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Sandra Pereira Magina

Melhoria da brancura de pastas sulfito ácido de eucalipto

Improvement of acid sulphite eucalypt pulp brightness

À minha família, em especial ao meu marido Paulo e à minha filha Joana

o júri

presidente

Prof. Dr. Vítor Brás de Sequeira Amaral
professor associado do Departamento de Física da Universidade de Aveiro

Prof. Dr. Dmitry Victorovitch Evtyugin
professor associado do Departamento de Química da Universidade de Aveiro

Prof. Dr. Ana Paula Coelho Duarte
professora associada do Departamento de Ciências e Tecnologias do Papel da Universidade da Beira Interior

palavras-chave

Eucalipto, sulfito, magnésio, branqueamento, oxigénio, peróxido de hidrogénio, ditionito.

resumo

De acordo com a prática realizada na indústria, o branqueamento de pasta sulfito ácido de eucalipto é realizado por um processo TCF de dois estágios E(O)P-EP obtendo-se uma brancura final de 88,5-89,0% ISO. A sua utilização compreende a produção de papéis de impressão e escrita, papéis especiais, "tissue", viscose, entre outras aplicações. As exigências futuras do mercado na área da produção de papel especial e, às vezes, de impressão exigem um grau de brancura de pasta de 90-91% ISO. Com o objectivo de viabilizar a utilização da pasta sulfito ácido de eucalipto nesta área executaram-se estudos no sentido de aumentar o seu grau de brancura minimizando o impacto a nível do preço e investimento requerido na indústria.

Estudaram-se os parâmetros envolvidos na sequência fabril, tendo-se obtidos resultados satisfatórios. Estes resultados foram confirmados através da realização de um ensaio à escala industrial. Como não foi atingido o objectivo de obter uma pasta de grau de brancura 91% ISO, foram utilizados catalisadores/ iniciadores de peróxidos no estágio EP que permitiram obter um incremento na brancura final da pasta de apenas 0.1-0.3% revelando-se ineficazes para o objectivo pretendido. Propôs-se um estágio complementar utilizando vários reagentes, incluindo ozono, dióxido de cloro, hipoclorito e ditionito. Todos os reagentes oxidantes verificaram-se ineficazes excepto o ditionito. O estágio redutor complementar à sequência de branqueamento permitiu alcançar, à escala laboratorial, o grau de brancura de pasta de 90.5%. Um ensaio à escala industrial confirmou este resultado bem como a viabilidade de implementar esse estágio nas instalações existentes da CAIMA. Finalmente, implementou-se um pré-estágio pressurizado com oxigénio à sequência de branqueamento que permitiu alcançar uma brancura final de pasta de 91.4%.

keywords

Eucalypt, sulphite, magnesium, bleaching, oxygen, hydrogen peroxide, dithionite.

abstract

According to established industrial practice, the magnesium-based acid sulphite eucalypt pulp is bleached by a two-stage E(O)P-EP TCF bleaching sequence allowing a final pulp brightness of 88.5-89.0% ISO. This pulp founds applications for the production of viscose, tissue and printing papers among others. The further market developments, for instance, application for some printing and special papers, request the pulp brightness improvement to 90-91% ISO without significant increase of its price and investments to the existing bleaching facilities.

Aiming to improve the acid sulphite eucalypt pulp brightness from 88-89% to 90-91% ISO the conditions of the conventional E(O)P-EP bleaching were optimised. This allowed the increase of final pulp brightness to about 90%. Several hydrogen peroxide catalysts/ activators (TAED, CyA and PAG) and peracetic acid were applied at the second EP stage tough without significant improvement of the pulp brightness. A complementary stage to the bleaching sequence was studied using ozone, chlorine dioxide, hypochlorite and dithionite. All the oxidative reagents revealed to be ineffective in the final bleaching stage. On the other hand, the use of dithionite in the complementary final stage allowed obtaining 90.5% ISO brightness of the pulp. An industrial scale experiment confirmed these results as well as the feasibility of implementing this technology using the CAIMA's facilities. Finally, a peroxide-reinforced oxygen pre-delignification stage to the bleaching sequence was studied allowing reaching a final brightness of 91.4%.

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INTRODUCTION

The pulp and paper industry is of great importance for the worldwide economy, since the production and consumption of pulp and paper products have increased dramatically in the last decades. The industries of this sector are dynamic in all related fields: from the forest (*e.g.*, genetic improvement of species and biotechnological applications) to the recycling of the final products/ by-products. The most important industries are from E.U.A, Canada, Japan, Finland and Sweden even though recent industries especially from Brazil and Indonesia have emerged.

In Portugal, the pulp and paper sector is the 4th liquid exporting branch in the national economy, after the textile, leather and wood industries. From 1997 to 2004, the production of pulp increased 15 %, while the production of paper increased 55 % in the same period. Since 2000, the production of eucalypt pulp has increased, whereas the production of pine pulp slightly decreased [1].

In particular, sulphite pulps are produced for different end uses namely for the production of viscose, acetate fibres, tissue and other kind of papers. Sulphite mills usually operate with two-stage bleach plants giving raise to pulps with typical values of ISO brightness around 86% to 88%. The standard combination of stages is a TCF (Totally Chlorine Free) bleaching sequence where a pre-bleaching stage with oxygen and hydrogen peroxide (E(O)P) is followed by a final stage with hydrogen peroxide (EP). However magnesium-based sulphite pulps are difficult to bleach to a very high brightness (up to 90% ISO) using a TCF bleaching process.

CAIMA Indústria de Celulose S.A. (Altri Group SGPS S.A.) is the only portuguese company in the pulp and paper sector producing sulphite pulp. In financial terms, it is a flexible company, balanced and competitive with one strong position in the European market. In 2003, *CAIMA* mill produced 105,025 tons of magnesium-based TCF bleached sulphite pulp from eucalypt and, by the end of 2006, the production raised 10 %, reaching 115,000 tons of pulp per year [2].

Further technical developments presume the increasing of pulp quality parameters according to mutual market demands. The brightness is one of these parameters. The main goal of this study was the improvement of the acid sulphite eucalypt pulp brightness from

conventional 88-89% to 90-91% within the same bleaching sequence, without implementation of new bleaching stages. This work is composed of five main parts: (1) bibliographic review; (2) experimental section; (3) results and discussion; (4) conclusions; and (5) references.

1. BIBLIOGRAPHIC REVIEW

The bibliographic review is divided into four parts where the first one is a brief description of the chemical composition of wood; the second part describes the sulphite pulping process including the chemical reactions that occur during the process and the use of magnesium as the base; the third part depicts the pulp bleaching including general features of the process and, subsequently, a description of each bleaching chemical agents used during the master project; and, finally, the last part deals with the strength properties and characteristics of bleached pulp.

1.1. CHEMICAL COMPOSITION OF WOOD

Wood is composed of macromolecular cell wall components such as cellulose, hemicelluloses and lignin, and minor low-molecular-weight components such as ash-forming minerals and extractives, all together forming a cellular structure. The proportions and chemical compositions of lignin and hemicelluloses are different in softwoods and hardwoods, while cellulose is a structurally common component. Wood composition and structure is of great importance to understand the chemical reactions including those occurring during pulping and beaching processes. In this review, a special emphasis was done to describe the chemical composition of *Eucalyptus globulus* wood, which was used in the present study.

Chemical composition of eucalypt wood varies between species [3,4], between trees of one species [3], within trees [3] and between geographical location [4]. *Eucalyptus globulus Labill* is composed of approximately 50.0– 54.0 % of cellulose, 19.2– 21.5 % of acid insoluble lignin, 1.0– 2.0 % of soluble lignin, 18.0– 22.0 % of pentosans, 2.0– 3.0 % of total extractives and 0.3– 0.4 % of ashes [4].

1.1.1. Cellulose

Cellulose is the main constituent of wood [5] and consists of a linear homopolysaccharide composed of D-anhydroglucopyranose units which are linked together by β- (1 → 4)-glycosidic bonds (Figure 1). Each D-anhydroglucopyranose unit possesses hydroxyl groups at C-2, C-3and C-6 positions. The hydroxyl groups at both ends of the cellulose chain show different properties: the C-1 end has reducing properties, while the glucose end group with a free C-4 hydroxy group is a non-reducing one [6].
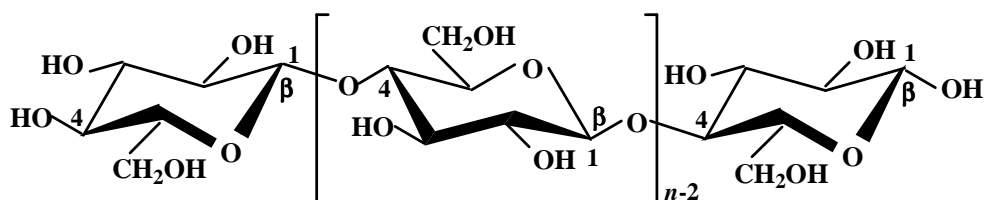
Figure 1. Molecular structure of cellulose (adapted from [6]).

The molecular size of cellulose can be defined by its degree of polymerization (*DP*) which corresponds to the **n** in the formula of cellulose shown in Figure 1. The *DP* values of cellulose differ widely depending on origin and pre-treatment. For instance, the *DP* of native cotton is up to 12000, while the *DP* of wood pulp is in the range of 600-1200 [6].

The three hydroxyl groups in each glucose unit of the cellulose molecule are able to undergo chemical reactions as well as to interact with other hydroxyl groups forming strong hydrogen bonds. In the solid state, cellulose molecules aggregate by mean of intramolecular hydrogen bonds (where OH-groups of adjacent glucose units in the same cellulose molecule link together) and intermolecular hydrogen bonds (where OH-groups of adjacent cellulose molecules link giving rise to supramolecular structures) leading to a polymer with crystalline regions alternated with amorphous regions. It has been found that cellulose crystallinity is higher in kraft pulps than in sulphite pulps [7]. Due to its fibrous structure and strong hydrogen bonds, cellulose has a high tensile strength and is insoluble in most solvents.

Native cellulose, also known as cellulose-I, has a monoclinic unit cell, with dimensions of 0.835 nm for the a-axis, 1.03 nm for the b-axis, 0.79 nm for the c-axis and 84° for the β-angle (Figure 2a). With respect to the orientation of the cellulose molecules, two neighbouring molecules are in anti-parallel directions which means that they are in a reverse position with respect to one another. Thus, among five cellulose chains in the elementary cell, four are in the same direction and one (central) is in anti-parallel direction [8]. Based on ^{13}C NMR studies, it has been found that there are two crystalline forms of cellulose I, designated as cellulose I_α and cellulose I_β, and that the crystalline component of cellulose I corresponds to a mixture of these two forms [9].

