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THE USE OF FENTON CHEMISTRY FOR REDUCING THE REFINING ENERGY DURING TMP PRODUCTION – THE EFFECT OF FREE FERROUS AND FREE OR CHELATED FERRIC IONS

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ABSTRACT

The potential of using acid hydrogen peroxide under Fenton conditions to lower the electrical energy consumed during the production of Black spruce (*Picea mariana*) thermomechanical pulp (TMP) was investigated in pilot scale. The chemical system, which consisted of ferrous sulphate, hydrogen peroxide and optionally an enhancer (such as a chelating agent), was evaluated as an inter-stage treatment. The produced TMPs were thoroughly characterised in order to explain the effect of the chemical system on fibre development and to be able to propose a mechanism for the impact on refining energy reduction. The possibility to improve the optical properties by washing, chelating and sodium dithionite or hydrogen peroxide bleaching the treated pulps was evaluated. The system of lignocellulosic material, a Norway spruce (*Picea abies*) TMP, and Fenton chemistry was also evaluated in a model study to understand more about how conditions such as e.g. initial pH, dissolved organic material and reaction time affect the reactions. Ferrous and ferric ions (free and chelated) and different anions were evaluated. Moreover, it was examined whether hydroxyl radicals could be detected and monitored.

The results obtained in pilot scale showed that it is possible to significantly reduce the specific energy consumption by approximately 20% and 35% at a freeness value of 100 ml CSF or a tensile index of 45 Nm/g by using 1% and 2% hydrogen peroxide respectively. The energy reduction was obtained without any substantial change to the fractional composition of the pulp, although tear strength was slightly reduced, as were brightness and pulp yield. No major differences between the reference pulp and the chemically treated pulps were found with respect to fibre length, width or cross-sectional dimensions. However, the acid hydrogen peroxide-treated pulps tended to have more collapsed fibres, higher flexibility, a larger specific surface area and a lower coarseness value. The yield loss

accompanying the treatment was mainly a consequence of degraded hemicelluloses. It was also found that the total charge of the chemically treated pulps was higher compared to the reference pulps; something that may have influenced the softening behaviour of the fibre wall.

A washing or chelating procedure could significantly reduce the metal ion content of the chemically treated TMPs. The amount of iron could be further reduced to a level similar to that of untreated pulps by performing a reducing agent-assisted chelating stage with dithionite. The discoloration could not, however, be completely eliminated. The brightness decrease of the treated pulps was therefore not only caused by the greater iron content in the pulp, but was also dependent on the type of iron compound and/or other coloured compounds connected with the acid hydrogen peroxide treatment. Oxidative bleaching using hydrogen peroxide was more effective than reductive bleaching using sodium dithionite in regaining the brightness that was lost during the energy reductive treatment.

From the model study and by using a chemiluminescence method, it could be concluded that hydroxyl radicals were present in the system of Fenton chemicals and lignocellulosic material (TMP). Initial pH, retention time, pulp consistency, type of catalyst (free or chelated) and dissolved organic material had an impact on the reactions between TMP and acid hydrogen peroxide. Different anions (sulphate, nitrate and chloride) of ferric ion salt gave a similar catalytic effect. There appeared to be more reactions with the TMP when there was less dissolved organic material in the liquid phase from the start. A catalyst of ferrous sulphate had a greater impact on the pulp (increased total fibre charge and carbonyl groups, more dissolved organic material in filtrate) than ferric ions chelated with ethylenediaminetetraacetic acid at an initial pH of about 3-7. If using ferric-EDG (ethanol diglycinic acid) as catalyst, the measured effect on the pulp was similar or less compared to using ferrous sulphate. Ferric-EDG, however, gave higher hydrogen peroxide consumption and more detectable hydroxyl radicals than using ferrous sulphate (initial pH 5-8). It is likely that the iron catalyst must bind to the TMP, or be in close proximity to it, for the hydroxyl radicals to be able to react with the material.

A mechanism was proposed: the hydroxyl radicals generated in the Fenton reaction will probably attack and oxidise the available outer fibre surfaces, weakening these layers, and simultaneously dissolve some of the organic material. This can facilitate fibre development, give a better bonding pulp and reduce the electrical energy required during refining.

Keywords: TMP, Energy reduction, Hydrogen peroxide, Fenton's reagent, Ferrous ions, Ferric ions, Refining, Chelation, EDTA, EDG, Black spruce, Norway spruce, Inter-stage treatment, Pulp and paper properties, Bleaching, Sodium dithionite, Brightness, Metals, Fibre properties, Hydroxyl radicals, Total fibre charge, TOC, COD, Carbonyl groups

SAMMANFATTNING

En undersökning i pilotskala om sur väteperoxid (Fentons reagens) har potential att sänka elenergikonsumtionen vid tillverkning av termomekanisk massa (TMP) av gran (*Picea mariana*) har genomförts. Det kemiska systemet bestod av järn(II)sulfat, väteperoxid och ibland en hjälpkemikalie (såsom komplexbildare) och systemet utvärderades som en mellanstegsbehandling. De termomekaniska massor som framställdes karakteriserades noggrant för att förklara kemikaliesystemets effekt på fiberutvecklingen och för att föreslå en mekanism för hur energikonsumtionen påverkas. Möjligheten att förbättra optiska egenskaper genom att tvätta, komplexbinda och bleka de behandlade massorna med ditionit eller väteperoxid utvärderades. Systemet lignocellulosa, en TMP av gran (*Picea abies*), och Fentonkemikalier undersöktes vidare i en modellstudie för att förstå mer om hur betingelser som start pH, löst organiskt material och reaktionstid påverkar reaktionerna. Järn(II)- och järn(III)katalysatorer (fria och komplexbundna) och olika anjoner utvärderades. Dessutom undersöktes det om hydroxylradikaler kunde detekteras och kvantifieras.

Resultaten från pilotstudien visade att det är möjligt att signifikant minska den specifika energikonsumtionen med ungefär 20 respektive 30%, jämfört vid freeness 100 ml CSF eller dragstyrka 45 Nm/g, genom att använda 1% respektive 2% väteperoxid. Energireduktionen uppnåddes utan att ändra massans komposition av fraktioner, dock minskades rivstyrkan något, liksom ljusheten och utbytet. Det var inga stora skillnader mellan referensmassan och de kemiskt behandlande massorna med avseende på fiberlängd, -bredd eller -tvärsnittsdimensioner. Massorna behandlade med sur väteperoxid tenderar att ha mer kollapsade fibrer, högre flexibilitet, en större specifik ytarea och ett lägre coarsenessvärde. Utbytesförlusten som följde med behandlingen var i huvudsak en konsekvens av att hemicellulosa löstes ut. Det kunde också konstateras att totalladdningen hos de kemiskt behandlade massorna var högre jämfört med hos referensmassorna, något som kan ha påverkat mjukningen i fiberväggen.

Ett tvätt- eller komplexbildarförfarande kunde minska metallinnehållet avsevärt hos de kemiskt behandlade termomekaniska massorna. Mängden järn kunde ytterligare minskas till samma nivå som i obehandlade massor genom att utföra ett komplexbildarsteg förstärkt med reduktionsmedlet ditionit. Missfärgningen kunde dock inte helt elimineras. Ljushetssänkningen hos de behandlade massorna var inte enbart orsakat av det högre järninnehållet i massan utan också beroende av typen av järnförening och/eller andra färgade föreningar som bildas vid den sura väteperoxidbehandlingen. Oxidativ blekning med väteperoxid var mer effektivt än reduktiv blekning med natriumditionit för att återfå den ljushet som förlorats under energireduktionsbehandlingen.

Från modellstudien och genom användandet av en kemiluminiscensmetod kunde slutsatsen dras att hydroxylradikaler var närvarande i systemet av Fentonkemikalier och lignocellulosamaterial (TMP). Val av start pH, reaktionstid, massakoncentration, typ av katalysator (fri eller komplexbunden) och löst organiskt material hade effekt på reaktionerna mellan massa och sur väteperoxid. Användandet av järn(III)salt med olika anjoner (sulfat, nitrat och klorid) gav liknande katalytisk effekt. Det verkade som det var mer reaktioner med massan om det var mindre löst organiskt material i vätskefasen från start. En större effekt på massan (högre total fiberladdning och fler karbonylgrupper, mer löst organiskt material i filtratet) uppmättes om järn(II)sulfat användes som katalysator jämfört med om järn(III)joner komplexbundna med etylendiamintetraättiksyra användes när start pH var ungefär 3-7. När Fe(III)-EDG (etanoldiglycinsyra) användes som katalysator uppmättes liknande eller mindre effekt på massan som när järn(II)sulfat användes. Järn(III)-EDG gav dock högre väteperoxidkonsumtion och fler detekterade hydroxylradikaler jämfört med järn(II)sulfat (start pH 5-8). Troligen måste järnkatalysatorn binda till den termomekaniska massan, eller vara i dess omedelbara närhet, för att hydroxylradikalerna skall kunna reagera med materialet.

En mekanism föreslogs; vid Fenton reaktionen bildas hydroxylradikaler som troligen attackerar och oxiderar de tillgängliga yttre fiberytorna, försvagar dessa, och samtidigt löser ut en del av det organiska materialet. Detta kan underlätta fiberutvecklingen, ge en mer bindande massa och sänka behovet av elektrisk energi under raffineringen.

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LIST OF PAPERS

This thesis is mainly based on the following five papers, hereafter referred to by their Roman numerals:

Paper I — Energy efficient refining of Black spruce TMP by using acid hydrogen peroxide: Part 1. A pilot plant study
Walter, K., Paulsson, M. and Wackerberg, E.
Nordic Pulp and Paper Research Journal, 2009, 24(3), 255-265.

Paper II — Energy efficient refining of Black spruce TMP by using acid hydrogen peroxide: Part 2. Washing, chelating and bleaching studies
Walter, K., Paulsson, M. and Wackerberg, E.
Nordic Pulp and Paper Research Journal, 2009, 24(3), 266-272.

Paper III — Energy efficient refining of Black spruce TMP by using acid hydrogen peroxide: Part 3. Chemical and morphological characterisation
Walter, K., Paulsson, M. and Wackerberg, E.
Journal of Pulp and Paper Science, 2010, 36(1-2), 2-9.

Paper IV — Acid hydrogen peroxide treatment of Norway Spruce TMP: a model study using free ferrous ions and ferric ions chelated with EDTA as catalysts
Walter, K., Paulsson, M. and Hellström, P.
Journal of Wood Chemistry and Technology, 2013, 33(4), 267-285.

Paper V — Acid hydrogen peroxide treatment of Norway Spruce TMP: the effect of an extended pH range when catalysed by free ferrous and free or EDG/EDTA-chelated ferric ions
Walter, K., Paulsson, M. and Engstrand, P.
Accepted for publication in Journal of Wood Chemistry and Technology.

AUTHOR'S CONTRIBUTION TO THE REPORTS

The author's contributions to the papers in the thesis are as follows:

Paper I — Planning for and participating in the pilot trial, interpretation of results, and writing the article in co-operation with Magnus Paulsson and Eva Wackerberg.

Paper II — Experimental work, interpretation of results, and writing the article in co-operation with Magnus Paulsson and Eva Wackerberg.

Paper III — Preparation of pulps (analyses conducted by PFI, Trondheim and Innventia, Stockholm), interpretation of results, and writing the article in co-operation with Magnus Paulsson and Eva Wackerberg.

Paper IV — Experimental work, interpretation of results and writing the article. The development of the hydroxyl radical and spectrophotometric iron analytical methods was done together with Pia Hellström.

Paper V — Experimental work, interpretation of results, and writing the article. Experiments of decomposition of hydrogen peroxide into pressure increase (incl. method development) were conducted by Pär Nilsson.

RELATED MATERIAL

Energy efficient refining of Black spruce TMP by using Fenton chemistry
Walter, K., Paulsson, M. and Wackerberg, E.
Proceedings of the 27th International Mechanical Pulping Conference, Sundsvall, Sweden, June 1-4, 2009, 286-291.

Energy efficient production of TMP by using acid hydrogen peroxide: factors affecting the hydrogen peroxide consumption
Walter, K., Paulsson, M., Hellström, P. and Nilsson, P.
Proceedings of the 28th International Mechanical Pulping Conference, Xi'an, China, June 26-29, 2011, 484-487.

Acid hydrogen peroxide treatment of Norway Spruce TMP: the effect of free and chelated iron as catalysts
Walter, K., Paulsson, M. and Hellström, P.
Fundamental Mechanical Pulp Research Seminar, Åre, Sweden, January 29-31, 2013, 6-7.

1 INTRODUCTION

Efficient utilisation of energy and lignocellulosic products are issues of great importance to both industry and society. The production of mechanical and chemimechanical pulps is an efficient way of using the available virgin fibre resources since the yield of these manufacturing processes is high and the environmental impact relatively low. The light scattering and bulk properties of high-yield pulps are exceptional and not easily obtainable with other pulp types. The poor brightness stability and the relatively low maximum obtainable brightness level are the major obstacles to using high-yield pulps even in long-life, high-quality papers. Mechanical and chemimechanical pulping processes are, however, electrical energy intensive (Muenster et al. 2005). From a global perspective, the development of solutions that substantially reduce energy consumption while maintaining pulp quality is the most important issue for the high-yield pulp and paper industry.

The amount of electricity needed for fibre separation and development is dependent on many factors, such as the type of wood raw material used, the pulping process chosen and the intended end-use of the produced pulp. The specific energy consumption (SEC) for producing thermomechanical pulps (TMPs) can be up to 3-3.5 MWh/bdt (Jackson, Wild 1999; Ali (Viforr), Salmén 2005; Francis et al. 2006; Viljakainen 2006), and consequently the electrical power cost has a considerable impact on the total production cost and thus profitability. In the newsprint industry, the energy component accounts for 25 to 50% of the total cost (Jackson, Wild 1999; Forsyth, Ahmad 2009). The significant increase in energy costs that has taken place in recent years due to deregulation of the power industry in combination with legislation or incentives to reduce greenhouse gas emissions and increased energy demands throughout the world has intensified efforts to increase energy efficiency in the refining process. Global production of mechanical pulp containing paper grades has decreased by about 6% during the last three years and the forecast is that it will continue to decrease over the next five years by 1.9%, 0.2% and 0.4% annually, for newsprint, uncoated mechanical and coated mechanical paper grades respectively (Source: RISI, February 2013). One way for a mill to survive in the mature markets (Europe and North America) is to lower costs. At FSCN, Mid Sweden University, extensive research is currently under way aimed at reducing the electrical energy consumption by 50% when manufacturing mechanical pulps. The initiative for the research programme E2MP (Energy Efficiency Mechanical Pulping) was taken by four large TMP producers in Scandinavia: Holmen, Norske Skog, SCA and Stora Enso, and two supplier companies: Andritz and Metso.

A vast number of energy-reducing strategies and technologies ranging from process control and machinery to chemistry and biotechnology have been

proposed for the mechanical pulping process (see Section 2.3). When introducing a new energy-reducing technology, it is of great importance that the final pulp quality is not diminished. High-yield pulp quality comprises the highest possible strength and optical properties. If these properties are altered by an energy-reducing method, the method can still be viable if the pulp properties are recovered satisfactorily, for example through bleaching, and if the overall economics (including equipment, chemicals, the mill's energy balance etc.) are favourable to the mill. The profitability of an energy-reducing method will ultimately be mill-specific.

1.1 Objectives

This work was aimed at evaluating the potential of hydrogen peroxide (H_2O_2) and $FeSO_4$ at an acidic pH, i.e. Fenton chemistry, to reduce electrical refining energy while preserving softwood thermomechanical pulp properties. The chemical system was used as an inter-stage treatment on Black Spruce (*Picea mariana*) TMP in pilot plant refining. The produced TMPs were investigated with respect to strength and optical properties as well as morphological and chemical characterisation in order to explain the effect the chemical system has on fibre development. Moreover, the study was aimed at minimising the impact of the added iron on final pulp brightness by elucidating the effect of washing, chelating and bleaching on metal removal and brightness increase.

Another objective was to evaluate the system of lignocellulosic material and Fenton chemistry in a more fundamental way to understand more about how conditions such as initial pH, dissolved organic material and reaction time affect the reactions. Coarse pulp from Norway spruce (*Picea abies*) TMP was treated with chemicals in a model study. Iron catalysts of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, different anions and forms (free and chelated) were evaluated. Moreover, it was examined whether hydroxyl radicals could be detected and monitored.

A third objective was to propose a mechanism for refining Fenton treated lignocellulosic material.

1.2 Contents description

Section 2 presents the background to the research reported in this thesis. The chemical constituents of wood are briefly presented (Section 2.1) and the mechanical and chemimechanical pulping processes are described (Section 2.2). The suggested methods for energy reduction in high-yield pulping processes are reviewed (Section 2.3). Fenton chemistry and iron catalysts are presented and

discussed together with some theory about hydroxyl radicals and lignocellulosic material (Section 2.4).

Section 3 presents the conditions at the pilot plant trial (Section 3.1) and during the model study (Section 3.2). The hydroxyl radical analysis method is described (Section 3.2.1) and also a method that uses increased pressure for calculating the amount of hydrogen peroxide that was decomposed into oxygen (Section 3.2.2). The carbonyl group analysis is described (Section 3.2.3). Other experimental details can be found in the appended papers.

Section 4 presents and discusses the results obtained in this work. The pilot study is presented (Section 4.1) with chemical charges and reactions (Section 4.1.1). The results of the pilot plant trial are reported: specific energy consumption (Section 4.1.2), strength properties (Section 4.1.3) and optical properties (Section 4.1.4). A thorough morphological and chemical characterisation is presented (Section 4.1.5). Metal removing trials (Section 4.1.6), bleaching and the generation of chemical oxygen demand are reported (Section 4.1.7).

The model study is presented (Section 4.2). The detection method of hydroxyl radicals, adapted for the system of acid hydrogen peroxide and pulp, is discussed (Section 4.2.1). The results from using free ferrous/ferric ions (Section 4.2.2) or chelated ferric ions (Section 4.2.3) as catalysts are reported and discussed.

A mechanism for refining Fenton treated pulp is proposed (Section 4.3). Some unpublished results from full-scale (Section 4.4) and bench trials (Section 4.5) are communicated.

Section 5 reports the conclusions drawn from this work.

Section 6 presents some recommendations for future work in the area of acid hydrogen peroxide and energy efficient refining.

Cited references are included in Section 8.

The Appendices 1-3 include the most important data obtained in the pilot plant trial, the bleaching trials and the model study.

2 BACKGROUND

This section presents background information necessary for understanding the results presented in this thesis. First is an overview of the components of wood. Next is a short description of the mechanical and chemimechanical pulping processes, followed by a review of suggested methods for energy reduction in the aforementioned processes. Energy reducing methods that combine different types of technology are presented under the subsection of their main technology. Finally, there is an explanation of Fenton chemistry, including free or chelated iron as catalysts, which is the basis for the chemical system used in this work to lower the energy consumption during production of thermomechanical pulp.

2.1 Wood components and the layer structure of the fibre

More detailed information can be found in, for example Fengel and Wegener (1989), Lewin and Goldstein (1991), Sjöström (1993), Back and Allen (2000), Hon and Shiraishi (2001), Ek et al. (2009a) and Heitner et al. (2010).

Wood is a biological material that possesses unique properties and has a wide range of applications. The properties of wood depend on the structure of the chemical components forming its ultrastructural elements, which are combined to create the cell walls of the fibres (tracheids, libriform fibres) that together with parenchyma cells, ray tracheids and vessels compose the wood tissue. The main chemical components are cellulose, lignin and hemicelluloses. A minor, but for pulp and papermaking processes important, part consists of extractives and inorganic material.

Cellulose is the dominating cell wall component (40-45% of the dry wood weight), located largely in the secondary wall. Cellulose is a polysaccharide consisting of β-D-glucopyranose units linked together by (1 → 4)-glycosidic bonds. The molecule of cellulose I (all naturally occurring cellulose) is linear with a degree of polymerisation (DP) of 7,000-10,000 units and forms intra- and intermolecular hydrogen bonds. The individual cellulose chains are organised in bundles in the form of microfibrils, in which highly ordered (crystalline) regions are present but also less ordered (amorphous) regions. The microfibrils are the building blocks of fibrils, which are the constituents of fibres. The fibrous structure and hydrogen bonding give the cellulose a high tensile strength and make it insoluble in most solvents. Strong acids and bases, concentrated salt solutions and various metal complexes are able to dissolve cellulose.

Hemicelluloses are heteropolysaccharides, in contrast to cellulose which is a homopolysaccharide. Similar to cellulose, the hemicelluloses (20-30% of the dry wood weight) function as supporting material in the cell walls. The monomeric components of hemicelluloses are D-glucose, D-mannose, D-galactose, D-xylose, L-

arabinose and small amounts of L-rhamnose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid and D-galacturonic acid. The polysaccharide molecules are usually branched to various extents and have a DP of 100-200 units. Hemicelluloses can be dissolved in strong alkali and are more easily hydrolysed by acid than cellulose is. The greater solubility depends on their more amorphous structures and lower molecular weights.

The hemicelluloses in softwoods differ in composition and structure from those in hardwoods. In softwoods, the galactoglucomannans are the principal hemicelluloses (about 20% of the dry wood weight). They have a linear or possibly slightly branched chain of (1 → 4)-linked β-D-glucopyranose and β-D-mannopyranose units. Single-unit side chains comprised of α-D-galactopyranose are linked to the backbone chain by (1 → 6)-bonds. The hydroxyl groups at the C-2 and C-3 positions of the backbone are partly acetylated (about one acetyl group per 3-4 hexose units). Softwoods also contain 5-10% (by weight) arabinoglucuronoxylan, which consists of a framework of (1 → 4)-linked β-D-xylopyranose units. The backbone chain is partially substituted at C-2 by 4-O-methyl-α-D-glucuronic acid and at C-3 by α-L-arabinofuranose units. The principal monosaccharides in softwood hemicelluloses, in decreasing abundance, are: mannose, xylose, glucose, galactose and arabinose. Softwoods also contain other polysaccharides, e.g. starch and pectins, in minor quantities.

In hardwoods, glucuronoxylan is the major component of hemicellulose (15-30% of the dry wood weight). It has a backbone of (1 → 4)-linked β-D-xylopyranose units, which is partially substituted by acetyl groups (about seven per ten xylose units) and 4-O-methyl-α-D-glucuronic acid groups at the C-2 and/or C-3 position. Glucomannan occurs at an amount of 2-5% (by weight) in hardwoods and is composed of (1 → 4)-linked β-D-xylopyranose and β-D-mannopyranose units. The principal monosaccharides in hardwood hemicelluloses, in decreasing abundance, are: xylose, mannose, glucose, galactose and minor amounts of arabinose and rhamnose. Hardwoods also contain minor amounts of other polysaccharides, partly of the same type as those present in softwoods.

Lignin is the third major wood cell wall component and occurs in softwoods at an amount of 26-32% (by weight) and in hardwoods at 20-25% (by weight). The functions of lignin in wood are several: lignin provides stiffness to the cell wall, glues cells together, decreases water transport across the cell wall, counteracts attacks from micro-organisms and acts as a barrier to enzymatic degradation of the cell wall. Lignins are three-dimensional branched and to some extent cross-linked heterogeneous network polymers of phenylpropane units with many different linkages leading to an irregular structure, which is not yet fully understood. Lignins are polymerized primarily from three monomers: coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol. The main lignin precursor in softwoods, producing guaiacyl lignin, is coniferyl alcohol, while both coniferyl alcohol and

sinapyl alcohols are the main precursors of the so-called syringyl-guaiacyl lignin found in hardwoods. About two-thirds or more of the phenylpropane units in lignin are linked by ether bonds, the rest by carbon-carbon bonds. There are also linkages between lignin and hemicellulose and possibly also between lignin and cellulose.

Extractives consist of a large number of different compounds that are soluble in neutral organic solvents or water. Usually they occur at an amount of less than 10% (typical 1.0-2.0% in Norway spruce and 2.5-4.8% in Scots pine), although the concentration can be much higher in certain parts of the wood structure, e.g. in heartwood, branches, roots and areas of sore irritation. The main classes of extractives are: terpenoids, steroids, fats, waxes and phenolic substances such as stilbenes, lignans, flavonoids and tannins. Different types of extractives have different biological functions in the wood, e.g. fats and fatty acids are energy sources, steroids are part of enzymatic systems and resin acids and phenolic extractives protect against micro-organisms and insects.

The inorganic material content of woods that grow in temperate zones is low, 0.1-1%. The highest content is found in the needles, leaves and bark. The main metal components are calcium, potassium and magnesium, usually originating from different metal salts deposited in the cell walls and lumina. The most commonly occurring metal salts are carbonates, silicates, oxalates, and phosphates. The metals are partly bound to carboxylic groups present in xylan, pectin and extractives or are held by the wood components through complexing forces. Manganese and iron can be present in amounts of up to 100 mg/kg, whereas only trace amounts of some other metals can be found. The inorganic compounds are often essential for wood growth. Remaining heavy metals such as iron and manganese can detrimentally affect the brightness, bleachability and brightness stability of a pulp.

The chemical compounds described above are organised in a way that forms the ultrastructure of the fibre. In Figure 1, the wood fibre is schematically illustrated, showing the different layers that build up the cell wall: the primary wall (P), the three layers of the secondary wall (S1, S2, S3) and the warty layer (W). The fibres are held together by the middle lamella (ML). The hollow centre inside the mature fibre is called lumen. The primary wall has irregularly oriented cellulose fibrils. The secondary wall has different orientations of the cellulose fibrils (fibril angles) for each of the three layers, with the lowest fibril angle in the S2 layer. The layers have differing thicknesses: P and S3 have the thinnest walls and S2 has the thickest wall (cf. Figure 1 and Figure 2).

The various layers of the fibre wall have different physical and chemical properties and one reason for this is that the distribution of chemical compounds is not uniform throughout the cell wall, see Figure 2. The highest concentration of lignin can be found in the middle lamella (especially in the cell corners), but most of the

lignin occurs in the S2 layer because of the high cell wall volume of this layer (Panshin, DeZeeuw 1970).

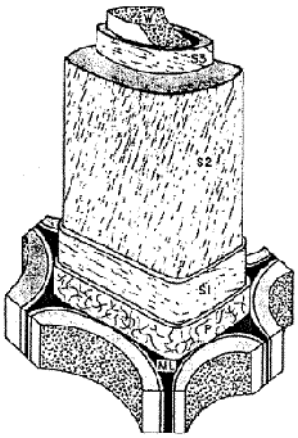


Figure 1. A schematic illustration of the wood fibre, showing the middle lamella (ML), the primary wall (P), the secondary wall layers (S1, S2, S3) and the warty layer (W) (Côte 1967).

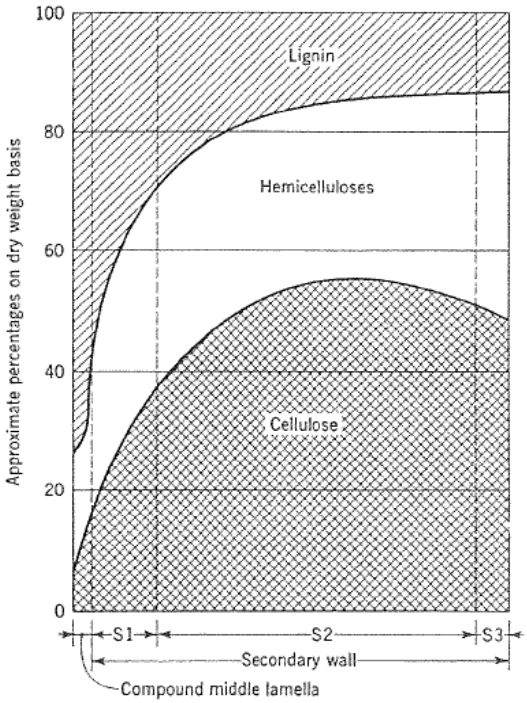


Figure 2. Approximate distribution of the main chemical components in the different layers of a softwood fibre (Panshin, DeZeeuw 1970). The compound middle lamella includes the primary wall of the adjacent fibres.

2.2 Mechanical and chemimechanical pulping

More detailed information can be found in, for example Kappel (1999), Sundholm (1999), Blechschmidt et al. (2006), Ek et al. (2009b), Suess (2010) and Hart and Rudie (2012).

