as pulp quality, bleaching costs, and energy consumption may favor ECF bleaching over TCF bleaching. As a result, ECF continues to be the dominant bleaching technology with a worldwide share of >90% of all bleached chemical pulp production (Sixta 2006). Taking into account the reported global annual production of 407 million tons of paper in 2015 (Santos et al. 2016a), further technological improvements in the ECF bleaching processes could provide major positive environmental and economic impact.

An interesting approach for developing ECF bleaching further is to apply catalytic bleaching with added (H$_{\text{cat}}$) or in situ formed (D$_{\text{cat}}$) hypochlorous acid (Chenna et al. 2013). This novel alternative is currently under development and aims at intensifying the bleaching and decreasing the use of energy and chemicals. H$_{\text{cat}}$ uses a tertiary amine, such as triethyldiamine or 1,4-diazabicyclo[2.2.2]octane (DABCO), as the catalyst and hypochlorous acid as the bulk oxidant for degradation of HexA and lignin.

This thesis starts with a brief introduction into the principles of bleaching. After that, chemical bleaching sequences and individual bleaching stages will be described in detail. Meanwhile, the importance of chlorammonium cations and their reactivity with unsaturated structures will be presented.

The aim of the dissertation was to create understanding of the chemical basis of tertiary amine catalyzed hypochlorous acid pulp bleaching and how this catalytic stage could help to revolutionize the present pulp bleaching practices. The thesis compared several alternative sequences that contain of a catalytic stage with normal ECF bleaching in respect of chemical consumption and pulp characteristics. Special attention was paid on developing a catalyst that was simultaneously stable and highly reactive in the presence of hypochlorous acid. In addition to laboratory bleaching trials, stopped flow spectrophotometry (SFS) was applied to study the self-decomposition and oxidation reactions of the chlorammonium cations. The thesis ended with conclusions describing the overall work and the advantages of the developed catalytic bleaching concept and the advantage of applying short catalytic pulp bleaching.
2. Background

2.1 Principles of bleaching

The bleaching process can be split into two parts on an industrial scale: pre-bleaching and final bleaching. In prebleaching lignin is mainly removed with a relatively large chemical dosage. Indeed, the brightness still remains quite low at this stage. The aim of final bleaching is to raise the brightness to 88 – 94% ISO and to remove the impurities of the pulp (Suhr et al. 2015). Thus, shives, dirt particles, extractives, and other undesired components are removed in addition to the residual lignin and HexA (Sixta 2006). The most used bleaching chemicals are sulfuric acid, chlorine dioxide, sodium hydroxide, hydrogen peroxide, ozone, oxygen, and peracetic acid. Bleaching is carried out in towers in mill processes and the pulp is washed between the stages. A final screening is needed to remove the rest of the impurities before the pulp goes to the drying machine (Kringstad and Lindström 1984).

To reduce chlorine dioxide consumption in the bleaching stages and the amount of sulfur components in the bleaching filtrates is the target of bleaching development (Alajoutsijärvi 2014).

2.2 Chemical pulp bleaching sequences

Pulp bleaching is a process that has paved the improvement path for many years (Bajpai 2012). The first industrial pulp bleaching process consisted of one or two hypochlorite (H) stages at 3% consistency, which caused extensive damage to the fibers. In addition, it generated effluents with high amounts of halogenated compounds (Pouyet et al. 2014). Consequently, bleaching led to both environmental and health problems (Ferro 2017). As a solution to these problems, multistage bleaching with various chemicals, including oxygen delignification (O), chlorine dioxide stage (D), alkali extraction stage (E), acid extraction stage (A), peroxide stage (P) and ozone stage (Z) appeared during the 20th century.

Currently a wide range of industrial bleaching sequences is used depending on the type and quality of the incoming pulp or brown stock. Two of the main characteristics for choosing the sequences is the wood source and incoming kappa number. The kappa number range of softwood pulps entering the bleaching process is 15-30 corresponding to 2-4% lignin content, while hardwood pulps have a lower kappa number in the range of 10-20 with a lignin content of 1-2% (Sixta et al. 2013). Three or four stages of bleaching are used on oxygen delignified
hardwood pulps; however, four or more stages are used for bleaching of softwood pulps (Fiskari 2002; Granholm et al. 2010)

2.2.1 Oxygen delignification

Oxygen delignification is a chemical process for removing lignin from unbleached pulp by oxygen pressure in alkaline conditions (Sixta et al. 2013). Oxygen is a strong reagent that removes 30% to 50% lignin from the brown stock (Heitner et al. 2010).

Oxygen delignification are benefits economically and environmentaly. From an economical point of view, reagents, such as caustic soda (NaOH), oxidized white liquor, and the oxygen applied in oxygen delignification are low-priced. Indeed, the recovery cycle in kraft pulping produces NaOH (Sixta et al. 2013). The brown stock is washed by the oxygen delignification filtrate to reduce the amount of effluents from the pulp mill. Furthermore, these filtrates are combusted producing energy in the recovery boiler. Consequently, the biological water treatment plant and the environment are shielded from potential pollutants from the oxygen delignification stage (Mcdonough 1989). Additionally, the utilization of other bleaching reagents such as chlorine dioxide, hydrogen peroxide or ozone will be diminished. In the sphere, the oxygen stage generates a lower environmental impact (Akim et al. 2001).

Oxygen delignification is highly selective toward lignin removal at the end of the kraft cooking process. Consequently, a higher yield on wood is generated compared with extended cooking to lower kappa number (Chakar et al. 2000).

Molecular oxygen, O₂, is a mild oxidant with a high electronegativity and a tendency for accepting electrons. It has three possible electron configurations, a triplet stage and two singlet states (Figure 1). The most common and stable type of oxygen is the triplet configuration with two parallel spin electrons at \( \pi^* \) orbital. Therefore, oxygen is a free radical with capability of reacting with high electron density chemical structures. In the end, stable radicals arise through one-electron abstraction (Heitner et al. 2010).

\[
\begin{align*}
\pi^* & \quad \text{triplet state} \\
{^3\Sigma_g^-} & \\
\uparrow \downarrow & \\
\text{singlet state} & \\
{^1\Delta_g} & \\
\downarrow \uparrow & \\
\text{singlet state} & \\
{^1\Sigma^+_g} &
\end{align*}
\]

**Figure 1.** Electron spin states of oxygen in the \( \pi^* \) orbital (Suess, 2010).

Oxygen oxidizes organic substances and converts into water in four subsequent one electron transfer steps (Figure 2). The first step in the oxygen reduction process yields superoxide ion radical (OO⁻). This negative ion is in an equilibrium with the hydroperoxy radical (HOO⁻). These radicals have higher oxidation potential than oxygen itself. Therefore, they can gain another electron to generate peroxide dianion (O₂⁻²) and hydroperoxide anion (HOO⁻), respectively. These anions then exist in equilibrium with hydrogen peroxide. In a third step,
hydrogen peroxide accepts an electron to form hydroxide anion (HO⁻) and a hydroxyl radical (HO•). At last, hydroxyl radical obtains another electron and transforms into water or hydroxide ion (Suess 2010).

\[
\begin{align*}
O_2 + e^- + H^+ & \rightarrow OO^- + H^+
\end{align*}
\]

\[
\begin{align*}
OO^- + e^- + H^+ & \rightarrow HOO^-
\end{align*}
\]

\[
\begin{align*}
HOO^- + e^- + H^+ & \rightarrow HOOH \rightarrow O^- + H^+
\end{align*}
\]

\[
\begin{align*}
HOOH + e^- + H^+ & \rightarrow HOH + HO^-
\end{align*}
\]

\[
\begin{align*}
HOH + HO^- + e^- + H^+ & \rightarrow 2H_2O
\end{align*}
\]

**Figure 2.** Four-step oxygen reduction into water. Modified after (Suess, 2010).

Oxygen delignification has been claimed to split into three steps consisting of initiation, propagation, and termination reactions (Figure 3). Increasing the temperature or providing reactive substrates is essential to initiate the oxidation. One way to activate the substrate is alkaline conditions where free phenolic groups are ionized, resulting in anionic sites with high electron density (Heitner et al. 2010).