(a) (b)
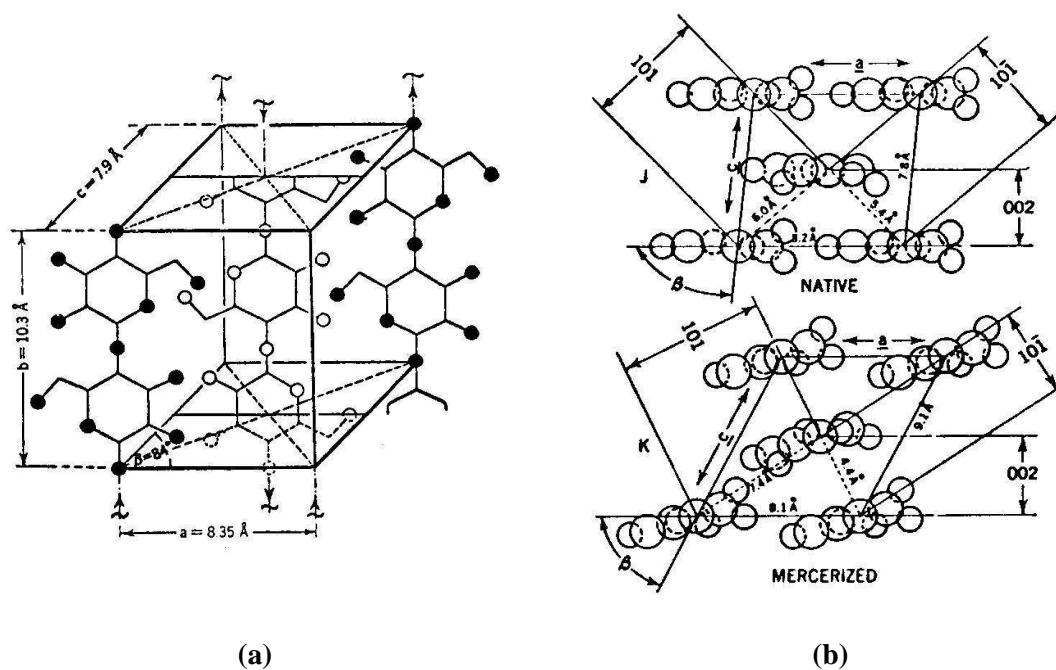
Figure 2. (a) Cellulose-I unit cell structure of native cellulose according to Meyer, Mark and Misch; and (b) view down the long axis (b-axis) of the unit cell of native (cellulose-I) and mercerized (cellulose-II) celluloses according to Meyer, Mark and Misch and Andress, respectively [adapted from 8]

Besides cellulose-I, cellulose can also adopt other polymorphic crystal structures. Mercerized cellulose, also known as cellulose-II, is obtained when native celluloses are

treated with strong alkaline solutions or when native celluloses are precipitated from solution. Cellulose-II has a different crystal structure than cellulose-I giving rise to a different X-ray diffractogram. Comparing with cellulose-I, in cellulose-II, the dimensions of the unit cell are different due to changes in the hydrogen bonds. Cellulose-II has a monoclinic unit cell, with dimensions of 0.814 nm for the a-axis, 1.03 nm for the b-axis, 0.924 nm for the c-axis and 62º for the β-angle. In cellulose-II, the anti-parallel arrangement of the molecules also occur but two staggered cellulose molecules rotated by 180º around their axis in a twofold helical screw conformation [8]. The differences between cellulose-I and cellulose-II are shown in Figure 2b.

1.1.2. Hemicelluloses

Hemicelluloses are heteropolysaccharides and represent about 20-30% of dry wood [5]. They are composed of hexoses (D-glucose, D-mannose, D-galactose), pentoses (D-xylose, L-arabinose) and small amounts of deoxy-hexoses (L-rhamnose), and uronic acids (D-glucoronic acid, 4-*O*-methyl-D-glucoronic acid and D-galacturonic acid). Hemicelluloses usually have shorter molecular chains than cellulose, having side-groups and, in some cases, being branched. Hardwoods usually contain more hemicelluloses than softwoods and the sugar composition and structure are different.

Hemicelluloses are mainly xylans (pentosans) or glucomannans (hexosans). In hardwood species, compared to the portion of xylan, the glucomannans are of minor importance consisting of 3-5 %. Xylans are hemicelluloses with a homopolymer backbone of xylose units which are linked by β-(1→4)-glycosidic bonds. Hardwood xylans chains are laced, at irregular intervals, with groups of 4-*o*-methylglucuronic acid bonded with a α-(1→2)-glycosidic linkage to the xylose units. Many of OH-groups at C-2and C-3 of the xylose units are substituted by *o*-acetyl-groups [10]. A fragment of *o*-acetyl-4-*o*-methylglucuronoxylan from hardwood is represented in the formula in Figure 3. On the average, in hardwood xylans, every tenth xylose unit is linked to a side group of 4-*o*-methylglucuronic acid [10].
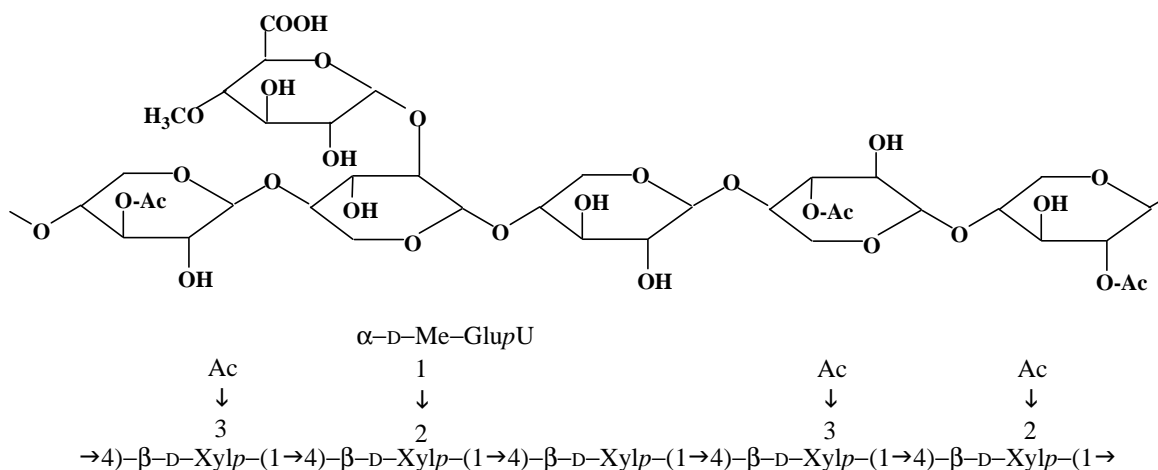
Figure 3. Chemical structure of O-acetyl-4-O-methylglucuronoxylan from hardwood [10].

In general, softwood xylans differ from hardwood xylans by the lack of acetyl groups and by the presence of arabinofuranose units linked by α-(1→3)-glycosidic bonds to the xylan backbone. Thus, softwood xylans are arabino-4-*o*-methylglucuronoxylans [10]. A fragment of the molecule is shown in Figure 4. Softwood xylans have a higher portion (about 20– 30 %) of 4-*o*-methylglucuronic acid than hardwood xylans [10].
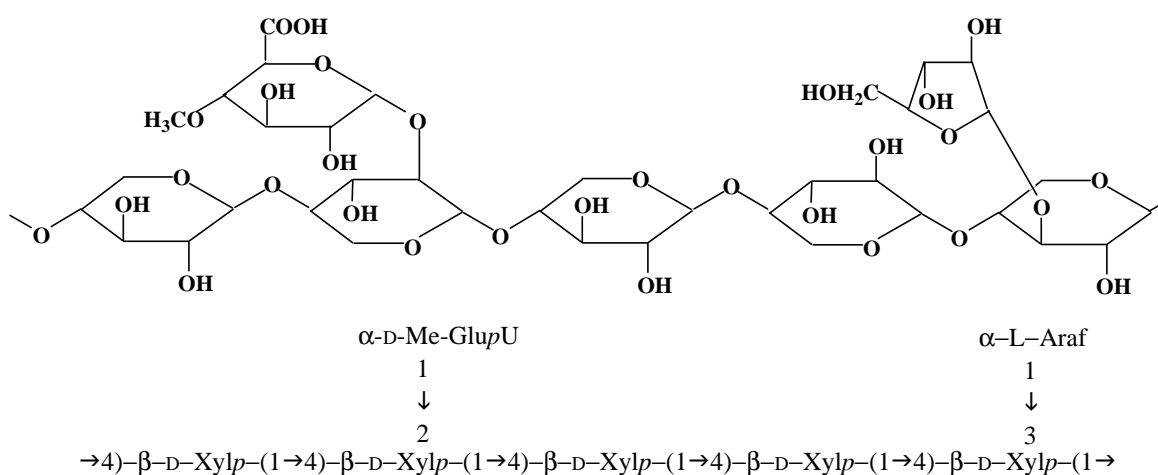
Figure 4. Chemical structure of arabino-4-O-methylglucuronoxylan from softwood [10].

[β–D–Xyl*p*]–(1→4)–[β–D–Xyl*p*]$_7$–(1→4)–[β–D–Xyl*p*]$_{42}$–(1→4)–[β–D–Xyl*p*]$_2$–(1→4)–[β–D–Xyl*p*]$_{24}$–(1→4)–[β–D–Xyl*p*]–

4–O–Me–α–D–Glc*p*A   4–O–Me–α–D–Glc*p*A   4–O–Me–α–D–Glc*p*A

Rhamnoarabinogalactan–α–D–Gal*p*   Glucan–D–Glc*p*

–(1→4)–[β–D–Xyl*p*]$_6$–(1→4)–[β–D–Xyl*p*]$_{15}$–(1→3)–[α–L–Rha*p*]–(1→2)–[α–D–Gal*p*A]–(1→4)–[β–D–Xyl*p*]

Ac   Ac   Ac
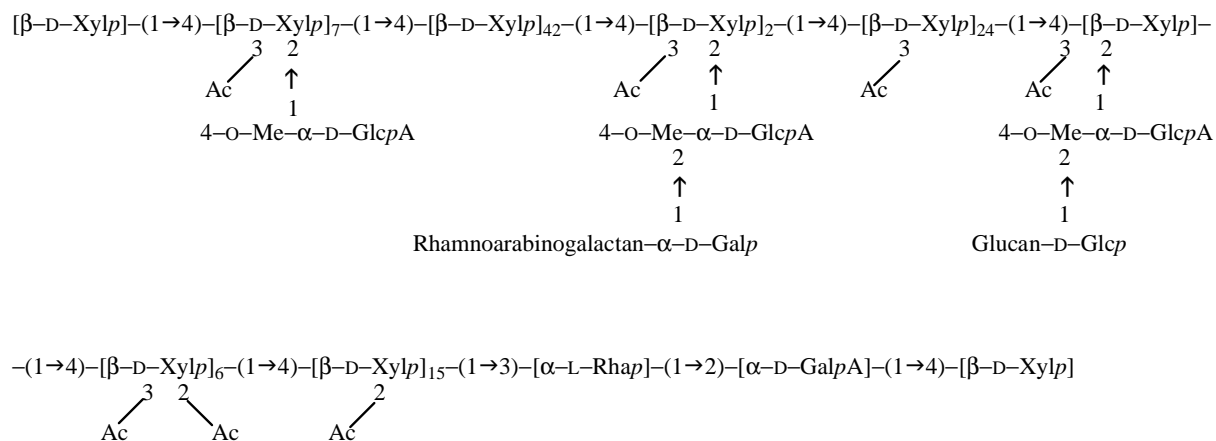
Figure 5. Structure of the heteroxylan from *Eucalyptus globulus* Labill [12].

As already mentioned, hardwood hemicelluloses are mainly composed of glucoronoxylan (*o*-acetyl-4-*o*-methylglucurono-β-D-xylan), which is the main component, and glucomannan (β-D-glucopyranose and β-D-mannopyranose units linked by (1→4) bonds). Recently, an empirical structure for the heteroxylan from *Eucalyptus globulus* wood has been proposed [11,12], consisting of *o*-acetyl-(4-*o*-methylglucorono)xylan ramified with galactan and glucan side-chains (Figure 5).