Of all paper pulp produced, mechanical pulp accounts for about 20% while the larger part comprises chemical pulp. Mechanical pulping uses one of two main principles: grinding or refining. When producing groundwood (GW) pulp, wood logs are pressed against a rotating grindstone to produce fibres and fragments. In refining (e.g. RMP, refiner mechanical pulp), wood chips are defibrated and fibres further treated between refiner discs, with either one or both of the discs rotating. Mechanical pulping, also called high-yield pulping, normally results in a yield of 96-98% for Norway spruce (*Picea abies*). Chemimechanical pulping results in a lower yield, 80-95%, since the chips have been pre-treated with lignin softening chemicals before refining. Thermomechanical pulping (TMP) and chemithermomechanical pulping (CTMP) use pressurised refining at elevated temperatures. Before refining, the chips are pre-heated with steam (TMP) or pre-heated and pre-treated with chemicals (CTMP). For softwoods, the most commonly used chemical is sodium sulphite under slightly alkaline conditions. When producing hardwood CTMP, a larger amount of alkali is used in order to modify the carbohydrates and facilitate fibre separation and development. The production of alkaline peroxide mechanical pulp (APMP), where alkaline hydrogen peroxide and peroxide stabilising agents are added prior to and, in some cases, during refining, has increased over recent decades and is an alternative to the sulphite-based chemimechanical pulping processes.

2.2.1 Refining

The largest part of the high-yield pulps are produced in disc refiners. In the refiner, into which the chips are fed, the fibres are separated and fibrillated. The refining process usually continues in one or several subsequent refiners where further fibrillation occurs. The separation of the fibres is very important as it determines the character of the fibres obtained. Weakening of the fibre wall or middle lamella affects where the fibre separation occurs in the wood (Figure 3). Lignin softening by elevated temperature (TMP) fractures the fibres in the secondary (S1, S2) and the primary wall (P) whereas lignin softening by chemicals, e.g. sulphonation (CTMP), leads to greater rupturing in the primary wall and in the middle lamella (ML). Refining at low temperatures (RMP), i.e. when the wood and lignin are stiffer, results in a more uncontrolled fibre rupture across the cell wall.

The refining process comprises several mechanisms: the defibration when the fibres are separated and the fibre development when fragments and fine material (fines) are peeled off from the fibre wall, making the fibre fibrillated, see Figure 4.

The fibrillated fibre often has thinner walls (lower coarseness), is more flexible and collapses more easily than the unfibrillated fibre. The fibrillated surface also has a higher bonding ability. The produced fines improve the strength and light scattering properties of the final paper. Papers produced from mechanical pulps are characterised by high bulk, high light scattering ability and opacity, and good printing properties.

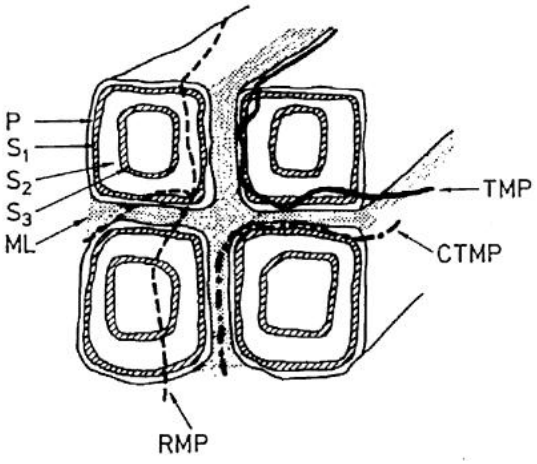


Figure 3. Schematic diagram of fracture zones in softwood fibres in different high-yield pulping processes (Htun et al. 1993).

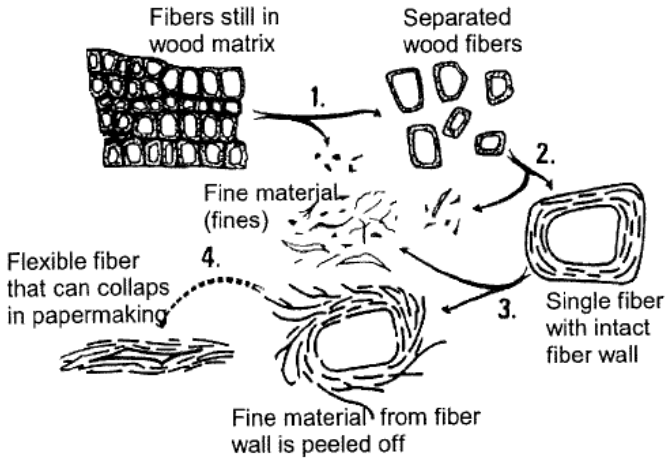


Figure 4. A hypothetical description of the fibre separation and development in a refining process (Sundholm 1993).

2.2.2 Bleaching

The aim when bleaching mechanical or chemimechanical pulps is to increase brightness/whiteness by eliminating coloured groups in the lignin without dissolving the wood constituents. Several factors influence the final brightness of the bleached high-yield pulp, mostly the initial brightness of the wood, the bark content, the mechanical defibration process, the bleaching conditions and the chemicals utilised. The light absorption coefficient, *k*, and light scattering coefficient, *s*, determine the brightness of the pulp. The light absorption coefficient measures the coloured matter in the pulp. The colour in mechanical pulp mainly originates from lignin that contains conjugated systems, chromophores, which absorb light and give the lignin its colour. Larger amounts of extractives in the wood may also make a small contribution to the colour. Bark in the pulp increases the *k* value. The high temperature during defibration will generate new chromophoric structures and thus increase the *k* value of the unbleached pulp (Karlsson 2010 and references cited therein).

Bleaching of mechanical or chemimechanical pulps is based on destroying the above-mentioned coloured groups in the lignin. The aim is not to dissolve the lignin as when bleaching chemical pulp since this would decrease the yield dramatically and the high-yield pulp properties would be lost. Lignin decolourisation is achieved by using oxidative or reductive bleaching chemicals. The higher the brightness target, the more complicated the bleaching technology becomes.

Reductive bleaching can be performed using, for example, dithionite (hydrosulphite), sodium borohydride, formamidin sulphinic acid (FAS), or other sulphite chemicals. Sodium dithionite ($Na_2S_2O_4$) is the most common reductive bleaching agent. Normal charges are 0.5% to 1.0% dithionite (calculated on bone dry pulp). Bleaching with dithionite is typically conducted at a moderately acidic pH. This will favour the yield compared to alkaline hydrogen peroxide bleaching. The presence of oxygen as well as too low pH levels leads to decomposition reactions. In order to avoid air, dithionite bleaching is preferably performed at low consistency or, if modern de-aerating pumps are used, medium consistency. The bleaching temperature is between 50°C and 80°C and the retention time is 15-60 minutes. Most of the bleaching occurs within the first 15 minutes. As the number of available chromophores for the reductive bleaching is limited, a brightness plateau is reached at a dithionite charge of between 1.0 and 1.5%. The brightness can be increased by about 10-12 ISO units by using dithionite under optimum conditions.

The most common oxidative bleaching agent is hydrogen peroxide (H_2O_2) used at an alkaline pH. Other possible oxidative bleaching chemicals are peracetic acid, ozone, percarbonates and perborates. Hydrogen peroxide bleaching is performed together with an alkali source as sodium hydroxide or magnesium hydroxide to

produce the active perhydroxyl anion (HOO^-). The amount of alkali is optimised (typically 1-3% NaOH) for each peroxide charge (typically 1-5%), retention time and bleaching temperature. The initial pH is about 11.5 when sodium hydroxide is used as alkali source and decreases during bleaching. Adding more alkali or increasing the temperature will increase the perhydroxyl anion concentration but more alkali will also promote decomposition and alkali darkening reactions. Lower temperatures require longer retention times to reach the same brightness. Hydrogen peroxide bleaching is performed at medium consistency (12%-20%) or high consistency (20%-40%). Higher consistency improves bleaching efficiency. Sodium silicate is used as an additive; 1-3% can improve the bleaching results by several brightness units. The exact mechanism of the function of sodium silicate is not known but it is believed, for example, to stabilise the hydrogen peroxide and act as a pH buffer. When magnesium hydroxide is used instead of sodium hydroxide, the pH is lower and more constant during bleaching, which can reduce the need for sodium silicate. Bleaching by adding hydrogen peroxide to the refiner is sometimes used as an alternative to a conventional bleach plant. The temperature and consistency is high and the mixing is good, although the retention time is much shorter.

Hydrogen peroxide decomposition to oxygen and water under bleaching conditions can be caused by high temperature, high alkali charge or high levels of transition metals. Metals in the pulp may derive from the wood itself, the process equipment or the process water. Since transition metals, particularly manganese, iron and copper, catalyse the decomposition of hydrogen peroxide, high levels will reduce the potential to bleach to a high brightness. Consequently, transition metals are removed before bleaching by treatment with a chelating agent, such as diethylenetriaminepentaacetic acid (DTPA) or ethylene-diaminetetraacetic acid (EDTA), followed by a washing stage. Another option is to remove the metals by using an acidic treatment.

Very small amounts of lignin are dissolved from the pulp under hydrogen peroxide bleaching conditions. Lignin side chains are cleaved and quinones are oxidised and carboxylic acids are introduced. The main compounds that are dissolved are acetic acid (from acetyl groups on hemicelluloses), formic and oxalic acids and low molecular weight carbohydrates. Also, some of the extractives are dissolved during hydrogen peroxide bleaching. The dissolved and colloidal substances, measured as chemical oxygen demand (COD), for example, are interrelated with the alkali charge. Using magnesium hydroxide as alkali source will lower the COD in the effluent compared to sodium hydroxide because of the lower pH. Maximum brightness after hydrogen peroxide bleaching can be about 82% ISO for softwood pulp and about 86% ISO for hardwood pulp, i.e. the brightness can be increased by about 20-22 ISO units under optimum bleaching conditions.

2.3 Energy reduction

The high electrical energy demand during mechanical pulping was pointed out as "the Achilles' heel of mechanical pulping" more than thirty years ago (Pöyry 1977) and it has always been a reason for process development. In recent years, there has been an increasing focus on energy reduction in mechanical pulp research and development. The specific energy consumption (SEC) for producing TMPs can be up to 3-3.5 MWh/bdt (Jackson, Wild 1999; Ali (Viforr), Salmén 2005; Francis et al. 2006; Viljakainen 2006) and consequently the electrical power cost has a major impact on the total production cost and thus the profitability.

High-yield pulping processes utilise the facts that the lignin in the wood matrix can be softened and that the fibre wall structure can be weakened by heat or chemicals. The separated fibres must be developed (fibrillated, delaminated) before the fibres are suitable for papermaking. An ideal mechanical pulp produces a sheet of paper with high opacity, brightness, bulk and smoothness. The pulp must also have sufficient strength properties, otherwise more reinforcement (chemical) pulp is needed. The chemical pulp has a higher cost and lower opacity and bulk.

It is well known that only a minor part of the energy applied to the refiner is used for fibre separation and fibre development (Hartler 1980; Salmén et al. 1999). The rest of the energy applied is converted to heat. The heat is generated when the more or less freely moveable viscoelastic fibres are fatigued by thousands of impacts in the refiner. Although a large proportion of the impacts do not directly break down the fibres, they are probably necessary to weaken the wood and fibre structure in the right places (Salmén et al. 1999). There is still much potential to improve energy efficiency, such as by directing the shear and compression forces to the right place in the fibre wall (Muenster 2008).

The TMP systems installed today are expected to consume at least 10% less energy than the systems installed previously (Sabourin et al. 2007), but this is not enough and many companies are pursuing new and more energy efficient solutions that are also viable in existing installations. A vast number of energy reducing strategies and technologies have been proposed ranging from process control and machinery to biotechnology (cf. e.g. Cannell 1999; Rodden 2003 and references cited therein). Some of the processes mentioned below can reduce the specific energy consumption considerably, but seldom without detrimental effects on the pulp and paper properties. Furthermore, many of the technologies are capital intensive and/or have high operational costs that result in no or very little economic benefits for the mills.

In this thesis, the focus is on methods aimed at obtaining a printing grade pulp with the use of less electrical energy during refining. If an energy reducing method is associated with deteriorated pulp properties, the additional cost (e.g. more

chemical pulp or more bleaching chemicals) for producing a pulp with the right properties must be compared with the cost savings due to energy reduction during refining. The amount of electricity needed for fibre separation and development is dependent on many factors, such as the type of wood raw material used, the pulping process chosen and the intended end-use of the produced pulp. The profitability of an energy reducing method is ultimately mill specific.

2.3.1 Optimisation of process conditions

Several concepts with increased processing temperature and intensity in the refining process have been developed in recent decades. The Thermopulp process was introduced by Sunds Defibrator in 1995 as a modification of the TMP process (Höglund et al. 1997). The pulp from the primary refiner is subjected to a high temperature treatment (160-170°C) for a short period of time (a few seconds) in a thermomixer and in the second refiner. The higher temperature reduces the disc gap and this increases the refining intensity. The temperature treatment makes the fibres more flexible, resulting in less damage during the intense refining. The first refining stage is conducted under standard TMP conditions to obtain fibre separation typical for TMP (cf. Figure 3). The higher temperature causes a brightness loss of about 1% ISO compared to standard TMP. The specific energy consumption can be reduced by 10% to 20% at equivalent freeness and tensile index. One advantage of the Thermopulp process is that it is easy to run periodically in a mill. High-temperature TMP reject refining has been shown in full scale to have the potential to reduce energy consumption by about 15% at a certain freeness level (Norgren et al. 2004). These results are maybe to be expected as the conditions are the same as those in the Thermopulp process.

The RTS-TMP process was introduced as an energy saving TMP process by Andritz (Muenster, Dahlqvist 1995; Sabourin et al. 1996; Muenster 2008). After pre-steaming the chips at atmospheric pressure, the chips are heated for a short residence (R) time of 10-20 seconds at a high temperature (T) of about 165°C prior to high speed (S) primary stage refining. The high temperature makes the fibres more resistant to the harsh intense refining. Brightness loss can be avoided because of the short retention time. The optimised refining intensity led to a reduction in SEC of about 15% at similar freeness and with similar or higher strength properties in pilot plant refining (Sabourin et al. 1996).

High-temperature chemithermomechanical pulping (HTCTMP) can produce high bulk pulp from birch using considerably lower energy input than standard CTMP, which is pre-heated at a lower temperature (Vesterlind, Höglund 2006). A temperature increase from 130°C to 160°C could lower the SEC in pilot refining by about 30% for a specific freeness and internal bond strength (Scott-Bond).

Another energy saving TMP process is low-consistency (LC) refining used as a final stage. The addition of LC refining at mill scale can reduce energy consumption by 5%-8% for a given freeness and/or increase capacity (Musselman et al. 1996). There is an increased risk of fibre cutting, although this can be avoided by good control of the refining intensity. It has also been shown in pilot trials that a low-consistency post-refining stage of spruce HTCTMP at very low specific energy input can comprise a process for producing paperboard pulp. The process gave high bulk for a specific internal bond strength, although fibre cutting was seen (Klinga et al. 2008). High temperature LC refining is another more energy efficient approach (Muenster et al. 2006; Sandberg 2007). The reason for the lower SEC remains unclear. It has been proposed that the energy reduction can be explained by the higher refining intensity, more efficient energy transfer in water, a higher degree of fibre swelling or the very narrow and well controlled disc gap (Muenster et al. 2006). By chemically pre-treating TMP (cf. Sections 2.3.3 and 2.3.5 below) with alkaline hydrogen peroxide, the pulp was made more resistant to cutting during the subsequent LC laboratory refining (Chang et al. 2010), while ozone pre-treatment could promote tensile development during the LC refining (Chang et al. 2012). The effect of LC refining at mill scale was studied when two mechanical pulping lines were compared, one line had two stages with high consistency (HC) single disc (SD) refining and the other line had HC double disc (DD) refining with subsequent LC refining (Andersson et al. 2012). At similar tensile index and freeness, the DD-LC line reduced the energy consumption by 400 kWh/adt compared with the SD-SD line.

Several new and improved refiner segments have been developed during the past decade. Segments with new geometry, e.g. low energy (LE™) segments (Bergquist, Vuorio 1998; Bergquist et al. 2008) and Turbine™ segments (Huhtanen et al. 2004), have quite recently been put into industrial use and are reported to give a reduction in SEC. Trials using various abrasive segments indicate potential to reduce energy consumption, but these segments have not yet been put into industrial use due to problems with control of the refiner, limited operating lifetime of segments and a degradation of pulp quality (poor strength properties) (Somboon, Pynnönen 2008). Evaluation of grit segments at pilot plant scale has shown that optimising the refining intensity can achieve an energy reduction of up to 10% at a specific freeness level and tensile strength with no distinct difference in pulp quality (Somboon et al. 2009).

Some mills have achieved a reduction of SEC through increased refiner production rates (see Cannell 1999). However, the reasons for and extent of the energy savings are difficult to estimate as they are unique to each system. Also, a reduced primary stage refining consistency (e.g. from 50% to 40%) is reported to give a SEC reduction of up to 7% for a specific freeness value (Cannell 1999).

2.3.2 Mechanical pre-treatments

Different approaches to increase the destruction of the wood prior to refining have been tested as methods to decrease the energy demand in subsequent refining (Gorski et al. 2010 and references cited therein). Mechanical compressive treatments of wood chips prior to refining could be a way of transferring mechanical energy to wood more efficiently. The methods are aimed at modifying the viscoelastic behaviour of pre-heated wood by exposing the wood to well-directed shear and compression forces (Muenster 2008). Energy savings of between 6% and 9% at equivalent freeness and burst index respectively are reported using compressive pre-treatment at pilot scale (Frazier, Williams 1982; Sabourin 1998; Kure et al. 1999). A modified wood chipping process, inducing increased compressive damage to the chips, gave an energy reduction in subsequent pilot refining of about 15%, compared at similar freeness (Hellström et al. 2012). By measuring the energy used under different loading conditions of wood pieces, it has been shown that the deformation in compression loads require larger amounts of energy than the deformation in combined (shear and compression) loads (De Magistris, Salmén 2006).

Electron beam pre-treatment (irradiation) can affect the wood structure if the intensity is high enough. Energy savings of up to 25% can be achieved in pilot refining when comparing at the same freeness but not, however, when comparing a specific tensile or tear strength (Granfeldt et al. 1992). By introducing an impregnation step with magnesium or sodium bisulphite (cf. Section 2.3.3 below) before irradiation in the so-called ETMP-process, energy savings between 30% and 40% in laboratory refiner have been reported when compared at similar freeness (Gailat et al. 2011). The tensile strength was slightly decreased however.

The potential for energy reduction by using wood shavings instead of chips has been shown to be about 25% for a specific tensile index (Ali (Viforr), Salmén 2005). The targeted deformation that occurs when manufacturing the shavings probably results in more favourable fibre deformation before refining.

2.3.3 Chemical pre-treatments

Chemical modifications of wood and fibres often affect the softening and swelling behaviour. In the CMP, CTMP and APMP processes, either sulphonic acid groups (sulphonation) or carboxylic acid groups (carboxylation) are incorporated into the lignin to lower the lignin softening temperature (Salmén 1995). These chemical treatments also affect the swelling since the added groups are hydrophilic. However, chemimechanical pulps are mainly used for board, fluff and tissue applications and have other properties than the pulp used for normal printing papers. The same chemical treatments with much less chemicals or other chemical treatments have been tested with the aim of producing energy efficient “TMP-like” printing paper grade pulp. The majority of the suggested methods add the

chemicals to the wood chips prior to refining, i.e. as a chemical pre-treatment. A few inter-stage treatments of coarse pulps have also been suggested (see Section 2.3.5). The application of chemicals for enhanced refining of softwood TMP has so far only been used to a limited extent by the industry.

Mild sulphonation is a chemical pre-treatment method that has the potential to save energy in high-yield pulping. Refiner trials at both pilot and mill scale with low charges (0.1% to 0.15% Na_2SO_3/dry weight of wood) result in about a 15% reduction in SEC for a specific freeness and tensile index (Axelson, Simonson 1982a; 1982b; 1983a; 1983b). The difficulty is in targeting the narrow range of sulphonation that gives the energy reduction. The mechanism has been proposed to be related to selective sulphonation of the primary wall (Westermark et al. 1987; Peng et al. 1992). Later research suggests that it is related to swelling and softening due to loss of lignin-protein and lignin-pectin bonding (Stevanic, Salmén 2008). Mechanical (Impressafiner) and sulphite pre-treatment of chips before double-disc refining were evaluated at mill scale by Nelsson (2011). The energy consumption during refining was reduced by 6% with the mechanical treatment and by 12-15% with the sulphite treatment, in both cases when compared at a certain tensile index. Moreover, mechanical or sulphite pre-treatment increased or decreased, respectively, the light scattering coefficient of the pulp. Gas phase sulphonation is another proposed method that has been shown to have the potential to reduce SEC in a laboratory refiner by up to 20% for a specific freeness or tensile index (Svensson et al. 1994).

The use of oxalate or oxalic acid as a chemical pre-treatment has been tested at pilot scale and has shown potential as an energy saving method for TMP refining (Swaney et al. 2003; Houtman, Horn, 2011). A degradation of the cell wall is reported and sugars constituting hemicelluloses are found to be the main target of oxalate. Energy savings of about 20% were achieved in laboratory refining for a specific freeness level (Meyer et al. 2005). The use of diethyl oxalate on wood chips prior to refining of spruce TMP has been reported to provide energy savings at laboratory scale of up to 40% for a specific freeness level (Kenealy et al. 2007). Strength properties were improved, although their absolute values were unusually low. Problems with scaling must be taken into consideration, however, when oxalate is used in a high-yield pulping process. The use of ozone at different stages of the TMP process has been studied. The energy savings reported from pilot and laboratory refining vary from 5% to 30% depending on the wood species, addition point and ozone charge (Petit-Conil et al. 1998; Petit-Conil 2003).

Alkaline treatment in the refiner zone increases fibre swelling and has been reported to give SEC reductions of up to 30% (depending on the sodium hydroxide NaOH charge) for a specific tensile index (Hartler 1980). The energy savings were accompanied by lower yield and lower brightness. The addition of alkaline hydrogen peroxide to refiners is a well-known technology (Strunk, Meng 1989)

that besides brightening the pulp also can lower the energy demand in both pilot and mill refining (Åkerlund et al. 1979; Harrison et al. 2008). Hydrogen peroxide treatment introduces carboxylic acid groups into the lignin. The hydrogen peroxide treated wood in Na^+ form has both a low lignin softening temperature and a high degree of swelling (Hammar et al. 1995), which should be positive for energy efficient refining. The previously mentioned APMP process (see Section 2.2), where chips are impregnated with alkali and hydrogen peroxide prior to refining, has been applied to hardwood with considerable energy reductions in pilot refining compared with bleached chemithermomechanical pulp (BCTMP) (Bohn, Sferrazza 1989). The APMP process applied to softwood has shown the same SEC as for BCTMP at the same freeness and pulp quality and the advantage claimed is that it does not need a separate bleach plant (Bohn, Sferrazza 1989). It is important to compare SEC in APMP processes with SEC in standard CTMP or TMP processes, including bleaching to the same brightness and strength properties in order to draw the right conclusions about energy reductions.

2.3.4 Biotechnical pre-treatments

Fungal treatment of wood chips or coarse pulp has been explored since the 1970s to lower the specific energy consumption during mechanical pulping (Ander, Eriksson 1975; Akhtar et al. 1998). White-rot fungi are of prime interest since the potential exists to degrade both wood polysaccharides and lignin. The benefits of using white-rot fungi in mechanical pulping are the substantial energy reduction and the improved paper strength properties that can be obtained, although these achievements are at the expense of lower brightness due to the formation of quinones, lower light scattering ability and lower yield. It has been shown that TMP pulps from spruce can be produced in laboratory refiners using 13% less refining energy for a given freeness (Setliff et al. 1990). The technical difficulties (long pre-treatment times, addition of nutrients, inhibition of undesirable micro-organisms etc.) of implementing this technology in existing operations present a serious drawback.

Enzymatic pre-treatments of chips, using several different enzymes (e.g. cellulase, hemicellulase, laccase, pectinase or xylanase), have been studied with the aim of reducing energy consumption in mechanical pulping. The results are very varied but significant energy reductions, sometimes compared at similar strength and sometimes compared at similar freeness (with strength losses), have been achieved in laboratory or pilot refining (Pere et al. 2000; Mansfield 2002; Peng et al. 2003; Hart et al. 2009; Lecourt et al. 2010; Meyer et al. 2012). It is difficult to draw any conclusions about the optimum enzyme treatment for spruce TMP.

2.3.5 Inter-stage treatments

Chemicals used to lower the SEC during refining can be added at various stages of a mechanical or chemimechanical pulping process. One alternative is to add chemicals before fibre separation (cf. the pre-treatment methods described above), another is to add chemicals in-between or during refining stages (inter-stage treatment). The first approach could have the potential to influence the fibre separation mechanism and thereby the resulting pulp properties to a greater extent than the second approach. The pre-treatment method, however, has the drawback of being more capital intensive since some type of impregnation equipment is normally needed. The second approach, such as using the primary refiner as mixing equipment, has the advantage of being cheaper and could be directly applicable in a thermomechanical pulping process consisting of two or more refiners in series. The potential energy reduction could still be considerable for an inter-stage approach if the first refining stage is performed with a low energy input. This is supported by the fact that most of the energy used in a high-yield pulping process is consumed during fibre development (flexibilisation, fibrillation, generation of high-quality fine material etc.) and not fibre separation (Campbell 1934; Kano et al. 1983; Sundholm 1993).

One process that uses inter-stage treatment is the OPCO process (developed by the Ontario Paper Company), which is a thermomechanical or mechanical pulping process combined with a reactor for chemical treatment (Knuutila, Barnet 1984). The reactor can be placed either after refining or between the refining stages in a TMP process. The resulting product combines the high yield and fibrillation of mechanical pulp with the high flexibility and bonding ability of chemical pulps. The main changes in the properties of OPCO pulps as compared to TMP pulps are: improved dry and wet strength properties, high density, lower shive content and lower light scattering coefficient. OPCO pulp can be used to replace kraft or sulphite pulps in newsprint or other paper grades.

Some of the studies described above that have used chemical pre-treatments for ozonation and sulphonation, for example, have also tested inter-stage treatments. One sulphonation study, where 2-5% sodium sulphite was added either as a pre-treatment or to the eye of a pilot refiner, concluded that the refiner addition was favourable with respect to energy reduction to a given tensile index and gave a SEC reduction of at least 20% (Högman, Hartler 1988). Earlier results showed that for a given specific energy input in pilot refining, inter-stage treatment at a given sulphonate content (above 1%) led to higher strength and light scattering ability than did pre-treatment for the same sulphonate content (Heitner et al. 1982).

The effect of adding oxygen, hydrogen peroxide, sodium bisulphite, peracetic acid or sodium hydrosulphite as inter-stage treatment between laboratory refining stages was compared (Delisle et al. 2012) and some of these chemicals were also

used to only treat the long fibre fraction (Lin, Lanouette, 2012). The most promising treatments were oxygen or sodium bisulphite. The addition of chemicals to the refiner is also used for bleaching purposes (Åkerlund et al. 1979; Strunk, Meng 1989; Chute et al. 1995) and energy reductions have been reported, for example, for refiner bleaching with magnesium hydroxide and hydrogen peroxide (Harrison et al. 2008).

A combination of mechanical pre-treatment of chips, increased refining intensity and chemical inter-stage treatment after defibration, called ATMP (Advanced Thermomechanical Pulp), has reduced the specific energy consumption in pilot production by 12-42% (Johansson et al. 2011; Gorski et al. 2011), compared at similar tensile index. The ATMP process adds an Impressafiner and a Fiberizer before the normal refining stages. Chemicals such as bisulphite or hydrogen peroxide were charged to the primary refiner.

2.4 Fenton system

More detailed information about the Fenton reaction and Fenton-like systems can be found in, for example Haber and Weiss (1934), Barb et al. (1951a; 1951b), Walling (1975), Goldstein and Meyerstein (1999), De Laat et al. (2004) and the review articles Edwards and Curci (1992), Goldstein et al. (1993), Koppenol (1993), Sychev and Isaak (1995) and Pignatello et al. (2006).