**Initiation**

\[
\begin{align*}
RO^- + O_2 & \rightarrow RO^+ + O_2^-
\end{align*}
\]

\[
\begin{align*}
RH + O_2 & \rightarrow R^+ + HOO^-
\end{align*}
\]

**Propagation**

\[
\begin{align*}
R^- + O_2 & \rightarrow RO_2
\end{align*}
\]

\[
\begin{align*}
RO_2 + RH & \rightarrow RO_2H + R^+
\end{align*}
\]

**Termination**

\[
\begin{align*}
RO^- + R^- & \rightarrow ROR
\end{align*}
\]

**Figure 3.** Main reactions during oxygen delignification, where R can be lignin or polysaccharides. (Heitner et al. 2010).

During oxygen delignification both random cleavage of carbohydrates and subsequent end-wise degradation may occur. The most common one is random oxidation in the unbleached pulp, leading to cellulose scission (Johansson and Ljunggren 1994; Gierer 1997; Suess 2010). Therefore, it is better to remove only half of the incoming lignin with oxygen to save the yield and properties of the pulp. The rest of the delignification may be continued in the subsequent bleaching stages with less destructive and more selective reagents (McDonough 1989; Heitner et al. 2010).

**2.2.2 Catalytic bleaching (H\textsubscript{cat})**

This section summarizes the main known features of the novel catalytic bleaching stage, H\textsubscript{cat}. H\textsubscript{cat} uses a tertiary amine as a catalyst with hypochlorous acid (HOCl) as a reagent. This technology is currently under development, and hence, there is limited literature available on it.
Previous investigations (Prütz 1998; Brogdon 2009; Waschulin 2016) on chlorine dioxide (ClO₂) bleaching show that the reagent attacks phenolic lignin producing HOCl, which then reacts rapidly with HexA and non-phenolic lignin. Accordingly, the \textit{in situ} formed HOCl is essential for pulp bleaching. The reactivity of HOCl is augmented with a tertiary amine \(R_3N\), such as 1,4-diazabicyclo[2.2.2]octane known as DABCO. It reacts with HOCl producing a chloroammonium cation \(R_3N^+\text{Cl}\). This cation is a stronger nucleophile than HOCl. Indeed, a higher reduction in kappa number happens when using HOCl and DABCO than with only HOCl (Chenna et al. 2013).

![Figure 4. Structure of 1,4-diazabicyclo[2.2.2]octane (DABCO).](image)

A small charge of DABCO in the presence of NaOCl/HOCl at room temperature when bleaching oxygen delignified eucalyptus kraft pulp decreases the kappa number by half in less than ten minutes (Chenna et al. 2013). The kappa number reduction happens mainly by oxidation of HexA, whereas part of the residual lignin is degraded too. Figure 5 presents the advocated scheme for lignin and HexA degradation in the \(H_{\text{cat}}\) stage.

![Figure 5. HexA and lignin oxidation route in \(H_{\text{cat}}\) stage. Modified from (Chenna, et al. 2013).](image)

This stage can also be considered as a substitute of the acid hydrolysis stage (A). The catalytic system degrades both HexA and lignin that is unreactive in the A stage. Although the \(H_{\text{cat}}\) stage consumes chemicals, it does not require high temperature and long reaction time that are typical for the A stage to obtain similar HexA degradation.

The main operational parameters for \(H_{\text{cat}}\) bleaching are pH, time, catalyst dosage, and active chlorine charge. High lignin and HexA degradation happens in a wide range of pH in the \(H_{\text{cat}}\) stage. However, results show that the greatest kappa reduction and the lowest Adsorbable Organic Halogen (AOX) generation occurs at an initial pH of 4 to 5. More than 50% of HexA and lignin degradation takes place in the first from minutes of the reaction. Chloroform forms with prolongation of the time without any further beneficial effect on HexA removal. The catalyst dosage is another important factor for an efficient HexA and lignin degradation. Since a higher charge of catalyst could decrease the efficiency of the
process, the proposed and consequently verified concentration of DABCO is below 0.1%. The verified active chlorine charge is 1% (Chenna et al. 2016).

2.2.3 Hypochlorite bleaching

Hypochlorite as a bleaching reagent for cloth and wood pulp has been applied since its discovery in 1789 (Daneault et al. 1983; Lindström and Österberg 1986; Bajpai 1999; Adorjan et al. 2006). Hypochlorite was added to circulating pulp in order to obtain desired brightness in a single stage (H stage) (Czepiel 1959). The commercial usage of a chlorination stage during the 1930’s in multistage bleaching sequences led to lower demand for hypochlorite as the sole bleaching reagent (Colodette et al. 2002). Therefore, multistage pulp bleaching sequences of hypochlorite, chlorine, and chlorine dioxide, such as CEH, CEHEH, CEHD, etc., were popular in order to produce a pulp with high brightness (ca. 88% ISO).

The hypochlorite (H) stage was normally operated at 9-14% consistency. One important parameter in the H stage bleaching was the required charge of active chlorine (Bajpai 2012). Conventionally, 1-5% active chlorine on pulp was applied during only the H stage, however, the total active chlorine usage exceeded 8% in many cases (Carr et al. 1996). The H stage was performed as short as 8 min at 80 °C or as long as 90 min at the more conventional 35 °C (Czepiel 1959). The initial and final pH of the reaction system were other important parameters to control cellulose degradation (Johansson and Ljunggren 1994; Parthasarathy and Colodette 2003; Lehtimaa et al. 2010a).

Hypochlorite was the major bleaching oxidant for generations (Rook 1977). However, toxic polychlorinated dioxins in river waters were discovered that were linked to the H and C stage bleaching processes (Suess 2010; Wang et al. 2012). As a solution, the D stage replaced the C and H stages as the main bleaching stage in pulp bleaching lines.

2.2.4 Chlorine dioxide bleaching (D)

Chlorine dioxide as a bleaching oxidant received commercial recognition starting from 1946 (Kolar et al. 1983). However, until the 1980’s chlorine dioxide was not used extensively for delignification but was mainly used as a brightening agent in the final stages of bleaching. The advantage of using chlorine dioxide was to enable production of high brightness kraft pulp without yield loss. However, it was much more expensive than chlorine/hypochlorite. Indeed, it was environmental concerns that led the industry to diminish elemental chlorine usage and adopt its substantial and later complete, replacement with chlorine dioxide (Tarvo et al. 2010).

Currently, chlorine dioxide (ClO$_2$) is one of the main delignification and bleaching chemicals, which can be introduced at the beginning or in the middle of the bleaching sequence. ClO$_2$ performs as a delignification agent if applied right after cooking or oxygen delignification; that stage is called D$_0$. On the other hand, if ClO$_2$ is introduced after an alkali extraction or other bleaching stages, it operates as a brightening agent. The stage is named D$_1$ or D$_2$, according to the number of chlorine dioxide stages applied in the final bleaching (Sixta et al.
Chlorine dioxide degrades lignin selectively. Besides, it has low impact on polysaccharides and low emissions of AOX compared to chlorine bleaching (Nie et al. 2015).

Chlorine dioxide is a radical with one electron vacant space in the outer orbital (Figure 6) (Suess 2010).

![Resonance structures of chlorine dioxide](image)

Figure 6. Resonance structures of chlorine dioxide (Suess 2010).

Unfortunately, undesired reactions such as formation of quinones, which are considered as chromophores and are insoluble in water, also take place during bleaching with ClO₂. (Ferro 2017)(Figure 7).

![Effect of chlorine dioxide on phenolic structures](image)

Figure 7. Effect of chlorine dioxide on phenolic structures (Tarvo et al. 2009; Ferro 2017).
In general, both two molecules of ClO$_2$ in the reaction with free phenolic lignin produce a HOCl molecule. However, HOCl, or its equilibrium form, Cl$_2$, reacts fast with lignin, it generates AOX (Tarvo et al. 2009).