1.1.3. Lignin

Lignin is the second most abundant biopolymer in wood and constitutes approximately 30 % of the dry weight of softwoods and about 20 % of the dry weight of hardwoods. Lignin is an amorphous and polyphenolic three-dimensional polymer that derives mainly from the polymerization of three hydroxycinnamyl alcohol monomers differing in their degree of methoxylation, p-coumaryl, coniferyl and sinapyl and alcohols (Figure 6). These monolignols produce, respectively, p-hydroxyphenyl (**H**), guaiacyl (**G**) and syringyl (**S**) phenylpropane units which constitute the lignin polymer. Hardwood lignins consist principally of **G** and **S** units and traces of **H** units, whereas softwood lignins are composed mostly of **G** units with low levels of **H** units [5].
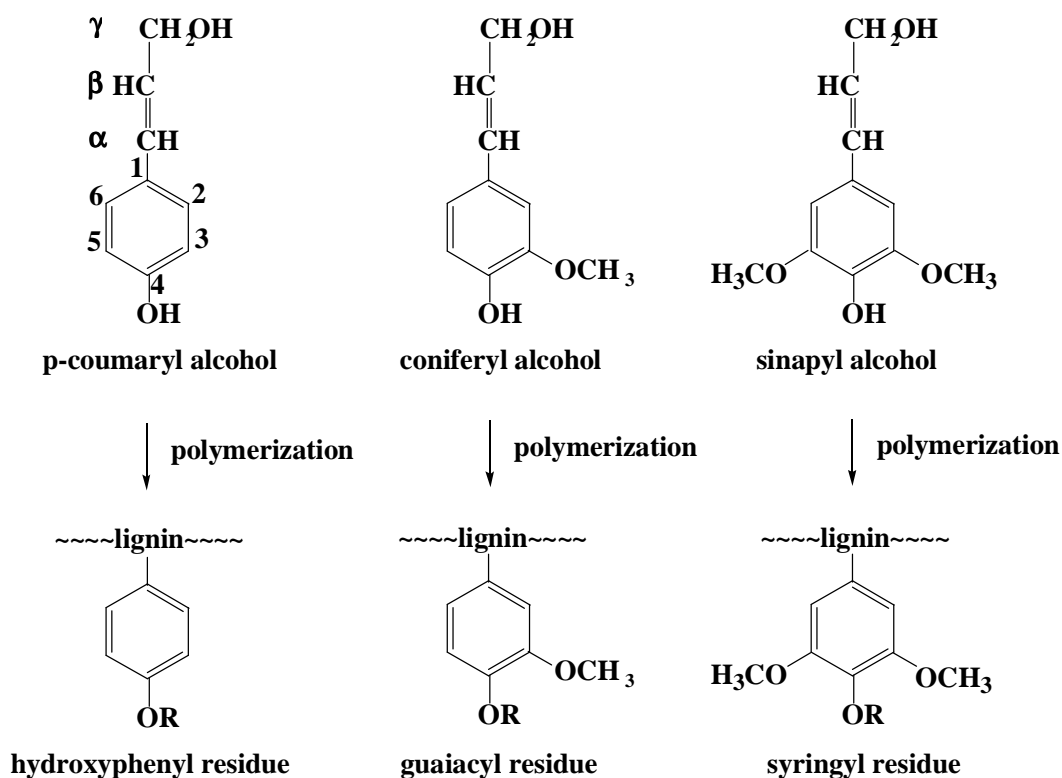
Figure 6. Structures of the three monolignols and the residues derived from them.

Lignification is the process in which the structural units are linked together via radical coupling reactions. Each type of precursor may form several types of bonds with other precursors giving rise the structures with different linkages: alkyl-*o*-alkyl, aryl-*o*-aryl, alkyl-alkyl, alkyl-aryl and aryl-aryl types. The most prominent type of linkage both in softwood and hardwood lignins is the β-*o*-4 linkage which represents approximately half of all interunit linkages (Figure 7). Among other stucutres, those of aryl-aryl (5-5') and alkyl-alkyl types (β-β') are rather abundant. In the hardwood lignin, the abundance of diaryl ether structures (4-*o*-5') may be also significant [13]. In contrast, the amount of β-1 and β-5 structures in hardwood lignins is less pronounced than in softwood lignins, which is determined by a low proportion of G units in the formers.

Monolignols can also form bonds to other cell wall polymers in addition to lignin, to polysaccharides and thus forming a very complex three-dimensional network. The statements for lignin as a non-ordered macromolecule are essentially due to three reasons: the heterogeneity of lignin structure, the morphological aspects of lignin incorporation

within the polysaccharidic structure and the non-homogeneity of isolated lignin-polysaccharides complexes [10].
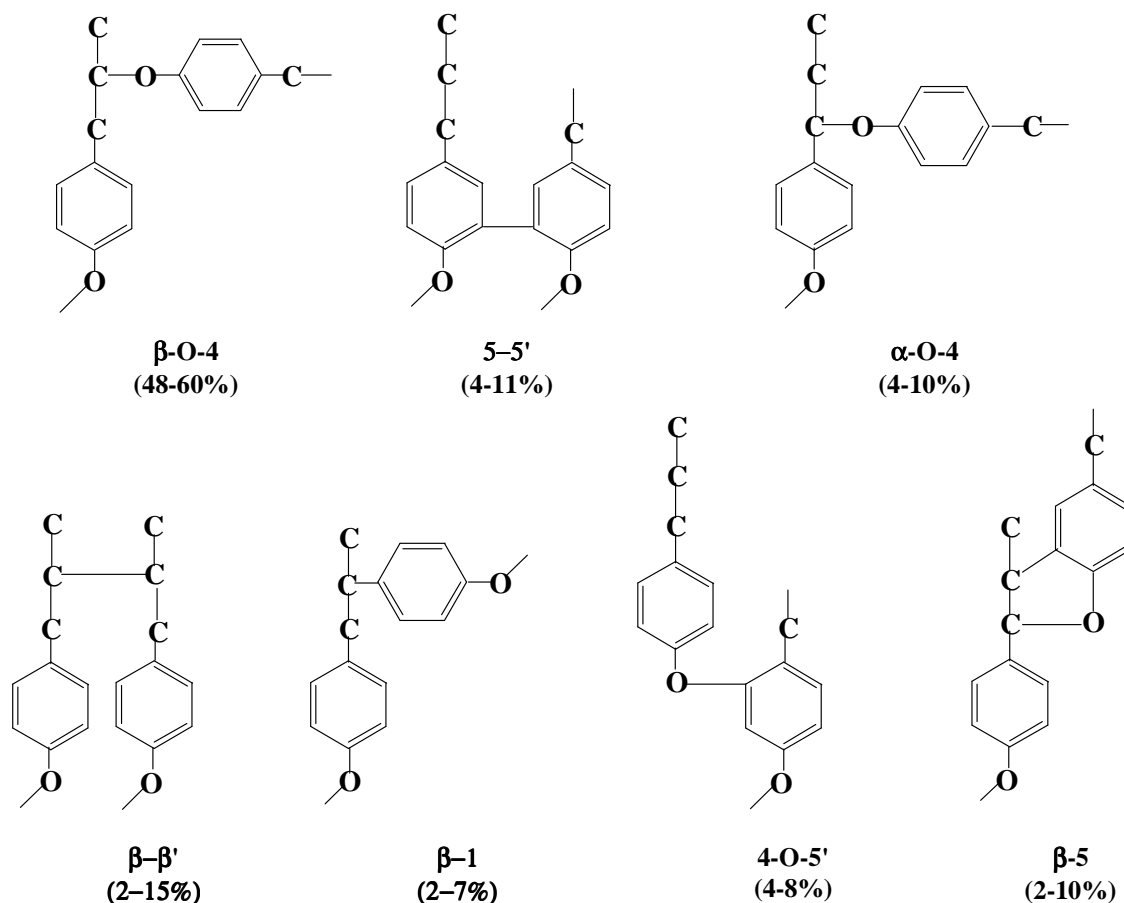
Figure 7. Linkages between the phenylpropane units in lignin [13,14].

Essentially four functional groups can be found in lignin: methoxyl, phenolic and aliphatic hydroxyls, carbonyl and carboxyl groups. Table 1 summarizes the amounts of functional groups per phenylpropane unit (C_6C_3) in softwood and hardwood lignin.

The molecular weight determination of isolated lignins varies depending on the isolation method used. The isolated lignins are mixtures of polymer fragments of considerable polydispersity. Recent studies employing sophisticated mass spectrometry techniques showed that the molecular weight of isolated lignin preparations does not exceed 8000 Da being in average around 3000 Da [13].

Table 1. Functional groups of lignin (per 100 C_6C_3 units) [5].

Group	Softwood	Hardwood
Methoxyl	92-97	140-160
Phenolic hydroxyls	15-20	15-20
Aliphatic hydroxyls	90-100	100-110
Carbonyl	10-15	10-15
Carboxyl	2-3	2-3

Benzyl ester linkage

Benzyl ether linkage

Phenyl glycosidic linkage
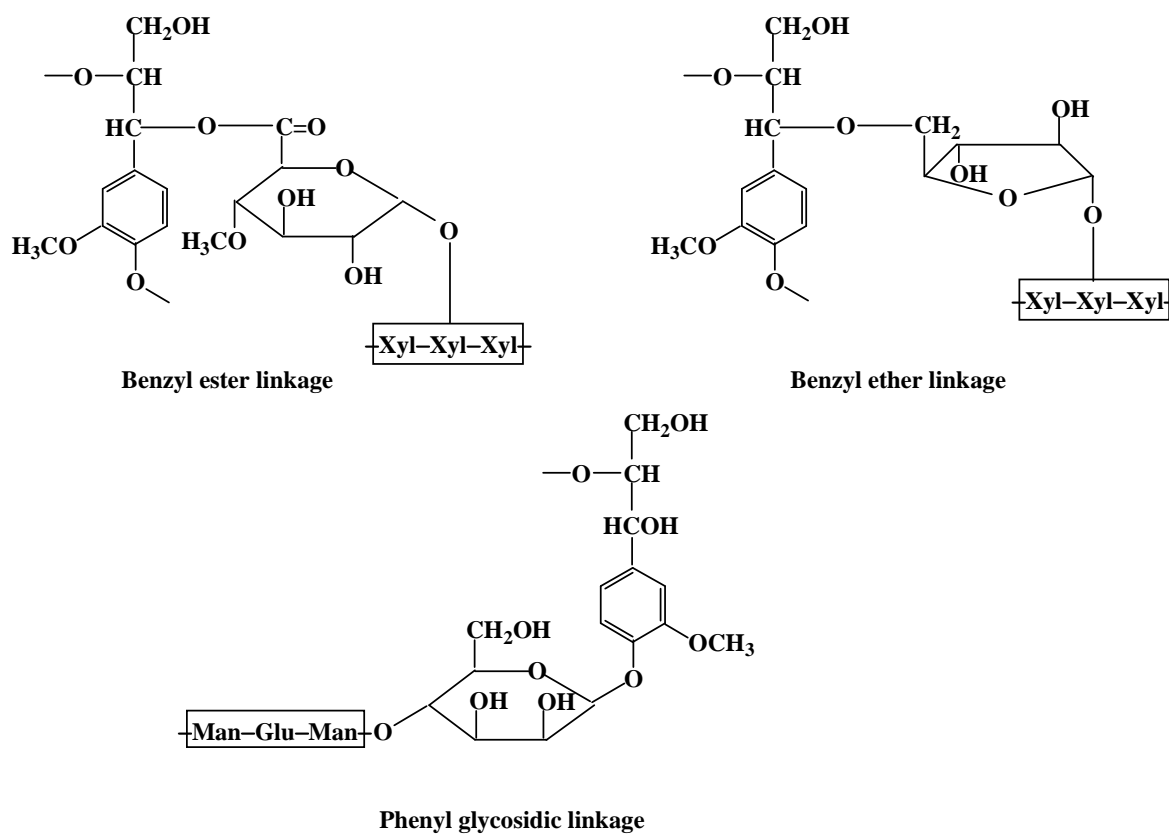
Figure 8. Most frequently suggested types of lignin-polysaccharides linkages [10].