The reactions are, for example, relevant to biological chemistry and the treatment of hazardous wastes. The number of scientific articles on the application of Fenton chemistry in waste treatment has increased over the years (Pignatello et al. 2006 and references cited therein). Water treatability studies with dye wastes, pulp bleaching wastes, agricultural effluents, landfill leachates and surfactants are reported. Recent studies have explored the possibility of using Fenton chemistry for degrading contaminants in soil and ground water. The involvement of Fenton chemistry in the early phase of lignin biodegradation by fungi is not fully elucidated but is debated (Goodell et al. 1997; Hammel et al. 2002; Bohlin 2008; Arantes et al. 2009a).

2.4.1 Free ferrous/ferric ions

The Fenton reaction refers to the decomposition of hydrogen peroxide to highly reactive hydroxyl radicals (HO•) via a reaction pathway involving soluble ferrous ions (Fe^{2+}) at an acidic pH, see Reaction 1 in Figure 5. The name of the Fenton reaction refers to H. J. H. Fenton who, in 1894, published his work about oxidation of tartaric acid in the presence of hydrogen peroxide and low concentrations of ferrous salts (Fenton 1894). The Reaction 1 was proposed by Haber and Weiss (1934). The formed ferric ions (Fe^{3+}) can slowly be transformed to Fe^{2+} by a reaction consuming H_2O_2 under the formation of hydroperoxyl radicals (HOO•), see

Reactions 2 and 3 in Figure 5. This means that the ferrous ions are recycled and can act as a catalyst in the oxidation system. Organic compounds (RH) such as lignocellulosic materials can be oxidised in radical chain reactions. The formed hydroxyl radicals may also oxidise Fe^{2+} to Fe^{3+} or decompose H_2O_2 to water and HOO•. The formed hydroperoxyl radicals can react with both the ferric and ferrous ions or combine and generate hydrogen peroxide. If the Fenton reaction starts with ferrous ions, ferric ions are almost instantly formed (especially when a large molar excess of hydrogen peroxide is present) and since the iron acts as a catalyst in the Fenton system, both valence states should be present simultaneously. Theoretically therefore, it should be of minor importance whether the reaction starts with ferrous or ferric ions. However, differences have been reported, and when starting with ferrous ions a burst of hydroxyl radicals is formed and an initial rapid degradation phase takes place (Pignatello et al. 2006).

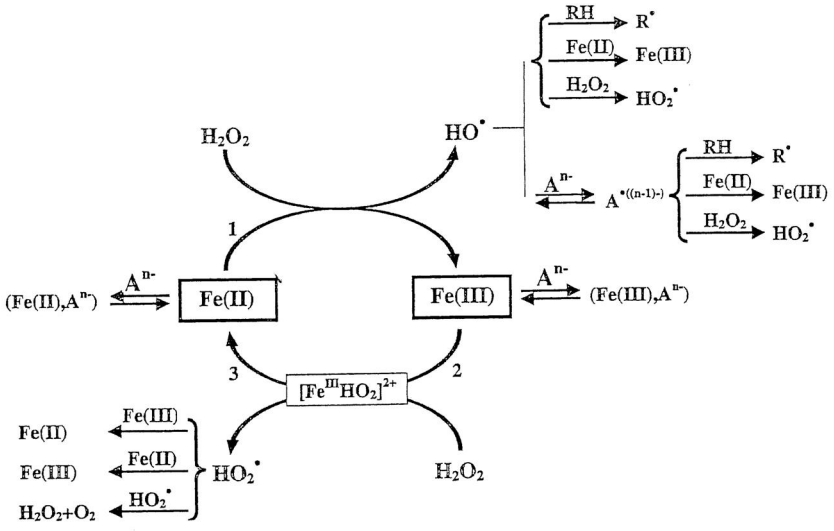


Figure 5. Simplified reaction scheme for the Fenton system (De Laat et al. 2004). A^{n-} = inorganic anion, RH = organic compound.

The reactions of the Fenton system are influenced by the inorganic anions (A^{n-}), the ligand attached to the metal ion and the nature of the organic compounds present (De Laat et al. 2004). Furthermore, De Laat et al. (2004) showed that the rates of reaction between ferrous ions and hydrogen peroxide follow the order sulphate > perchlorate = nitrate = chloride ions, whereas the efficiency of the oxidation reaction between ferric ions and hydrogen peroxide decreased in the presence of chloride and sulphate ions. It is also known that the Fenton system can be broadened to other lower valence transition metals that have one-electron redox

couples [e.g. Co(I)/Co(II), Cu(I)/Cu(II), Mn(II)/Mn(III), Ti(III)/Ti(IV)] and organic hydroperoxides (e.g. alkyl hydroperoxides, ROOH) or hypohalous acids (e.g. HOCl). The catalytic decomposition of cellulose by hydrogen peroxide was tested with a number of substitutes for ferrous sulphate (e.g. ferric sulphate, ferric chloride, copper sulphate etc.) and ferrous or ferric salts were the most effective with a slight advantage for ferrous sulphate (Kang, Hwang 2000). Different ferrous and ferric complexes and the numerous radical intermediates, generated oxidation products (e.g. alkyl and alkoxyl radicals, hydroxylated derivatives and carboxylic acids) and consecutive reactions make the Fenton system complicated. In addition to the complexity of the many reactions, the Fenton system is dependent on pH, temperature and concentration.

The catalysis of hydrogen peroxide decomposition by iron in dilute solutions is, however, not presently fully elucidated and the role of the hydroxyl radical is disputed. Besides the theory described above, which is based on the participation of free radicals, a conceptually different theory exists wherein the ferryl ion (FeO^{2+}) is regarded as the active intermediate and not the hydroxyl radical (cf. Sychev, Isaak 1995).

2.4.2 Iron complexes used as Fenton catalysts

A commonly observed pH optimum of the Fenton reaction is about 3 (Kang, Hwang 2000; Pignatello et al. 2006), which is due to the formation of less Fenton-reactive precipitated ferric species at higher pH levels. Chelation extends the pH range over which iron is soluble and chelation may also accelerate Reaction 1 (see Figure 5). Studies have shown that hydroxyl radicals can be produced with iron complexes such as Fe-EDTA (ethylenediaminetetraacetic acid) or Fe-NTA (nitrilotriacetic acid) (Walling et al. 1975; Singh, Hider 1988). However, chelation may retard the regeneration reaction of ferrous iron, scavenge HO• or produce ferryl species instead of the desired hydroxyl radicals (Pignatello et al. 2006). If the hydroxyl radical production is accelerated, diminished or inhibited depends on e.g. the type of ferric complex used and/or the type of organic substrate present (Koppenol, Butler 1985; Sun, Pignatello 1992; Addy, Gilbert 1995; Kang, Hwang 2000; Bissey et al. 2006). For example, the availability of a free (open or occupied by e.g. water) coordination site on the iron is required for catalysis (Graf et al. 1984). The redox potential of the iron influences the reaction and it can be altered depending on the stability constants of the ferrous chelate and the ferric chelate (Bond, Jones 1959). It has been seen that a stable complex such as iron-EDTA forms fewer hydroxyl radicals compared to a less stable iron chelate such as iron-NTA (Singh, Hider 1988). The ligands with very high affinity for ferric ion are those with correct stereochemical arrangement around the metal ion, e.g. DTPA (diethylenetriaminepentaacetic acid), which consequently forms even fewer hydroxyl radicals than ferric-EDTA (Singh, Hider 1988). The ability of the ligands

to react (or scavenge) the hydroxyl radicals may also have an effect. Either free or complexed organic ligands can be attacked by the oxidant. It may be advantageous with oxidised complex if iron remains soluble and acts as a catalyst long enough to perform the treatment of the substrate. The activity of the oxidised complex can be enhanced compared with that of the original complex (Sun, Pignatello 1992).

EDTA forms a strong complex with ferric ions, which has a stability constant (log K) of 25.1 (Chabarek, Martell 1959). The ferric ion is coordinated to four O atoms and two N atoms of EDTA and a water molecule, i.e. seven-coordinated, in a pentagonal bipyramidal shape (Higginson, Khan 1983; Solans et al. 1984) and thus has a free coordination site. Fe-NTA has a stability constant of 15.9 (Chabarek, Martell 1959) and the ferric ion coordinates with two NTA in a pentagonal bipyramidal coordination with one carboxylate group uncoordinated (Clegg et al. 1984). Another iron ligand of similar size to NTA, i.e. ethanol diglycinic acid [EDG, also called hydroxyethyliminodicetic acid (HEIDA or HIMDA)], was used as ferric complex and catalyst in a Fenton-like reaction to effectively degrade pesticides in water and soil at a pH of about 6 (Sun, Pignatello 1992; Pignatello, Baehr 1994; Pignatello, Day 1996). Both EDG and NTA were the most reactive ferric chelates with respect to oxidation of 2,4-dichlorophenoxyacetic acid by H_2O_2, while EDTA was inactive in that study (Sun, Pignatello 1992). EDG has a stability constant of 11.6 (Chabarek, Martell 1959) and thus forms a weaker complex with ferric ions compared with EDTA or NTA. It is possible that the ferric ion which is chelated with EDG has several free coordination sites. The exact coordination structure of Fe-EDG is not known, however, there are indications that polynuclear chelates are formed from the hydroxy forms of Fe-EDG (Gustafsson, Martell 1963).

2.4.3 Fenton-like reactions with lignocellulosic material

There have been several investigations using Fenton's reagent together with wood or lignocellulosic materials such as pulp or models of its components. Among the research areas investigated are fibre-board production (Westermark, Karlsson 2003; Widsten et al. 2003; Qian et al. 2004; Yelle et al. 2004; Pino et al. 2005), lignosulphonate bleaching (Walker et al. 1999), kraft pulp beating (Qian et al. 2002), degradation of lignin (Bentivenga et al. 2003) and treatment of lignosulphonates (Areskogh, Henriksson 2011), as well as treatment of recycled unbleached softwood kraft pulp (Mocchiutti et al. 2010) and degradation of pulp mill effluents (Catalkaya, Kargi 2007; Arantes, Milagres 2007). There are also studies into how Fenton chemistry may play a role in fungal degradation of wood (Goodell et al. 1997; Hammel et al. 2002; Bohlin 2008; Arantes et al. 2009a) and it is proposed that oxalate and low molecular weight compounds are involved by chelating and reducing the ferric ions (Goodell et al. 1997; Arantes, Milagres 2006).

The half-life of the hydroxyl radical, formed by the Fenton reaction, is approximately 10^{-9} seconds, which means that its reactions take place practically at

the site of generation (Sies 1993). The hydroxyl radical is a very strong oxidant with reported standard reduction potential of between 1.8 V in neutral solution and 2.7 V in acidic solution (Buxton et al. 1988). Furthermore, the hydroxyl radical reacts rapidly with organic compounds by adding to unsaturated bonds, abstracting H from C-H bonds or by adding to aromatic rings (Buxton et al. 1988), therefore it reacts with both lignin and carbohydrates in lignocellulosic material. It is proposed that there is a selectivity of hydroxyl radicals, when reacting with lignin and carbohydrate models, that is about 5-6 in favour of the lignin structures (Ek et al. 1989). The oxidation of carbohydrates initiated by hydroxyl radicals can lead to carbonyl groups, which in alkaline solution can cause cleavage of the cellulose chain (Ek et al. 1989). The depolymerisation reactions, viscosity loss, can decrease the strength of the fibre (Gellerstedt 2009). However, hydroxyl radicals that are produced outside wood fibres have been shown to have little influence on the viscosity (Lind et al. 1997). It has therefore been proposed that during oxygen delignification, it is the superoxide driven Fenton reaction at the inside of the fibres that may lead to fibre fracture (Reitberger et al. 2001). Hydroxyl radicals are also said to be partly delignifying (Ragnar 2000), they alone cannot degrade aromatic structures into aliphatic structures (Reitberger et al. 2001), but by hydroxylating aromatic rings they introduce handles for other bleaching agents to attack (Ragnar 2000). It has been shown that the Fenton reaction can both depolymerise and polymerise different lignin types, e.g. depolymerisation of steam-exploded lignin from beech (Bentivenga et al. 2003) and polymerisation of lignosulphonates (Areskogh, Henriksson 2011). When Fenton´s reagent was used to degrade black liquor lignin, low concentrations of hydrogen peroxide (5 and 15 mM) caused the lignin to polymerise, while high concentrations (60 mM) caused depolymerisation (Araujo et al. 2002). A decrease in phenolic groups of the lignin and lignosulphonate, respectively, was observed after oxidation (Araujo et al. 2002; Areskogh, Henriksson 2011). Research using Fenton based reactions on wood has shown demethoxylation of lignin (Arantes et al. 2009b).

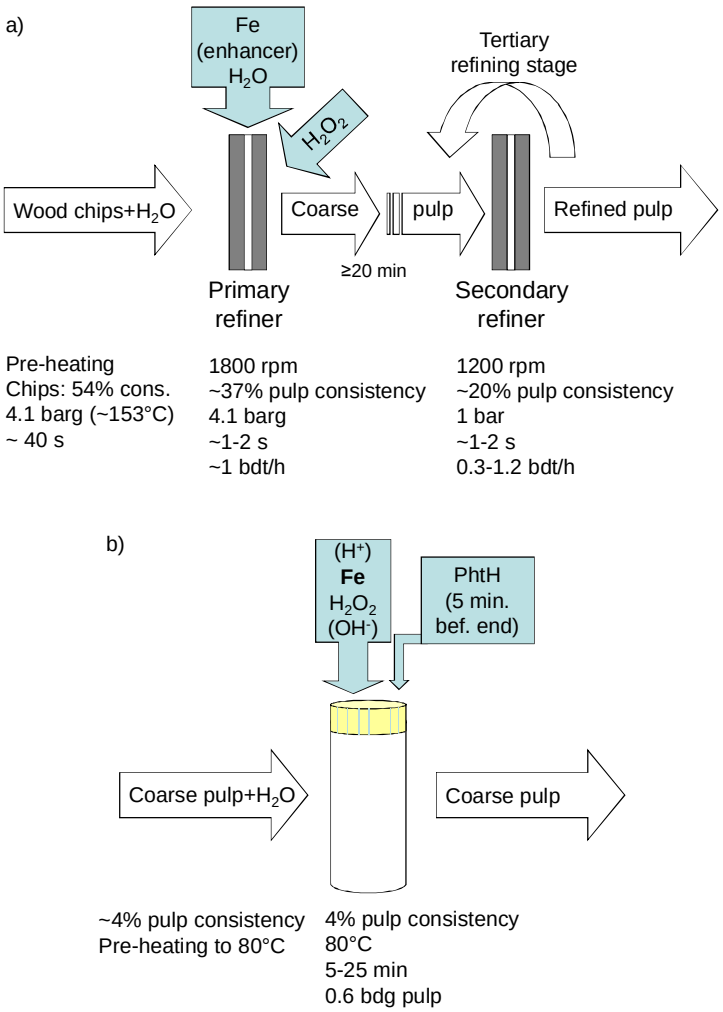
3 EXPERIMENTAL

This experimental section deals mainly with the conditions of the pilot plant trial and the model study. It also explains how hydroxyl radicals were monitored and how increased pressure was used to calculate hydrogen peroxide that decomposed into oxygen. There is a short description of the method used for determination of carbonyl groups (not included in Paper I-V). Experimental details can be found in the appended papers.

3.1 Pilot plant trial (Papers I, II and III)

TMPs were produced from Black spruce (*Picea mariana*) wood chips at the Andritz pilot plant facility in Springfield, OH, USA. A three-stage refining setup was used and the energy input was varied in the last refining stage to obtain pulps with different freeness levels (see Figure 6a). The wood chips were pre-heated at 4.1 barg steaming pressure for 40 seconds prior to refining. A single disc 36" pressurised refiner (Andritz Sprout-Bauer 36-1 CP) was used in the first refining stage and a double disc 36" atmospheric refiner (Andritz Sprout-Bauer 401) in the second and third refining stages. The energy input in the primary refining stage was approximately 500 kWh/bdt, and in the second refining stage approximately 1,000 kWh/bdt. In most cases, three tertiary refining stages were performed with a targeted energy input of 400, 800 and 1,200 kWh/bdt, respectively. The energy consumption for producing the Black spruce reference TMP in the pilot plant was close to commercial operation (cf. Jackson, Wild 1999). The metal content in the chips and in the pulps produced is shown in Table 7.

The chemicals used in the trial were added according to an inter-stage approach; the ferrous sulphate (and enhancer when used) was added to the refiner eye and the hydrogen peroxide to the blow line of the pressurised first-stage refiner (cf. Table 1 and Figure 6a). The ferrous sulphate and the enhancer were thoroughly mixed before addition to the refiner eye. The pilot plant is a batch process, which inevitably leads to a retention time between the refining stages of at least 20 minutes, something that may have an impact on the chemical reactions prevailing. The retention time per refiner was estimated at 1-2 seconds. All trial series were performed under identical conditions, meaning that the variation in specific energy consumption and resulting pulp and paper properties is a result of the chemicals added during the trial. The addition levels of chemicals are given as 100% calculated on bone dry (bd) wood.



Figures 6a-b. The setups of the pilot plant trial at Andritz (a) and of the model study (b). See Papers IV and V for more detailed information e.g. the type of iron catalysts and enhancers used.

3.2 Model study (Papers IV and V)

Primary refined pulp of Norway spruce (*Picea abies*) was obtained from a Swedish mill. The pulp consistency was 43.8% and the freeness was 370 ml CSF. The content of transition metals in the pulp (mg/kg) was: Cr, <0.1; Cu, 0.5; Fe, 5.0; Mn, 58; and Ti, 0.1. The pulp was stored in the freezer at -20°C before further use. Deionised water was used in all trials unless otherwise stated (see Paper IV).

The setup of the model study is illustrated in Figure 6b. Pulp and deionised water were preheated to 80°C, after which iron containing catalyst and hydrogen

peroxide were added to the pulp suspension in that order. If the pH was adjusted, the acid was added before the iron catalyst and the alkali was added after H_2O_2 in order to prevent the iron from precipitating. After each chemical addition, the sample was mixed and finally placed into a water bath of 80°C for, in most cases, 5 to 25 minutes. A probe of phthalic hydrazide (PhtH) was added to be present, normally at five minute intervals, see Section 3.2.1 below about hydroxyl radical detection. The start concentration of chemicals was 0.30 mmol Fe/L (17 mg Fe/L, 400 g Fe/b.d.t.), 0.15 mol H_2O_2/L (5.0 g H_2O_2/L, 120 kg/b.d.t.) and 0.17 mmol PhtH/L in all trials. Following the reaction, the pulp was dewatered and liquids were filtrated before immediate analyses of chemical oxygen demand (COD), total organic carbon (TOC), hydroxyl radicals and dissolved iron. Coefficients of variance were 16% for COD, 12% for TOC, 12% for hydroxyl radicals and 7% for dissolved iron (based on seven replicates). Residual hydrogen peroxide (determined with iodometric titration) and pH were measured on unfiltered liquids (based on seven replicates, coefficients of variance were 3% and 0.9%, respectively). Most trials were performed with 0.6 g bd pulp at 4% pulp consistency in 50 mL plastic tubes (see Figure 6b), since this gave a fast and time accurate procedure when dosing the chemicals and analysing the filtrates. For pulp analyses such as total fibre charge and metal ion content, and for trials with higher consistency, a procedure was used with a greater amount of pulp in a plastic bag.

3.2.1 Hydroxyl radical detection

The main methods used for detecting hydroxyl radicals are 1) spin trapping, 2) reactions with known scavengers and identification of the products formed, 3) analysis of the relative yields of the products formed in the reaction of the oxidising unit with one or two reactants and 4) use of oxygen isotope effects (Goldstein et al. 1993). Here, a chemiluminescence (CL) method, originating from a work by Reitberger and Gierer (1988) was chosen as the basis for the hydroxyl radical detection, but with some modifications. The method is based on the reaction of hydroxyl radicals with the scavenger phthalic hydrazide (PhtH). The formed hydroxylated PhtH produces detectable light at subsequent oxidation. The CL method has previously been used to measure hydroxyl radicals in different types of pulp or wood applications (Walker et al. 1999; Backa et al. 1992; Backa et al. 1997; Nilvebrant, Stenman 2003). In this study, the CL method has been used qualitatively and as a complement to other analyses.

In the original procedure, the PhtH was present during the entire reaction. A modified procedure in which the probe is exposed to hydroxyl radicals for a limited time period to avoid degradation of the hydroxylated PhtH was described by Walker et al. (1999). A similar modified method was used in this study. The deviation from the original procedure was that, in all trials except when noted, the PhtH was present in a maximum of five-minute intervals. For example, to analyse

the hydroxyl radicals that were formed during 15 minutes of reaction, three separate reaction vessels (5, 10 and 15 minutes) were used. The PhtH was not present during the entire reaction but only during the final five minutes, i.e. added at time zero for reactions of zero to five minutes (vessel 1), at time five minutes for reactions of five to ten minutes (vessel 2) and at time ten minutes for reactions of ten to fifteen minutes (vessel 3). The accumulated chemiluminescence (CL) was obtained by adding the values from the separate intervals (vessels). Not all five-minute intervals were measured in all cases, but some values were interpolated from data of adjacent measured intervals (Paper V). In the example above, the value from vessel 2 (five to ten minutes) should then be interpolated from the values of vessel 1 and 3. The accumulated CL was obtained by adding the values from the separate intervals (measured and/or interpolated). For the CL analysis, a luminometer (Unilite NG) was used and the CL value after 20 minutes of emission was used for evaluation in this study.

A further modification of the original procedure was that the strength of the buffer solution was doubled, i.e. 2 M sodium carbonate and 50 mM EDTA tetrasodium salt were used, to ensure an alkaline environment and to avoid further hydroxyl radical production or PhtH hydroxylation during the CL analysis.

3.2.2 Hydrogen peroxide decomposition into pressure increase

For a few trials, the reaction was performed in a reactor (non-stirred pressure vessel from Parr, N4774) containing 4.0 g bd pulp. The preheating (including reactor) and mixing procedure was performed in a similar way as for the other trials (described above in Section 3.2) but the water bath had a set temperature of 85°C since the temperature decreased to about 75°C during the opening and closing procedure and the time to increase the temperature in the reactor took longer than in the small plastic tubes. The average temperature during the 25 minutes of reaction time was about 80°C and the pulp consistency was 4%. The final temperature of the pulp suspension was about 85°C. The temperature and pressure in the reactor were logged throughout the procedure.

A calibration curve for decomposed hydrogen peroxide and pressure increase was made by the reaction of a certain amount of hydrogen peroxide with an excess of potassium permanganate, $KMnO_4$, and sulphuric acid, H_2SO_4. In an acid solution, a small excess of potassium permanganate (controlled by having a slightly violet solution after the reaction) should decompose all of the hydrogen peroxide into oxygen according to Equation 1 (Schumb et al. 1955).

$$2\ KMnO_4 + 5\ H_2O_2 + 3\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ O_2 \quad (1)$$

The measured pressure increase was corrected by subtracting the increased steam pressure of water (Perry et al. 1997), which originated from the temperature increase. When acid hydrogen peroxide treatment of pulp was performed, the decomposed hydrogen peroxide could be determined by using the pressure increase. Following the reaction, the pulp was dewatered and the residual hydrogen peroxide was measured in the liquids. The results are presented in Paper V.

3.2.3 Carbonyl group content

The carbonyl group content of a few pulps that were treated with different iron catalysts in the model study were determined by Innventia, Stockholm. The method used the fact that hydroxide ammonium chloride forms an aldoxime with the carbonyl groups. The content of carbonyl groups is proportional to the amount of nitrogen. The nitrogen content was determined by catalytic combustion and detection of nitrogen in a chemiluminescence detector in an Antek MultiTek from PAC.

4 RESULTS AND DISCUSSION

This section presents a summary of the results presented in Papers I-V. The pilot trial with subsequent evaluation (energy, pulp properties, chemical and morphological characterisation) is described in Section 4.1 and Papers I and III. The washing, chelating and bleaching trials on pilot plant produced pulps are also included in Section 4.1 (Paper II). The model study evaluating different conditions and iron catalysts (e.g. free and chelated) is described in Section 4.2 and Papers IV and V, together with the detection of hydroxyl radicals. Moreover, a proposed mechanism is described in Section 4.3. Finally, some information from full-scale trials and initial wing-refining trials is included in Sections 4.4 and 4.5, respectively.

4.1 Pilot study

The acid hydrogen peroxide system was used as an inter-stage treatment in a pilot study to chemically modify high-freeness Black spruce (*Picea mariana*) thermomechanical pulp (TMP) with the aim of lowering the electrical energy consumption during subsequent refining. The acid hydrogen peroxide system is here defined as the chemicals and reactions involved in the Fenton system, i.e. hydrogen peroxide with a ferrous salt at an acidic pH, according to the reactions described in Figure 5.

4.1.1 Chemicals (Paper I)

Table 1 shows the amount of chemicals added during the pilot plant trial. A TMP produced under standard pH conditions (pH 4.8, denoted TMP Ref) and a TMP produced under more acidic conditions (pH 3.8, TMP Acid Ref) were used as references. Two hydrogen peroxide levels (about 1 and 2%) and two ferrous sulphate levels (0.08 and 0.14-0.15%) were tested. The charge of ferrous sulphate was rather high but was chosen to be sure that all of the added hydrogen peroxide was consumed during refining. Three of the trial series also included an enhancer (oxalic acid/sodium-oxalate, Na_4EDTA or veratryl alcohol). The ratio between the enhancer and ferrous sulphate was about 1:1 (mole:mole) and the enhancer and ferrous sulphate were thoroughly mixed before addition to the inlet of the refiner.

Sodium oxalate/oxalic acid (abbreviated Ox in text, figures and tables) was chosen as an enhancer in the chemical system since it is known that oxalate is produced by wood-degrading fungi (Goodell et al. 2002; Henry 2003) and several research groups have shown that sodium oxalate/oxalic acid has the potential to lower the specific energy consumption during refining (Swaney et al. 2003; Meyer et al. 2005). One prerequisite for using oxalic acid/sodium oxalate, however, is that the addition level is low to minimise possible problems with deposits. Ethylenediaminetetraacetic acid, sodium salt (Na_4EDTA), was used as an enhancer together with ferrous ions to form the catalyst Fe-EDTA to examine the possibility

to reduce the well-known discoloration caused by iron (Gellerstedt et al 1983; Janson, Forsskåhl 1989; Ni et al. 1997; Ni et al. 1998a; Ni et al. 1999; Peart, Ni 2001, Narvestad et al. 2013). Fe-EDTA can also extend the pH range over which iron is soluble (cf. Section 2.4.2). Furthermore, it is at present debated whether the hydroxyl radical formation in the Fenton reaction decreases or increases in the presence of chelating agents such as EDTA (Walker et al. 1999; Pignatello et al. 2006; Li et al. 2007). Veratryl alcohol (3,4-dimethoxybenzyl alcohol, VA) is one of the proposed ligands that participate in the complex reactions that prevail during the biodegradation of wood (Hattori, Shimada 2001). Veratryl alcohol is transformed into a veratryl alcohol cation radical ($VA^{+\bullet}$) that could degrade the wood constituents. Veratryl alcohol was tested as an enhancer since it may direct the oxidation towards the lignin constituent.

Table 1. The chemicals used for each pilot trial series.

Pilot trial series	Added chemicals (% of bone dry wood)		
	H_2O_2	$FeSO_4 \times 7\ H_2O$	Enhancer
TMP Ref	n.a.[1]	n.a.[1]	n.a.[1]
TMP Acid Ref[2]	n.a.[1]	n.a.[1]	n.a.[1]
HP A	1.0	0.08	n.a.[1]
HP B	1.1	0.15	n.a.[1]
HP C	2.2	0.08	n.a.[1]
HP D	2.1	0.14	n.a.[1]
HP A Ox	1.0	0.08	0.04 Oxalic acid 0.04 Sodium oxalate
HP A EDTA	1.1	0.08	0.12 Na_4EDTA
HP D VA	2.0	0.14	0.09 Veratryl alcohol

[1]n.a. = no addition.
[2]The pH was adjusted by adding 0.19% (of bone dry wood) H_2SO_4 to the refiner eye.

The metal ion content of the wood chips and TMPs with a freeness value of approximately 100 ml CSF can be found in Table 7, Section 4.1.6. The iron content increased from 13 mg/kg for the wood chips to 25 and 64 mg/kg for the TMP reference and TMP acid reference respectively. This was an effect of the iron content of process waters and the release of iron from process equipment. The iron levels of the chemically treated pulps (160-320 mg/kg) correlated well with the amount of iron that was introduced via the ferrous sulphate addition. Furthermore, the calcium and magnesium contents were enriched during refining, whereas the manganese content decreased by 15-35% (Table 7).