Delignification in the chlorine dioxide stage is fast. HOCl and Cl$_2$ react with lignin and HexA and most of the AOX is formed in the first five minutes of the reaction (Lehtimaa et al. 2010b). Moreover, low pH has shown to enhance formation of AOX and OX (Lehtimaa 2010b; Tarvo et al. 2010). It is known that a fraction of the AOX is formed from HexA; hence, removing HexA prior to D$_0$ stage will lead to lower AOX formation as well as a decrease the oxidant consumption (Freire et al. 2003; Lehtimaa et al. 2010).

Chlorine dioxide does not react with cellulose at acidic pH, whereas HOCl and Cl$_2$ can react with the xylan-bound HexA (Figure 8). The importance of HexA removal is especially critical for bleaching hardwood pulps. Because their xylan content is high, the delignification or bleaching capacity of ClO$_2$ is reduced (Freire et al. 2003). Some solutions have been proposed to deal with HexA, the first one is to apply a hot acid stage (A) before the D$_0$ stage; the second one is to conduct a hot chlorine dioxide bleaching (90°C to 95 °C for more than two hours) instead of the normal D$_0$ stage (Marechal 1993; Brogdon 2001; Ventorim et al. 2008).

2.2.5 Ozone bleaching (Z)

Ozone (O$_3$) is one of the most powerful oxidizing agents used in pulp bleaching (Lemeune et al. 2000; Jablonský et al. 2004; Pouyet et al. 2013). O$_3$ is an electrophile specie that reacts with most organic structures. Although it reacts easier...
and faster with lignin than with carbohydrates, reduction products of O₃, especially hydroxyl radical, degrade carbohydrates quite easily (Sevastyanova 2005).

The main disadvantages of ozone are its low solubility in water, low selectivity, and toxicity. Ozone must be produced on site and used immediately after it is generated because of its high reactivity and relatively short lifetime (Freire et al. 2006). Nevertheless, O₃ can be considered to replace chlorine dioxide in TCF bleaching or to reinforce ECF bleaching. It is usually recommended to use alkali extraction after the ozone stage, although, the combination Z/D stage without a subsequent alkali extraction stage produces better results.

One of the most important parameters in ozone bleaching like other stages is pH. The lowest kappa number, highest viscosity, and brightness are obtained at pH 2-4.

2.2.6 Alkali extraction (E or EOP)

The alkali extraction (E) is conducted to remove acidic lignin degradation products from the D and Z stages. NaOH is the alkali which ionizes and solubilizes the acidic components. This stage may be enhanced by the addition of oxygen and/or hydrogen peroxide to reach higher brightness values and lower residual kappa numbers. Consequently, the extraction stage is called EO, EOP or EP, respectively. The controlling parameter of alkali extraction stages at modern mills is pH that should ideally be kept in the range of 10.5-11 (Suess 2010). Therefore, it is recommended to avoid an overdose of NaOH and a consequent undesired high pH (Reid and Morissette 2005).

An important point during the E stage is the neutralization of lignin-derived acidic groups in order to increase the solubility of oxidized lignin and achieve a higher degree of delignification. In other words, this process removes the high-molecular-weight oxidized lignin, which requires alkaline pH in order to be dissolved (Kringstad and Lindström 1984). The NaOH requirement will depend on the kappa number of the incoming pulp and it can be as high as 20-50 kg/ODT (Suess 2010).

Alkali extraction enhances the access of oxidants to new sites and allows the pulp to be oxidized further by removing the oxidized lignin (Kringstad and Lindström 1984; Heitner et al. 2010).

2.2.7 Peroxide bleaching (P)

The P stage refers to using hydrogen peroxide as the last bleaching and brightening stage (Zhang et al. 2013). The main difference between the peroxide reinforced alkali extraction (EP) and the P stage is that the added proportion of hydrogen peroxide is higher in the P stage. Currently, the P stage is preferred for ending the bleaching sequences because it provides a high brightness stability by attacking the residual chromophores, mostly quinones, selectively (Rosenau et al. 2007b). Besides the brightening reactions, hydrogen peroxide can undergo decomposition to radical species that reduce the efficiency and selectivity of the bleaching (Carter 1996).
Hydrogen peroxide is applied in alkaline conditions under which the perhydroxyl anion is responsible for nucleophilic reactions with chromophoric carbonyl structures and pulp brightening (Freire et al. 2000). Catalytic decomposition of hydrogen peroxide in the presence of transition metals produces oxygen, which can also react with lignin, degrading it. Furthermore, the catalytic reactions produce hydroxyl radicals (HO•) which are prone to degrade cellulose besides lignin (Parthasarathy and Colodette 2003). Therefore, a prior treatment with chelating agents to eliminate transition metals is recommended. Additionally, it is suggested to add MgSO₄ in order to protect carbohydrates from degradation by hydrogen peroxide (Lapierre et al. 2000).

2.3 Brightness stability

As depicted in Figure 9, kraft pulping leads to the creation of chromophores at the very first chemical processing stage (Loureiro 2012). The only way to remove the residual lignin and chromophores is to apply selective chemicals in the following bleaching processes in order to obtain the desired brightness development (Rosenau et al. 2007b). However, the brightness of the bleached pulp can be seriously reduced at the drying section, and during the storage and transportation of pulp bales. Indeed, brightness stability is a very important issue in the case of market pulp (Rollinson 1968; Jääskeläinen et al. 2009). The unwanted phenomenon is called brightness reversion. It may be affected by several factors, including the intrinsic chemical composition of pulp, and external variables such as the temperature, moisture and, to a lesser degree, the effect of light (Logenius et al. 2008) (Liitiä and Tamminen 2007). Nowadays, the ageing reactions of either residual lignin or carbohydrates of bleached pulps are the main debatable reason for the reversion (Rosenau et al. 2007b; El-Sakhawy 2005).

![Figure 9. Simplified diagram of a kraft pulp fibreline representing stages where chromophores are created (yellowed blocks) and removed (bleaching) (Loureiro 2012).](image)

Deposition of models of oxidized carbohydrates or their dehydration products, such as 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (furfural), over different cellulosic substrates have shown the enhancement of chromophore formation upon ageing (Pedroso and Carvalho 2003; Simeonova et al. 2007; Brogdon 2009; Rosenau et al. 2011). Additionally, the effect of transition metals in ageing reactions has been also confirmed (Granstrom et al. 2001; Simão et al. 2005; Beyer et al. 2006; Lachenal et al. 2009).

There are two different experimental ageing methods, dry and wet thermal ageing. Wet thermal ageing is considered a more relevant method for measuring and predicting the brightness stability of kraft pulps. The reason is that both temperature and moisture affect brightness on the drying machine and during shipment and storage of pulp bales where reversion mainly occurs (Figure. 9) (Łojewski et al. 2010; Loureiro 2012). However, some ageing tests performed at
elevated temperature and moisture contents may not show the phenomena occurring during natural ageing (Rollinson 1968; Granstrom et al. 2001; Beyer et al. 2006; Liitä and Tamminen 2007).

In general, the residual chromophores are difficult to analyze due to their minute presence (ppm or even ppb range) in fully bleached pulps (Oliveira et al. 2006; Schedl et al. 2017). The analysis of chromophores in bleached pulps after ageing may involve their extraction and chemical characterization. In recent studies, researchers isolated the residual chromophores from bleached chemical pulps to characterize and consequently identify the important chromophore structures (Schedl et al. 2017). An important structural moiety was identified in several residual chromophores, which was the 2-hydroxy-1,4-benzoquinone originating from carbohydrates (Sevastyanova 2005). These chromophores arise from condensed degradation products of oxidized monosaccharides (Rosenau et al. 2007a). The finding of the same compounds in lignin-free cotton linters confirmed their origin from (oxidized) carbohydrate structures rather than from lignin fragments (Perrin et al. 2014). However, it is still not clear whether their main origin is cellulose or hemicelluloses (Pedroso and Carvalho 2003; Beyer et al. 2006).