Lignin is not simply deposited between the cell wall polysaccharides, but it is linked and associated with at least part of them. Besides hydrogen bonds, van der Waals forces and

chemisorption, chemical linkages are involved in the interaction of lignin and polysaccharides. For this reason, lignin-carbohydrate complex (LCC) and lignin-polysaccharide complex (LPC) designations are used [10]. The most frequently suggested types of covalent linkages between lignin and polysaccharides are ether linkages, ester linkages and glycosidic bonds, and they are shown in Figure 8.

Eucalyptus globulus lignin is of **S/G** type having a molar proportion **H**:**G**:**S** of 2-3:12-16:82-86 including a high abundance of β-O-4 structures and units linked by α-O-4 bonds, low proportion of phenylcoumaran structures and different kind of β-β' substructures [13].

1.1.4. Low-molecular-weight compounds

The low-molecular-weight compounds are composed of organic and inorganic material. Inorganic substances include mainly potassium, calcium and magnesium. The organic material, which is a small fraction of wood components and is soluble in neutral organic solvents or water, is known as extractives. The extractives are very important in the wood processing for pulp and paper production [5]. Particularly, extensive studies have been performed to identify their structures in *Eucalyptus globulus* [15,16,17,18,19].

The extractives include completely different types of compounds such as phenolic compounds (phenolic compounds, tannins, stilbenes, lignans and flavonoids), terpenes and related compounds that derive from isoprene units, and aliphatic compounds such as fatty acids that occur in the free form or as triglycerides and aliphatic alcohols. Figure 9 shows some examples of extractives compounds that can be found in hardwood.

Aliphatic compounds

COOH   Palmitic acid

COOH   Oleic acid

OH   1-Nonadecanol

Sterols

HO   **β–Sitosterol**

HO   **β–Sitostanol**

Phenolic compounds

COOH

R₁   R₂

OH

Vanillic acid   R₁ = OCH₃, R₂ = H
Syringic acid R₁ = R₂ = OCH₃
Gallic acid   R₁ = R₂ = OH

Ellagic acid

COOH

R₁   R₂

OH

p-Coumaric acid R₁ = R₂ = H
Caffeic acid   R₁ = H, R₂ = OH
Ferulic acid   R₁ = H, R₂ = OCH₃
Sinapic acid   R₁ = R₂ = OCH₃
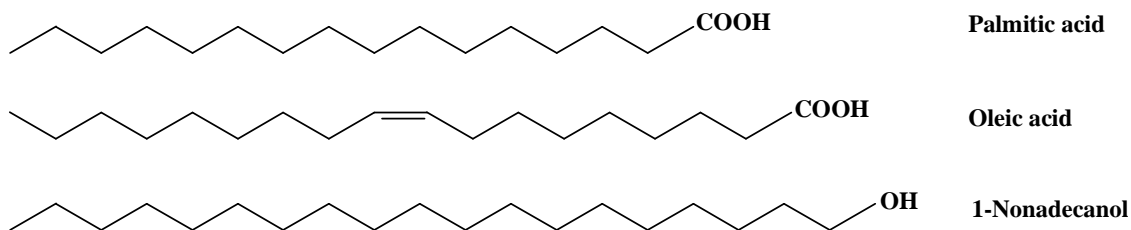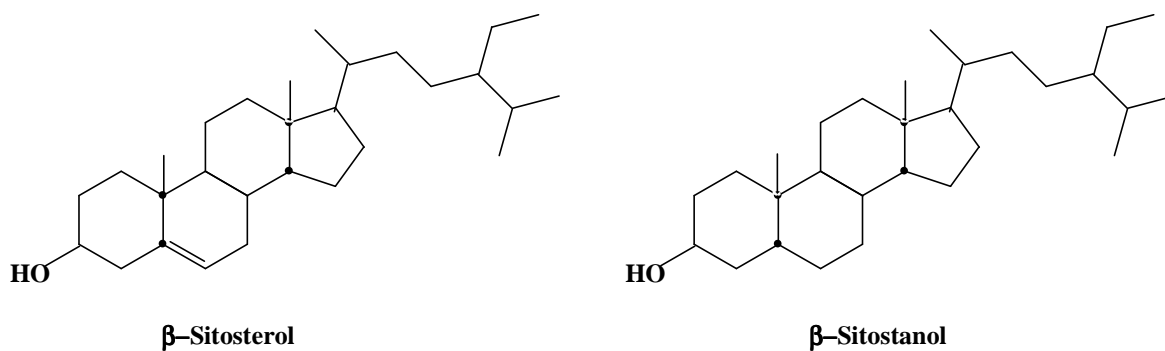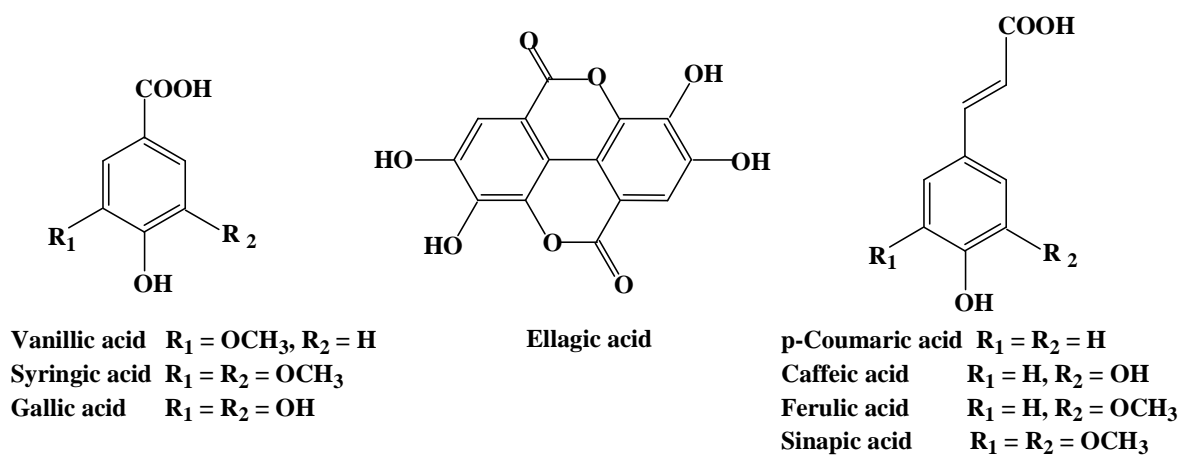
Figure 9. Structures of some extractive compounds found in wood.

1.2. PULPING

Pulping is the process converting wood or non-wood material to separated pulp fibres (pulp). Processes range from purely mechanical, in which the wood is ground into fibres by disk refiners or grindstones, to chemical, in which the fibres are separated by chemical degradation and dissolution of lignin. In fact, the main goal of chemical pulping is to remove selectively the lignin without extensive degradation of carbohydrates, and also remove extractives and other chromophoric structures in residual lignin or other components, which are already present in wood or generated during pulping. Nowadays, most of all the world production of chemical pulps is based on kraft and sulphite processes. In kraft pulping, wood chips are cooked in a solution of sodium hydroxide (*NaOH*) and sodium sulphide (*Na₂S*), while in sulphite cooking a solution of sulphurous acid (*H₂SO₃*) and bisulphite ion (HSO_3^-) is used. The kraft process dominates because it produces stronger pulps than in the mechanical processes and allows the efficient recovery of chemicals thus minimizing the pollutants release. However, the process of selectivity is less efficient than in the sulphite pulping and the pulp obtained is more difficult to bleach.

1.2.1. Sulphite Pulping

Calcium-based acid sulphite pulping of wood for the production of chemical pulps was introduced more than one century ago. In the mid time, other bases than calcium have been put in use, namely magnesium, sodium and ammonium, giving rise to four major sulphite processes that are acid, bisulphite, neutral and alkaline and all together cover the whole range of pH. For this reason, sulphite process is so versatile giving rise to the production of pulps with different yields and properties that may be used for all commercial applications, namely the acid sulphite pulping is the main process for the production of dissolving pulps [20].

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The main advantages of sulphite pulping are the high brightness of unbleached pulp and the good bleachability of the pulp. However, there are three main factors that make sulphite pulping less competitive, namely its sensitivity to the wood raw-material, the relatively low strength properties of pulps and the difficulty of recovering of the cooking reagents. Nevertheless, nowadays recovery of chemicals from the system is possible especially when magnesium is used as the base. On the other hand, studies have been done to use the lignosulphonates from the sulphite spent liquor for the production of valuable products such as vanillin [21,22], fine chemicals for pharmaceutical chemicals [23], ethanol [24] and for construction [25].

1.2.1.1. The chemistry of sulphite pulping

During a pulping, there are three main phases that co-exist simultaneously: solid, liquid and gaseous phase, which are under permanent mass and heat exchange. In the sulphite process, a mixture of sulphurous acid (H_2SO_3) and bisulphite ion (HSO_3^-) is used to attack the lignin, leading to the formation of sulphonated lignin fragments that are soluble in the cooking liquor. Figure 10 shows the equilibria of the components in aqueous solutions of sulphur dioxide [26]. The relative concentrations are functions of pH and temperature. Pulping temperatures are usually in the range of 130-170ºC.

$$SO_2 + H_2O \xleftrightarrow{pKa} H_2SO_3 \left(SO_2 \cdot H_2O\right) \xleftrightarrow{\sim 2} H^+ + HSO_3^- \xleftrightarrow{\sim 7} 2H^+ + SO_3^{2-}$$
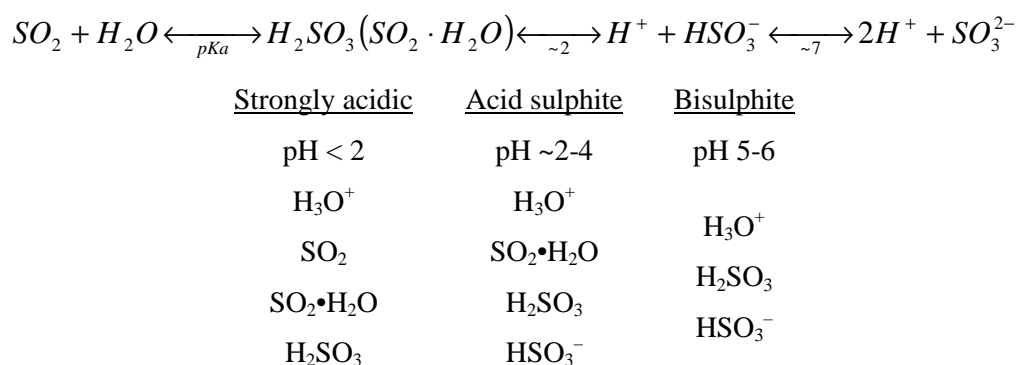
Strongly acidic	Acid sulphite	Bisulphite
pH < 2	pH ~2-4	pH 5-6
H_3O^+	H_3O^+	H_3O^+
SO_2	$SO_2 \bullet H_2O$	H_2SO_3
$SO_2 \bullet H_2O$	H_2SO_3	HSO_3^-
H_2SO_3	HSO_3^-	

pH – adjustment with hydroxides(oxides) of Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+}

Figure 10. Reactive chemical species in acid sulphite pulping processes [26].