Table 2 shows the amount of residual hydrogen peroxide and the pH value for the different trial series at different positions in the TMP line. Most of the added

hydrogen peroxide was still left after the primary refining stage (i.e. shortly after addition) and in most cases there was still peroxide present after the secondary refining stage. The addition of Na_4EDTA slowed down the consumption of hydrogen peroxide and increased the pH somewhat (Table 2), which was also observed in the model study (Figure 25, Section 4.2.3). It is also clear that all, or nearly all, of the added hydrogen peroxide was consumed during fibre processing. The final pH value of the acid hydrogen peroxide-treated thermomechanical pulps was in the range of 3.2-3.7. The lower pH was a consequence of the addition of hydrogen peroxide and ferrous sulphate, and probably also of the formation of low molecular weight organic acids (cf. total charge in Table 6) during the course of the reaction (cf. Manini et al. 2006). A similar pH decrease was observed in the model study, see Figure 25a.

Table 2. The residual hydrogen peroxide content and pH value at various positions in the pilot TMP line.

Pilot trial series	After 1st refining stage		After 2nd refining stage		Final pulp	
	H_2O_2 (%)	pH	H_2O_2 (%)	pH	H_2O_2 (%)	pH
TMP Ref	n.a.[1]	4.8	n.a.[1]	n.d.[2]	n.a.[1]	4.9
TMP Acid Ref	n.a.[1]	3.8	n.a.[1]	n.d.[2]	n.a.[1]	3.8
HP A	0.78	5.1	0.31	3.9	0.07	3.6
HP B	0.78	3.9	0	3.5	0	3.4
HP C	1.97	4.3	0.34	3.3	0.04	3.3
HP D	1.89	4.0	0.38	3.3	0	3.2
HP A Ox	0.88	4.2	0	3.5	0	3.3
HP A EDTA	0.92	4.8	0.94	4.2	0	3.7
HP D VA	1.99	4.1	0.40	3.2	0.03	3.2

[1]n.a. = no addition.
[2]n.d. = not determined.

4.1.2 Energy reduction (Paper I)

It is evident that a substantial energy reduction was obtained with the chemical system, compared at similar freeness or tensile index, and that the extent of electrical energy reduction was primarily a function of the amount of hydrogen peroxide applied (Figures 7a-b). There was no significant difference between the two TMP references (TMP Ref and TMP Acid Ref) as regards energy consumption for a constant freeness value, i.e. the lower pH of the acid hydrogen peroxide system cannot explain the reduction in specific energy consumption (SEC). At a freeness level of 100 ml CSF (newsprint grade pulp), about 20% lower SEC was obtained with the addition of 1% hydrogen peroxide (trial series HP A and HP B) and about 35% with the addition of 2% hydrogen peroxide (series HP C and HP

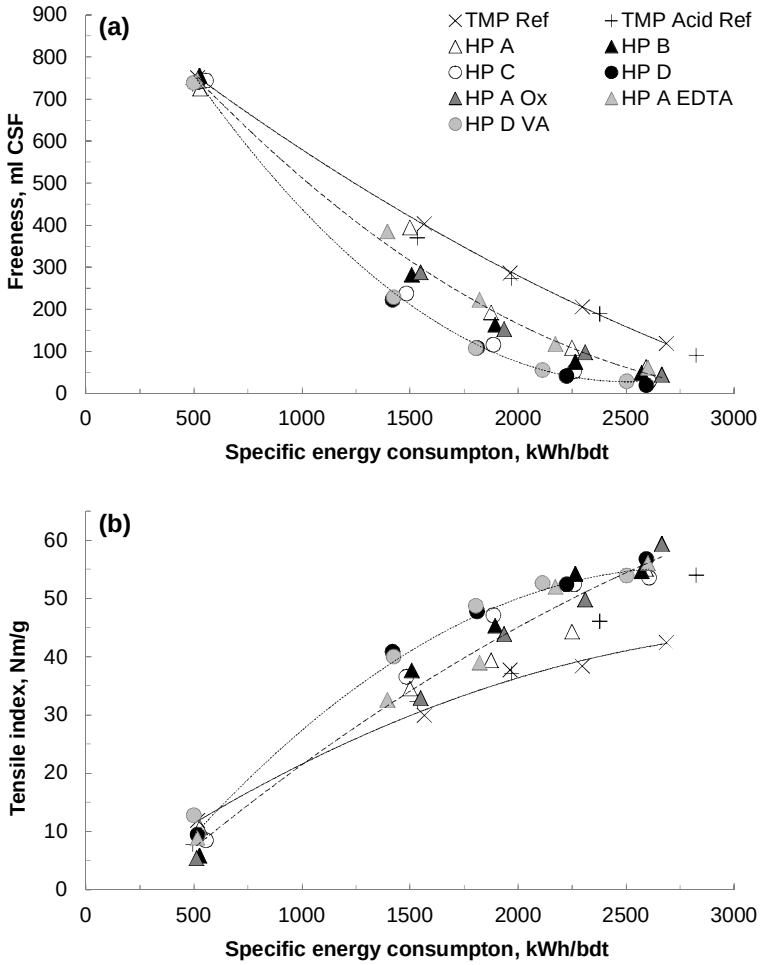
D). No clear effect of increasing the amount of ferrous sulphate could be seen, something that indicates even the low addition level of ferrous sulphate was too high for the hydrogen peroxide charge used. None of the tested enhancers (oxalic acid/sodium oxalate, Na_4EDTA or veratryl alcohol) influenced the specific energy consumption to any significant extent.

It is essential not only to compare the electrical energy consumption at a constant freeness level, but also at a constant strength property or another pulp and paper property that is important for the intended end-product. If a comparison is made between the TMP reference and the acid hydrogen peroxide-treated pulps at a constant tensile index of 45 Nm/g instead of a constant freeness value of 100 ml CSF, the same general conclusions can be made, i.e. the low hydrogen peroxide trials (series HP A and HP B) and the high low hydrogen peroxide trials (HP C and HP D) reduced the electrical energy used for refining by about 25% and 35%, respectively, compared to the TMP reference (Figure 7b).

4.1.3 Strength properties (Paper I)

The strength properties of mechanical or chemimechanical pulps are of the utmost importance and influence the cost of the resulting wood-containing paper, runability on the paper machine and printing press and the end-performance of the produced paper and paperboard product (e.g. printability, dusting and linting tendencies). A method that reduces the electrical energy consumption during production of high-yield pulps is therefore of limited interest to the pulp and paper industry if it simultaneously leads to a substantial reduction in the physical properties of the pulp/paper.

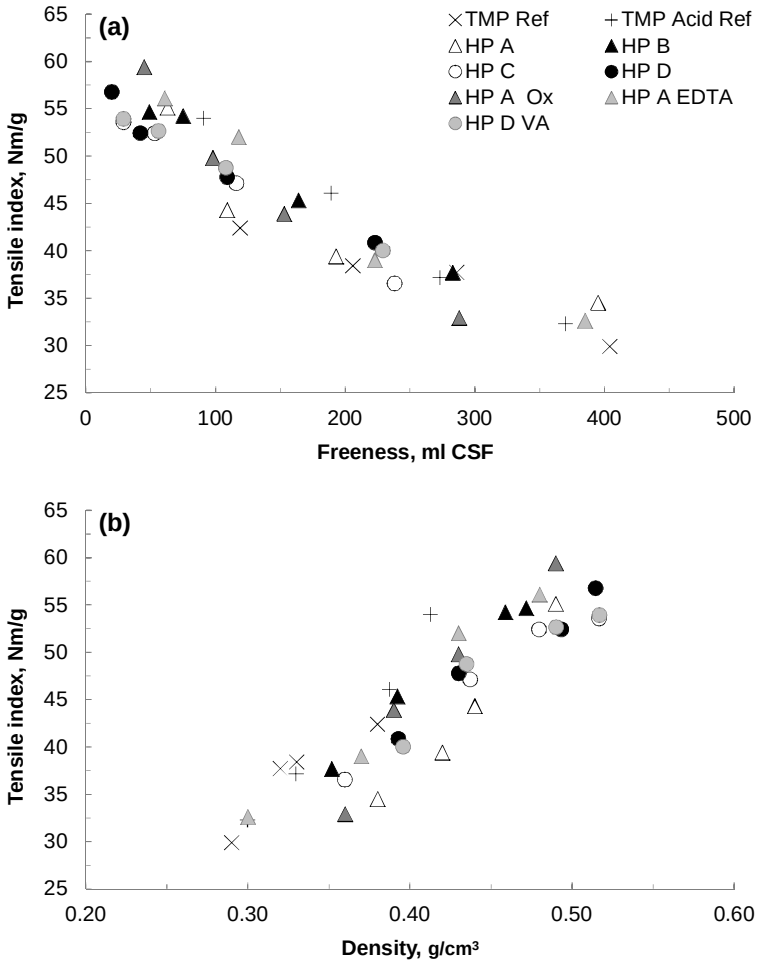
Figure 8a shows the tensile index as a function of freeness. At a freeness value of 100 ml CSF, the tensile index for the chemically treated pulps was the same or higher than the tensile index for the TMP reference. A slight reduction in the tensile index may be seen for a hydrogen peroxide addition level of 2% (series HP C and HP D) at lower freeness values when compared to the TMP acid reference. The tensile index is normally a function of the density of the paper sheet. When looking at Figure 8b, it is evident that the tensile-density relationship was somewhat different for the acid hydrogen peroxide-treated pulps compared to the reference pulps. The chemically treated pulps have a higher density (lower bulk) at a fixed tensile strength compared to the references. This can partly be a result of the higher flexibility of the fibres (Section 4.1.5), which may lead to a high contact (bonding) area. The oxidative treatment also led to an increased total charge of the pulp (Table 6), which may be one reason for improved fibre bonding potential (cf. model study, Section 4.2.3 and Figure 29). The somewhat higher density could be negative for products where a high bulk (stiffness) is desirable (e.g. paper board applications).



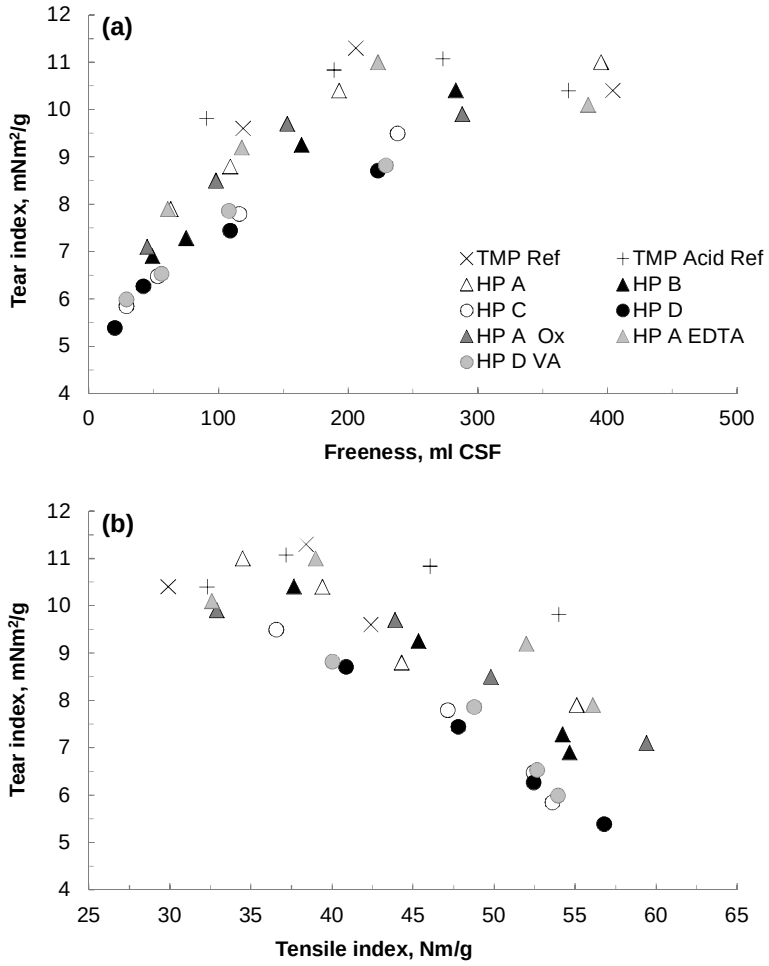
Figures 7a-b. Freeness (a) and tensile index (b) as a function of the specific energy consumption for TMP references and acid hydrogen peroxide-treated pulps. The amount of chemicals used in each pilot trial series can be found in Table 1. Trend lines are drawn for the TMP reference and the acid hydrogen peroxide-treated pulps (1% and 2% H_2O_2), respectively. The legends are given in Figure 7a.

The tear strength is influenced by the fibre length, the strength of the individual fibres and the bonding ability of the fibre material. The chemical inter-stage treatment lowered the tear index by 5-10% and about 20% for the low (1%) and high (2%) addition level of hydrogen peroxide, respectively when the comparison was made at a freeness value of 100 ml CSF (Figure 9a). When comparing with the TMP acid reference at a tensile index of 45 Nm/g, the reduction in the tear index was up to 15% depending on the amount of hydrogen peroxide added (Figure 9b). The lower tear strength could be explained to a lesser extent by a slight reduction

in fibre length (cf. Figure 5c in Paper I), and possibly also by some reduction in the internal fibre strength. This is not unlikely, since radicals are generated during the hydrogen peroxide decomposition (cf. Sections 2.4 and 4.2).



Figures 8a-b. The tensile index as a function of freeness (a) and density (b) for TMP references and acid hydrogen peroxide-treated pulps. The amount of chemicals used in each pilot trial series can be found in Table 1. The legends are given in Figure 8a.



Figures 9a-b. The tear index as a function of freeness (a) and tensile index (b) for TMP references and acid hydrogen peroxide-treated pulps. The amount of chemicals used in each pilot trial series can be found in Table 1. The legends are given in Figure 9a.

4.1.4 Optical properties (Paper I)

The optical properties of high-yield pulps are becoming more and more important since the brightness (whiteness) requirements for improved newsprint and many uncoated and coated magazine paper grades (e.g. SC, LWC, MWC) have been raised in recent years (Hill et al. 2010). Hence, the brightness and brightness stability of a pulp are important quality parameters and should not be altered in a detrimental way if possible.

Figure 10 shows the brightness and Figures 11-12 the light scattering and light absorption coefficients as a function of the degree of pulp refinement for the

different trial series. The brightness increases slightly when the freeness value decreases, which is a consequence of the increased light scattering ability of the pulps (cf. Figure 11). With the amount of chemicals applied in this trial, the acid hydrogen peroxide system lowered the brightness considerably. At a freeness level of 100 ml CSF, the acid hydrogen peroxide-treated series HP A EDTA and HP A lost 6 and 7 ISO brightness units compared to the references (TMP Ref, TMP Acid Ref) whereas the brightness decrease was more than 9 brightness units for the rest of the trial series. The decrease in brightness is a consequence of the increase in the light absorption coefficient (Figure 12). The slightly lower light scattering ability for most of the acid hydrogen peroxide-treated pulps also contributed to the brightness decrease. The variation in light scattering coefficient was large for the chemically treated pulps, however, especially at low freeness values. The effect of using enhancers was small; Na_4EDTA and veratryl alcohol increased the brightness somewhat whereas oxalic acid/sodium oxalate generated a darker pulp.

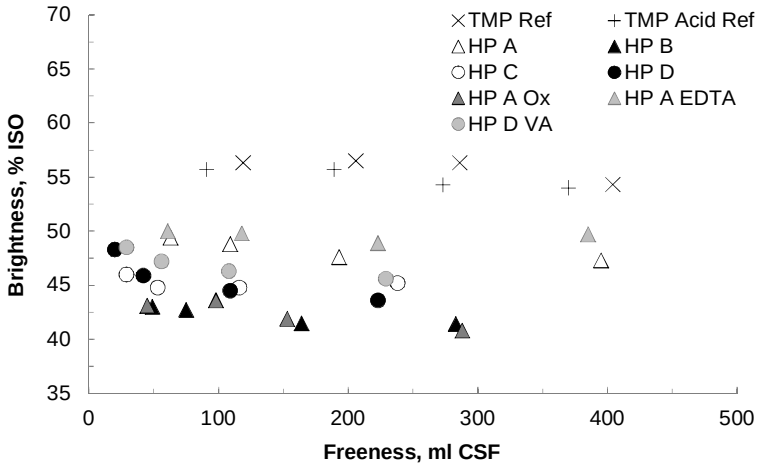


Figure 10. The brightness as a function of freeness for TMP references and acid hydrogen peroxide-treated pulps. The amount of chemicals used in each pilot trial series can be found in Table 1.

There could be several explanations for the discoloration that occurred. One obvious reason is the precipitation of iron salts when the pH is raised and another is the generation of ferric iron during the course of the reaction. The formation of coloured ferric complexes with wood constituents is another plausible explanation and it is well known that many lignin-metal and extractive-metal complexes are highly coloured (Gore, Newman 1964; Janson, Forsskåhl 1989; Ni et al. 1997; Ni et al. 1998a; Ni et al. 1999; Peart, Ni 2001; Ghosh, Ni 1998). The formed radicals (cf. Figure 5) may also generate new lignocellulosic structures that directly or indirectly (together with metal ions) contribute to the observed discoloration.

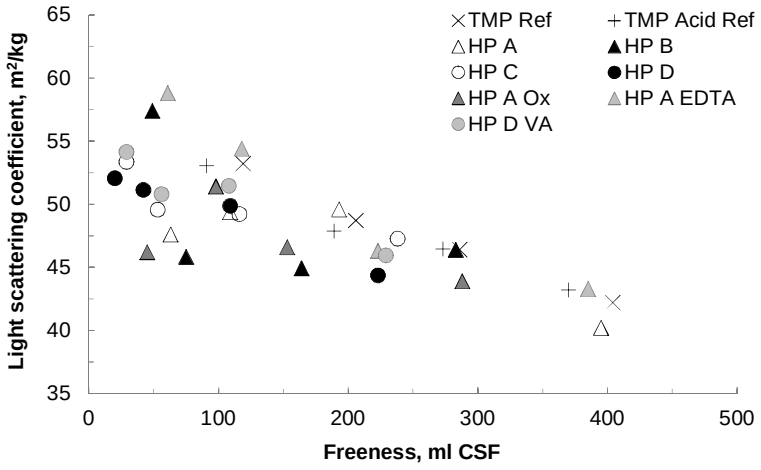


Figure 11. The light scattering coefficient (at 557 nm, CIE/Y filter) as a function of freeness for TMP references and acid hydrogen peroxide-treated pulps. The amount of chemicals used in each pilot trial series can be found in Table 1.

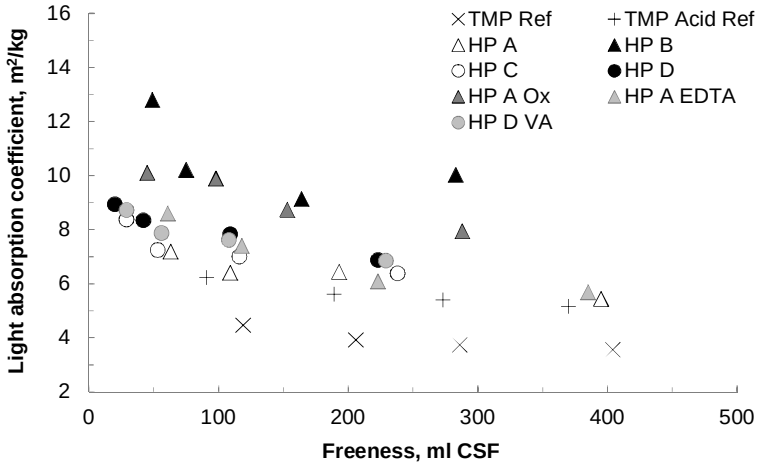


Figure 12. The light absorption coefficient (at 557 nm, CIE/Y filter) as a function of freeness for TMP references and acid hydrogen peroxide-treated pulps. The amount of chemicals used in each pilot trial series can be found in Table 1.

4.1.5 Characterisation of pulp and fraction properties (Paper III)

Pulps in the freeness range 90-120 ml CSF (cf. Table I in Paper III) were used for the morphological, chemical and charge analyses that are presented below. The difference in freeness value between the pulps will influence the pulp and fibre properties to some extent, something that has to be taken into consideration when the results are compared and analysed.

Characterisation of the pulps with respect to particle length, width and shape was performed using the STFI FiberMaster. In Figures 13 and 14, the particle length and width distributions for pulps are shown, while the corresponding distributions for long fibre (Bauer McNett P14/R30) fractions are shown in Figures 15 and 16. No major differences between the TMP references and the chemically treated pulps can be seen in the length distribution curves (cf. Figures 13 and 15). There is, however, a small difference in the particle-width distribution for the whole pulp at about 7 µm (Figure 14), but there is no difference in the width distribution of the long fibre fraction (Figure 16).

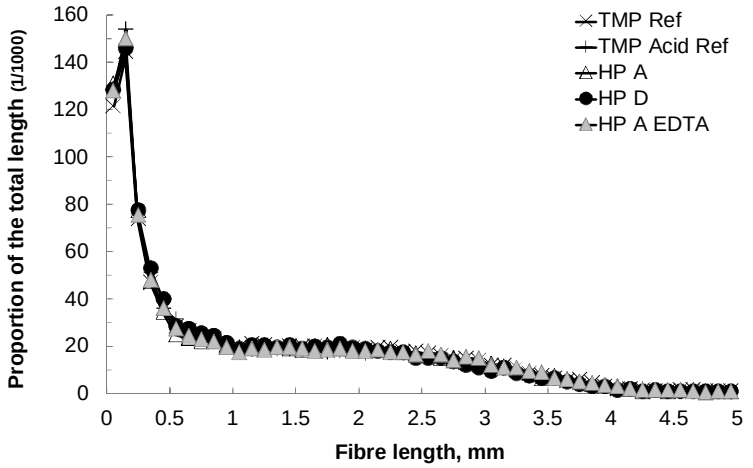


Figure 13. Particle length distribution for untreated and chemically treated pilot pulps.

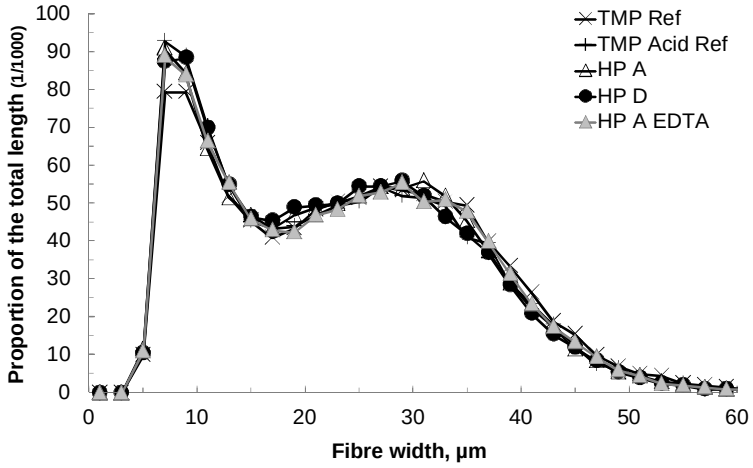


Figure 14. Particle width distributions for untreated and chemically treated pilot pulps.

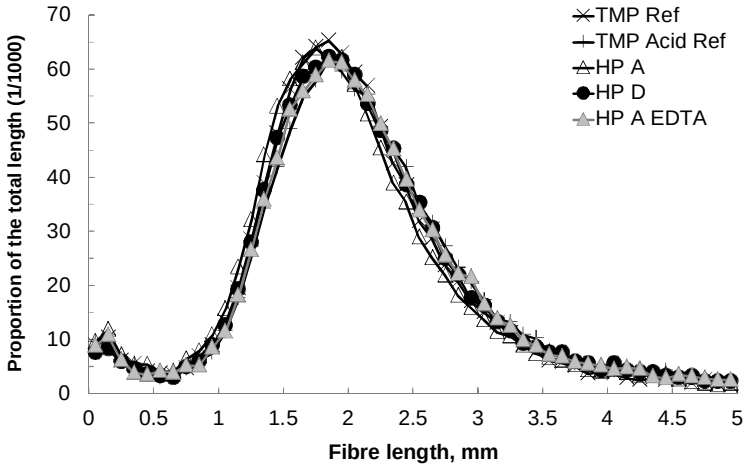


Figure 15. Fibre length distributions for untreated and chemically treated long fibre (Bauer McNett P14/R30) fractions from pilot trial.

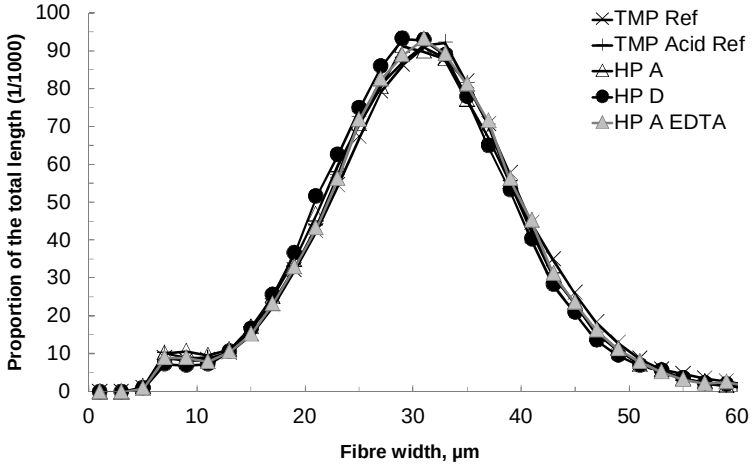


Figure 16. Fibre width distributions for untreated and chemically treated long fibre (Bauer McNett P14/R30) fractions from pilot trial.

Table 3 shows the length-weighted mean length and width for the pulp and long fibre fraction (P14/R30) as well as the mean coarseness and bendability for the long fibre fraction (P14/R30) and the specific surface area (SSA) for the long fibre fraction (P16/R30). There was no reduction in fibre length of the long fibre fraction and only a moderate length reduction of 0.1 mm (maximum) of the whole pulp, when comparing the TMP reference with the hydrogen peroxide-treated pulp HP D, which was subjected to the harshest reaction conditions. It should be noted that a reduction in fibre length of 0.05-0.1 mm is a minor change and that this will only marginally influence the strength properties of the resulting pulp and paper if the

strength of the individual fibres and the bonding potential of the material is unchanged.

Table 3. Length-weighted mean dimensions of pulp and long fibre (Bauer McNett P14/R30) fraction. The coarseness, bendability and sedimentation specific surface area (SSA) is given for the long fibre fraction (Bauer McNett P14/R30 or P16/R30). The confidence interval at 95% confidence is given in brackets.

Pilot trial series	TMP Ref	TMP Acid Ref	HP A	HP D	HP A EDTA
Length (mm)					
Whole pulp	1.24 (±0.00)	1.18 (±0.01)	1.21 (±0.02)	1.14 (±0.02)	1.24 (±0.01)
P14/R30	2.09 (±0.02)	2.21 (±0.01)	2.06 (±0.01)	2.16 (±0.01)	2.19 (±0.01)
Width (µm]					
Whole pulp	23.9 (±0.1)	22.8 (±0.0)	23.0 (±0.2)	22.7 (±0.1)	23.2 (±0.2)
P14/R30	31.6 (±0.2)	31.0 (±0.0)	30.8 (±0.1)	30.8 (±0.1)	31.2 (±0.1)
Coarseness (µg/m)					
P14/R30	127 (±8)	105 (±3)	114 (±5)	109 (±5)	112 (±4)
Bendability[1] (%)					
P14/R30	5.3 (±0.2)	5.7 (±0.1)	5.7 (±0.2)	6.0 (±0.1)	6.1 (±0.1)
SSA (m^2/g)					
P16/R30	8.3	11.2	10.3	9.5	n.d.[2]

[1]The bendability is reported for the fibre-length class 1.5-3.0 mm.
[2]n.d. = not determined

The particle width of the pulp and the long fibre fraction of the chemically treated pulps (HP series) and the TMP acid reference pulp was somewhat reduced compared to the particle width of the TMP reference pulp (Table 3). In addition, the coarseness value of the long fibre fraction decreased as a result of adding chemicals (H_2SO_4; $H_2O_2/FeSO_4$) during refining. The coarseness value is defined as the mass of fibres per unit length, which means that fibres with a lower value are generally more slender or have a larger proportion of thin-walled fibres. These results imply that more material was released from the acid hydrogen peroxide-treated fibres, which is probably a consequence of the radical (oxidation) reactions prevailing. Furthermore, fibre coarseness is known to decrease with falling yield (Scallan, Green 1975); the acid hydrogen peroxide treatment reduces the pulp yield by 1-3 percentage points (most for HP D series, see Figure 9 in Paper I). The reduction in particle width of chemically treated pulps may also be a consequence of the lower pH (3.2-3.8) during refining, i.e. mechanical treatment of a more brittle material (Ottestam, Sjögren 1997). However, the lower freeness value of the TMP

acid reference pulp can partly explain the lower fibre width and coarseness values of this pulp.