In general, the role of hemicelluloses in the brightness reversion of bleached chemical pulps has been addressed in previous literature (Ljungqvist et al. 2005; Beyer et al. 2006; Brogdon 2009). However, these studies were not focused on the component containing the major part of oxidized groups in pulp, namely carboxyl groups, such as the native uronic acids and the artificially introduced HexA (Brogdon 2009; Loureiro et al. 2010). On the other hand, the specific role of HexA on brightness reversion of bleached pulps has been the subject of many studies. It has been shown that there is a positive correlation between the amount of HexA and the extent of reversion (Rollinson 1968; Liitä and Tamminen 2007). However, in other studies HexA content did not explain the differences in brightness reversion among ECF bleached pulps (Pedroso and Carvalho 2003; Loureiro et al. 2010).

The multi-factorial nature of pulp brightness reversion complicates the understanding of the phenomenon and consequently finding solutions to tackle this puzzling problem.

### 2.4 Catalyst stability

Tertiary amines are present in natural and treated water from different sources (Mcardell et al. 2003; Miao et al. 2004; Park et al. 2009) with wide range of structural and chemical properties. The basicity and structure of tertiary amines lead to their catalytic power (Shah et al. 2011). It has been revealed that they promote very efficiently the interactions of HOCl with phenols, alkenes, nucleic acid constituents, and other substrates (Shah et al. 2011). It means that tertiary amines can catalytically modify and broaden the range of the activity of HOCl. However, these catalysts may change the pH profile of the reactivity of HOCl in different systems (Priuz 1998).
Tertiary amines react fast with HOCl and compose a chloroammonium cation. However, the stability of the composed cation depends on its stereochemistry and structure of the alkyl groups. Acyclic and monocyclic chloroammonium cations will decompose very fast if an α-carbon atom carries a hydrogen atom (H-C-N⁺-Cl) or a β-carbon has a nucleophilic substituent (X-C-C-N⁺-Cl).

Bicyclic tertiary amines where the nitrogen atom is in a bridgehead position, are relatively stable in the presence of HOCl (Figure 10). In this case, the H-C-N⁺-Cl torsion angle is unfavourable for elimination of HCl. (Vuorinen et al. 2013).

Figure 10. General scheme of stable tertiary amines (Vuorinen et al. 2013). X is N or C, and R₁–R₁₂ is the same or different alkyl group, halide, ester, alkoxide or hydrogen. Preferably, the alkyl is methyl or ethyl, the halide is chloride, the ester is formate, acetate or propionate ester and alkoxide is methoxide or ethoxide.
3. Materials and methods

3.1 Raw materials

Oxygen-delignified eucalyptus kraft pulps P1 and P2 were obtained from a Brazilian kraft pulp mill. Table 1 shows the properties of the pulps.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa number</th>
<th>HexA (mmol/kg)</th>
<th>ISO brightness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>11.4</td>
<td>66</td>
<td>57</td>
</tr>
<tr>
<td>P2</td>
<td>11.6</td>
<td>63</td>
<td>55</td>
</tr>
</tbody>
</table>

Ethylenediamine or DABCO (98%), acetonitrile, ethyl chloroacetate, and diethyl ether, sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), phosphoric acid (H₃PO₄), sodium hydroxide, sodium phosphate (NaH₂PO₄), bisodium phosphate (Na₂HPO₄), and trisodium phosphate (Na₃PO₄) were purchased from Sigma-Aldrich. N-Carboxymethyl-1,4-diazabicyclo[2.2.2]octane (CM-DABCO) was synthetized in the laboratory as described in the literature (Barczynski et al. 2009). KI solution, 0.2 M Na₂S₂O₃ (99.9%, VWR), and 2 M HCl (Merck) were used for quantification of ozone by iodometric titration. Sodium hypochlorite (NaOCl) as one the bleaching reagents was
purchased from VWR, and was measured before every experiment by iodometric titration as described in the standard method SCAN-C 29:72. Methyl 4-deoxy-β-L-threo-hex-4-enopyranosiduronic acid (HexA) was synthesized according to a previous procedure (Adorjan et al. 2006). Ultrapure water was produced by a Millipore Water purification system with a resistivity ≥ 18.2 MΩ cm. This ultrapure water was used to prepare all reaction solutions, except for NaOCl solutions that were diluted with deionized water.

Stock phosphate buffers (100 mM, pH 3-6) were prepared by mixing calculated (Goldberg et al. 2002) amounts of H₃PO₄, NaH₂PO₄, Na₂HPO₄, Na₃PO₄, and NaOH in water. Stock NaOCl solution (64 mM) was prepared by diluting the commercial NaOCl solution with ion exchanged water. The concentration of NaOCl was verified iodometrically using a Shimadzu UV2550 UV-Vis spectrophotometer as described by (Bichsel and Von Gunten 1999). Stock solutions of DABCO and CM-DABCO (32 mM) and HexA (38 mM) were prepared in water. The 64 mM NaOCl, 32 mM DABCO and CM-DABCO, and 38 mM HexA solutions were further diluted with water and buffer solutions, maintaining a constant buffer concentration for the kinetic experiments. For stopped flow spectrometry (SFS) mixed solutions of HexA, HOCl, and DABCO with molar ratio ([HexA]: [HOCl]: [DABCO] = 10:10:1) were prepared for better workability and flexibility in SFS. Fresh solutions were prepared daily and stored in amber bottles to prevent possible light induced degradation.

Chlorine dioxide (ClO₂) and ozone (O₃) were produced in the laboratory with a gas flow of 2.5 L/min due to their high reactivity and low stability. Ten liters of aqueous ClO₂ solution were produced by mixing 1000 g of oxalic acid, 265 g of potassium chlorate (KClO₃) and 1000 mL of distilled water in a Denso reactor. Ozone was produced in situ using a Wedeco GSO30 device. Concentrations of the active chemicals in solutions of ClO₂, NaOCl and H₂O₂ were measured experimentally by iodometric titration as described in the standard method SCAN-C 29:72 every day before running the bleaching experiments.

### 3.2 Pulp bleaching experiments

The bleaching experiments were performed in CRS engineering fluidizing medium consistency (MC) reactors, plastic bags, a low consistency glass reactor or a high consistency glass reactor, according to the case. The MC reactors were capable of handling 250 g batches of pulp at 10% consistency. A MC reactor constructed of titanium was used for bleaching with chlorine chemicals while a Teflon coated MC reactor was applied for the A, EOP, and P stages (Figure 11a). Alternatively, unpressurized MC bleaching (P and D) was carried out in plastic bags in a thermostated water bath. A low consistency Büchiglassuster reactor (2 L) made of borosilicate glass was used for H₂O₂ bleaching at 3% consistency (Figure 11b). Ozonation was carried out at 30% consistency in a glass reactor (Figure 11c).
After completing each bleaching stage, a liquid aliquot was withdrawn to quantify the residual active chlorine or peroxide concentration, as well as the final pH. Immediately after collecting the sample the pulp was washed once with hot water and twice with cold water by diluting the pulp to ca. 10% consistency after each filtration. Next, the pulp was centrifuged and homogenized to determine the dry matter content.

### 3.3 Pulp analyses

#### 3.3.1 UV resonance raman Spectroscopy

Aromatic lignin and HexA content were determined with UV resonance Raman (UVRR) spectroscopy (Jääskeläinen et al. 2005). The UVRR spectra were obtained with a Renishaw 1000 UV Raman spectrometer (Gloucestershire, UK), which was connected to a Leica DMLM microscope (Wetzlar, Germany) and an Innova 90C FreD frequency-doubled Ar+ ion laser (Coherent Inc., CA, USA). The excitation wavelength of the laser was 244 nm, power output 10 mW, and measuring transmittance 25%. The beam was directed through a 40X objective which the sample was rotated to prevent burning. The spectral resolution, which is ability to separate two bands close to one another was approximately 7 cm⁻¹. A diamond crystal was measured every day prior to sample measurements to ensure the repeatability and comparability of the sample band locations. The Raman spectra were linearly baseline-corrected to zero at two wave numbers (800 cm⁻¹ and 2000 cm⁻¹) with Grams AI spectroscopy software. All the collected spectra were normalized to cellulose peak at 1094 cm⁻¹.