The different chemical reactions of wood components can be subdivided into two groups: (1) reactions with involvement of sulphur components, such as formation of lignosulphonates, α-hydroxysuphonates, sugar sulphonates, sulphates and thiosulphates, and (2) reactions of the organic matter, such as acid hydrolysis of cellulose and hemicelluloses, lignin condensation, formation of organic acids, formic acid and acetic acid formation, and release of carbon dioxide from carbonyl groups [27]. A simplified scheme of the most important chemical reactions, chemical and phase equilibria occurring during sulphite pulping is shown in Figure 11.

GAS N_2, O_2

CO_2 SO_2 H_2O

SOLID **LIQUID**

$R\text{-}COOH \longrightarrow CO_2$ $2H_2O \leftrightarrow OH^- + H_3O^+$

$H_2O.SO_2 + H_2O \leftrightarrow HSO_3^- + H_3O^+$

$Lig \longrightarrow + \overline{\hspace{1cm}} HSO_3^- + H_2O \leftrightarrow SO_3^{2-} + H_3O^+$

$H_2SO_4 + H_2O \leftrightarrow HSO_4^- + H_3O^+$

$HSO_4^- + H_2O \leftrightarrow SO_4^{2-} + H_3O^+$

$H_2S_2O_3 + H_2O \leftrightarrow HS_2O_3^- + H_3O^+$

$HS_2O_3^- + H_2O \leftrightarrow S_2O_3^{2-} + H_3O^+$

$Lig\text{-}SO_3H \longleftarrow \longrightarrow Lig\text{-}SO_3H \leftrightarrow Lig\text{-}SO_3^- + H_3O^+$

$Lig\text{-}SO_3^- + H^+$

cellulose ⎫
hemicellulose⎬ $\longrightarrow$ ⎧ furfural
 ... ⎭ ⎨ acetic acid
 ...

side reactions

sulphate	$4HSO_3^- \longrightarrow$	$2SO_4^{2-} + HS_2O_3^- + H_3O^+$
α-hydroxysulphonate	$HSO_3^- + R\text{-}CHO \leftrightarrow$	$R\text{-}OH\text{-}SO_3^-$
sugar sulphonate	$nHSO_3^- + R\text{-}CHO \longrightarrow$	$R(COOH)SO_3^- + HS_2O_3^-$
aldonic acid	$2HSO_3^- + 2R\text{-}CHO \longrightarrow$	$2R\text{-}COOH + S_2O_3^{2-} + H_2O$
carbonic acid	$2HSO_3^- + 2HCHOOH \longrightarrow$	$2CO_2 + S_2O_3^{2-} + 3H_2O$

Figure 11. Scheme of phase equilibria and chemical reactions during acid sulphite pulping [27].

The reactions of lignin during acid sulphite pulping have been studied using phenolic and non-phenolic model compounds. Acid sulphite pulping is characterized by extensive sulphonation of benzylic carbon atoms (predominantly in the α-position) in phenolic and non-phenolic units (Figure 12). The cleavage of α-ether bonds leads to the intermediate formation of a benzylic cation which is sulphonated [28]. Sulphonation can also take place at the γ-carbon in the case of stilbenes structures with highly electrophilic γ-carbon atoms [29]. Together with sulphonation reactions, two other reactions occur in parallel or competitively, namely degradation and condensation of lignin [28]. Condensation of lignin is highly undesirable giving rise to dark-coloured and insoluble aromatic compounds.

R = H, alkyl, aryl

R_1 = H, neighbouring lignin unit

R_2 = neighbouring lignin unit
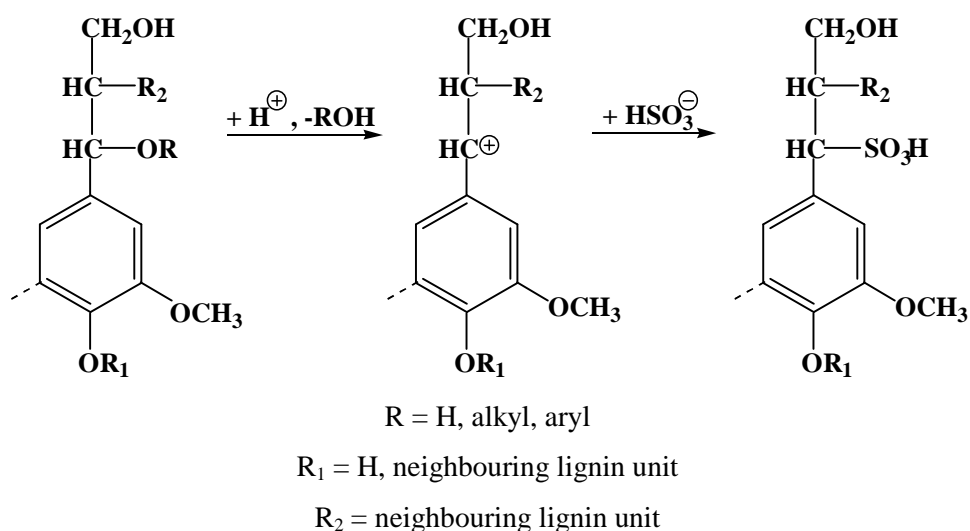
Figure 12. General scheme for the reactions of lignin units during acid sulphite pulping [29].

In the acid sulphite pulping, a high sensitivity to the wood raw-material remains a problem due to the fact that phenolic extractives have a tendency to condense with lignin structures at a very low pH. On the other hand, the combination of low acidity and not too high temperature favour sulphonation instead of lignin condensation [30].

The hydrolysis of hemicelluloses gives rise to a pulp with a lower yield; although, cellulose is relatively stable to chemical attack by the sulphite liquor, usually reducing in its degree of polymerization. However, when a yield of about 45% is reached, cellulose

becomes vulnerable to hydrolysis reactions [31]. As a rule, the yield of acid sulphite pulp is high as 3– 6 % than the kraft pulps.

1.2.1.2. The magnesium base in sulphite pulping

At the beginning of its use and until the mid 1950's, sulphite pulping process used calcium as the base due to its low cost (from limestone $CaCO_3$) and the lack of environmental regulations. However, this base presents several chemical limitations, which interfered in further sulphite process development. First, calcium is soluble only below pH 2.3 and only in its bisulphite form. Second, when calcium bisulphite solutions are heated, deactivation of the bisulphite takes place leading to calcium sulphite precipitation. Therefore, using calcium base, high charges of free SO_2 and low cooking temperature must be used interfering to the production rate improvements and the pulp quality [20].

Then, soluble bases were used to replace calcium (magnesium, sodium and ammonium bases) allowing the improvement of this sulphite pulping process by extending the raw materials used and the production of different kind of pulps with different applications; also methods to recover the bases and the sulphur were developed.

Magnesium base started to be used in a large scale during the commercial sulphite pulping in the 1960's. Since MgO is at least ten times more expensive than CaO, full chemical recovery is essential. Apart from cost, magnesium base shows advantages in sulphite process due to its chemical nature: (1) magnesium bisulphite solutions are stable up to 5.6 while the limit solubility of calcium bisulphite is at pH 2.3, and (2) magnesium sulphite is more soluble than calcium sulphite. For this reason, magnesium base can be used for acid-bisulphite, bisulphite and bisulphite-sulphite pulping [20].

In order to obtain pulps with different properties, different solutions in the magnesium sulphite process can be used:

$$H_2O + SO_2 \rightarrow SO_2 aq., \text{ free acid solution}$$

$$Mg(OH)_2 + SO_2 aq.(excess) \rightarrow Mg(HSO_3)_2 + SO_2 aq., \text{ acid bisulphite}$$

$$Mg(OH)_2 + 2SO_2 \rightarrow Mg(HSO_3)_2, \text{ bisulphite, Magnefite}$$

$Mg(HSO_3)_2 (excess) + Mg(OH)_2 \rightarrow Mg(HSO_3)_2 + MgSO_3$, "neutral Magnefite"

$Mg(HSO_3)_2 + Mg(OH)_2 \rightarrow 2MgSO_3 + 2H_2O$, magnesium sulphite solution

$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2$, bisulphite
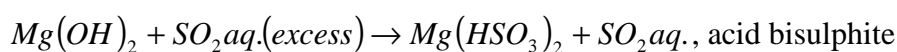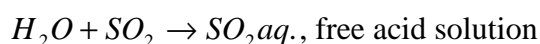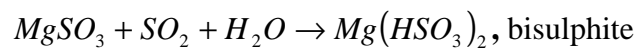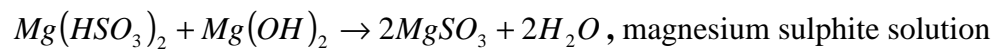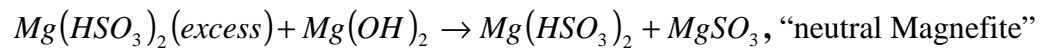
1.3. BLEACHING

To produce white pulps, the pulping process is accompanied by deeper delignification stages, usually oxidative, which are complex and may provoke environmental problems. This sequence of stages to improve the pulp brightness is called bleaching. There are two main types of bleaching: lignin-preserving bleaching and lignin-removing bleaching. Lignin-removing bleaching is a continuation of lignin degradation that was not removed during the pulping process but with more selective chemicals and under lower temperature. This process involves converting the lignin into soluble substances that can be eliminated by alkaline extraction. In lignin-preserving bleaching, chemicals react with lignin leading to a decolourized lignin without removing it from the pulp. This method is mostly used for mechanical pulp in which the major lignin remains. Lignin-removing bleaching is the most widely used method for chemical pulps. Table 12 presents most of the bleaching chemicals used in the industry including their function, advantages and disadvantages.

Most of the oxidants preferentially attack electron-donor phenolic and ethylenic structures in lignin; therefore, these oxidants initiate electrophilic reactions that degrade lignin and involve cations and/or radicals intermediates depending on the media pH. On the other hand, some species promote nucleophilic reactions that do not degrade lignin but eliminate chromophors. These reactions are essentially reductive and involve carbonyl- and conjugated carbonyl-containing structures. These reactions also occur in lignin-degrading processes after the initial attack of an electrophile [32]. Figure 13 shows the reactive sites attack in lignin and carbohydrates by electrophiles and nucleophiles [33].

Due to environmental regulations and market demands, the pulp and paper industry has been forced to find bleaching chemicals to substitute chlorine-based chemicals especially chlorine. Nowadays, most of pulp and paper industries produce ECF (elemental Chlorine Free) or TCF (Totally Chlorine Free) bleached pulps. ECF-bleaching denotes bleaching in a sequence where chlorine dioxide can still be used, but where chlorine and hypochlorite stages are excluded. TCF-bleaching, on the other hand, is performed without using any chlorine-based bleaching chemicals.

Table 2. Functions, advantages and disadvantages of bleaching chemicals (adapted from [33]).