The bendability is reported for the fibre length class 1.5-3.0 mm, which represents the majority of the fibres in the long fibre fraction P14/R30. Mechanical pulp fibres have a bendability range of about 0-15%, with lower values corresponding to less flexible fibres. The acid hydrogen peroxide treatment resulted in higher values (Table 3) and, thus, less stiff and more conformable fibres. The increased bendability of the TMP acid reference may be at least partly explained by the lower freeness value of this pulp.

The specific surface area of fibres provides information about the defibration process and bonding ability, and increases during refining. The SSA will increase with reduced particle size and must therefore be determined on a defined size fraction. The specific surface area is influenced by both the degree of external fibrillation and the apparent density of the fibres. However, it is difficult to separate the relative influence of external fibrillation and fibre cross-sectional dimensions on the sedimentation SSA (Wakelin 2004). A higher SSA is associated with larger cell wall diameters, thinner cell walls and a higher fibrillation degree, which is desirable for producing printing paper. It is evident that the chemically treated pulps (HP A and HP D) have a significantly higher specific surface area for the long fibre fraction (P16/R30) compared to the TMP reference (Table 3). The lower freeness of the TMP acid reference may explain the higher SSA for this pulp.

Table 4 shows the cross-sectional characteristics and collapse index of the Bauer McNett R50 fibre fraction. The frequency distribution of the fibre collapse index of individually intact fibres (fraction R50) is given in Figure 17. No significant differences were found with respect to the fibre cross-sectional dimensions (fibre perimeter, fibre wall area, fibre wall thickness). Differences were found in the fibre cross-sectional shape (e.g. lumen form circle, collapse index), which can be interpreted as the fibres' potential to collapse. Fibres of pulp treated with high charges of hydrogen peroxide and iron (series HP D) had the highest collapse index and thus most flattened fibre cross-sectional shape, while fibres in the two reference pulps (TMP Ref and TMP Acid Ref) had the opposite characteristics. These findings are supported by the bendability measurement of the long fibre fraction, which ranked fibres of the hydrogen peroxide-treated pulp HP D as the most flexible (cf. Table 3).

The degree of fibre splitting (given as fibre split index) was generally low with only minor differences between the four series (Table 4). The fibre split index denotes the area proportion of split and fragmented fibres relative to all fibre material examined in a given population. Pöhler and Heikkurinen (2003) reported that refining intensity at the first stage determined the increase in the proportion of split fibres in the later refining stages. Since the acid hydrogen peroxide treatment

was performed after the first refining stage, the extent of fibre splitting was possibly already set to a great extent.

Table 4. Cross-sectional fibre dimensions and shape and collapse index of the Bauer McNett R50 fibre fraction. Mean values, with confidence intervals in brackets at 95 percent confidence level.

Trial series	TMP Ref	TMP Acid Ref	HP A	HP D
Number of analysed fibres	861	809	971	906
Fibre split index (%)	7.4	6.3	7.1	7.7
Fibre perimeter (µm)	84.7 (±2.2)	84.6 (±2.1)	86.4 (±2.1)	84.0 (±2.1)
Fibre wall area (µm^2)	150 (±5)	155 (±5)	153 (±4)	151 (±5)
Fibre wall thickness (µm)	2.44 (±0.07)	2.43 (±0.07)	2.40 (±0.06)	2.46 (±0.07)
Variation of the local wall thickness (µm)	0.52 (±0.02)	0.51 (±0.01)	0.51 (±0.01)	0.52 (±0.01)
Fibre form circle	0.55 (±0.02)	0.56 (±0.02)	0.53 (±0.02)	0.52 (±0.02)
Lumen form circle	0.44 (±0.02)	0.44 (±0.02)	0.40 (±0.02)	0.38 (±0.02)
Fibre collapse index, intact fibres	0.52 (±0.02)	0.50 (±0.02)	0.56 (±0.02)	0.58 (±0.02)

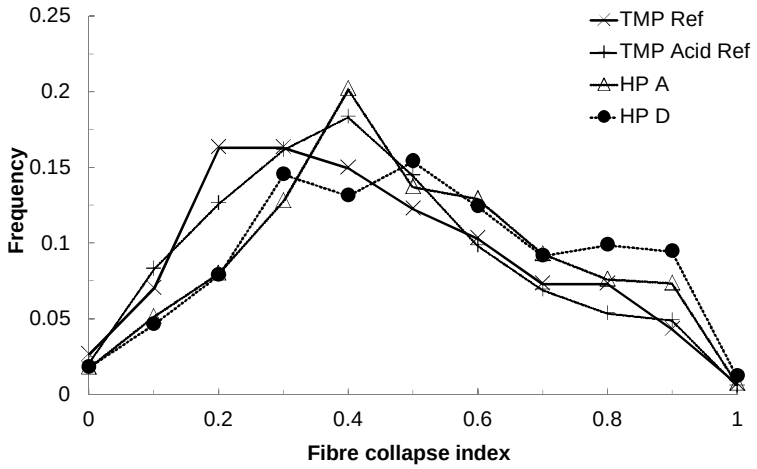


Figure 17. The fibre collapse index (frequency distribution) of individually intact fibres (Bauer McNett R50) of reference and acid hydrogen peroxide-treated pulps.

When comparing the different fibre types of the intact fibre populations (Table 5) the differences are too small to draw any definite conclusions. However, there is a tendency for a higher proportion of wide and thin-walled fibres and at the same time lower proportions of the other fibre types when analysing the intact fibres of TMP acid reference and low hydrogen peroxide-treated HP A pulp compared to

the TMP reference and high hydrogen peroxide-treated HP D pulp. These differences may point to a more effective refining treatment in terms of splitting or cutting of the coarsest (wide and thick-walled) fibres of TMP acid reference and the HP A pulp. Since the wide and thin-walled fibres (earlywood fibres) are more easily split (Reme et al. 1999; Nesbakk, Helle 2002), it may also partly be a consequence of the lower amount of split fibres in these pulps (cf. Table 4), which will give rise to a larger proportion of intact fibres. Again, the differences in the degree of fibre splitting and fibre types are small, and it is evident that the acid hydrogen peroxide treatment does not substantially change the character of the fibres.

Table 5. Intact fibres of the Bauer McNett fraction R50. Proportions (in per cent) of different fibre types classified according to fibre wall thickness (T) and fibre perimeter (FP).

Trial series	TMP Ref	TMP Acid Ref	HP A	HP D
Narrow and thin-walled (T<4 µm, FP<80 µm)	44.6	41.7	41.9	42.6
Narrow and thick-walled (T>4 µm, FP<80 µm)	7.5	6.8	6.6	8.9
Wide and thin-walled (T<4 µm, FP>80 µm)	43.5	49.1	48.8	45.0
Wide and thick-walled (T>4 µm, FP>80 µm)	4.4	2.5	2.7	3.4

The total charge increases by 15-20% for the acid hydrogen peroxide-treated pulps compared to the TMP reference pulp (Table 6). The change in charge is not consistent; the surface charge is unchanged with the exception of the HP A pulp where the surface charge decreases by about 30%. The surface charge is dependent on the amount of acidic groups and the specific surface area of the whole pulp that is accessible for the polyelectrolyte to adsorb onto. There is a possibility for the surface charge to decrease if the charged material (fines and fibre surface) is dissolved into the solution by the hydrogen peroxide treatment, measured as increased COD (cf. Figure 20). Both total charged groups and surface charged groups have been shown to be important to tensile strength (Zhang et al. 1994). A higher charge gives increased fibre hydrophilicity and increased fibre swelling and will influence the softening properties of the lignocellulosic material (Salmén 1995). An increase in fibre swelling makes fibres more flexible by plasticisation of the fibre wall, and this will facilitate fibre bonding. The differences in charge could eventually indicate a more selective modification of the fibre wall. If the acid hydrogen peroxide treatment influences the cross-link structures of lignin and/or hemicelluloses, this may also affect the amount of charged groups and/or fibre flexibility (Zhang et al. 1994). The total charge was evaluated further in the model study (Section 4.2.3).

Table 6. Total and surface charges of unwashed pulps.

Trial series	Total charge (µeg/g)	Surface charge (µeq/g)
TMP Ref	105 (±5)	48 (±2)
TMP Acid Ref	97 (±5)	34 (±2)
HP A	124 (±6)	37 (±2)
HP D	126 (±6)	47 (±2)
HP A EDTA	122 (±6)	46 (±2)

Prior to the chemical characterisation of the pulps, a thorough hot (70°C) water wash was performed, and the washing waters (effluents) were collected. The chemical composition of washed pulps as well as wood raw material (chips), is given in Paper III, Table VI, and the chemical composition of the material that was removed from the pulps through the effluents is presented in Paper III, Table VII. The analysis yield of the wood and pulp samples, i.e. the amount of material that could be identified, was between 93.6% and 96.3%, and most of the analysed differences were within the experimental errors. This means that the results obtained by characterising the washed pulps can only support a hypothesis. Analysis of the effluents will therefore be important in strengthening the hypothesis.

Generally, the difference in chemical composition of the washed pulps was small. The chemical characterisation of the two reference pulps indicates that there was no major effect caused by lowering the pH from 4.8 (TMP Reference) to 3.8 (TMP acid reference). The introduction of acid hydrogen peroxide during refining decreases the pulp yield by 1-3 percentage points; more for the harsh treatment conditions (HP D) than for the mild conditions (HP A) (see Section 4.1.7). The results presented in Tables VI and VII (Paper III) show that it was primarily the hemicelluloses that were affected by the chemical treatment. The monosaccharides attached to the hemicellulose backbone (i.e. arabinose and galactose) and xylose and mannose were dissolved to a greater extent as a result of the acid hydrogen peroxide treatment. Also, some glucose was dissolved, which mainly originated from the glucomannan. This means that the chemically treated pulps contained relatively more cellulose and lignin. Furthermore, the extractive content was slightly higher, something that was probably a consequence of the acid treatment conditions. The addition of the ferrous catalyst as a Fe-EDTA complex (HP A EDTA) seemed to have some beneficial effect on preserving the pulp yield. The yield was calculated (cf. Equation 2) from the COD values (Figure 20) which in turn can both increase and decrease as a result of the Fenton reaction (cf. discussion in Paper IV). The chemical characterisation showed that it was

primarily fewer carbohydrates that were dissolved by adding EDTA (cf. Table VII, Paper III).

4.1.6 Metal removal (Paper II)

It is clear that the amount of ferrous sulphate added to the system influences the discoloration, and since the addition level of ferrous sulphate was most likely too high (cf. discussion in Section 4.1.1) the potential to diminish the discoloration should be considerable. Washing and chelating experiments were performed in order to examine whether it was possible to reduce the iron content of the pulps and thereby regain some of the brightness that was lost during the chemical treatment. Furthermore, the removal of metals from pulps is an essential step in bleaching processes based on oxygen-containing chemicals. Transition metals (especially iron and copper) can also cause the decomposition of dithionite.

A thorough water wash (W) at 70°C could substantially reduce the metal ion content of chemically treated pulps, for example between 50% and 70% of the added iron could be reduced by washing (Table 7). In the model study it was observed that the iron content increased in the solution as the reaction proceeded (see discussion in Section 4.2.2 and Figure 23). Additionally, about 80% to 90% of the manganese in the acid hydrogen peroxide-treated pulps could be washed out compared to only about 30% and 60% from the TMP reference and TMP acid reference respectively. An acidic water wash (W_A) at pH 2.3 could reduce the manganese content by as much as 90% to 95% for the low hydrogen peroxide-treated pulps HP A and HP A EDTA, i.e. almost as effective as treating the pulp with Na_5DTPA in a chelating (Q) stage (Table 7). A W_A procedure could also reduce the iron content somewhat more compared to washing with water or chelating with Na_5DTPA.

A treatment with a chelant in combination with a reducing agent ($Na_2S_2O_4$), i.e. a Q_Y-stage, was the most effective of all the evaluated methods for reducing iron content (Table 7). The iron content after a Q_Y stage of the acid hydrogen peroxide-treated pulp HP A is similar to the iron content of the conventional chelated TMP reference. These results are in line with a previous study by Ni et al. (1998b), showing that a Q_Y stage is more efficient at removing transition metal ions from TMPs than chelation alone.

Table 7. Metal ion content before and after washing and chelating treatment of selected pulps.

Treatment and pilot trial series	Metal ion content (mg/kg)				
	Ca	Cu	Fe	Mg	Mn
Wood chips	910	0.1	13	110	95
After refining					
TMP Ref	1100	0.2	25	250	82
TMP Acid Ref	1100	0.5	64	250	76
HP A	1100	<0.1	170	250	75
HP B	1000	0.2	320	220	66
HP C	1000	0.2	160	200	71
HP D	960	<0.1	310	200	62
HP A Ox	1100	0.4	180	250	69
HP A EDTA	1100	<0.1	160	250	71
HP D VA	1100	0.6	290	220	74
Water wash, W (70°C)					
TMP Ref	900	0.4	24	180	58
TMP Acid Ref	550	0.6	48	90	36
HP A	340	0.2	76	40	16
HP B	270	0.3	120	30	13
HP C	280	0.2	46	20	10
HP D	270	0.3	80	20	9.7
HP A Ox	350	0.3	59	40	14
HP A EDTA	340	0.2	50	40	17
HP D VA	270	0.3	57	20	9.7
Chelation, Q (50°C)[1]					
TMP Ref	950	0.1	23	200	4.6
TMP Acid Ref	830	<0.1	34	160	3.9
HP A	690	0.2	71	120	3.7
HP B	640	<0.1	100	120	19
HP C	710	0.1	37	100	3.6
HP D	640	<0.1	68	90	3.1
HP A Ox	800	<0.1	53	130	5.4
HP A EDTA	700	0.1	41	120	3.2
HP D VA	720	<0.1	56	100	18
Acidic water wash, W_A (50°C, pH 2.3)					
HP A	100	<0.1	62	<20	5.2
HP A EDTA	100	<0.1	32	<20	4.6
Reducing agent assisted chelation, Q_Y (50°C)[1]					
TMP Ref	930	0.1	12	190	1.5
HP A	750	<0.1	20	130	4.8

[1]0.2% Na_5DTPA was used for all trial series except for HP D where 0.4% Na_5DTPA was used.

4.1.7 Brightness increase (Paper II)

Pulps with a freeness of about 100 ml CSF (cf. Table 1 in Paper II) were used for the washing, chelating and bleaching trials presented below.

The possibility to regain the brightness that was lost during the chemical treatment was examined by washing and chelating experiments followed by bleaching. The brightness of the pulps after washing and chelating is presented in Table 8. A thorough water wash (W) at 70°C could raise brightness by a maximum of 2.3 ISO units. During the Q_Y stage, the brightness of the TMP reference and hydrogen peroxide-treated HP A pulps increased by about five ISO brightness units, mainly due to the bleaching effect of the dithionite. The brightness of the acid hydrogen peroxide-treated pulp HP A (51.7% ISO) could therefore not be restored to the level of the TMP reference pulp (56.1% ISO), even though the iron levels of Q_Y-treated HP A pulp and conventional chelated TMP reference pulp were equivalent (cf. Table 7). The discoloration of the treated pulps was thus not only caused by a higher iron content in the pulp but also the type of iron compound and/or other coloured compounds connected with the acid hydrogen peroxide treatment had a substantial effect. All brightness values in Table 8 were measured at AkzoNobel Pulp and Performance Chemicals (ANPP) and the brightness values before treatment differed somewhat from the brightness values obtained at Andritz (cf. Figure 10 and Appendix 1). The reason for this is not clear but it may be the transportation of unwashed pulps from Andritz, USA, to ANPP, Sweden and/or the different equipments/methods used for determining the brightness.

Table 8. The brightness before and after washing or chelating of selected pulps. The abbreviated treatments are explained in Section 4.1.6 and Table 7.

Pilot trial series	Brightness (% ISO)				
	Before	W (70°C)	Q (50°C)	W_A (50°C, pH 2.3)	Q_Y (50°C)
TMP Ref	56.2	56.9	56.1	n.a.[1]	60.9
TMP Acid Ref	55.0	55.4	55.3	n.a.[1]	n.a.[1]
HP A	46.7	48.1	47.6	47.3	51.7
HP B	43.1	45.1	44.6	n.a.[1]	n.a.[1]
HP C	43.3	45.0	43.8	n.a.[1]	n.a.[1]
HP D	42.4	44.7	43.5	n.a.[1]	n.a.[1]
HP A Ox	43.9	45.3	45.1	n.a.[1]	n.a.[1]
HP A EDTA	49.4	50.7	50.2	49.5	n.a.[1]
HP D VA	43.4	44.4	43.3	n.a.[1]	n.a.[1]

[1]n.a. = not analysed.

Medium consistency dithionite bleaching (Y) was performed at a temperature of 60°C using 1% $Na_2S_2O_4$. The brightness gain after bleaching with dithionite alone

was about seven ISO brightness units for both the TMP reference and hydrogen peroxide-treated HP A EDTA series (Figure 18). The addition of 0.1% Na_4EDTA to the bleaching solution in the Y stage increased the brightness by one additional brightness unit for the same two pulps, i.e. a total brightness gain of about eight ISO units was achieved. It was also beneficial if the pulps were chelated with 0.2% Na_5DTPA before bleaching, and with this sequence (Q Y) the TMP Ref and HP A EDTA series gained a maximum of 8.5 ISO brightness units.

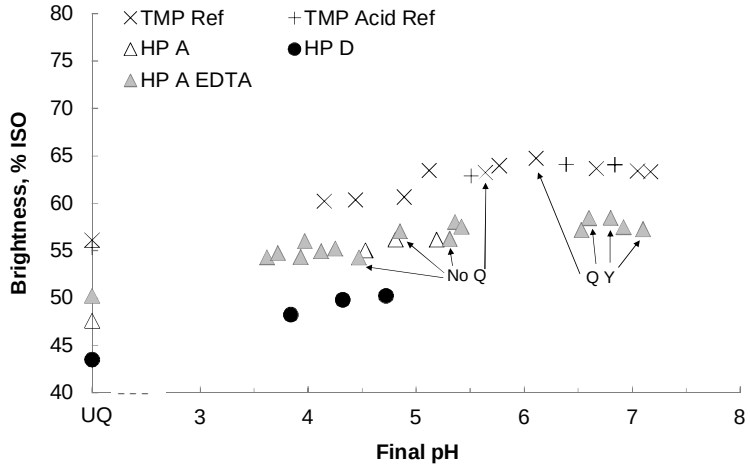


Figure 18. The ISO brightness of unbleached and chelated (UQ, y-axis) and dithionite (1% addition) bleached pilot pulps. 0.2% Na_5DTPA was added before bleaching (marked Q Y in the figure), 0.1% Na_4EDTA was added to the bleaching solution (unmarked) or no chelating agent was used before or during bleaching (marked No Q).

In general, the reference pulps and the acid hydrogen peroxide-treated pulps had about the same maximum brightness increase in the Y stage. Consequently, the brightness gap between the unbleached references and the acid hydrogen peroxide-treated pulps could not be eliminated by reductive bleaching, at least not for the iron level used in this work. However, the brightness could be recovered to the unbleached level of the references for the low hydrogen peroxide-treated trial series HP A and HP A EDTA.

High consistency hydrogen peroxide bleaching (P) was performed at a pulp consistency of 25% and a temperature of 70°C. The hydrogen peroxide charge was varied between 1-6% and alkali-optimised to reach the highest brightness. Figure 19 presents the ISO brightness values obtained at the optimum total alkali charges. The discoloration caused by the acid hydrogen peroxide treatment was reduced after the oxidative bleaching but not completely eliminated. The difference between the hydrogen peroxide-treated HP A EDTA pulp and the TMP reference

pulp was six brightness units before bleaching but lowered to about 2.5 units after bleaching with 6% hydrogen peroxide. A hydrogen peroxide charge of about 4.8% was needed to reach an ISO brightness of 75% for the HP A pulp whereas the corresponding hydrogen peroxide charge was about 3.2% for the TMP reference (Figure 19). The manganese content of the hydrogen peroxide-treated HP B and HP D VA series was high after the Q stage (about 20 mg/kg, see Table 7) and the obtained brightness after hydrogen peroxide bleaching would have been higher if the manganese content had been reduced more in the chelating stage. It can further be concluded that oxidative bleaching of the chemically treated pulps using 1% hydrogen peroxide will give higher brightness gains compared to reductive bleaching with 1% dithionite (cf. Figures 18 and 19).

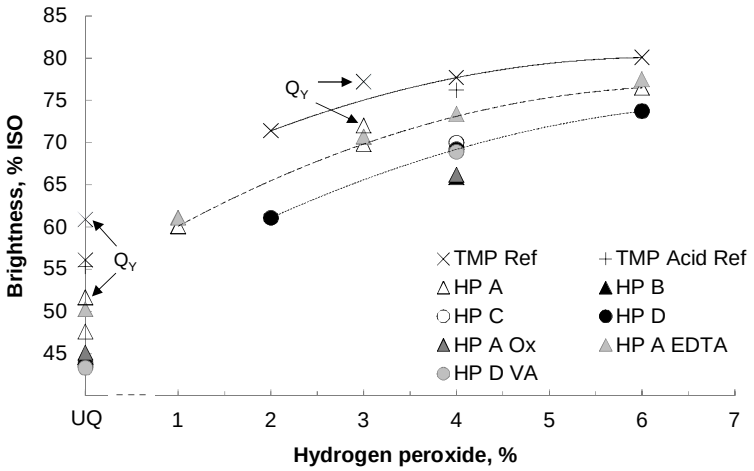


Figure 19. ISO brightness as a function of hydrogen peroxide charge in the bleaching stage at optimum alkali charge for untreated and acid hydrogen peroxide-treated pilot pulps. The unbleached chelated pulp brightness can be found on the Y-axis, denoted UQ. Trend lines are drawn for the TMP Ref, HP A and HP D pulps. Reducing agent-assisted chelated pulps are denoted Q_Y.

Hydrogen peroxide bleaching was also performed after a reducing agent-assisted chelating (Q_Y) stage with 0.5% dithionite. The Q_Y treatment alone increased the brightness by about five ISO units compared to conventional Q treatment (see Y-axis, Figure 19). The positive effect of a Q_Y treatment remains to a great extent after bleaching; the brightness improvement compared to Q P is 2-3 ISO units with the Q_Y P sequence with a 3% hydrogen peroxide charge (Figure 19). Both the TMP reference pulp and the hydrogen peroxide-treated HP A pulp have the same brightness development after a Q_Y stage. By exchanging the Q stage for a Q_Y stage, the hydrogen peroxide charge in the subsequent bleaching stage can be reduced to approximately 3.8% and the HP A pulp can still reach an ISO brightness of 75%. The corresponding hydrogen peroxide charge for the untreated TMP reference was

about 2.5% for the Q_Y P sequence. The additional cost of chemicals needed during bleaching have to be compared with the cost savings from the energy reduction during refining. The profitability of the concept is ultimately mill-specific.

In Figure 20 the amount of dissolved substances (measured as chemical oxygen demand, COD) is shown for the water phases of refined pulps (After refining), hot (70°C) washed pulps (W), chelated pulps (Q) and pulps that are hydrogen peroxide bleached to 74-75% ISO (P). COD was also used (together with TOC) as a measure of chemical reactions with the pulp in the model study (see discussions in Section 4.2.2 and Paper IV). After a thorough hot water wash the COD was of the same magnitude as the COD measured in the water phase of the refined pulps together with the COD removed during a chelating (Q) stage (Figure 20). The hot washing procedure is described in Paper I. The acid hydrogen peroxide system increased the amount of organic compounds that was released both before and after alkaline hydrogen peroxide bleaching. More alkali was needed in the oxidative bleaching stage in order to obtain maximum brightness at a given hydrogen peroxide charge. The increased alkali charge can largely explain the increase in COD after bleaching the chemically treated pulps. The enhancer Na_4EDTA, which was added during refining, had a beneficial effect, and the amount of COD released for the HP A EDTA series was of the same magnitude as for the TMP acid reference series during H_2O_2 bleaching (Figure 20). It is evident that the amount of dissolved substances will decrease during hydrogen peroxide bleaching if the brightness loss, which occurs as a consequence of the acid hydrogen peroxide treatment, can be reduced.

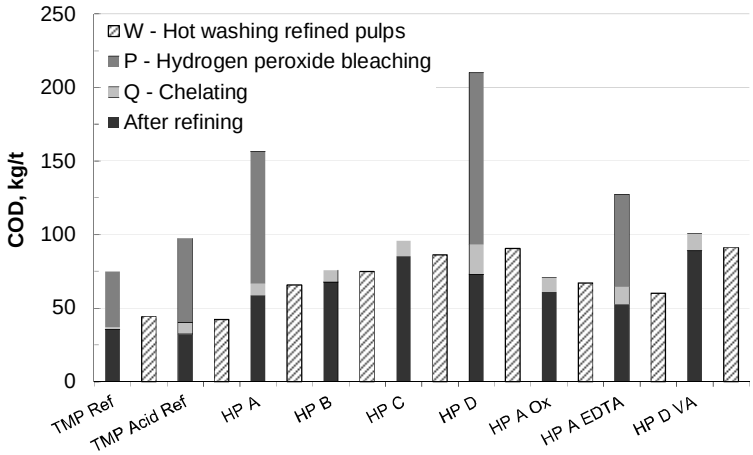


Figure 20. The chemical oxygen demand (COD) produced at different stages when processing untreated and acid hydrogen peroxide-treated pilot pulps. The brightness of the bleached pulps was 74-75% ISO.

There is no simple and straightforward way to determine the pulp yield in a mechanical or chemimechanical pulping process. The measured pulp yield is dependent on many factors such as wood raw material, processing conditions, pulping principle and the extent of washing. Most of the wood constituents that are dissolved during processing can be found in process waters and effluents as dissolved substances or as colloidal particles. In addition, volatile organic compounds (e.g. terpenes, low molecular weight alcohols, organic acids) are released during processing. Normally, the unbleached pulp yield for softwood thermomechanical pulps is about 96-97% (Holmbom et al. 2005). In the present investigation, the COD value obtained after the hot washing procedure (Figure 20) was used when calculating the pulp yield (%, bone dry) according to Equation (2), which is based on Åkerlund (1978) and Bertolotti et al. (1982).

$$\text{Pulp yield (\%)} = 1000 / (\text{COD [kg/t]} \times 0.75 + 1000) \times 100 \qquad (2)$$

The yield loss of the chemically treated pulps as compared to the yield of the TMP reference was then determined (Figure 9, Paper I) for pulps with freeness values of approximately 100 ml CSF. The acid hydrogen peroxide system generated a yield loss of approximately 1-3% units depending on the amount of chemicals added or the hydrogen peroxide that was consumed (cf. Papers IV, V and Walter et al. 2011).

4.2 Model study

The model study was focused on evaluating the acid hydrogen peroxide system together with lignocellulosic material in greater detail and under carefully controlled conditions, which can be difficult to perform at pilot or full scale. The influence of reaction pH, retention time, type of iron catalyst, and the amount of dissolved organic material on the reaction was examined. The knowledge gained in this study is important in order to optimise the chemical system and to gain a deeper understanding of the dominating factors for easier implementation of the energy reduction concept at full scale. Primary refined pulp of Norway spruce (*Picea abies*) was treated with iron containing catalyst and hydrogen peroxide in laboratory scale, while no refining was involved. Chemical charges of 5.0 g H_2O_2/L (0.15 mol/L) and 17 mg Fe/L (0.30 mmol/L) were examined. The chosen charges originate from the chemical concentrations that are in the liquid phase of 25% pulp consistency and when 50 g Fe and 15 kg H_2O_2 per tonne of pulp are charged, which were found to be suitable levels in earlier laboratory studies (Walter et al. 2011). The experimental details could be found in Section 3 and Papers IV and V.