#### 3.3.2 Kappa number

Kappa number was measured according to SCAN-C 1:00, revised 2000. Fully bleached pulp typically have a kappa number lower than one (Suess 2010).

#### 3.3.3 Viscosity

Viscosity was measured according to SCAN-CM 15:99, revised on 1999.
3.3.4 Production of sheets

Sheets of each trial stage were produced according to SCAN-CM 11:95. The sheets were used for brightness and UV Raman measurements.

3.3.5 Brightness

Pulp brightness was determined according to SCAN-C 11:75. Full ISO brightness of hardwood pulps is > 90% whereas full ISO brightness of softwood pulps is defined to be > 88% (Suess 2010).

3.3.6 Carbonyl group content and molar mass distribution

The CCOA method with carbazole-9-carboxylic acid 2-(2-aminoethoxy)-ethoxy amide (CCOA) as the carbonyl-selective fluorescence label was applied to measure the content of carbonyl groups (Röhrling et al. 2002; Potthast et al. 2003, 2005). The pulp was suspended in a zinc acetate buffer with dissolved CCOA at pH 4 and agitated at 40 °C for 7 days in order to complete labelling. After labelling, the pulp was dissolved in DMAc/LiCl (9% w/v), and then diluted to 0.9% w/v with DMAc/LiCl. At the end, it was analyzed by a gel permeation chromatograph (GPC) equipped with multiple-angel laser light scattering (MALLS), fluorescence, and RI detectors.

3.3.7 Organically bound chlorine in pulp (OX)

OX was measured with the Trace Elemental Instruments Xplorer analyzer with the help of an auto sampler. Pulp samples from bleaching trials were treated according to the ISO 9562 method for the evaluation of OX. The relative error in OX measurements was 2%.

3.3.8 Brightness reversion test

Pulp hand sheets were prepared according to ISO 3688. The ISO brightness was measured (ISO 2470:2002) at 457 nm with an Elrepho 2000 Datacolor Reflectometer (Datacolor Inc., Lawrenceville, NJ, USA). The brightness reversion tests were carried out according to ISO 5630-3 (80 °C, 65% R.H. for 48 h). The post color numbers (PCN) were calculated according to the equation defined by (Giertz and McPherson 1956; Zhou et al. 2011). To understand the problem of brightness reversion, it is critical to establish reliable methods of quantifying the brightness drop in the aging test. The most commonly used techniques are through the measurements of brightness loss (ΔR457 in % ISO), PCN and increase in b* coordinate (Δb*) across aging. Although the best method of expressing reversion is still a matter of debate, in this study reversion is always reported as ΔR457 (% ISO) values, since only pulps of similar brightness values are compared.
3.3.9 Time-gated Raman spectroscopy

The time-resolved Raman measurements were carried out using a Raman spectrometer (Timegate Instruments, Oulu, Finland) consisting of a 532 nm Nd:YVO microchip pulsed laser (pulse width <100 ps, repetition rate 40-50 kHz, average output power ~20-30 mW) and a time-gated complementary metal-oxide semiconductor (CMOS) single-photon avalanche diode (SPAD) 128 × 8 matrix, detector. The spectral resolution was ~10 cm⁻¹. Photobleaching effects were mitigated using a sample enclosure equipped with a rotating plate where the samples were placed on a metal wafer and rotated using constant speed during the laser exposure. A BAC100 Raman probe delivered the laser beam onto the samples (B&W Tek, Newark, DE, USA). An electronic delay generator was applied in order to move the gate in 50-ps steps for collecting time-resolved Raman spectra datasets (Rojalin et al. 2016).

3.4 Stability of catalyst

3.4.1 Kinetic measurements

The fast reaction kinetics were followed by using a double mixing Bio-Logic SFM-3000 stopped flow mixer coupled with, an ASPEN TIDAS diode array spectrophotometer. A quartz microcuvette with an optical path length of 0.015 mm was used for most of the kinetic studies. The mixer was thermostated with a water flow to an accuracy of ±0.1 °C. The kinetic data were processed with BioKine software from Bio-Logic. All the kinetic experiments were carried out in triplicate.

A series of experiments was carried out to study the kinetics of the DABCO/CM-DABCO catalyzed oxidation of HexA by HOCl. The concentration of Cl(I) (6 mM) and pH (3-6) were varied while the concentrations of DABCO/CM-DABCO (0.6 mM), HexA (6 mM) and the phosphate buffer (10 mM) and temperature (25 °C) were kept constant. The first mixer of the SFS system was used to make the dilutions of Cl(I) in the buffer and the second mixture to add the solution of DABCO/CM-DABCO and HexA in buffer. The dead time of the reactor system, i.e., the time elapsed from pushing the reaction mixture from the mixer 2 to the cuvette, was 0.2 ms. The reaction mixture was pumped to the cuvette (dead time 0.2 ms) and the absorption spectra were recorded at 200-500 nm in intervals of 2 ms.

3.4.2 Chemometric modelling and computational aspects

The relative concentration of HexA was calculated from the spectral data using a chemometric approach. First, the spectra were preprocessed by removing the time points corresponding to the first 14 ms, before which the reagents were not fully mixed in the cuvette, and by restricting the wavelength range to 201-350 nm, which was the range that contained the most useful information and was least likely to show any non-linear response. Second, a constant baseline was
removed from these spectra by subtracting their minimum value. The pre-processed spectra were then analysed by Multivariate Curve Resolution – Alternating Least Squares (MCR-ALS), which is a method that computationally decomposes analytical data into the spectral and concentration profiles of its pure components. For a detailed description of MCR-ALS, the reader can consult other references such as (de Juan et al. 2014 and Jaumot et al. 2015). Briefly, MCR-ALS finds a factorization of the experimental data matrix D according to the bilinear model \( D \approx CS \), where C and S are the matrices of pure concentration and spectral profiles, respectively. The method begins by choosing the number of components, determining an initial estimate for C or S and by noise-filtering the data by Principal Component Analysis (PCA). Next, the estimated profiles are iteratively optimized by calculating one matrix (either C or S, using the bilinear relationship mentioned above), modifying it via the application of appropriate constraints, and then doing the same for the other matrix in alternating fashion. Many types of constraints have been developed to express the available knowledge on physical, chemical and mathematical properties of the investigated system. The optimization is stopped after a pre-set number of iterations or when the matrices do not significantly change between consecutive iterations. For the data analyzed in this work, the number of components was determined using PCA and usually set at three, except in few cases in which it was two or one. Initial estimates of S were determined using an algorithm based on SIMPLISMA (Jaumot et al. 2015), a method that finds the least-mixed profile within a data set. The employed constraints were non-negativity (for both spectral and concentration profiles) and closure, i.e. the total initial concentration of the species in the microcuvette, which was 4.2 mmol/L.

The obtained concentration profiles were fitted with kinetic equations of 1st and 2nd order, i.e., respectively:

\[
[\text{HexA}] = [\text{HexA}]_0 e^{-kt} \quad \text{(Eq. 1)}
\]

and

\[
[\text{HexA}] = \frac{[\text{HexA}]_0}{1 + kt[\text{HexA}]_0} \quad \text{(Eq. 2)}
\]

Where \([\text{HexA}]\) is the concentration of HexA, \([\text{HexA}]_0\) is its initial concentration, and \(t\) is the reaction time. \([\text{HexA}]\) and \([\text{HexA}]_0\) were often interpreted as relative concentrations (paper 4), so \([\text{HexA}]_0\) was conveniently normalized to 1. Whenever the reaction profile stabilized at a plateau above zero (paper 4), a constant offset term was added to the equations.