Name	Formula	Function	Advantages	Disadvantages
Oxidant				
Chlorine	Cl_2	Oxidize and chlorinate lignin	Effective, economical delignification; good particle removal	Organochlorine formation; highly corrosive
Hypochlorite	NaOCl	Oxidize, decolourize and solubilize lignin	Easy to make and use; low cost	Can cause loss of pulp strength; chloroform formation
Chlorine dioxide	ClO_2	1) Oxidize, decolourize and solubilize lignin 2) In small amounts with Cl_2, protects against cellulose degradation	Achieves high brightness without loss of pulp strength; good particle bleaching	Must be made on-site; some organochlorine formation; cost; highly corrosive
Oxygen	O_2	Oxidize and solubilize lignin	Low chemical cost; provides chloride-free effluent for recovery	Requires significant capital equipment when used in large amounts; potential loss of pulp strength
Hydrogen peroxide	H_2O_2	Oxidize and decolourize lignin	Easy to use; low capital cost	High chemical cost; poor particle bleaching; can cause loss of pulp strength
Ozone	O_3	Oxidize, decolourize and solubilize lignin	Effective; provides chloride-free effluent for recovery	Must be made on-site; poor particle bleaching and pulp strength; cost
Reductant				
Hydrosulphite	$Na_2S_2O_4$	Reduce and decolourize lignin in high-yield pulp	Easy to use; low capital cost	Decomposes readily; limited brightness gain
Alkali				
Sodium hydroxide	NaOH	Hydrolize chlorolignin and solubilize lignin	Effective and economical	Darkens pulp

There are three main TCF bleaching processes, oxygen, hydrogen peroxide and ozone bleaching, which exhibit similar characteristics, namely, common reagents (oxygen and hydrogen peroxide) and common intermediary radical species (superoxide($O_2^{\bullet-}$)/ hydroperoxyl ($HO_2^{\bullet}$) and hydroxyl ($HO^{\bullet}$) radicals) originated from these reagents. These radical species have very different functions concerning the degradation of aromatic and

aliphatic structures; however, in all three TCF bleaching processes, hydroxyl radicals attack carbohydrate structures, being the main cause of the limited selectivity of TCF bleaching [34]. Some studies have been carried out to improve TCF bleaching of sulphite [35,36] and thus increase the final pulp brightness remaining intact the pulp properties.

Sites of attack by electrophiles

(non-conjugated units)   (ring-conjugated units)
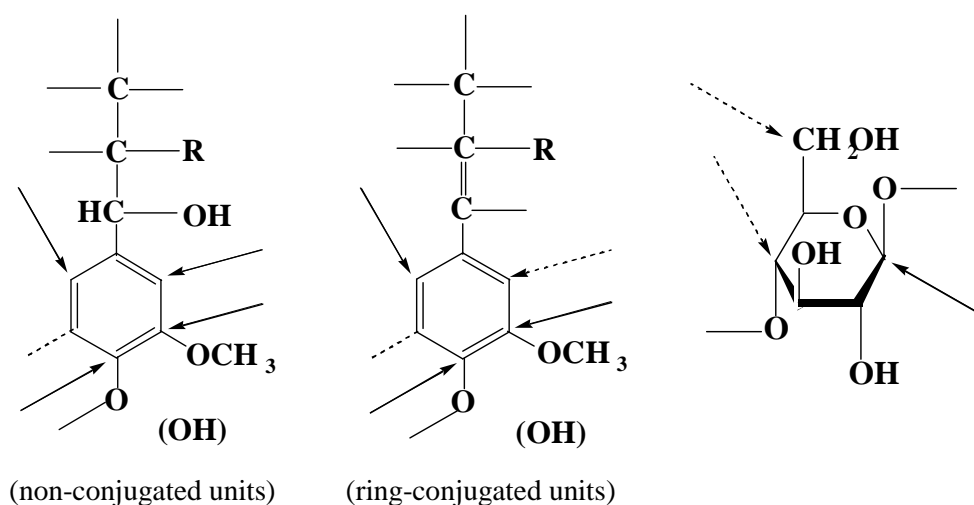
Sites of attack by nucleophiles

(non-conjugated units)   (ring-conjugated units)
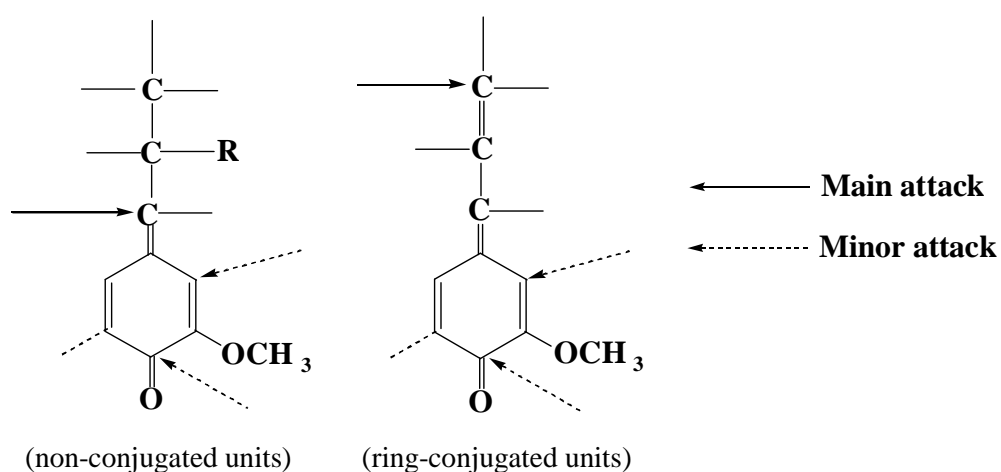
Figure 13. Reactive sites in lignin and carbohydrates units [32].

1.3.1. Chlorine-based bleaching: chlorine dioxide and hypochlorite

Chlorine dioxide was firstly used to replace chlorine in pulp bleaching allowing the production of high pulps brightness without loss of pulp strength. Nowadays, chlorine dioxide is one of the most important bleaching chemicals because it reacts preferentially with lignin and only in small extent with carbohydrates.

When chlorine dioxide reacts with pulp, several chlorine-based intermediates are formed, including hypochlorous acid ($HOCl$), chlorine (Cl_2) and chlorate (ClO_3^-), which is a non-reactive species [37].

Chlorine dioxide primarily reacts with phenolic groups in unbleached lignin during the delignification stage [37]. Studies using a softwood kraft pulp show that chlorine dioxide delignification gives rise to the formation of quinone and muconic structures onto the oxidized lignin, generally in a 2:1 ratio, respectively; and most of the quinone structures are *o*-quinones [38] (Figure 14). Chlorine dioxide reveals to have a small effect on the structure of cellulose fibres since no change in the cellulose degree of polymerisation is observed [39].

Several parameters influence the efficiency of chlorine dioxide, namely, chemical charge and residual pH, time and temperature, pulp consistency, amounts of chlorine and chloride ions, washing efficiency and carryover composition [40].

Before using chlorine dioxide, hypochlorite was the preferable chemical for pulp bleaching because it could be produced in dry form and shipped over long distances. However, it has some drawbacks including the fact that hypochlorite is a chlorine-based chemical (giving organochlorides) and, during pulp bleaching, chloroform is formed [41].
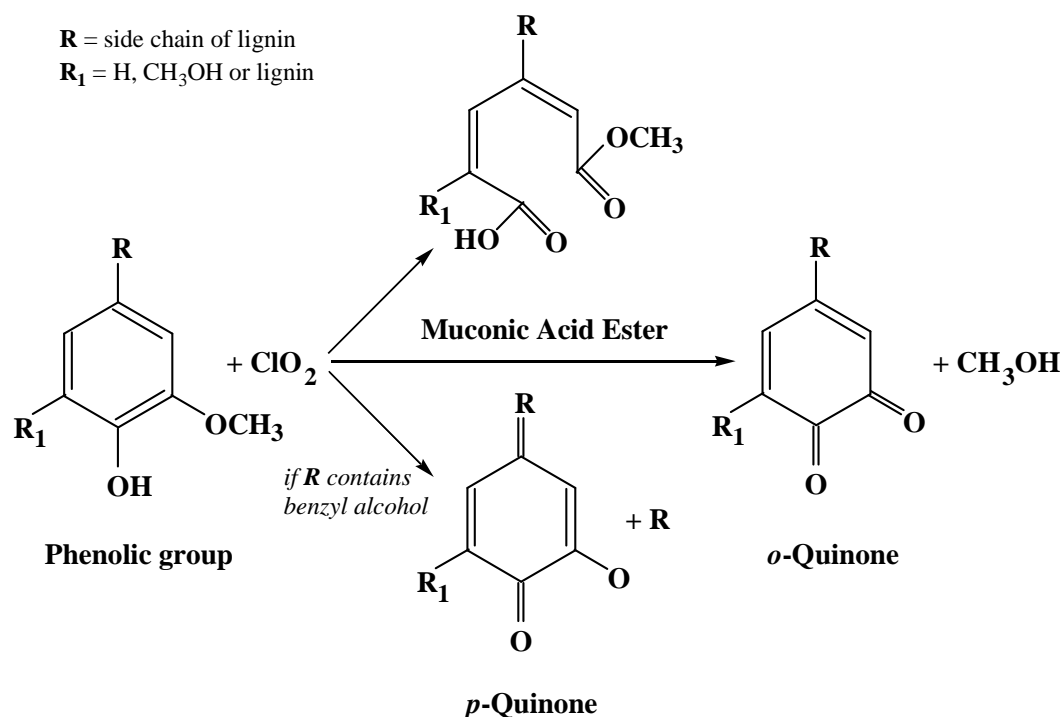
Figure 14. Reactions of ClO₂ with representative phenolic groups of residual lignin during a ClO₂ delignificatin stage [38].

1.3.2. Oxygen bleaching

The use of oxygen as a bleaching agent, usually occurring under pressure, has expanded in the recent decades due essentially to oxygen bleaching efficiency, which is in the range of 35-50%, and environmental benefits. Under the typical alkaline conditions used in oxygen bleaching, several oxygen species are formed according to the following steps, which include radical chain reactions involving lignin and carbohydrates [42].

Initiation	$RO^- + O_2 \rightarrow RO^\bullet + O_2^{-\bullet}$
	$RH + O_2 \rightarrow R^\bullet + HO_2^\bullet$
Propagation	$R^\bullet + O_2 \rightarrow RO_2^\bullet$
	$RO_2^\bullet + RH \rightarrow RO_2H + R^\bullet$
Termination	$RO^\bullet + R^\bullet \rightarrow ROR$
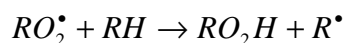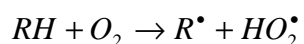
Because oxygen is a weak oxidant, reactions have to be promoted by raising temperature or by providing a reactive substrate. In typical oxygen bleaching, the substrate is activated by ionization of the free hydroxyl groups under alkaline conditions [42].

Oxygen has the main advantage being an environmental friendly bleaching agent; however, its main disadvantages are the high costs associated to initial capital costs, the all system used, steam, maintenance and a high overall process complexity, and the need of a recovery system. An additional disadvantage is the fact that oxygen is a non-selective bleaching agent especially at high delignification degrees, up to 50%, attacking carbohydrates. The decrease of chlorine-based oxidizing chemicals consumption leads to decrease in the amount of chlorine-based by-products originated as well as in biochemical oxygen demand (BOD), chemical oxygen demand (COD) and colour. [42].

The main oxygen bleaching process variables are as follow [42]:

- **Time and temperature**, since the decrease of kappa number with time exhibits two dissimilar stages depending on the presence of two types of lignins removed in a different way: in the first one, the kappa number drops rapidly while during the second one the kappa number drops slowly. When there is enough alkali, kappa number drops indefinitely, on the other hand a limiting kappa number decreasing is reach when all alkali is consumed. Delignification accelerates with temperature increase and the point of alkali consumption is reached much more rapidly at high temperatures (about 130ºC) than at low temperatures (about 85ºC).