4.2.1 Formation of hydroxyl radicals (Paper IV)

First, some results to introduce the chemiluminescence (CL) method used for detecting the formed hydroxyl radicals during the acid hydrogen peroxide treatment. For more information about the CL method, see also Section 3.2.1. The method is based on the reaction of hydroxyl radicals with the scavenger phthalic hydrazide (PhtH). It is known that the CL method has a pH dependence, similar to all hydroxyl radical detection methods based on aromatic hydroxylation, that is most pronounced above pH 10 (Backa et al. 1997). Furthermore, the substrate (e.g. pulp, dissolved organic material) present (Backa et al. 1997), the distance between the probe and the formed hydroxyl radical (e.g. due to localisation of the iron, presence of chelating agents, concentration of substrate) and the pH dependence of the standard reduction potential of the hydroxyl radical (Buxton et al. 1988) can all influence the CL analysis. Therefore, in this study the CL analysis was only used qualitatively and as a complement to the other analyses.

When PhtH was added to a room tempered solution (pH 3.2) of ferrous sulphate and hydrogen peroxide, it can be seen in Figure 21 that about 150,000 RLU (relative light units) were measured at the start; i.e., hydroxyl radicals were present and could be detected. After about 25 minutes of reaction, the CL value started to decrease, which indicated that the chemiluminescent form of PhtH (hydroxylated PhtH) was degraded. To avoid this, the PhtH was not present during the entire reaction time but exposed to the reaction for five minutes at a time. The accumulated CL value was obtained by adding the CL values from the separate five-minute intervals. This modified method showed that the amount of hydroxyl radicals increased throughout the time period examined (Figure 21). When the temperature was increased to 80°C, it was not possible to detect hydroxyl radicals in the solution since, even after a few minutes (<5), the chemiluminescent form of PhtH had been degraded. This is because there was no substrate present, such as pulp, for the hydroxyl radicals to react with. When pulp was added to the reaction, it was possible to detect hydroxyl radicals at a temperature of 80°C. To ensure that the degradation of the chemiluminescent form of PhtH is not too extensive, an accumulated CL value of a solution where PhtH was present for two times 2.5 minutes should be similar to that of a solution where PhtH was present for five minutes. This was tested at 0.1% and 1% pulp consistency, with $FeSO_4$ as catalyst and at low pH (3.2); i.e., where the Fenton reaction should give a high output (Figure 22). It can be seen that at 1% pulp consistency the CL values after two times 2.5 minutes and after five minutes are similar, but at 0.1% consistency the CL value after two times 2.5 minutes is significantly higher than after five minutes. This indicates that at 80°C and with the present chemical charges, the degradation of hydroxylated PhtH is of minor importance if used in five-minute intervals at a pulp consistency of 1% or higher. The chemiluminescence value decreased when the pulp consistency increased from 1% up to 25%, which probably was the effect

of hydroxyl radicals reacting with pulp instead of with PhtH (Figure 22). The exact distribution of hydroxyl radicals that have reacted with the pulp and/or the probe is thus not possible to completely elucidate in this system. A calibration with gamma radiation (Backa et al. 1997) could probably solve this problem if it is considered to be important in future evaluations.

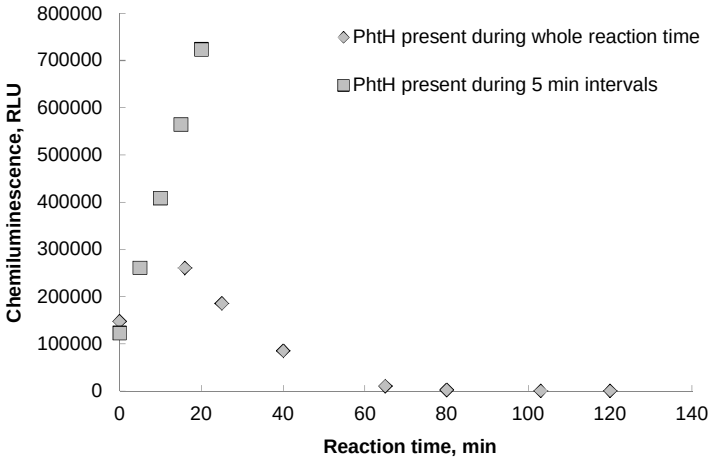


Figure 21. Chemiluminescence at room temperature in an acid hydrogen peroxide solution (no pulp present). Ferrous sulphate was used as catalyst and the initial pH was 3.2. Phthalic hydrazide (PhtH) was present in the solution throughout the entire reaction or in five minutes intervals.

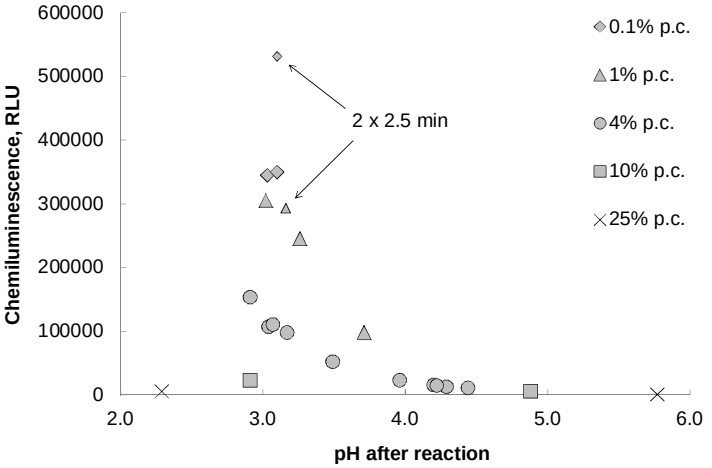


Figure 22. Chemiluminescence as a function of pH after reaction while varying the pulp consistency (p.c.). Ferrous sulphate was used as a catalyst and the reaction time was five minutes (large symbols) or 2.5 + 2.5 minutes (small symbols) at 80°C.

To determine the chemiluminescence during five minutes (4% pulp consistency, 80°C) when no iron catalyst was added, a series of experiments were conducted. At pH 5.3 (no acid added) the chemiluminescence was 7,600 RLU and 6,900 RLU, with and without hydrogen peroxide present. The corresponding values at pH 3.2 were 7,800 RLU (with H_2O_2) and 7,700 RLU (without H_2O_2). Hence the transition metals originally present in the pulp (in mg/kg: Cr, <0.1; Cu, 0.5; Fe, 5.0; Mn, 58; Ti, 0.1.) give only a very small contribution to the CL value (less than 1,000 RLU) and no effect on the pulp (no increase in COD and no decrease in pH after 20 minutes reaction (Paper IV, also cf. Walter et al. 2011). Consequently, when no iron catalyst is added, the dominating part of the background CL value is not associated with hydroxyl radicals formed from hydrogen peroxide. In Figure 26a, the background level of chemiluminescence is shown as a shaded area.

4.2.2 Free ferrous/ferric ions (Papers IV and V)

If the Fenton reaction starts with ferrous ions, ferric ions are almost instantly formed (especially when a large molar excess of hydrogen peroxide is present) and since the iron acts as a catalyst in the Fenton system, both valence states should be present simultaneously. Theoretically therefore, it should be of minor importance whether the reaction starts with ferrous or ferric ions. However, differences have been reported and when starting with ferrous ions, a burst of hydroxyl radicals is formed and an initial rapid degradation phase takes place (Walling 1975). Ferrous and ferric sulphate [$FeSO_4$ and $Fe_2(SO_4)_3$] were compared when the pH at the start of the reaction was 3.2 and 5.3 and the reaction time was 5 and 15 minutes, see Table 9. To follow the chemical work that was exerted on the pulp, the increase in dissolved organic material in the filtrate was measured by analysing both the total organic carbon (TOC) and the chemical oxygen demand (COD). A large increase in TOC or COD should indicate more reaction with the pulp but the results should be interpreted carefully since both TOC and COD can increase and decrease (cf. Section 2.4 and Paper IV) as a consequence of the Fenton reaction. The charge of hydrogen peroxide was 5 g/L and the reason for sometimes analysing a residual hydrogen peroxide over 5 g/L is discussed in Section 4.2.3. The analyses of filtrates from hot (80°C) and room tempered slurries are presented with error bars in Figure 25b. The chemiluminescence, presented in thousands of relative light units (kRLU), was interpreted qualitatively as accumulated detected hydroxyl radicals. At both pH levels, when ferrous and ferric ions were used, the pH decreased as the reaction proceeded, indicating the formation of carboxylic groups, similar to the results in the pilot study. As a result of the logarithmic pH scale, the increase in acidity was greatest when the initial pH was 3.2. At an initial pH of 3.2, ferrous and ferric sulphate gave similar results, while at initial pH 5.3 there is a tendency to a slightly greater reaction (after 15 minutes) when ferrous sulphate is used (lower pH, higher TOC and iron in solution). The effect of the lower solubility of ferric ions at higher pH is thus very small.

Table 9. Initial and final pH, residual hydrogen peroxide, iron content, total organic carbon (TOC), chemical oxygen demand (COD) and accumulated chemiluminescence (CLack) of the filtrates from the reacted pulp suspensions. The reaction temperature was 80°C and the hydrogen peroxide and iron concentrations at the start were 5.0 g/L and 17 mg/L, respectively.

Initial pH	Reaction time (min)	pH after reaction	Residual H_2O_2 (g/L)	Fe in solution (mg/L)	TOC (g/L)	COD (g/L)	Clack (kRLU)
Catalyst $FeSO_4$							
3.2	5	3.1	5.1	5.7	0.31	0.77	144
	15	2.9	4.3	11	0.74	2.4	376
5.3	5	4.4	5.4	3.9	0.31	0.65	13
	15	3.6	4.8	5.7	0.72	1.6	85
Catalyst $Fe_2(SO_4)_3$							
3.2	5	3.1	4.9	5.9	0.31	1.2	123
	15	2.9	4.5	10	0.63	2.3	366
5.3	5	4.7	4.9	3.3	0.32	0.90	18
	15	4.1	4.8	3.2	0.44	1.5	72
Catalyst $Fe(NO_3)_3$							
3.2	5	3.2	5.3	5.7	0.36	0.76	112
	15	2.8	4.6	9.9	0.82	2.1	348
5.3	5	4.8	5.4	4.9	0.39	0.88	12
	15	4.0	4.7	4.2	0.49	1.6	58
Catalyst $FeCl_3$							
3.2	5	3.1	5.2	5.1	0.31	0.95	113
	15	2.9	4.5	9.9	0.81	2.5	322
5.3	5	4.7	5.4	4.3	0.30	1.0	17
	15	4.1	4.7	4.1	0.47	1.7	66

To evaluate the effect of anions in the investigated system, three different anions (sulphate, nitrate and chloride) of ferric ion salt were compared, see Table 9. There are investigations (De Laat et al. 2004) asserting that the anion of the iron salt may influence the Fenton reaction while others (Halliwell 1965) conclude that the anion is not important and that ferrous sulphate was slightly superior to ferric salts. There was no significant difference between the anions and the ferric ions. There was, however, a difference depending on initial pH.

The amount of iron in the solution at various stages of the reaction can add information about any eventual differences between the catalysts examined, Figure 23. If only $FeSO_4$ and acid (initial pH 3.2) was added to the warm pulp suspension,

the iron in the liquid phase decreased from an initial 17 mg/L to about 12 mg/L, with the remainder likely to have been left on the pulp. If H_2O_2 was also added to the $FeSO_4$-acid-pulp mixture, the iron in the liquid phase decreased to about 6 mg/L. Thus, from the reaction with hydrogen peroxide, more iron will bond to the pulp. One reason could be that ferric ions bind more easily to cellulose than ferrous ions do (Xu, Goodell 2001). The effect of temperature was not apparent; no significant difference between 20 and 80°C was observed. As the reaction proceeded, the iron content in the solution increased again. This occurred at pH 3.2 and 5.3 but the increase was more pronounced at the lower pH. After 35 minutes, the iron in the solution was again almost 17 mg/L. The interpretation was that iron, first bonded to the pulp, was released as the reaction proceeded and that the iron in the solution was associated with the dissolved organic material (Paper IV). For the higher pH level, there is a possibility that the catalyst, in its ferric form, is at least partly precipitated to relatively inactive Fe^{3+}-species (Sylva 1972; Gallard et al. 1999). However, it has been shown that when increasing the pH (i.e. from about 2 to 7) more iron will be adsorbed by the cellulose (Xu, Goodell 2001). There was no significant difference between different iron catalysts in Figure 23.

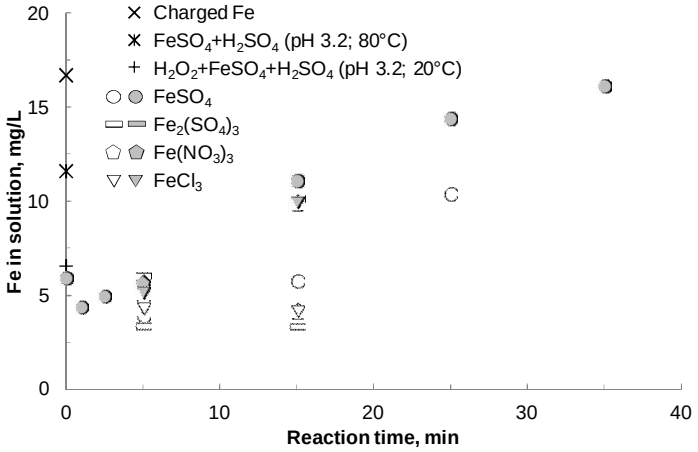


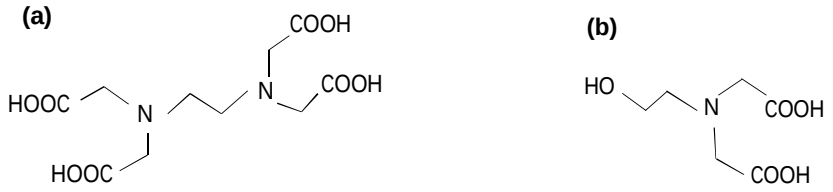
Figure 23. The iron content in the solution as a function of reaction time when ferrous ions ($FeSO_4$) or ferric ions with different anions; sulphate [$Fe_2(SO_4)_3$], nitrate [$Fe(NO_3)_3$] or chloride ($FeCl_3$), was used as a catalyst. The initial pH was 5.3 (open symbols) or 3.2 (filled symbols) and the reaction was performed at 4% pulp consistency and 80°C. The charged Fe amount was 17 mg/L (X on Y-axis).

In a mill system, it is not unusual to have a high level of dissolved organic material in the recirculating water, especially if the degree of closure is high. The effect of having three different levels of dissolved organic material present during reaction was therefore examined when ferrous sulphate was used as a catalyst and initial

pH was 3.2. The results (presented in Paper IV) indicated that hydrogen peroxide (or its formed products) reacted with the pulp in all of the cases studied. However, in a cleaner system, there was more reaction with the fibre material based on a faster COD increase and a lower amount of dissolved iron in the filtrates. The hydrogen peroxide (or its formed products) also reacted with the dissolved organic material, i.e. there was a small decrease in COD during the first five minutes of reaction and a higher amount of dissolved iron catalyst likely to be bonded to the dissolved organic material. The high COD level present in the reaction system may have partly deactivated the iron catalyst, as indicated by the slightly lower hydrogen peroxide consumption.

4.2.3 Iron complexes as Fenton catalysts (Paper V)

Chelation of iron can make the iron soluble at higher a pH and two different chelates, ferric EDTA (Fe-EDTA) and ferric EDG (Fe-EDG) were evaluated as catalysts in the system of acid hydrogen peroxide and TMP. The results of using the ferric chelates were compared with using ferrous sulphate ($FeSO_4$). It is important to find a catalyst that functions well at a higher pH, closer to the one used in the TMP process. EDTA (Figure 24a) forms a stronger complex with ferric ions than EDG (Figure 24b) and they have stability constants (log K) of 25.1 (Chaberek, Martell 1959) and 11.6 (Chaberek, Martell 1959) respectively. A few different molar ratios between ferric ion and chelating agent were examined.

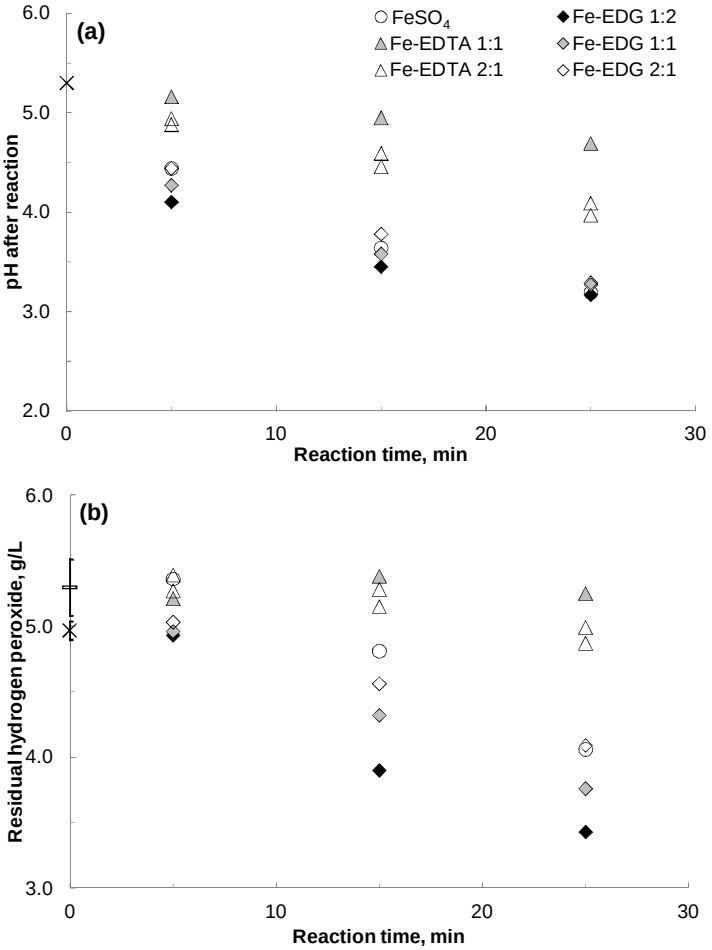


Figures 24a-b. The structures for the chelating agents ethylenediaminetetra acetic acid (EDTA) and ethanoldiglycinic acid (EDG) (b).

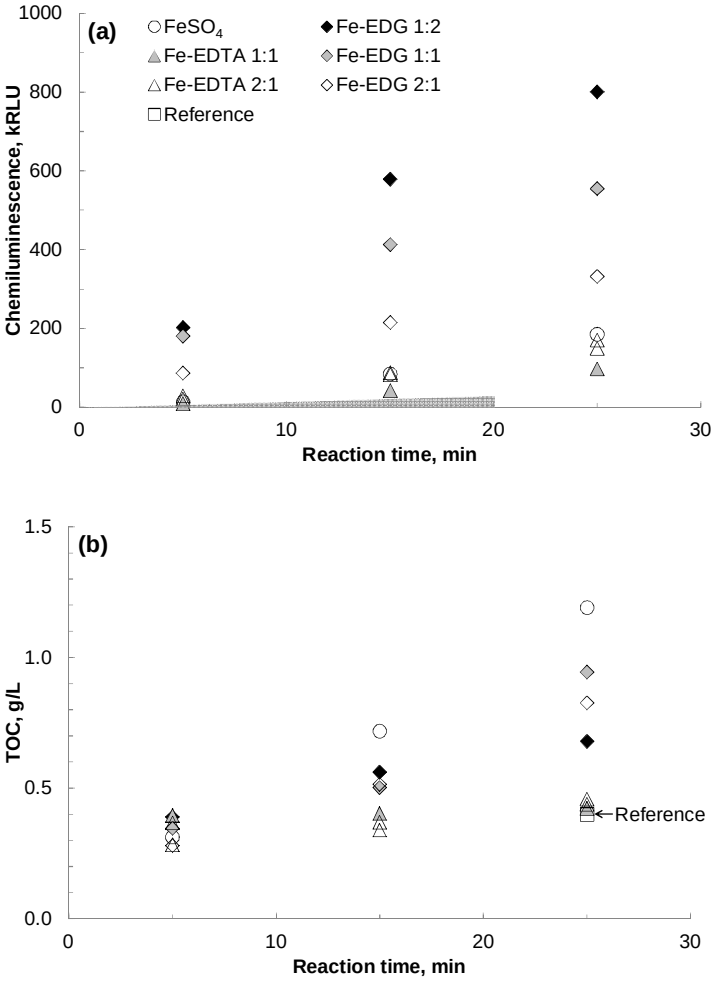
The effect of using different catalysts during 5 to 25 minutes and at an initial pH of 5.3 is shown in Figures 25 and 26. The pH decreased as the reaction proceeded, indicating the formation of acidic groups, see Figure 25a. When using Fe-EDTA as a catalyst, the final pH was not affected as much as when using ferrous ions or Fe-EDG, which show a similar pH decrease. The pH decrease was more pronounced when ferric ions exceeded EDTA (2:1). The greatest amount of hydrogen peroxide was consumed when ferrous sulphate or Fe-EDG was used as catalyst, especially Fe-EDG at a molar ratio 1:2, see Figure 25b. The effect on hydrogen peroxide consumption, when using Fe-EDTA as a catalyst, was very small or non-existent. The charge of hydrogen peroxide was 5 g/L but if nothing was consumed, as when

only hydrogen peroxide was added to the hot pulp slurry and then directly analysed, the analysis showed a value above 5 (line on y axis in Figure 25b). It is likely that the pulp consistency increased somewhat when handling the hot pulp slurry; the water was vaporised and the measured concentration of hydrogen peroxide was therefore too high. This explanation was supported by the fact that the correct amount of 5 g/L was analysed if only hydrogen peroxide was added to room temperature pulp slurry (the cross on y axis in Figure 25b). In Figure 26a, the background level of chemiluminescence (no catalyst, initial pH 3.2, 4% pulp consistency, 80°C) is shown as a shaded area up to 20 minutes. At initial pH 5.3, the greatest amount of hydroxyl radicals were detected when Fe-EDG was used and the results correlate well with the amount of hydrogen peroxide consumed, cf. Figures 25b and 26a. The effect of different catalysts on pulp treatment was evaluated by analysing TOC in the filtrate, see Figure 26b. When the catalyst $FeSO_4$ or Fe-EDG was used, the TOC value increased substantially, while Fe-EDTA gave no increase compared with a reference (i.e. heating the pulp without H_2O_2 and catalyst at 80°C and 4% pulp consistency). In spite of the small effects seen on pH, residual hydrogen peroxide and chemiluminescence by using Fe-EDTA, at least at a molar ratio 2:1, no effect on the dissolved organic material could be seen. Both ferrous ions and Fe-EDG increased TOC extensively but the Fe-EDG showed lower values compared to ferrous ions, although the consumed hydrogen peroxide and detected hydroxyl radicals indicated more reaction, see Figures 25b and 26a-b. The reason for this is probably a difference in where the hydroxyl radicals reacted, with the pulp, with the dissolved organic material or with the PhtH.

The iron content and pH in the solution after 5 and 25 minutes of reaction when chelated ferric ions were used as catalyst are shown in Table 10. For this set of experiments, the initial pH was 5.3, the charged Fe content was 17 mg/L and an inductively coupled plasma (ICP) instrument was used for Fe determination. When Fe-EDTA 1:1 was used, the iron content of the liquid phase was almost constant over time, which shows that probably very little iron was bonded to the pulp. When ferric ions were in excess of EDTA (2:1), more iron had disappeared from the solution. It is possible that some of the ferric ions were not chelated by EDTA and thus bonded more easily to the pulp. When Fe-EDG was used, more iron was probably bonded to the pulp and the increase in the solution after 25 minutes of reaction supports the results with increased TOC in the solution, see Figure 26b. The results for Fe-EDG are more similar to the result for ferrous sulphate, even though the increased iron in the solution during the reaction was not as great as for ferrous ions at pH 3.2, cf. Figure 23. It is likely that the iron must bind to the pulp to be close enough for the hydroxyl radicals to react with the pulp.



Figures 25a-b. The pH after reaction (a) and residual hydrogen peroxide (H_2O_2) (b) as functions of different reaction times when ferrous ions ($FeSO_4$) or chelated ferric ions (Fe-EDTA or Fe-EDG) were used as catalyst. Initial pH was 5.3 and the reaction was performed at 4% pulp consistency and 80°C. The Xs on the Y-axes represent start values. The start value of H_2O_2 is analysed with standard deviations at both room temperature (X, four replicates) and at 80°C (▭, seven replicates), when only 5 g H_2O_2 /L was added to a 4% pulp suspension. The legends are given in Figure 25a.



Figures 26a-b. The chemiluminescence (a) and total organic carbon (TOC) (b) as functions of different reaction times when ferrous ions ($FeSO_4$) or chelated ferric ions (Fe-EDTA or Fe-EDG) were used as catalyst. Initial pH was 5.3 and the reaction was performed at 4% pulp consistency and 80°C. The shaded area in (b) represents the chemiluminescence level when no iron catalyst was added. Reference was pulp treated at similar conditions but without chemicals. The legends are given in Figure 26a.

Table 10. The iron content and pH in the solution following the reaction when chelated ferric ions (Fe-EDTA or Fe-EDG) were used as a catalyst. An inductively coupled plasma (ICP) instrument was used for Fe determination. The initial pH was 5.3 at 4% pulp consistency and 80°C and the charged Fe content was 17 mg/L.

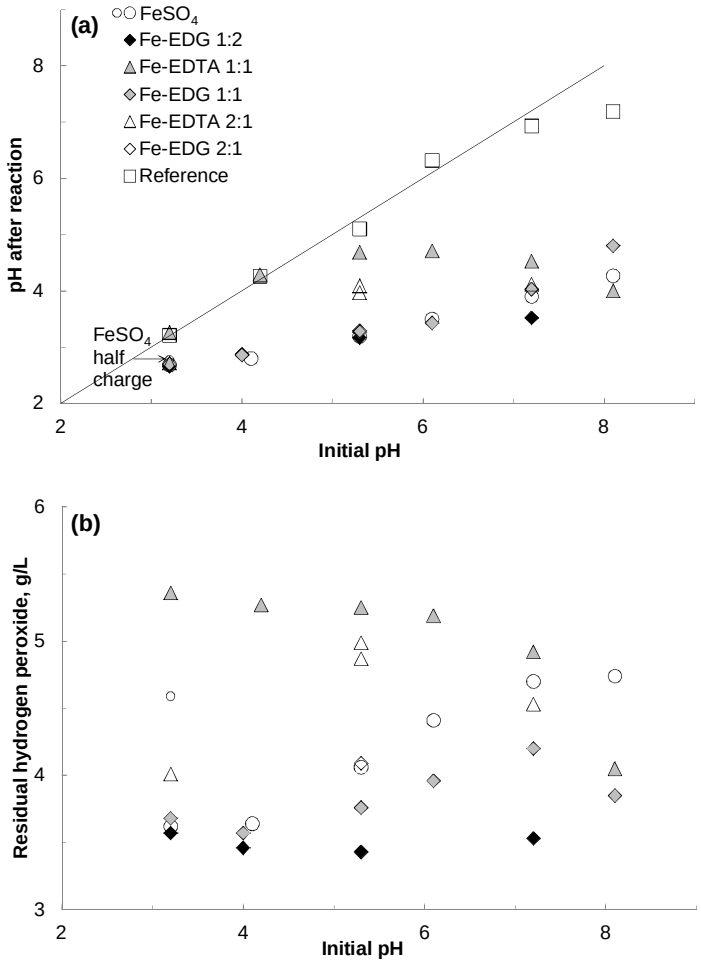
Catalyst	Molar ratio Fe:complex	Reaction time (min)	pH after reaction	Fe in solution (mg/L)
Fe-EDTA	1:1	5	5.2	16
		25	4.5	15
	2:1	5	4.7	11
		25	3.7	9.5
Fe-EDG	1:2	5	3.6	9.5
		25	3.1	14
	1:1	5	3.9	6.0
		25	3.1	11
	2:1	5	4.2	6.9
		25	3.2	9.1

The chelated catalysts and ferrous sulphate were examined when the initial pH was varied from 3.2 to 8.1. The results obtained after 25 minutes of reaction are presented in Figures 27, 28 and 29. Results after 5 and 15 minutes can be found in Appendix 3. Compared to the reference, ferrous sulphate and Fe-EDG gave a pH decrease over the entire examined pH region, see Figure 27a. Since pH has a logarithmic scale, the increase in proton concentration was highest at low pH (cf. Paper V, Figure 4b). The sample with ferrous sulphate containing a half charge of iron (8.5 mg/L) at initial pH 3.2 was added to be compared with Fe-EDTA 2:1 if maybe half of the ferric ions were acting as free. The $FeSO_4$ "half charge" behaved similarly to Fe-EDTA 2:1, i.e., a large pH decrease when the initial pH was 3.2.