The initial reaction rates were obtained from the concentration profiles by calculating the average slope between the first point at 16 ms and the point that first satisfied one of these two conditions: i) \([\text{HexA}] < 90\%[\text{HexA}]_0\) or ii) \(t > 0.5\) s. Prior to this calculation, the spectra were smoothed to reduce random noise. This method provides an underestimation of the real initial rates, but is still adequate for comparing the reactions with each other. The rate constants for the decomposition of DABCO was obtained by fitting the initial reaction rates vs. delay time using eq. 1 with the constant offset term.
4. Results and discussion

This chapter summarizes the results obtained from the bleaching sequences performed using the methods summarized in the previous chapter presented more comprehensively in papers 1-4. Moreover, results on the stability and reactivity of the catalysts, DABCO and CM-DABCO, toward oxidation of HexA by HOCl are presented.

4.1 Bleaching studies

4.1.1 Intensified and short catalytic bleaching of eucalyptus Kraft pulp (paper 1)

The experimental results presented here show that eucalyptus kraft pulps can be bleached extremely efficiently by combining a tertiary amine catalyzed hypochlorite (Hcat) prebleaching with ozone (Z) bleaching. Although the brightness
is already high after the ozone stage, full brightness is easy to achieve with an additional treatment with alkaline peroxide. This short $\text{Hcat} - \text{Z} - \text{P}$ sequence results in residual lignin and HexA contents on the same or lower level as in the best ECF bleached pulps. In addition, the pulp viscosity remains at a high level that is not typical for pulps that have been bleached with ozone and peroxide (Table 2).

Table 2. Changes in kappa number, HexA and lignin contents, brightness and viscosity of oxygen delignified kraft pulp during the $\text{Hcat} - \text{Z} - \text{P}$ bleaching sequence (Paper 1).

<table>
<thead>
<tr>
<th></th>
<th>$\text{O}_3$ (%)</th>
<th>$\text{H}_2\text{O}_2$ (%)</th>
<th>pH</th>
<th>$T$ (°C)</th>
<th>$t$ (min)</th>
<th>$\kappa$</th>
<th>HexA (mmol/kg)</th>
<th>Lignin (%)</th>
<th>Brightness (%)</th>
<th>Viscosity (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11.4</td>
<td>66</td>
<td>100</td>
<td>57</td>
<td>1129</td>
</tr>
<tr>
<td>$\text{Hcat}$</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>25</td>
<td>10</td>
<td>5.9</td>
<td>30±0.1</td>
<td>64</td>
<td>69</td>
<td>1103±10</td>
</tr>
<tr>
<td>$\text{Hcat-Z}$</td>
<td>0.3 (0.28)</td>
<td>-</td>
<td>2.5</td>
<td>25</td>
<td>2</td>
<td>3.3</td>
<td>≤3±0.12</td>
<td>12</td>
<td>81</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Hcat-Z}$</td>
<td>0.4 (0.32)</td>
<td>-</td>
<td>2.5</td>
<td>25</td>
<td>2</td>
<td>2.8</td>
<td>≤3±0.12</td>
<td>10</td>
<td>82</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Hcat-Z}$</td>
<td>0.5 (0.46)</td>
<td>-</td>
<td>2.5</td>
<td>25</td>
<td>3</td>
<td>2.5</td>
<td>≤3±0.12</td>
<td>10</td>
<td>84</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Hcat-Z-P}$</td>
<td>0.3</td>
<td>0.6</td>
<td>11.2</td>
<td>60</td>
<td>30</td>
<td>1.2</td>
<td>2.6±0.1</td>
<td>9</td>
<td>85</td>
<td>1060±15</td>
</tr>
<tr>
<td>$\text{Hcat-Z-P}$</td>
<td>0.3</td>
<td>0.6</td>
<td>11.2</td>
<td>60</td>
<td>60</td>
<td>1.1</td>
<td>2.5±0.2</td>
<td>9</td>
<td>86</td>
<td>1015±10</td>
</tr>
<tr>
<td>$\text{Hcat-Z-P}$</td>
<td>0.3</td>
<td>0.6</td>
<td>11.2</td>
<td>85</td>
<td>30</td>
<td>1</td>
<td>2.3±0.1</td>
<td>9</td>
<td>87</td>
<td>1060±12</td>
</tr>
<tr>
<td>$\text{Hcat-Z-P}$</td>
<td>0.5</td>
<td>0.3</td>
<td>11.2</td>
<td>85</td>
<td>60</td>
<td>1.3</td>
<td>1.1±0.2</td>
<td>7</td>
<td>86</td>
<td>1090±10</td>
</tr>
<tr>
<td>$\text{Hcat-Z-P}$</td>
<td>0.5</td>
<td>0.6</td>
<td>11.2</td>
<td>85</td>
<td>60</td>
<td>0.9</td>
<td>0.8±0.1</td>
<td>6</td>
<td>66</td>
<td>1080±15</td>
</tr>
</tbody>
</table>

Figure 12. UVRR spectra of oxygen delignified eucalyptus kraft pulp (a), treated first with DABCO and HOCl (b), then with ozone (0.3%) (c) and finally with 0.6% peroxide for 30 min at 60 °C (d), for 60 min at 60 °C (e) and for 30 min at 85 °C (f) (paper 1).

The catalytic treatment also increased the brightness of the pulp (Table 2). One of the difficulties of bleaching is to remove all residual lignin with oxidants. Therefore, we decided to apply ozone, because of its high reactivity, in the second bleaching stage. The acidity of the medium is the key parameters of ozone bleaching. Because the delignification in this stage has been reported to be most efficient at pH 2–3, we selected to carry out the ozonation at pH 3. For practical
reasons, we chose to use high consistency ozonation in the laboratory experiments. Ozone with the charge of 0.4% lowered the kappa number by half. The final kappa number depended slightly on the amount of ozone used (Table 2).

The UVRR spectra of the pulps (Figure 12) confirmed that ozone oxidized the most of the residual HexA (1655 cm\(^{-1}\)) and lignin (\(\approx 1605\ cm^{-1}\)). An increase in the Raman scattering intensity at \(\approx 1700\ cm^{-1}\) was an indication of oxidized lignin structures.

The ISO brightness (Figure 12) was increased to 81–84%, depending on the charge of ozone (Table 2). In order to get full brightness, we bleached the pulps further with alkaline peroxide. Hydrogen peroxide is known as a bleaching agent that oxidizes many of the chromophores and the possible remaining carbonyl groups present in pulp for stabilizing its viscosity.

The peroxide bleaching stage increased the brightness by 2–6% and led to 85–88% final brightness, depending on the conditions in the ozone and peroxide bleaching stages. The viscosity of the pulp remained almost unchanged throughout the bleaching (Table 2). This finding was somewhat unexpected because both the ozone and peroxide stages are known for their ability to depolymerize cellulose to some extent.

As a conclusion of this part of study, the effects of several reaction parameters, including chemical charges, temperature, and time, on DABCO-catalyzed bleaching of an oxygen delignified eucalyptus kraft pulp followed by the Z and P stages to obtain fully bleached pulp were studied. Since the HexA and residual lignin content were low, the content of muconic acids from oxidation of lignin was obviously low too. Consequently, the low contents of HexA and muconic acids could explain the stability of cellulose toward ozone after the catalytic bleaching (Pouyet et al. 2013).

4.2 Analyses of bleached pulp from short catalytic investigation

4.2.1 Wet chemical analyses (Paper 2)

After obtaining the fully bleached pulp from the H\(_{\text{cat}}\)ZP sequences, we analyzed the organically bound chlorine (OX) (Figure 13), molar mass distribution of each stage to confirm the high viscosity of the stages and carbonyl group content (CO) (Table 3).
Figure 13. OX of oxygen-delignified pulp bleached in laboratory sequentially with 0.1% DABCO and 1% active chlorine (H_cat), varying amounts (0.3-0.5%) ozone (Z), and hydrogen peroxide (0.3-0.6%) (P) (paper 2).