- **Alkali charge**, because when it is increased, the delignification and the cellulose degradation are promoted.

- **Oxygen pressure**, when is lower than 4 atm, the delignification occurs only in a small extension when compared to the same alkali charge and temperature.

- **Consistency**, which, at a constant alkali charge, has a small effect on delignification and carbohydrate degradation.

In order to increase oxygen efficiency as a delignifying agent, some additives may be applied, namely (i) reinforcement with hydrogen peroxide or peracids; (ii) addition of activators or catalysts, including polyoxometalates (POMs) and nitrogen-based activators in peroxide-reinforced oxygen delignification stage [43] between others; (iii) pulp pre-

treatment prior to oxygen delignification; (iv) two-stage oxygen delignification with or without a washing stage between the two oxygen stages [44,45].

The reinforcement of oxygen with hydrogen peroxide combines the bleaching effect of hydrogen peroxide and the delignifying effect of oxygen. Comparing with oxygen delignification stage, hydrogen peroxide-reinforced oxygen delignification stage gives rise to the increased pulp brightness due to reducing kappa numbers without the viscosity drop. On the other hand, reinforcing oxygen stage with hydrogen peroxide allows to work at low temperatures (90ºC instead of the usual 110-120ºC) giving rise to pulps with increased brightness and similar kappa numbers [44,45]. Peracetic acid has also been used to reinforce oxygen delignification but high costs and hazardous handling are hindered to its utilization. A new method to avoid this problem has been proposed, where hydrogen peroxide reacts with pentaacetyl glucose, which is a safe and non-toxic chemical, generating peracetic acid *in-situ* [46].

POMs have been claimed to be promising catalysts for the selective lignin oxidation under anaerobic conditions [47,48,49,50] and aerobic conditions [51,52,53] with special attention focused in the use of POMs with the Keggin structure [53,54,55,56,57] .The feasibility of POM-catalyzed oxygen delignification has been confirmed at pilot-scale [58].

1.3.3. Peroxide bleaching

Hydrogen peroxide is a delignifying and bleaching agent that is able to bleach pulps to brightness around 80-83% without significant lignin removal [59]. Usually, chemical pulp bleaching involves mainly electrophilic reactions of hydrogen peroxide as delignifying agent and mechanical pulp bleaching involves nucleophilic reactions and lignin-retaining bleaching [32].

In alkaline medium, hydrogen peroxide (H_2O_2) is in equilibrium with hydroperoxide anion (HO_2^-), a strong nucleophile that is believed to be the active species that reacts with chromophoric structures in lignin [59,60]:

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$$
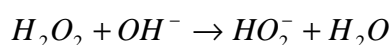
In hydrogen peroxide bleaching, there are two main competing reactions: (1) the bleaching process where hydroperoxide anion reacts with carbonyl and conjugated carbonyl groups in lignin destroying them leading to a pulp brightness increase and (2) the parallel reaction of the hydrogen peroxide decomposition into water and oxygen. In order to maximize hydrogen peroxide efficiency as a lignin-retaining bleaching agent and minimize pulp degradation, its decomposition should be as minimized as possible. However, some of its decomposition products participate in delignification and bleaching reactions. Therefore, hydrogen peroxide decomposition should be controlled by: (1) using mild alkaline bleaching conditions, (2) using inorganic stabilizers such as magnesium sulphate and sodium silicate, and (3) removing transition metals by pre-treatment of the pulp with an acid or chelating agent [59].

The main decomposition products of hydrogen peroxide are hydroxyl radicals ($HO^{\bullet}$), and superoxide anion radicals ($O_2^{\bullet-}$). Because the half-life of hydroxyl radicals is very short, the effectiveness of radical species in increasing pulp brightness is influenced by whether peroxide decomposition occurs mainly in solution or in the fibre near the chromophoric groups of lignin. Hydroxyl radicals attack preferentially the phenolic units in lignin but also degrade to some extent carbohydrates [59].

At a temperature higher than 80ºC, hydrogen peroxide acts as a delignifying agent that promotes lignin dissolution being highly effective after an oxygen bleaching stage. There are three hydrogen peroxide delignifying processes: (1) hydrogen peroxide is directly applied to unbleached pulp, (2) hydrogen peroxide is applied after a stage where trace metal profile is changed, and (3) both oxygen and peroxide are used in a hydrogen peroxide-reinforced oxygen delignification. Hydrogen peroxide delignification results from the reaction of the decomposition products of the hydroperoxide anion with chromophoric groups in lignin. Therefore, the rate of peroxide decomposition is important for the extent of delignification and cellulose degradation [60].

The efficiency of hydrogen peroxide as a delignifying and bleaching agent may be affected by several parameters [59,60]:

- **Hydrogen peroxide charge**, during bleaching hydrogen peroxide rapidly decomposes; therefore, an increase in hydrogen peroxide charge leads to a higher pulp brightness.

- **Metals**, in alkaline medium, may catalyse (Fe, Cu and Mn) or stabilize (magnesium salts and sodium silicate) the decomposition of hydrogen peroxide. On the other hand, some inorganic species improve hydrogen peroxide selectivity (*e.g.* manganese provides less cellulose degradation). Some chelating agents like EDTA and DTPA used in a pulp pre-treatment improve peroxide delignification and bleaching effect as well as less cellulose degradation.

- **Temperature**, at 120ºC; hydrogen peroxide decomposition is very fast affecting negatively its selectivity. At atmospheric pressure, a temperature of 90ºC is a good compromise because it provides a high delignification rate with small extent cellulose degradation. Pressure may be applied leading to higher pulp brightness with decreased hydrogen peroxide charge. When oxygen is used to pressurize this stage, the maximum temperature should be below 130ºC in order to avoid further hydrogen peroxide decomposition.

- **Reaction time**, which should be as long as possible; however a too long retention time is economically difficult. In order to obtain certain pulp brightness, retention time may be shortened by increasing temperature of peroxide stage: good results are obtained in 120 minutes at 90ºC.

- **Chemical charge**, which is a function of hydrogen peroxide charges – Table 3 – since alkalinity must be in the optimum dosage in order to peroxide dissociates in the optimum hydroperoxide anion concentration and to improve pulp brightness. When the alkaline charge is above the optimum, hydrogen peroxide effectiveness is reduced and brightness reversion is observed.

- **Consistency**, when is as high as 25% enhances peroxide delignification; however, due to high investment costs that obliges, usually consistencies around 10% are used.

Activators or catalysts, including some transition metals [61] and transition metal peroxo complexes like a vanadium peroxo complex [62], nitrogen-based compounds especially cyanamide [63,64] and dicyandiamide [65], tetraacetylthylenediamine (TAED), peracids, namely peracetic acid and caro's acid, and pentaacetyl glucose between others, can be used to improve peroxide stage [44,45]. The activator or catalyst is added directly into the peroxide stage where it reacts with hydrogen peroxide leading to the formation *in-situ* of a more powerful oxidant.

Table 3. Optimum sodium hydroxide charge as a function of hydrogen peroxide charge in the delignification of softwood and hardwood kraft pulps [60].

H_2O_2 (% on pulp)	NaOH (% on pulp)
1	2-2.5
1.5	2-3
2	2-3
3	2.5-3.5
4	3-4

Operating conditions: 90ºC, 2h, 10-15% consistency.

The use of activators such as cyanamide allows to use a smaller amount of hydrogen peroxide or to use the same hydrogen peroxide dosage leading to an increase in pulp brightness [59]. Studies using lignin model compounds have been performed where cyanamide activated hydrogen peroxide reacts exclusively with free phenolic structures [66] via two reactions mechanisms, radical and ionic, where the predominant one is the radical mechanism [67]. This system, which is strongly dependent on pH and the cyanamide-to-peroxide ratio [67], gives rise to extensive lignin degradation [68].

TAED reacts with hydrogen peroxide and water giving rise to triacetylethylenediamine (TriAED) and diacacetylethylenediamine (DAED) with the release of two molecules of peracetic acid or acetic acid [69].

1.3.4. Ozone bleaching

Ozone is a powerful oxidizing agent used to bleach pulp but it is toxic in small amounts. There are basically two main disadvantages on using ozone in a bleaching stage: (1) during the ozone bleaching stage there is formation of ozonised pulp that is susceptible to alkaline degradation in the following bleaching stage, and (2) the low efficiency and selectivity of ozone as a bleaching agent. Even though ozone is very reactive, its use is restricted because ozone is generated in low concentrations diluted with a carrier gas, usually

oxygen. For this reason, the reactivity of ozone is defined by its own properties and those of the carrier gas. On the other hand, due to the low solubility of ozone in water, its reactivity is limited in aqueous systems where ozone must be transfered from the gas phase into the water in order to react [70].

In aqueous media, ozone reacts with organic materials resulting into the formation of hydroxyl ($HO^\bullet$) and superoxide ($O_2^{\bullet-}$) radicals:

$$RH + O_3 \rightarrow R^\bullet + HO^\bullet + O_2$$
$$RH + O_3 \rightarrow RO^\bullet + H^+ + O_2^{\bullet-}$$
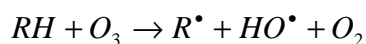
In acidic solutions, superoxide is the initially formed radical species, however, in the presence of oxygen and ozone, superoxide is easily converted into the hydroxyl radical and also hydroxyl radical into superoxide [71].

Several variables affect the reactions between ozone and the pulp, pulps properties and commercial reliability, such as mass transfer, pulp consistency, ozone charge, effect of pH, time, temperature, additives, metal effects, presence of residual organic matter and pulp treatment before ozone stages. Mass transfer of ozone to the active sites in pulp fibre occurs mainly in three steps: (1) ozone convection in the phase, gaseous or liquid, in which fibres are dispersed, (2) ozone dissolution in the water surrounding the individual fibres; and (3) ozone diffusion to the reaction site [70].

It would be of great interest to prevent or decrease the reaction of ozone with carbohydrates during the ozone bleaching stage by increasing its efficiency and selectivity. This may be achieved by using an oxalic acid additive or by performing a sodium borohydride-based post-treatment. Oxalic acid protects cellulose and facilitates lignin removal resulting in increased brightness and viscosity, while sodium borohydride post-treatment reduces carbonyl groups leading to increased viscosity and brightness. The combination of using oxalic acid as additive and a sodium borohydride-based post-treatment gives rise to better results than when used individually [72].

According to published results [73,74], using ozonated water for the final bleaching of chemical bleached pulps allows the gain of some percents of final brightness.

1.3.5. Hydrosulphite (dithionite) bleaching

Another approach for bleaching is to reduce chromophoric structures instead of the usual oxidative processes. The effect of reducing agents depends on the redox potential of the system [5]:

$$H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \qquad\qquad \left(E^\circ = -0.20V\right)$$

$$S_2O_4^{2-} + 4HO^- \rightarrow 2SO_3^{2-} + 2H_2O + 2e^- \qquad\qquad \left(E^\circ = -1.12V\right)$$

$$BH_4^- + 8HO^- \rightarrow B(OH)_4^- + 4H_2O + 8e^- \qquad\qquad \left(E^\circ = -1.24V\right)$$
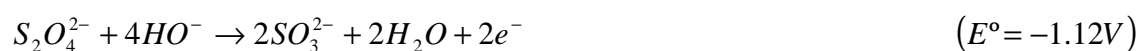
The respective standard redox potential for the quinone structures in the residual lignin are around 0.7-0.9 V. Therefore, quinone structures can be reduced to the corresponding hydroquinones by sodium dithionite and sodium borohydride. Since sodium borohydride needs special security cares and is very expensive, sodium dithionite is the most common chemical agent used for the lignin-preserving bleaching of semichemical and thermomechanical pulps.