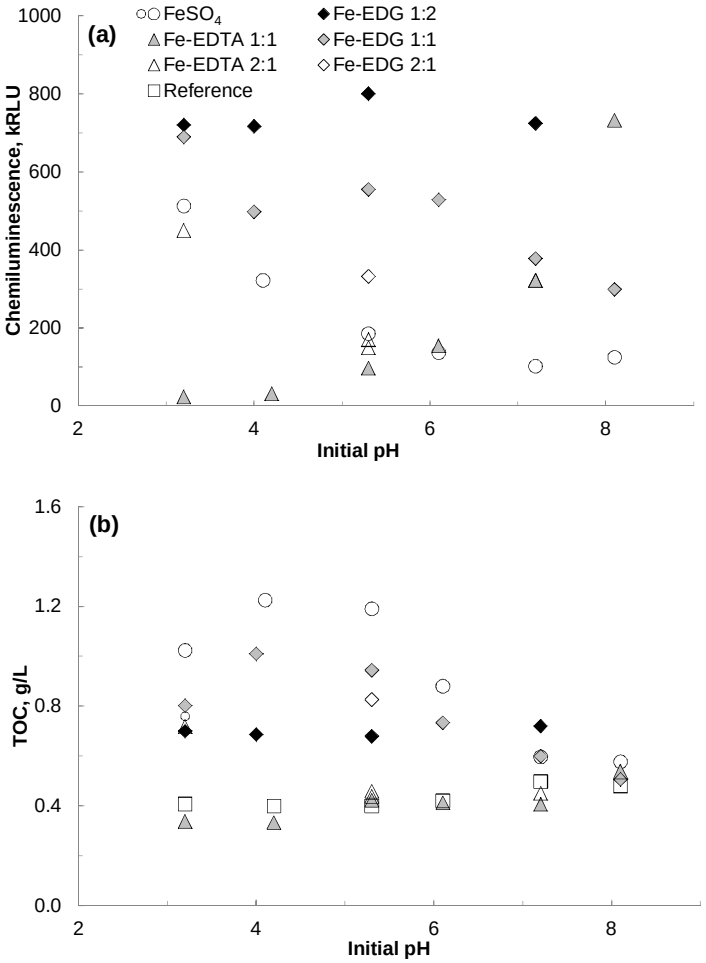
The use of ferrous sulphate as catalyst gave a high hydrogen peroxide consumption at initial pH 3-4 while decreasing at higher pH (Figure 27b), just as has been observed in other laboratory trials (Walter et al. 2011), larger scale trials (not published, Section 4.4) and following the theory of the Fenton reaction. Using Fe-EDG resulted in high hydrogen peroxide consumption over the whole pH region evaluated, especially when the molar ratio was 1:2. The use of Fe-EDTA resulted in low hydrogen peroxide consumption with the exceptions of molar ratio 1:1 at initial pH 8.1 and molar ratio 2:1 at initial pH 3.2. The molar ratio 2:1 gave similar residual hydrogen peroxide as ferrous sulphate "half charge" albeit not exactly the same. The detected hydroxyl radicals correlated well with the residual hydrogen peroxide, see Figures 27b and 28a. It should be noted, however, when

varying the pH greatly, that the CL method shows a pH-dependence, see discussion in Section 4.2.1. The fraction of hydroxyl radicals scavenged by PhtH can vary with pH but also probably with chelating agents, which makes it difficult to compare absolute values of CL in this complex system. Examining the amount of organic material (as TOC) in the filtrate revealed how these reactions had affected the lignocellulosic material, see Figure 28b. Between pH 3 and 6, when the catalysts $FeSO_4$ or Fe-EDG were used, the TOC value increased substantially, while Fe-EDTA gave no increase when compared with the reference. An exception was Fe-EDTA with a molar ratio of 2:1 at pH 3.2, which had the same TOC value as ferrous sulphate "half charge".

The total fibre charge, determined by conductometric titration, of some of the reacted pulps could be an alternative measure of the amount of chemical work that was exerted on the pulp. Total fibre charge measures the amount of acidic groups, which are predominantly carboxylic acids in TMP. Fibre charge is important for the strength of the paper since it increases fibre swelling potential and thereby the flexibility of the fibre wall and this facilitates fibre bonding (Katz et al. 1981; Engstrand et al. 1991; Zhang et al. 1994). Acid hydrogen peroxide treatment gave an increase in total fibre charge of pilot plant produced pulps (Table 6) and it is possible that this could be at least one reason for the reduced refining energy to a constant tensile index. The fibre charge of untreated pulp in this study was 73 µekv/g. The reference treatments with water only gave no increase in total fibre charge, see Figure 29. All acid hydrogen peroxide treatments resulted in an increase of total fibre charge and using ferrous sulphate or Fe-EDG as catalysts gave an increase of at least 50%. For Fe-EDTA catalysed samples, the total fibre charge was higher at the conditions (1:1 molar ratio, pH 8.1 and 2:1 molar ratio, pH 3.2), which also gave indications of more reaction when evaluating the other parameters as discussed above (see Figures 27 and 28). There are some correlations, although not perfect, between total fibre charge and TOC or proton increase (see Paper V, Figures 6b-c). Similar to total fibre charge, these parameters indicate to what extent the pulp was treated chemically. However, the TOC and the proton increase were analysed in the filtrate and the total charge was analysed on the fibres, i.e. the pulp. High chemiluminescence values indicate conditions with a lot of hydroxyl radicals formed and a possibility to treat pulp to higher total fibre charge. However, the highest chemiluminescence values did not necessarily give the highest total fibre charge, since it depended on where the hydroxyl radicals reacted, with the pulp, with the dissolved organic material or with the PhtH.



Figures 27a-b. The pH after reaction (a) and residual hydrogen peroxide (b) as functions of initial pH when ferrous ions ($FeSO_4$) or chelated ferric ions (Fe-EDTA or Fe-EDG) were used as catalyst. Reaction time was 25 minutes at 4% pulp consistency and 80°C. Reference was pulp treated at similar conditions but without chemicals. Small circle is half the Fe charge (8.5 mg/L) when $FeSO_4$ was used as catalyst. The legends are given in Figure 27a.



Figures 28a-b. The chemiluminescence (a) and total organic carbon (TOC) (b) as functions of initial pH when ferrous ions ($FeSO_4$) or chelated ferric ions (Fe-EDTA or Fe-EDG) were used as catalyst. Reaction time was 25 minutes at 4% pulp consistency and 80°C. Reference was pulp treated at similar conditions but without chemicals. Small circle is half the Fe charge (8.5 mg/L) when $FeSO_4$ was used as catalyst. The legends are given in Figure 28a.

The increase in the content of carbonyl groups (where the carboxylic acids are included) is another measure of how much the lignocellulosic material was oxidised by hydrogen peroxide and different iron catalysts. The amount of carbonyl groups was determined for similarly treated pulps as for the total fibre charge analysis, see Table 11. When ferric-EDTA (1:1) was used as a catalyst the content of carbonyl groups was not raised more than for a hot water treatment (reference), at similar initial pH of 5.3. Using ferric-EDG as catalyst resulted in almost a doubled content of carbonyl groups compared to the reference at both initial pH levels (3.2 and 5.3). The ferrous catalyst ($FeSO_4$) caused a similar or

somewhat greater increase in carbonyl groups at initial pH 5.3 but the largest increase was at initial pH 3.2, where a maximum of 332 µmol carbonyl groups/g pulp was obtained. To sum up, the content of carbonyl groups when using different iron catalysts in the hydrogen peroxide treatment follows the same trend as the content of carboxylic acid groups (total fibre charge).

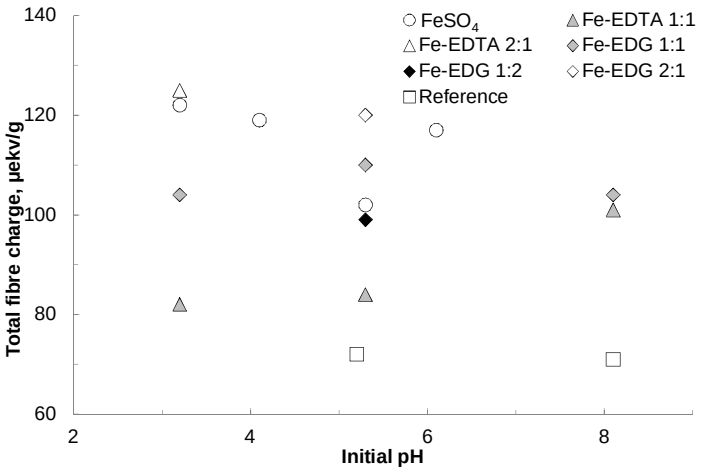


Figure 29. Total fibre charge as a function of initial pH when ferrous ions ($FeSO_4$) or chelated ferric ions (Fe-EDTA or Fe-EDG) were used as catalyst. Reaction time was 25 minutes at 4% pulp consistency and 80°C. Reference was pulp treated at similar conditions but without chemicals.

Table 11. Carbonyl group content when ferrous ions ($FeSO_4$) or chelated ferric ions (Fe-EDTA or Fe-EDG) were used as catalyst. Reaction time was 25 minutes at 4% pulp consistency and 80°C. Reference was pulp treated at similar conditions but without chemicals.

Catalyst	Initial pH	Carbonyl groups (µmol/g)
Non-treated pulp	n.a.	112
Reference	5.3	137
$FeSO_4$	3.2	332
	5.3	240
Fe-EDTA	3.2	123
	5.3	142
Fe-EDG	3.2	226
	5.3	233

The model study showed that different iron catalysts and the amount of dissolved organic material cause different reactions between hydrogen peroxide (or its

formed products) and lignocellulosic material. It was also shown, by a chemiluminescence method, that hydroxyl radicals are formed and that their amounts differ depending on the catalyst used. However, the studied system is very complex by containing mechanical pulp (consisting of all the wood components, cf. Section 2.1) and different Fenton catalysts (both free ferrous and ferric ions, precipitated iron and ferrous and ferric ions bounded to different ligands). Moreover, the varying pH levels influence e.g. the metal binding properties of pulp, the form of the iron, hydroxyl radical formation and its reactions with the probe phthalic hydrazide, the form of the pulp constituents, hydrogen peroxide and its formed products. For example, the standard reduction potential of the hydroxyl radical varies between 1.8 in neutral solution and 2.7 V in acidic solution (Buxton et al. 1988). Consequently, the chemiluminescence method was used qualitatively and as a complement to other analyses such as residual hydrogen peroxide, TOC, COD and fibre charge. Nevertheless, the detected hydroxyl radicals showed trends that fit well with the other analyses during many of the trials in the study and the most deviating results, when comparing free ferrous ions, ferric EDTA and ferric EDG as catalysts in the chemical system, also contributed to the information that these different iron catalysts show three different behaviours when they react with hydrogen peroxide and pulp.

The results from analysing TOC, COD, total fibre charge and carbonyl groups indicate the impact of hydrogen peroxide treatment on the pulp. The comparison of different iron catalysts and conditions showed that free ferrous or ferric ions at an acidic pH (initial pH 3.2) have a considerable impact on the pulp. There is still a considerable effect on the pulp from ferrous- or ferric-catalysed hydrogen peroxide treatment when raising the initial pH to 5.3 in the model study but also ferric-EDG-catalysed treatment shows a similar impact on the pulp. The ferric-EDTA-catalysed treatment gave almost no reaction with the hydrogen peroxide (below initial pH 7) and consequently affected the pulp very little in the model study and it seemed to coincide with the strongly bounded ferric ions (at molar ratio 1:1). In the pilot study, there was no acid addition to decrease initial pH but other chemicals and the reaction lowered the pH and this was enough to obtain major effects on the refining energy and on the pulp properties (e.g. freeness, strength and dissolved organic material), both with ferrous sulphate and ferrous sulphate together with EDTA. It is possible that at least part of the ferrous ions in the EDTA containing trial series were acting as free ions in the pilot study. It was somewhat surprising that ferrous- or ferric-catalysed treatments had a relatively large impact on the pulp at an initial pH as high as 5. Maybe the ferric ions formed a weak ferric-cellulose complex that was capable of participating in the redox reactions, at least up to pH 5-6. A consequence of the metal-binding sites in a biological material such as pulp is that, if Fenton-like reactions occur and hydroxyl radicals are produced, site-specific binding of the iron will result in site-specific reactions with

the pulp since hydroxyl radicals have an exceptionally low diffusion distance before reaction. Also, even if more hydroxyl radicals were detected with Fe-EDG, it may be that they were formed in the solution where Fe-EDG was present and was thereby scavenged by the probe (PhtH) to a greater extent. However, less residual hydrogen peroxide was left after a Fe-EDG-catalysed treatment than after a ferrous-catalysed treatment, which supports the indication that more hydroxyl radicals could have been formed. Moreover, the deviating chemiluminescence and residual hydrogen peroxide results show that the Fe-EDG catalyst is most probably not only acting as free ferric and ferrous ions, which could otherwise be suspected. Even if this model study indicates the excellence of ferrous sulphate, it is maybe not the best choice for full scale refining. At the higher pulp consistency, such as in a refiner, the radicals probably come closer to the pulp even if the iron is not bounded to the pulp. After all, it would be preferable not having the iron bounded to the pulp since it may form coloured groups with lignin and extractives or formed oxidation products and thereby decrease the brightness of the pulp. Moreover, the time is shorter (seconds) and the temperature is higher (>140°C) in the refiner. Since Fe-EDG seems to accelerate the reaction, this catalyst can be an interesting alternative in full-scale refining, provided that the complex will survive long enough at the high temperature and the chelated ferric ions come close enough to treat the pulp.

4.3 Proposed mechanism

The pilot study showed that the use of acid hydrogen peroxide as an inter-stage treatment during refining can significantly reduce electrical energy consumption. The results from the chemical and morphological characterisation (Section 4.1.5) of untreated and chemically treated pulps indicate that the Fenton treatment facilitates fibre development without cutting the fibres. The fibre length (unchanged or slightly decreased) and fibre width (slightly decreased), as well as the coarseness (lower), bendability (higher) and collapse index (higher) values (Section 4.1.5), support this. The differences in fibre morphology between untreated and acid hydrogen peroxide-treated pulps are very limited, and this is probably a consequence of the fact that the fibre separation mechanism is unaffected since the hydrogen peroxide is added at a point when the majority of fibres are already released from the wood matrix. However, some of the organic material will be dissolved, primarily hemicelluloses (Section 4.1.5), which will result in a higher COD (Section 4.1.7) and lower pulp yield (Section 4.1.7 and Paper I).

As the fibre cross-sectional dimensions did not vary significantly, it appears likely that the improved collapsibility and flexibility (Section 4.1.5) can be attributed to changes in the fibre wall structure. The analysis of charged groups in the pulps shows a somewhat higher total charge, but not surface charge, of the treated pulps

compared to the TMP reference (Section 4.1.5). A higher total charge for Fenton treated pulps was also confirmed in the model study (Section 4.2.3). The higher charge increases the fibre swelling potential and may thereby influence the softening behaviour of lignin in the fibre wall (Salmén 1995). The total charge could also have been considerably higher during refining since the method for total charge analysis includes a thorough wash, which can remove part of the charged material.

The hydroxyl radicals generated in the Fenton reaction (cf. Figure 5) and detected in the model study (Section 4.2) will most probably attack the available outer fibre surfaces (all organic wood constituents) with oxidised (carbonyl and carboxylic groups, Section 4.2.3) and dissolved organic material (COD/TOC in solution, Sections 4.1.7 and 4.2.) as a result. The charged pulp material can give better fibre bonding and consequently result in a higher tensile index at constant electrical energy consumption (Section 4.1.2) but the decreased freeness (Section 4.1.2) and small changes in fibre morphology (Section 4.1.5) show that there is also increased fibre development at constant energy consumption. The model study indicated that it is likely that the iron catalyst must bind to the lignocellulosic material, or be in close proximity to it, for the hydroxyl radicals to be able to react with the material (Section 4.2.3). High levels of dissolved organic material present in the reaction system, either by e.g. the addition of dilution water or as a product of the Fenton reaction, are also a target for the hydroxyl radicals to react with and it may also partly deactivate the iron catalyst (Section 4.2.2).

4.4 Experience from full scale (unpublished results)

A number of full-scale trials have been performed with different types and sizes of refiners (twin, SD, DD; 54-68") and subsequent dithionite or hydrogen peroxide bleach plants. The wood type used was spruce and the pulp produced was intended for different end products (news or magazine paper). The pH of the refined pulps was in the range of 3.5-4.0, the charge of hydrogen peroxide was 10-15 kg/bdt and the catalyst used was ferrous or ferric ions at a charge of about 130 g/bdt. The chemicals were, in most cases, charged with the dilution water to the refiner.

The results from full-scale trials consistently show a reduction in freeness for acid hydrogen peroxide-treated pulps compared with a reference at constant electrical refining energy consumption, under the prerequisite that hydrogen peroxide is consumed under Fenton conditions. The reduction in freeness is not caused by the acid conditions prevailing during refining or by cutting of the fibres. If the iron catalyst is omitted, the freeness is unaffected, indicating that the transition metal content originally present in the pulp is not enough. The Fenton reaction as well as the addition of iron causes an approximate brightness decrease of 2-4% ISO,

whereas the light scattering coefficient of the pulps is increased. Directly after refining, the tensile strength is not consistently improved but the strength development after further treatment (e.g. bleaching) is favorable for Fenton-treated pulps. Furthermore, the light scattering ability after bleaching, at a certain tensile strength, is improved. When compared at similar tensile strength and at a brightness of about 75% ISO, a reduction of the electrical refining energy of 10-40% has been obtained. The magnitude of the energy reducing effect of using acid hydrogen peroxide in full-scale refining can be influenced by several mill-specific factors, see Section 6 (Recommendations for future work).

4.5 Experience from wing refining (unpublished results)

The most serious obstacle when developing low energy refining concepts for TMP production is the lack of suitable small scale refiners that can predict the function in full scale refining. Besides the trials performed in pilot scale (Paper I-III), there was also initial trials conducted using a laboratory scale refiner, the wing defibrator (Asplund 1953). It was possible to repeat the results obtained at pilot scale with respect to freeness reduction when a high freeness Black spruce TMP was treated with Fenton chemicals prior to wing refining. Also trials with other types of high freeness mechanical and chemimechanical pulps were performed; Norway spruce TMP, Aspen *(Populus tremula*) CTMP, Norway spruce HTCTMP, and energy reduction to a constant freeness could be seen as a consequence of acid hydrogen peroxide treatment. The strength properties were not evaluated in this study. The wing defibrator can most likely be used to screen concepts for energy reduction. The time, temperature, pulp consistency and mechanical treatment in the wing defibrator differ considerably compared to a full-scale refiner. Any results obtained during wing refining therefore need to be verified in full scale. However, well controlled trials aimed at evaluating hydrogen peroxide consumption and hydroxyl radical formation are difficult to perform in the wing defibrator and the work presented in Papers IV-V was therefore chosen to be conducted without mechanical treatment.

5 CONCLUSIONS

The use of acid hydrogen peroxide under Fenton conditions (i.e., H_2O_2 and $FeSO_4$) as an inter-stage treatment during the pilot refining of Black Spruce thermomechanical pulp (TMP) has a considerable effect on electrical energy reduction. A reduction in the specific electrical energy consumption of 20-35% for a constant freeness value or a constant tensile index seems possible using 1-2% H_2O_2 with only marginally changed fibre dimensions or fractional composition of the pulp. The main drawbacks are lower brightness and a lower pulp yield in the magnitude of 1-3 percentage points. A chemical characterisation of the washed pulps and their effluents implies that the yield loss accompanying the chemical treatment is mainly caused by dissolution of hemicelluloses. There is little or no effect on the fibre morphology (fibre length, fibre width and cross-sectional fibre dimensions). However, the form of the fibres is somewhat influenced; the chemically treated fibres are more collapsed and flattened compared to the fibres of the reference. The long fibre fraction of the acid hydrogen peroxide-treated pulps has a slightly higher flexibility, lower coarseness value and a higher specific surface area, indicating higher external fibrillation. It was also found that the total charge of the acid hydrogen peroxide-treated pulps is higher compared to the reference pulps, something that may have influenced the softening behaviour of the fibre wall and the tensile index of the pulps.

The discoloration of the chemically treated pulps can largely be removed by hydrogen peroxide bleaching. The amount of ferrous sulphate added in the energy reduction system influences the resulting unbleached pulp brightness, although the discoloration is not only caused by higher iron content in the pulp as it is also dependent on the type of iron compound and/or other coloured compounds connected with the acid hydrogen peroxide treatment. The amount of iron in a chemically treated pulp can be reduced to the level of an untreated pulp by a reducing agent-assisted chelating stage. The bleaching results indicate that oxidative bleaching with hydrogen peroxide is more effective than reductive bleaching with dithionite. Depending on the pre-treatment strategy, it is possible to reach a brightness 75% ISO for the chemically treated pulp by using 3.8-4.8% hydrogen peroxide. The analogous hydrogen peroxide charge for the untreated TMP reference is 2.5-3.2%.

From the model study and by using a chemiluminescence (CL) method, it could be concluded that hydroxyl radicals are present in the system of Fenton chemicals and lignocellulosic material (TMP) and that their detected amount differs depending on the conditions used. All of the examined parameters [i.e., initial pH, retention time, pulp consistency, type of catalyst (free or chelated), and dissolved organic material] have an impact on the reactions between coarse thermomechanical pulp and acid hydrogen peroxide. The ferrous and ferric sulphate gave similar results at

an initial pH of 3.2 while there was a tendency for a slightly greater reaction when using ferrous sulphate at an initial pH of 5.3. Different anions (sulphate, nitrate and chloride) of ferric ion salt gave similar catalytic effect at initial pH of 3.2 and 5.3. There appeared to be more reactions with the TMP when there was less dissolved organic material in the liquid phase from the start.

The catalysts ferrous ions, ferric-EDTA (ethylenediaminetetraacetic acid) and ferric-EDG (ethanol diglycinic acid) behaved very differently. A catalyst of ferrous sulphate affected the pulp more than ferric ions chelated with EDTA (initial pH between 3.2 and about 7). However, at an initial pH of 7-8, the ferric-EDTA catalysed reaction resulted in similar or higher hydrogen peroxide consumption and more detectable hydroxyl radicals than the ferrous sulphate catalysed reaction. If using ferric-EDG as catalyst, the measured effect on the pulp was similar or less compared to using ferrous sulphate. Ferric-EDG, however, gave higher hydrogen peroxide consumption and more detectable hydroxyl radicals than using ferrous sulphate when the initial pH was 5-8. It is likely that the iron catalyst must bind to the lignocellulosic material, or be in close proximity to it, for the hydroxyl radicals to be able to react with the material.

The hydroxyl radicals generated in the Fenton reaction will probably attack and oxidise the available outer fibre surfaces, weakening these layers, and simultaneously dissolve some of the organic material. This can facilitate fibre development, give a better bonding pulp and lower the electrical energy demand during refining.

6 RECOMMENDATIONS FOR FUTURE WORK

The acid hydrogen peroxide system studied is complex and the work presented in in this thesis has not completely elucidated the system. There is still a lot of work that can be done to fully understand the chemical system and thereby the potential of the treatment. Below is a recommendation on important subjects for future studies that have been out of scope for this thesis work.

The effect of using acid hydrogen peroxide in full-scale refining in a mill is the most important step in validating the energy saving potential of the proposed treatment. The mill-specific refiner setup, mill water content, subsequent pulp treatment, energy balance, etc. can be decisive for a successful implementation. It is also possible that a chemical treatment changes the optimum production rate for the refiner. An increased production rate can have effect on the specific energy consumption (cf. Muhić 2010 and references cited therein).

The influence of where in the refining process (before, during and/or after fibre release) the Fenton chemicals are added could be of importance and should be evaluated.

In both pilot and model studies, the acid hydrogen peroxide was applied as an inter-stage treatment and the retention time was very long compared to what can be achieved in most full-scale refiner lines. Full-scale trials have shown that the short retention time during refining can be enough (Section 4.4) but it would be of interest to examine the effect of prolonged retention times between refining stages.

Research aimed at understanding the effect on, for example, refiner stability and the refiner's temperature profile is also recommended.

The effect of using weak iron complexes, such as Fe-EDG, in full scale should be evaluated.

There are suggestions of how to accelerate the Fenton reaction either by additives that speed up the redox cycle between ferrous and ferric ions, such as hydroxylamine (Chen et al. 2011) or 3,4-dihydroxyphenyl acetic acid (Arantes, Milagres 2006), or by e.g. using Mohr's salt as a catalyst instead of ferrous sulphate (Prousek, Palacková 2004). With use of the methods developed and described in this thesis, there is a possibility to time-efficiently screen a larger set of additives or catalysts.

To improve the hydroxyl radical detection, a calibration with gamma radiation (Backa et al. 1997) could be of interest.

The level of added ferrous sulphate was higher than necessary when producing the low energy pilot pulps evaluated in this study and lower iron levels should therefore be examined in order to reduce the discoloration and thereby further

improve brightness and bleachability. It is also important to continue to work with finding alternative non-iron-containing catalysts that work at a higher pH closer to the normal operating pH in a thermomechanical pulping line.

The effect of Fenton chemistry on the softening of the wood material could be investigated in e.g. the encapsulated split Hopkinson device.

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APPENDIX 1 – PILOT PLANT TRIAL DATA

Table 1.1. Specific energy consumption and pulp properties.