The H_cat stage introduced a significant amount of organically bound chlorine (OX) on the pulp. The subsequent treatments with ozone and peroxide lowered the OX content. The OX content of H_cat-Z-P bleached pulp is high (ca. 200 mg/kg) in comparison with its low residual lignin content (Paper 2).

The oxygen-delignified kraft pulp had a low carbonyl group content, which was only slightly increased in the DABCO catalyzed treatment with HOCl (Table 3). The subsequent ozonation more than doubled the amount of carbonyl groups, depending on the ozone dosage. The final alkaline peroxide bleaching again lowered the carbonyl content.

Two different types of carbonyl groups might be present in the pulp. Depolymerization of cellulose leads to new reducing end groups. Oxidation of any of the primary or secondary alcohol groups in cellulose or hemicelluloses generates carbonyl groups without polymer chain cleavage. Ozonation of the H_cat treated pulp increased the carbonyl content by ca. 10 mmol/kg while the increase in the molarity of the polysaccharides was < 5 mmol/kg. Thus, both depolymerization and oxidation of the polysaccharides took place. The molarity of the polysaccharides did not really change during the peroxide treatment while the carbonyl content of the ozonated pulp decreased by ca. 4 mmol/kg. Thus, it looks like the peroxide oxidized the alkali labile carbonyl groups without depolymerizing cellulose.

As it has been already discussed, the chloroammonium cation gives rise to electrophilic oxidation of HexA and lignin, with negligible effect on the carbonyl content. On the other hand, the carbonyl content is increased during ozonation and decreased in peroxide treatment that is in consistence with the theory and published literature (Pouyet et al. 2014).

The number and weight averaged molar mass values (M_n and M_w, respectively), together with the CO group and molarity (n) of the pulps are documented in Table 3.
Table 3. Parameters calculated from molar mass distributions and CO group of industrial ECF bleached pulp (ECF), industrial oxygen delignified pulp (OD), and the OD pulp bleached in the laboratory sequentially with 0.1% DABCO and 1% active chlorine (H\text{cat}), varying amounts (0.3-0.5%) ozone (Z), and hydrogen peroxide (0.3-0.6%) (P) (Paper 2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (kg/mol)</th>
<th>$M_n$ (kg/mol)</th>
<th>CO (μmol/g)</th>
<th>n (mmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECF</td>
<td>485</td>
<td>68</td>
<td>20.0</td>
<td>14.7</td>
</tr>
<tr>
<td>OD</td>
<td>1052</td>
<td>185</td>
<td>5.3</td>
<td>5.4</td>
</tr>
<tr>
<td>H\text{cat}</td>
<td>957</td>
<td>208</td>
<td>6.0</td>
<td>4.5</td>
</tr>
<tr>
<td>H\text{cat}Z (0.3%)</td>
<td>823</td>
<td>128</td>
<td>11.5</td>
<td>7.8</td>
</tr>
<tr>
<td>H\text{cat}Z (0.4%)</td>
<td>923</td>
<td>148</td>
<td>13.0</td>
<td>6.8</td>
</tr>
<tr>
<td>H\text{cat}Z (0.5%)</td>
<td>823</td>
<td>108</td>
<td>15.6</td>
<td>9.4</td>
</tr>
<tr>
<td>H\text{cat}Z (0.5%)P (0.3%)</td>
<td>612</td>
<td>89</td>
<td>11.1</td>
<td>11.2</td>
</tr>
<tr>
<td>H\text{cat}Z (0.5%)P (0.6%)</td>
<td>693</td>
<td>122</td>
<td>10.8</td>
<td>8.2</td>
</tr>
</tbody>
</table>

The H\text{cat}-Z-P bleaching removes the residual lignin and HexA from hardwood kraft pulps very selectively. Cellulose remains almost unattacked in the catalytic stage while the subsequent ozone stage moderately introduces some carbonyl groups in the pulp. The peroxide treatment reacts partly with the carbonyl groups. In spite of their low lignin, HexA and carbonyl group content, the H\text{cat}-Z-P bleached pulps underwent thermal yellowing during the artificial aging test. Highly conjugated unsaturated organic structures were formed during the discoloration.

### 4.3 Modification of catalytic bleaching studies

#### 4.3.1 Optimized catalytic bleaching sequences (Paper 3)

In this part, we aimed to optimize the catalytic bleaching sequences by applying a derivative of DABCO, and CM-DABCO, as the catalyst. In addition, we investigated whether new kraft pulp bleaching sequences with an initial chlorine dioxide (D) stage and an intermediate H\text{cat} stage could provide fully bleached pulps.

Table 4 presents the main operative parameters of the trials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>D$_0$</th>
<th>E</th>
<th>E$_{OP}$</th>
<th>H$_{cat}$</th>
<th>Z/D</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td></td>
<td>2.8</td>
<td>11</td>
<td>11</td>
<td>2.9</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Final pH</td>
<td></td>
<td>3</td>
<td>10.5</td>
<td>10.5</td>
<td>4.5-6</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>RT</td>
<td>RT/75</td>
<td>85</td>
</tr>
<tr>
<td>Time</td>
<td>min</td>
<td>30</td>
<td>60</td>
<td>60</td>
<td>10</td>
<td>1.1/15</td>
<td>60</td>
</tr>
<tr>
<td>CM-DABCO</td>
<td>%</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClO$_2$</td>
<td>% act.Cl</td>
<td>1.4</td>
<td></td>
<td></td>
<td>0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOCl</td>
<td>% act.Cl</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>%</td>
<td>0.7</td>
<td>0.5</td>
<td></td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>kPa</td>
<td>300</td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>%</td>
<td>0.75</td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>%</td>
<td>0.4</td>
<td></td>
<td></td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We found that CM-DABCO was more stable than DABCO in the presence of hypochlorous acid why we used a much lower catalyst dosage (0.01% on pulp) in the case of CM-DABCO. As expected, the brightness of the pulp after D$_0$ and E$_{OP}$ stages was markedly higher than after the E stage. However, this significant difference did not fully remain after the subsequent H$_{cat}$ and P stages (Figure
The highest ISO brightness of this set of trials (D_{0}E_{OP}H_{cat}P) was ca. 87% ISO. An even higher brightness level of 89% ISO was reached with H_{cat}Z/DP bleaching sequence. In this sequence, the initial H_{cat} stage reduced the kappa number remarkably by 8.5 units in slightly acidic conditions (final pH < 6).

Figure 14. Development of kappa number and ISO brightness in bleaching with sequences D_{0}EH_{cat}P, D_{0}EOPH_{cat}P, and H_{cat}Z/DP (Paper 3).
The UVRR spectra confirmed the higher efficiency of EOP over E stage as lower residual lignin and HexA content (Figure 15). However, the H_cat and P stages led to disappearance of this difference between the extraction stages. The residual content of lignin and HexA were identically low in all pulps after the P stage. The final normalized UVRR signal intensities of residual lignin and HexA were very low. These results demonstrated a very low kappa number that is typical of the best commercial bleached hardwood kraft pulps. The UVRR spectra proved again the efficiency of H_cat stage in removing HexA. However, this time the efficiency of H_cat in removing lignin was lower than in the previous investigation. The initial H_cat stage was more selective in lowering the kappa number in comparison with D_0 stage.

In this part, the results confirmed the great efficiency of tertiary amine catalyzed hypochlorous acid treatment in removing HexA and some lignin from eucalyptus kraft pulps. A novel discovery in catalytic bleaching was the high stability of using CM-DABCO as the catalyst in comparison with DABCO. The higher catalyst stability allows using lower catalyst dosages which is economically attractive. The experiments with the short H_catZ/DP sequence confirmed the earlier observation on the efficiency of ozone stage in combination with the catalytic stage.

### 4.4 Analyses of two tertiary amine catalysts

#### 4.4.1 Reactivity and stability of tertiary amine catalysts (Paper 4)

Finally, we investigated the reactivity and stability of two tertiary amine catalysts, DABCO and CM-DABCO, in the oxidation of HexA by hypochlorous acid. The reactions were conducted using SFS in combination with multivariate curve resolution methods to monitor the changes in the concentration of HexA, which were fitted to kinetic equations of first and second order.

The reactions performed in this study differed in speed and order, which means different mechanisms might be involved, depending on the experimental conditions.

Table 5 summarizes the most likely reaction orders observed for each case, while a few examples of kinetic fitting are shown in Figure 16.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>pH</th>
<th>Delay (ms)</th>
<th>10</th>
<th>100</th>
<th>1000</th>
<th>5000</th>
<th>10000</th>
<th>100000</th>
</tr>
</thead>
<tbody>
<tr>
<td>DABCO</td>
<td>3</td>
<td>1</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
</tr>
<tr>
<td>CM-DABCO</td>
<td>3</td>
<td>1</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2*</td>
<td>2*</td>
<td>2*</td>
<td>2*</td>
<td>2*</td>
<td>2*</td>
<td>2*</td>
</tr>
</tbody>
</table>

- Concentration profile does not reach zero. b Reaction order might be lower than 1. c Reaction has different stoichiometry. d Reaction order between 1 and 2.
Figure 16. Examples of kinetic fits from selected experimental conditions (catalyst, pH, and delay time): a) DABCO, pH 5, 100 ms; the profile follows clear 1st order kinetics. b) DABCO, pH 4, 100 ms; the kinetics are of 1st order, but the profile stops at a plateau before reaching zero; the fitting equation includes a constant offset term. c) DABCO, pH 3, 10,000 ms; the kinetics appear of order lower than 1st. d) CM-DABCO, pH 3, 10 ms; the kinetics seem to follow an order lower than 1st; additionally, the profile stops at a plateau (not exactly horizontal) before reaching zero. e) CM-DABCO, pH 6, 100 ms; the profile follows 2nd order kinetics. f) CM-DABCO, pH 4, 10 ms; the kinetics appear of an order intermediate between 1st and 2nd. g) DABCO, pH 4, 10,000 ms; the reaction follows 1st order kinetics, but the stoichiometry is different than 1:1 (offset included for fitting). h) DABCO, pH 5, 10,000 ms; the kinetics are of 2nd order, with stoichiometry different than 1:1 (offset included for fitting) (Paper 4).
HexA was disappeared by the 1st order kinetics with delay times of ≤ 1000 ms in the case of applying DABCO as the catalyst (Table 5). The 1st order reaction shows that DABCO existed almost completely as its chlorammonium cation independent of the concentration of HOCl and pH, because HexA and HOCl were added in a stoichiometric 1:1 ratio. A similar 1st order observation took place when CM-DABCO was applied as the catalyst at pH 4 and 5. At pH 3, the reaction order was clearly lower than 1 (Figure 16d). Because in the acidic conditions the protonated chlorammonium cation yields rapidly a more electrophilic chlorine species, such as Cl+, that reacts immediately with HexA. Therefore, the degradation rate of HexA varies only with the concentration of chlorammonium cation and, thus, the reaction would be zero order relative to HexA and HOCl.

On the other hand, CM-DABCO at pH 6 was not completely in the chlorammonium form so it showed mainly 2nd order kinetics (Figure 16e). Indeed, the concentration of chlorammonium would thus depend on the concentration of HOCl, leading to a 2nd order reaction or at least one between 1st and 2nd order.

As for the reactions using DABCO and delay times longer than 1000 ms, major changes were observed not only in speed but also in mechanism. In particular, for pH 4-6, the stoichiometry was clearly different than 1:1 and less than half of the HexA is consumed, see (Figures 16g and 16h). Since the reaction took longer than the observation time, the conditions were not suitable for an accurate evaluation of the reaction order, nor the exact stoichiometry. However, for pH 4 the reaction appeared to follow a 1st order mechanism (Figure 16g), while for pH 5-6, 2nd order was found (Figure 16h). In that case, the 2nd order could be simply explained because, in the complete absence of active catalyst, the reaction occurred directly between HexA and HOCl.

Figure 17 plots the initial reaction rates for each studied case. Since the reaction orders varied depending on the experimental conditions, the initial rate was preferred to kinetic constants as a more uniform way of comparing reaction speeds. The most obvious difference between DABCO (Figure 17a) and CM-DABCO (Figure 17b) was that, for the former, the initial rates followed an exponential decay, whereas for the latter they remained approximately constant, although they noticeably decreased with rising pH. This dependence can be explained by the higher reactivity of HOCl toward neutral HexA than the dissociated form.

Figure 17. Initial reaction rates vs delay time at different pH for DABCO (a) and CM-DABCO (b). For DABCO, all series of points are fitted with an exponential equation that includes a constant offset term. The rate constants derived from that fitting are plotted in c) as a function of pH (Paper 4).
5. Conclusions
This thesis covers several sequences with a new catalytic bleaching sequences using $H_{\text{cat}}$ technology followed by ozone and peroxide stages to prepare fully bleached pulps. The pulps were characterized by the quantification of carbonyl group content, and the reactivity and stability of the catalysts in the reaction of unsaturated components during pulp bleaching. Indeed, it was found that an initial catalytic stage followed by ozone and peroxide bleaching gave the most promising results. One of the main important achievements of this technology is preserving the viscosity and carbohydrates, which is confirmed by the carbonyl group content. However, the OX level was relatively high which possibly explained the observed brightness instability.

A catalytic amount of tertiary amine activates HOCl that leads to a very reactive chlorammonium cation species ($R_3N-Cl^+$). These cation species react with lignin and HexA in pulp fibers at room temperature in a few seconds. Actually, the activity of the catalyst can be improved by protecting one of the amino groups of DABCO by alkylation (carboxymethylation) which is called CM-DABCO. The individual $H_{\text{cat}}$ stage experiments with $0.01\%$ of CM-DABCO dosage leads to similar HexA removal as compared to the experiments with $0.1\%$ addition of DABCO. Hence, CM-DABCO is preferred as the catalyst for the $H_{\text{cat}}$ stage.

The stopped flow mixer experiments help understandings of the individual reactions taking place during the catalytic pulp bleaching conditions by selecting the relevant model compound. The HexA model compound studies show that HOCl along with tertiary amine catalysts can oxidize HexA. However, how the reaction proceeded strongly depends on pH. The initial rates of DABCO and CM-DABCO show that DABCO follows an exponential decay, whereas CM-DABCO remains approximately constant, although they noticeably decrease with rising pH.

The catalytic bleaching technology reduces the overall reaction time from several hours into few seconds in comparison with the current bleaching technology. The catalysis also increases the selectivity of the bleaching chemical toward HexA and lignin. Thus the consumption of active chlorine can be as low as 5-10 kg/t in comparison with today’s 20-25 kg/t in hardwood pulp bleaching. Due to the ultrafast reactions, huge bleaching towers become unnecessary and the investments costs are reduced because the number of bleaching stages can be reduced from the typical 4 to 2. The low chemical charges required may make it easier to close water cycles in the pulp mill. The emphasis is on validation of the technology on laboratory scale. The target is to verify the most potential process options with pilot and possibly mill trials.

For the future studies, it is worthful to apply the catalytic stage in combination of other effective reagents on softwood and different types of hardwood pulps. The selectivity of the bleaching will be monitored by yield, viscosity, and chemical consumption. The target is to decrease the consumption of the chemicals on a level in order to lead to lower chemical costs than in today’s mills. This technology is under development; however, it will revolutionize the pulp bleaching industry in the near future.


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Tertiary Amines in Catalytic Pulp Bleaching

Ghazaleh Afsahi