	SEC [kWh/t]	Freeness [ml CSF]	Density [cm^3/g]	Tear Index [mNm^2/g]	Tensile Index [Nm/g]	Burst index [$kPam^2/g$]	TEA [J/m^2]	Pulmac 0.10 [%]	Fiber length [mm]	Brightness [% ISO]	s [m^2/kg]	k [m^2/kg]
TMP Ref	518	751	0.24	4.9	11.9	0.42	3.5	16.2	n.d.	50.1	34.4	3.6
	1567	404	0.29	10.4	29.9	1.47	20.8	1.76	1.71	54.3	42.2	3.6
	1964	286	0.32	n.a.	37.7	1.91	31.9	0.92	1.68	56.3	46.4	3.7
	2297	206	0.33	11.3	38.4	2.24	31.5	0.32	1.68	56.5	48.7	3.9
	2687	119	0.38	9.6	42.4	2.63	30.4	0.24	1.61	56.3	53.2	4.5
TMP Acid Ref	494	735	0.19	3.8	7.8	0.29	2.5	16.8	n.d.	49.3	35.8	5.0
	1534	370	0.30	10.4	32.3	1.52	23.1	1.78	1.76	54.0	43.2	5.2
	1970	273	0.33	11.1	37.2	1.90	31.0	0.76	1.70	54.3	46.5	5.4
	2378	189	0.39	10.8	46.1	2.49	44.8	0.44	1.73	55.7	47.9	5.6
	2825	91	0.41	9.8	54.0	3.21	54.0	0.20	1.54	55.7	53.1	6.2
HP A	528	725	0.24	4.8	10.7	0.38	2.9	18.4	n.d.	42.4	32.8	5.8
	1500	395	0.38	11.0	34.5	1.68	27.6	1.20	1.70	47.3	40.2	5.4
	1875	193	0.42	10.4	39.4	2.41	32.2	0.24	1.61	47.6	49.6	6.4
	2250	109	0.44	8.8	44.3	2.91	34.3	0.08	1.61	48.8	49.4	6.4
	2592	63	0.49	7.9	55.1	3.33	48.1	0.02	1.55	49.4	47.6	7.2
HP B	526	755	0.19	3.2	5.8	0.26	1.4	25.5	n.d.	36.5	26.5	7.3
	1508	283	0.35	10.4	37.7	1.86	31.7	1.60	1.63	41.4	46.4	10.0
	1894	164	0.39	9.3	45.3	2.34	38.7	0.58	1.60	41.5	44.9	9.1
	2265	75	0.46	7.3	54.2	2.98	46.0	0.16	1.50	42.7	45.8	10.2
	2572	49	0.47	6.9	54.7	3.01	44.0	0.10	1.48	43.0	57.4	12.8
HP C	555	744	0.22	4.3	8.5	0.34	2.8	20.6	n.d.	40.5	29.7	5.5
	1483	238	0.36	9.5	36.6	1.79	30.7	1.56	1.54	45.2	47.3	6.4
	1885	116	0.44	7.8	47.1	2.42	40.3	0.26	1.55	44.8	49.2	7.0
	2259	53	0.48	6.5	52.4	2.75	43.8	0.14	1.44	44.8	49.6	7.2
	2606	29	0.52	5.8	53.6	3.11	45.6	0.08	1.34	46.0	53.4	8.4
HP D	516	740	0.22	4.5	9.5	0.38	2.7	18.0	n.d.	38.0	31.7	7.1
	1419	223	0.39	8.7	40.9	2.06	34.2	0.78	1.55	43.6	44.4	6.9
	1810	109	0.43	7.4	47.8	2.40	41.1	0.28	1.49	44.5	49.9	7.8
	2224	42	0.49	6.3	52.4	2.92	42.8	0.18	1.39	45.9	51.1	8.3
	2593	20	0.51	5.4	56.8	3.19	46.3	0.04	1.35	48.3	52.1	8.9
HP A Ox	512	743	0.18	3.2	5.4	0.26	1.5	22.8	n.d.	37.3	29.9	6.6
	1549	288	0.36	9.9	32.9	1.94	20.9	1.66	1.64	40.8	43.9	7.9
	1936	153	0.39	9.7	43.9	2.35	42.0	0.10	1.65	41.9	46.6	8.7
	2310	98	0.43	8.5	49.8	2.91	43.7	0.06	1.61	43.6	51.4	9.9
	2665	45	0.49	7.1	59.4	3.35	57.7	0.04	1.56	43.1	46.2	10.1
HP A EDTA	516	745	0.21	4.3	8.9	0.34	3.1	21.5	n.d.	45.9	30.3	4.5
	1395	385	0.30	10.1	32.6	1.55	23.7	1.82	1.78	49.7	43.3	5.7
	1822	223	0.37	11.0	39.0	2.11	35.3	0.36	1.69	48.9	46.3	6.1
	2173	118	0.43	9.2	52.0	2.89	51.6	0.20	1.61	49.8	54.4	7.4
	2601	61	0.48	7.9	56.1	3.02	52.7	0.04	1.56	50.0	58.8	8.6
HP D VA	499	739	0.26	5.7	12.8	0.46	4.5	14.6	n.d.	40.1	32.9	6.8
	1424	229	0.40	8.8	40.0	2.07	31.3	1.34	1.53	45.6	45.9	6.9
	1804	108	0.43	7.9	48.8	2.45	40.8	0.38	1.55	46.3	51.5	7.6
	2113	56	0.49	6.5	52.7	2.74	44.2	0.20	1.47	47.2	50.8	7.9
	2502	29	0.52	6.0	53.9	2.91	44.2	0.02	1.43	48.5	54.2	8.7

n.d.=not determined

n.a.=not available

APPENDIX 2 – BLEACHING DATA

Table 2.1. Dithionite ($Na_2S_2O_4$) bleaching data.

	$Na_2S_2O_4$ [%]	H2SO4 [%]	NaOH [%]	EDTA [%]	pH	Brightness [% ISO]	L*	a*	b*	COD [kg/t]
TMP Ref	10		0.20		5.6	63.2	91.1	-1.19	13.7	28.8
TMP Ref (Q before)	10		0.20		6.1	64.7	92.0	-1.14	13.9	14.4
TMP Ref	10	0.20		0.1	4.2	60.2	90.7	-0.74	15.8	24.9
(Y+Q)	10	0.10		0.1	4.4	60.3	90.7	-0.71	15.7	26.0
	10				4.9	60.6	90.4	-1.13	15.0	24.7
	10		0.05	0.1	5.1	63.4	91.6	-1.05	14.5	27.2
	10		0.20	0.1	5.8	64.0	91.7	-1.07	14.1	30.3
	10		0.30	0.1	6.7	63.7	91.7	-1.07	14.4	31.5
	10		0.40	0.1	7.1	63.4	91.7	-1.01	14.6	31.1
	10		0.50	0.1	7.2	63.3	91.7	-1.05	14.7	33.0
TMP Acid Ref	10		0.30	0.1	5.5	62.9	91.3	-0.97	14.5	29.9
(Y+Q)	10		0.40	0.1	6.4	64.1	91.8	-1.10	14.2	31.9
	10		0.50	0.1	6.8	64.1	91.8	-1.00	14.2	33.1
HP A	10		0.30	0.1	4.5	55.0	88.7	-0.61	17.4	39.7
(Y+Q)	10		0.40	0.1	4.8	56.1	89.4	-0.78	17.6	45.6
	10		0.50	0.1	5.2	56.1	89.2	-0.68	17.2	47.5
HP D	10		0.30	0.1	3.8	48.2	86.2	-0.12	20.2	50.1
(Q before)	10		0.50	0.1	4.3	49.8	87.1	-0.28	20.1	50.8
	10		0.60	0.1	4.7	50.2	87.2	-0.35	19.7	50.6
HP A EDTA	10		0.30		4.5	54.3	87.9	-0.91	16.7	35.7
	10		0.40		4.9	57.0	88.9	-1.17	15.8	
	10		0.50		5.3	56.2	88.7	-1.06	16.2	40.6
HP A EDTA	10		0.20		6.6	58.4	89.7	-1.02	15.7	17.0
(Q before)	10		0.30		6.8	58.4	89.8	-0.98	15.9	18.9
	10		0.40		7.1	57.3	89.3	-0.90	16.3	22.6
HP A EDTA	10	0.20		0.1	3.6	54.3	89.0	-0.39	18.5	33.1
(Y+Q)	10	0.10		0.1	3.7	54.7	89.1	-0.44	18.6	33.2
	10			0.1	3.9	54.3	88.7	-0.40	18.1	34.8
	10		0.05	0.1	4.0	56.0	89.6	-0.58	18.0	34.8
	10		0.10	0.1	4.1	54.9	89.2	-0.48	18.4	35.8
	10		0.15	0.1	4.3	55.2	89.2	-0.50	18.1	34.9
	10		0.30	0.1	4.6	55.3	89.0	-0.68	17.6	36.2
	10		0.40	0.1	5.4	58.0	90.2	-0.96	17.2	37.0
	10		0.50	0.1	5.4	57.5	90.1	-0.85	17.3	38.3
	10		0.60	0.1	6.5	57.2	89.7	-0.82	17.1	41.5
	10		0.70	0.1	6.9	57.5	89.7	-0.77	16.7	45.2

Table 2.2. Hydrogen peroxide (H_2O_2) bleaching data (continued on next page).

	H2O2 [%]	NaOH [%]	Silicate [%]	pH	Res H2O2 [%]	Brightness [% ISO]	L*	a*	b*	COD kg/t
TMP Ref	2	0.28	1.4	6.4	1.43	66.5	92.9	1.36	14.1	16.0
(Q before)	2	0.78	1.4	6.5	1.09	69.7	94.1	0.72	13.4	23.5
	2	1.28	1.4	7.4	0.73	70.8	94.5	0.26	13.2	33.0
	2	1.78	1.4	8.2	0.43	71.4	94.8	0.06	13.3	39.3
	2	2.28	1.4	8.5	0.25	70.6	94.6	0.06	13.5	49.6
	4	1.46	2.8	7.5	2.09	74.7	95.5	-2.54	11.4	39.3
	4	2.16	2.8	8.3	1.64	76.1	95.9	-2.80	11.2	50.2
	4	2.86	2.8	8.7	1.22	77.1	96.3	-2.93	11.0	60.4
	4	3.56	2.8	9.1	0.79	77.7	96.3	-2.88	10.6	71.0
	4	4.26	2.8	9.6	0.42	77.3	95.6	-0.83	9.8	79.4
	6	1.34	4.2	7.6	3.63	76.1	95.5	-0.45	10.6	41.7
	6	2.34	4.2	8.6	2.95	78.1	95.9	-0.91	9.6	57.3
	6	3.34	4.2	8.9	2.05	79.5	96.3	-0.99	9.3	72.2
	6	4.34	4.2	9.3	1.44	80.1	96.1	-1.12	8.4	86.2
	6	5.36	4.2	9.8	1.00	80.2	96.1	-1.00	8.3	94.2
TMP Ref	3	1.40	2.1	7.6	1.49	75.0	95.9	-2.80	12.0	37.1
(Q+Y before)	3	2.00	2.1	8.0	1.29	76.0	96.2	-2.94	11.6	45.2
	3	2.60	2.1	8.1	1.27	76.5	96.3	-2.87	11.4	46.8
	3	3.20	2.1	8.3	0.99	77.2	96.4	-2.96	11.2	55.9
TMP Acid Ref	4	1.40	2.8	7.5	1.88	73.0	94.7	-2.14	11.5	37.0
(Q before)	4	2.10	2.8	8.2	1.52	74.4	95.2	-2.43	11.2	48.9
	4	2.80	2.8	8.5	1.07	75.4	95.5	-2.67	11.0	59.0
	4	3.50	2.8	8.9	0.66	76.2	95.7	-2.66	10.6	67.9
	4	4.20	2.8	9.6	0.37	76.1	95.5	-2.55	10.4	77.3
HP A	1	0.20	0.7	5.9	0.57	57.0	89.5	-1.01	17.0	22.8
(Q before)	1	0.70	0.7	6.6	0.36	60.1	90.9	-1.48	16.3	29.4
	1	1.20	0.7	7.8	0.05	58.7	90.5	-1.50	16.9	39.2
	1	1.70	0.7	8.2	0.01	56.1	89.5	-1.37	17.7	49.5
	1	2.20	0.7	8.6	0.00	54.0	88.7	-1.24	18.4	60.4
	3	0.80	2.1	6.3	1.61	65.5	92.8	-1.99	14.6	32.8
	3	1.40	2.1	7.3	1.22	68.2	93.7	-2.33	13.9	44.2
	3	2.00	2.1	8.0	0.84	69.4	94.2	-2.64	13.7	54.8
	3	2.60	2.1	8.3	0.51	69.8	94.4	-2.77	13.7	66.0
	3	3.20	2.1	8.6	0.23	69.5	94.3	-2.78	13.9	79.4
	6	1.30	4.2	7.4	3.42	71.2	94.2	-2.38	12.2	46.9
	6	2.30	4.2	8.3	2.30	73.7	94.9	-2.61	11.4	66.5
	6	3.30	4.2	8.6	1.39	75.5	95.5	-2.78	10.8	92.0
	6	4.30	4.2	9.0	0.82	76.5	95.7	-2.82	10.4	114.9
	6	5.30	4.2	9.5	0.65	76.8	95.6	-2.74	10.1	127.2
HP A	3	1.40	2.1	7.8	1.42	69.8	94.5	-2.56	14.0	45.3
(Q+Y before)	3	2.00	2.1	8.1	1.04	70.3	94.8	-2.77	13.9	53.0
	3	2.60	2.1	8.3	0.76	71.3	95.0	-2.84	13.6	68.2
	3	3.20	2.1	8.8	0.40	72.0	95.2	-2.88	13.3	81.8

Table 2.2. Hydrogen peroxide (H_2O_2) bleaching data (continued from previous page).

	H2O2 [%]	NaOH [%]	Silicate [%]	pH	Res H2O2 [%]	Brightness [% ISO]	L*	a*	b*	COD [kg/t]
HP B	4	1.40	2.8	7.3	1.24	63.1	91.0	-1.41	13.7	48.8
(Q before)	4	2.10	2.8	8.1	0.72	64.9	91.8	-1.68	13.4	61.2
	4	2.80	2.8	8.4	0.40	65.9	92.4	-1.89	13.5	75.5
	4	3.50	2.8	8.8	0.13	65.5	92.3	-1.92	13.7	84.9
	4	4.20	2.8	9.8	0.04	61.0	90.8	-1.58	15.3	106.6
HP C	4	1.40	2.8	7.3	2.07	65.9	93.1	-2.26	14.8	50.3
(Q before)	4	2.10	2.8	8.1	1.64	67.8	93.7	-2.47	14.2	66.2
	4	2.80	2.8	8.5	1.18	69.1	94.1	-2.61	13.9	76.9
	4	3.50	2.8	8.7	0.74	70.0	94.5	-2.70	13.7	98.4
	4	4.20	2.8	9.1	0.40	70.3	94.6	-2.66	13.6	109.6
HP D	2	0.28	1.4	5.9	1.31	55.9	89.7	-1.08	18.3	32.2
(Q before)	2	0.78	1.4	6.1	0.94	59.0	90.8	-1.61	17.3	37.5
	2	1.28	1.4	6.9	0.56	61.0	91.7	-2.02	16.9	47.0
	2	1.78	1.4	7.9	0.27	61.1	91.9	-2.21	17.2	56.5
	2	2.28	1.4	8.2	0.08	60.4	91.7	-2.18	17.6	68.3
	4	1.46	2.8	7.3	1.75	65.6	93.2	-2.38	15.3	54.0
	4	2.16	2.8	8.1	1.26	67.6	93.8	-2.65	14.6	66.4
	4	2.86	2.8	8.5	0.83	68.6	94.1	-2.80	14.3	82.7
	4	3.56	2.8	8.7	0.48	69.2	94.5	-2.94	14.4	100.5
	4	4.26	2.8	9.2	0.17	68.5	94.0	-2.99	14.3	114.3
	6	1.34	4.2	7.0	3.21	68.3	93.8	-2.63	14.1	57.1
	6	2.34	4.2	8.3	2.16	70.6	94.4	-2.90	13.1	80.5
	6	3.34	4.2	8.6	1.30	72.4	94.9	-3.07	12.5	100.4
	6	4.34	4.2	8.9	0.75	73.7	95.3	-3.30	12.1	120.0
	6	5.36	4.2	9.4	0.50	74.0	95.2	-3.16	11.7	136.0
HP A EDTA	1	0.20	0.7	5.9	0.59	58.4	90.0	-1.08	16.4	19.7
(Q before)	1	0.70	0.7	6.9	0.26	61.1	91.3	-1.52	16.0	28.6
	1	1.20	0.7	8.0	0.06	60.5	91.2	-1.59	16.5	36.5
	1	1.70	0.7	8.3	0.01	57.5	90.1	-1.34	17.3	45.6
	1	2.20	0.7	8.6	0.00	55.2	89.2	-1.31	18.3	57.4
	3	0.80	2.1	6.3	1.58	66.8	93.1	-2.01	14.1	31.6
	3	1.40	2.1	7.7	1.20	69.8	94.1	-2.35	13.2	43.5
	3	2.00	2.1	8.1	0.87	70.3	94.4	-2.62	13.4	52.7
	3	2.60	2.1	8.3	0.53	70.7	94.6	-2.73	13.4	62.1
	3	3.20	2.1	8.6	0.27	70.8	94.6	-2.77	13.3	72.2
	6	1.30	4.2	7.5	3.25	72.7	94.8	-2.48	11.9	46.2
	6	2.30	4.2	8.4	2.29	75.1	95.4	-2.70	11.0	65.4
	6	3.30	4.2	8.7	1.46	76.8	95.9	-2.82	10.5	91.8
	6	4.30	4.2	9.1	0.94	77.5	96.0	-2.77	10.1	98.7
	6	5.30	4.2	9.6	0.77	77.8	95.9	-2.71	9.8	117.0
	4	2.50	2.8	8.5	1.12	72.4	94.7	-2.79	12.2	63.1
	4	3.20	2.8	8.6	0.76	73.1	95.0	-2.77	11.9	76.2
	4	3.90	2.8	9.2	0.41	73.4	95.0	-2.71	11.8	92.9
HP A Ox	4	1.40	2.8	7.4	1.63	61.7	90.4	-1.24	13.9	41.8
(Q before)	4	2.10	2.8	8.1	1.22	63.8	91.2	-1.50	13.4	56.4
	4	2.80	2.8	8.4	0.76	65.1	91.8	-1.74	13.3	68.5
	4	3.50	2.8	8.6	0.46	65.6	92.1	-1.88	13.4	80.8
	4	4.20	2.8	9.4	0.16	66.2	92.4	-2.01	13.4	103.7
HP D VA	4	1.40	2.8	7.5	1.53	66.4	93.5	-2.53	15.1	50.6
(Q before)	4	2.10	2.8	8.1	0.96	67.5	93.8	-2.66	14.7	61.0
	4	2.80	2.8	8.4	0.61	68.9	94.3	-2.86	14.4	82.2
	4	3.50	2.8	8.5	0.28	68.7	94.3	-2.96	14.6	102.2
	4	4.20	2.8	9.3	0.04	66.2	93.5	-2.65	15.4	115.6

APPENDIX 3 – MODEL STUDY DATA

Table 3.1. Reference treatment (water) and Fenton treatment with $FeSO_4$ as catalyst. Temperature was 80°C and pulp consistency was 4%. The charges of hydrogen peroxide and iron was 5 g/L and 17 mg/L, respectively.

Catalyst	Pulp amount [odg]	Time [minutes]	Type of pH adj.	Amount of 0.5M pH adj. [µl]	pH Start	Final pH	CL20 min [RLU]	CL measuring time [minutes]	CLack [RLU]	COD [g/L]	TOC [g/L]	Fe [mg/L] Spectroph.	Residual H_2O_2 [g/L]
Reference	0.6	25	H2SO4	40	3.2	3.2				1.12	0.41		
Reference	0.6	25	H2SO4	17	4.2	4.3				1.11	0.40		
Reference	0.6	25	H2SO4	2	5.3	5.1				1.13	0.40		
Reference	0.6	25	NaOH	12	6.1	6.3				1.28	0.42		
Reference	0.6	25	NaOH	25	7.2	6.9				1.47	0.50		
Reference	0.6	25	NaOH	37	8.1	7.2				1.43	0.48		
$FeSO_4$	0.6	15	NaOH	10	5.3	3.54	54771	5		1.18	0.55	6.9	4.7
$FeSO_4$	0.6	15	NaOH	10	5.3	3.57	58440	5		1.78	0.61	6.7	4.6
$FeSO_4$	0.6	15	NaOH	10	5.3	3.60	46887	5		1.25	0.53	6.6	5.0
$FeSO_4$	0.6	15	NaOH	10	5.3	3.60	49176	5		1.62	0.50	6.1	4.8
$FeSO_4$	0.6	15	NaOH	10	5.3	3.56	59015	5		1.77	0.60	6.9	4.8
$FeSO_4$	0.6	15	NaOH	10	5.3	3.61	47222	5		1.36	0.59	6.0	4.9
$FeSO_4$	0.6	2.5	H_2SO_4	30	3.2	3.1	82358	2.5	82358	0.53	0.24	4.9	5.2
		5			3.2	3.1	144375	5	144375	0.77	0.31	5.7	5.1
		15			3.2	2.9	106576	5	376427	2.36	0.74	11.1	4.3
		25			3.2	2.7	55364	5	512761	2.91	1.02	14.4	3.6
		35			3.2	2.5	29987	5	585423	3.74	1.27	16.1	3.1
$FeSO_4$	0.6	5	H_2SO_4	15	4.1	3.7	39605	5	39605	0.76	0.38	4.6	5.2
		15			4.1	3.1	87514	5	190679	2.20	0.66	8.9	4.4
		25			4.1	2.8	58370	5	321991	3.18	1.23	12.8	3.6
$FeSO_4$	0.6	5	NaOH	10	5.3	4.4	13455	5	13455	0.65	0.31	3.9	5.4
		15			5.3	3.6	42908	5	84545	1.63	0.72	5.7	4.8
		25			5.3	3.2	52904	5	185355	2.92	1.19	10.4	4.1
$FeSO_4$	0.6	5	NaOH	25	6.1	5.1	11005	5	11005	0.68	0.35	3.8	5.2
		15			6.1	4.1	27818	5	58235	1.07	0.51	4.1	5.1
		25			6.1	3.5	42999	5	136642	2.19	0.88	7.3	4.4
$FeSO_4$	0.6	5	NaOH	38	7.2	5.7	14534	5	14534	0.82	0.38	3.8	5.2
		15			7.2	4.6	18011	5	48818	0.97	0.44	3.4	5.1
		25			7.2	3.9	29417	5	101949	1.48	0.60	5.1	4.7
$FeSO_4$	0.6	5	NaOH	53	8.1	6.2	34414	5	34414		0.33	3.0	5.2
		15			8.1	5.1	16406	5	76230	0.81	0.47	2.0	5.0
		25			8.1	4.3	26802	5	124636	1.27	0.58	3.5	4.7

Table 3.2. Fenton treatment with Fe-EDTA as catalyst. Temperature was 80°C and pulp consistency was 4%. The charges of hydrogen peroxide and iron was 5 g/L and 17 mg/L, respectively.

Catalyst	Pulp amount [odg]	Time [minutes]	Type of pH adj.	Amount of 0.5M pH adj. [µl]	pH Start	Final pH	CL20 min [RLU]	CL measuring time [minutes]	CLack [RLU]	COD [g/L]	TOC [g/L]	Fe [mg/L] Spectroph.	Residual H_2O_2 [g/L]
Fe-EDTA	0.6	5	H_2SO_4	35	3.2	3.4	4415	5	4415	0.61	0.35	15.1	5.3
		15			3.2	3.4	4631	5	13569	0.68	0.36	14.3	5.3
		25			3.2	3.3	4876	5	23199	0.54	0.34	12.6	5.4
Fe-EDTA	0.6	5	H_2SO_4	15	4.2	4.4	5067	5	5067	0.71	0.28	18.1	5.3
		15			4.2	4.3	6480	5	17320.5	0.76	0.28	18.4	5.3
		25			4.2	4.3	7476	5	31774.5	0.81	0.33	12.7	5.3
Fe-EDTA	0.6	5			5.3	5.2	9935	5	9935	0.82	0.40	18.1	5.2
		15			5.3	5.0	17945	5	41820	0.79	0.40	17.7	5.4
		25			5.3	4.7	30801	5	96994	0.83	0.42	16.6	5.3
Fe-EDTA	0.6	5	NaOH	10	6.1	5.4	14017	5	14017	0.78	0.39	12.4	5.3
		15			6.1	5.0	29325	5	65013	0.78	0.41	17.5	5.3
		25			6.1	4.7	49574	5	154037	1.00	0.41	16.6	5.2
Fe-EDTA	0.6	5	NaOH	25	7.2	5.7	33641	5	33641	0.86	0.36	17.6	5.2
		15			7.2	5.0	74267	5	161862	0.91	0.40	15.0	5.1
		25			7.2	4.5	82290	5	322431	1.04	0.41	13.7	4.9
Fe-EDTA	0.6	5	NaOH	40	8.1	6.2	126436	5	126436	0.83	0.39	16.1	5.1
		15			8.1	4.8	150159	5	414893	0.92	0.34	12.1	4.7
		25			8.1	4.0	161729	5	732566	1.24	0.54	11.7	4.1
Fe-EDTA 2:1	0.6	5	H_2SO_4	35	3.2	3.2	51964	5	51964	0.64	0.24	10.7	5.2
		15			3.2	3.0	102617	5	231872	1.22	0.49	11.7	4.8
		25			3.2	2.7	111454	5	450361	1.94	0.72	14.0	4.0
Fe-EDTA 2:1	0.6	5	NaOH	10	5.3	4.9	28932	5	28932	0.68	0.37	10.6	5.3
		15			5.3	4.5	29496	5	87642	0.86	0.37	9.7	5.3
		25			5.3	4.0	45109	5	170054	1.04	0.44	9.4	4.9
Fe-EDTA 2:1	0.6	5	NaOH	10	5.3	4.9	21013	5	21013	0.68	0.28	9.9	5.4
		15			5.3	4.6	33833	5	82269	0.78	0.34	8.8	5.2
		25			5.3	4.1	33629	5	149629	1.01	0.46	8.7	5.0
Fe-EDTA 2:1	0.6	5	NaOH	35	7.2	5.7	72442	5	72442	0.65	0.29	9.5	5.0
		15			7.2	4.8	58293	5	196103	0.75	0.37	7.9	4.9
		25			7.2	4.1	64437	5	321905	1.11	0.45	7.8	4.5

Table 3.3. Fenton treatment with Fe-EDTA as catalyst. Temperature was 80°C and pulp consistency was 4%. The charges of hydrogen peroxide and iron was 5 g/L and 17 mg/L, respectively.

Catalyst	Pulp amount [odg]	Time [minutes]	Type of pH adj.	Amount of 0.5M pH adj. [µl]	pH Start	Final pH	CL20 min [RLU]	CL measuring time [minutes]	CLack [RLU]	COD [g/L]	TOC [g/L]	Fe [mg/L] Spectroph.	Residual H_2O_2 [g/L]
Fe-EDG	0.6	5	H_2SO_4	35	3.2	3.3	123784	5	123784	0.53	0.36	10.0	5.3
		15			3.2	2.7	193159	5	475415	1.20	0.49	13.6	4.3
		25			3.2	2.7	78248	5	689366	1.76	0.80	15.1	3.7
Fe-EDG	0.6	5	H_2SO_4	15	4	3.7	115889	5	115889	0.72	0.35	8.9	5.2
		15			4	3.1	111293	5	340773	1.78	0.64	11.1	4.3
		25			4	2.9	67363	5	497464	2.52	1.01	14.4	3.6
Fe-EDG	0.6	5	NaOH	15	5.3	4.3	180543	5	180543	0.74	0.35	7.5	5.0
		15			5.3	3.6	94508	5	412577	1.45	0.50	8.6	4.3
		25			5.3	3.3	63402	5	554934	2.41	0.94	11.3	3.8
Fe-EDG	0.6	5	NaOH	30	6.1	4.8	161181	5	161181	0.72	0.28	7.4	5.0
		15			6.1	3.9	91140	5	378482	1.23	0.44	7.4	4.4
		25			6.1	3.4	69681	5	528573	1.98	0.73	9.7	4.0
Fe-EDG	0.6	5	NaOH	55	7.2	5.5	133805	5	133805	0.73	0.32	5.0	4.9
		15			7.2	4.6	52077	5	278823	1.03	0.39	4.2	4.5
		25			7.2	4.0	48566	5	377711	1.50	0.60	6.2	4.2
Fe-EDG	0.6	5	NaOH	80	8.1	6.1	118537	5	118537	0.98	0.40	5.8	4.4
		15			8.1	5.0	39706	5	237365	1.16	0.37	4.3	4.0
		25			8.1	4.8	27710	5	298783	1.24	0.51	4.1	3.9
Fe-EDG 2:1	0.6	5	NaOH	15	5.3	4.4	86488	5	86488	0.74	0.28	6.2	5.0
		15			5.3	3.8	56885	5	215060	1.36	0.51	6.5	4.6
		25			5.3	3.3	58958	5	331939	2.13	0.83	9.2	4.1
Fe-EDG 1:2	0.6	5	H_2SO_4	40	3.2	3.1	93258	5	93258	0.64	0.27	13.3	5.3
		15			3.2	2.8	221738	5	472494	1.20	0.50	14.3	4.2
		25			3.2	2.7	91351	5	720390	1.68	0.70	16.2	3.6
Fe-EDG 1:2	0.6	5	H_2SO_4	20	4	3.6	154144	5	154144	0.71	0.29	12.7	5.1
		15			4	3.1	182265	5	504614	1.27	0.55	14.1	4.0
		25			4	2.9	80641	5	716708	1.74	0.69	15.7	3.5
Fe-EDG 1:2	0.6	5	NaOH	3	5.3	4.1	202137	5	202137	0.81	0.39	11.5	4.9
		15			5.3	3.5	183740	5	578816	1.20	0.56	12.8	3.9
		25			5.3	3.2	86668	5	800688	1.73	0.68	14.7	3.4
Fe-EDG 1:2	0.6	5	NaOH	35	7.2	4.7	201946	5	201946	0.79	0.39	10.0	4.5
		15			7.2	3.9	145261	5	520811	1.22	0.44	9.8	4.0
		25			7.2	3.5	87431	5	724588	1.78	0.72	12.2	3.5