Dithionite ions are converted to sulphite ions during bleaching; however some of the dithionite disproportionates leading to the formation of thiosulphate and hydrogen sulphite and, in the presence of oxygen, dithionite is oxidized (Figure 15) [75].

Dithionite reacts with lignin or lignin-derived carbonyl-conjugated structures such as *o*- and *p*-quinones, quinonemethides and the side chain of conyferaldehyde units [76], as shown in Figure 16.

$$Na_2S_2O_4 + H_2O$$

Disproportionation

$$NaHSO_3 + NaHSO_2 + PULP$$

Direct
oxidation

Decomposition $(2NaHSO_2)$

Lignin-retaining
bleaching

$$Na_2S_2O_3 + H_2O$$

$$NaHSO_4 \xleftarrow{[o]} NaHSO_3$$

$$Na_2S \dashrightarrow H_2S$$

BLEACHED PULP
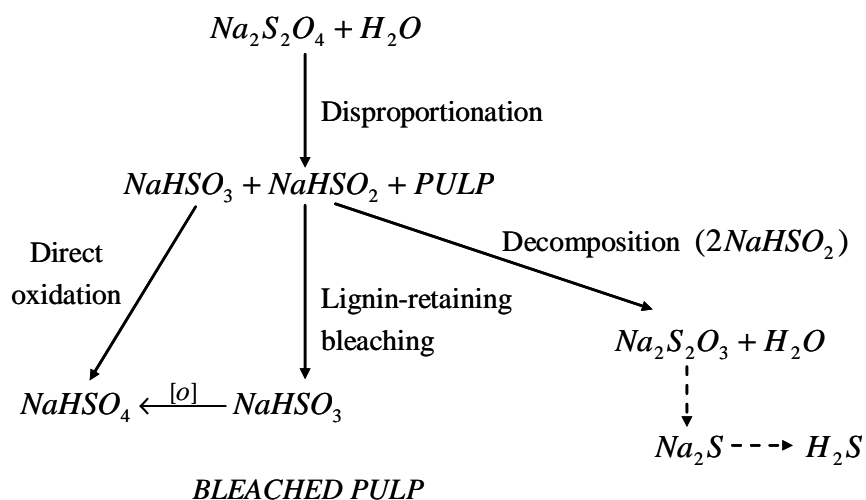
Figure 15. Main reaction pathways for degradation of sodium dithionite during bleaching [75].
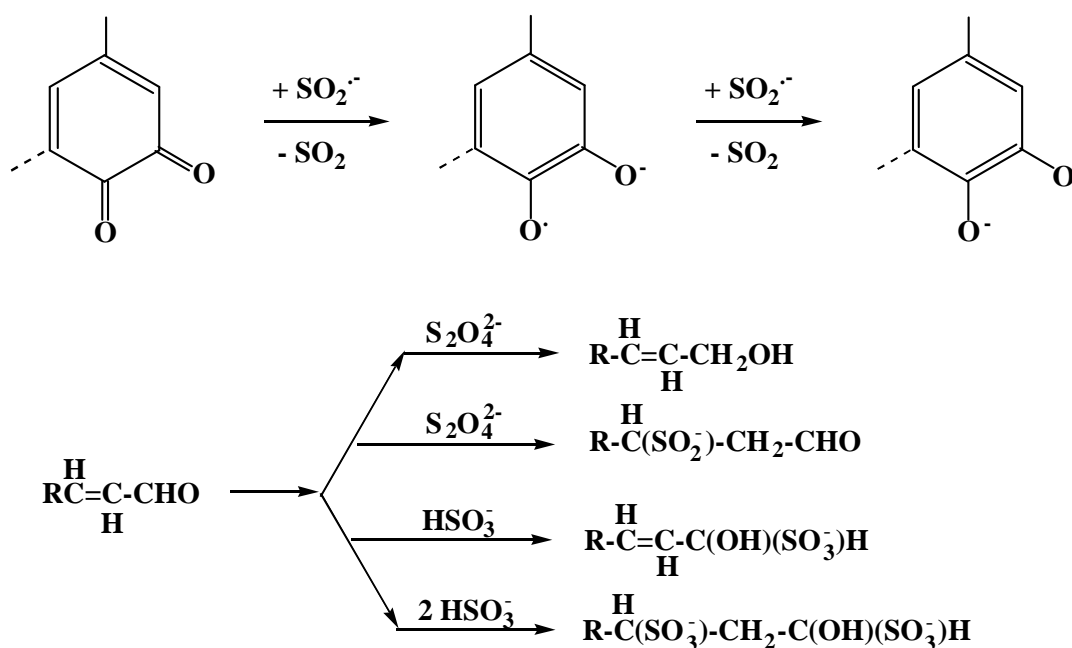
Figure 16. Elimination of quinone- and conyferaldehyde-type chromophores by reaction with dithionite and bisulphite ions [76].

1.4. The Properties of Bleached Pulp

Bleached chemical pulps are used for different types of products according to their specific properties. Depending on the end use of the pulp and to achieve the required quality of the final product, several properties have to be taken into account, namely strength properties, bulk, optical quality, hydrophobicity or ability to absorb water and other liquids, surface structure (for printing) and homogeneity [77]. Chemical analysis includes the determination of lignin content in pulp. The kappa number analysis is used in mills as a control parameter for two specific purposes: (1) to estimate the degree of the delignification during pulping, and (2) to calculate the chemical requirement for bleaching. The degree of polymerization of cellulose can be determined by measuring the viscosity of a cellulose solution of known concentration. Generally, all measurable pulp characteristics, excluding chemical properties, are grouped as physical properties. Usually, strength tests, which include burst, tear, tensile and folding endurance, are of great importance having a commercial value along with brightness [31].

Strength of sulphite pulp depends on pulping and bleaching conditions through carbohydrate degradation and dissolution. Acid sulphite pulping causes initial degradation of fibre structure while hemicelluloses dissolution is promoted by severe conditions during alkaline extraction, oxygen delignification and high-temperature peroxide stages resulting in a decrease of the strength properties of the bleached sulphite pulp [31].

Several studies have been performed to evaluate sulphite pulp properties and to understand the reasons that give rise to determined physical behaviour. Kraft pulps tend to be stronger, especially in tear strength, while sulphite pulps beat more easily. Several explanations have been proposed related to different chemical distributions in the fibre cell wall, different amounts of crystallinity in cellulose structure, variations in the surface chemistry of the fibres, different degrees of polymerisation of carbohydrates, between others [78].

2. EXPERIMENTAL PROCEDURES

2.1. PULP BLEACHING EXPERIMENTS

The industrial magnesium-based sulfite eucalypt pulp with kappa number of 18.8 from *CAIMA Indústria de Celulose S.A.* was used in the laboratory bleaching experiments carried out in 1-L stainless steel pressurized reactor PARR (model 4842). Figure 17 illustrates the two-stage bleaching sequence used.
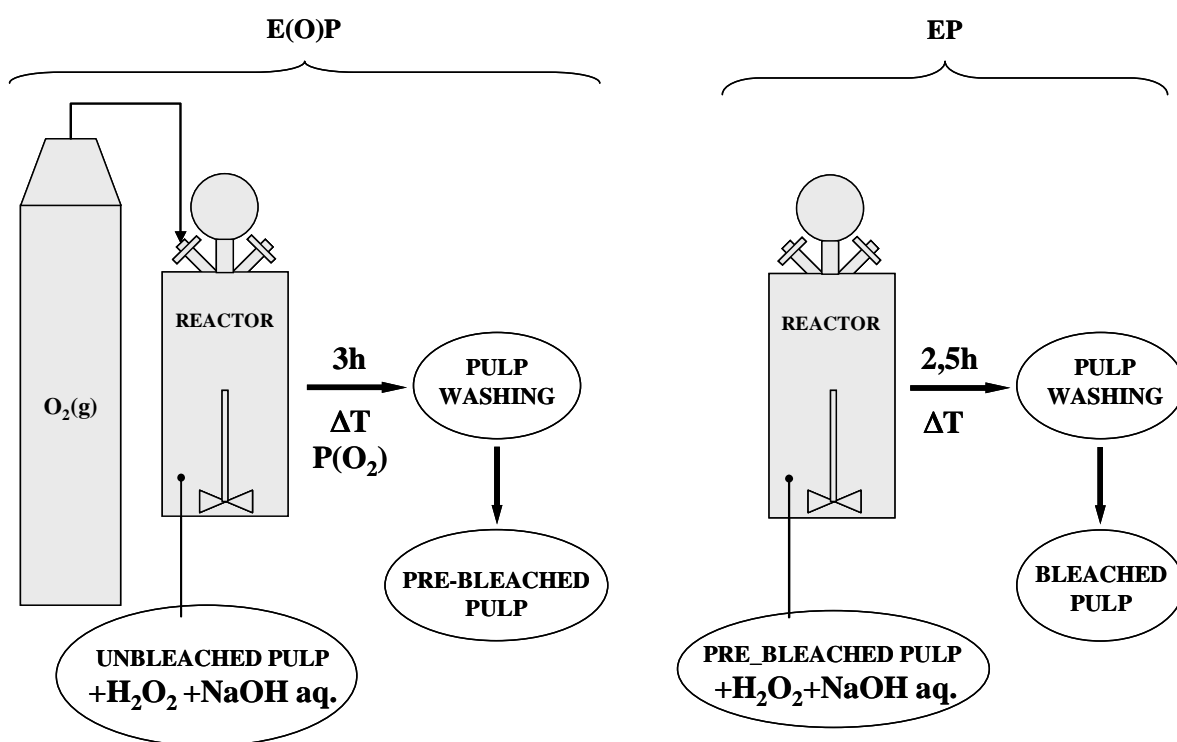
Figure 17. E(O)P-EP bleaching sequence used in the laboratory.

The E(O)P-EP bleaching sequence was performed using a 1L steel Parr reactor. All the reagents weights were calculated based on the unbleached dry pulp. The E(O)P stage

started by preparing the sodium hydroxide solution which was mixed with the unbleached pulp and to which the hydrogen peroxide was added. The mixture was purred into the reactor vessel and the reactor was safely closed. Then the reactor was pressurized with oxygen to a 2 bar pressure. The system was heated to reach the bleaching temperature (for example, 90ºC). When the intended temperature was reached, timing started. Finally, after a bleaching time of 3 hours, the reactor was cooled out and opened. The pulp was filtered and a portion of the sulphite liquor was collected for residual hydrogen peroxide quantification. The pulp was washed out with distilled water until neutral pH. After that the same reactor was used to perform the EP stage. The sodium hydroxide solution was prepared and the washed pulp and the hydrogen peroxide were added. The mixture was purred into the reactor vessel and the reactor was safely closed. Like in the previous stage, the system was heated to reach the bleaching temperature. And, after reaching the intended temperature, timing started. After a bleaching time of 2.5 hours, the reactor was cooled out and opened. The pulp was filtered and a portion of the sulphite liquor was collected for residual hydrogen peroxide quantification. The bleached pulp was washed out until neutral pH. Finally, the bleached pulp was air dried for further analysis.

2.2. PULPS ANALYSIS

Chemical and physical analyses were carried out for the relevant pulps; physical standard methodology is listed in Table 4 and chemical methodology is described below.

Residual hydrogen peroxide content [79]

After filtering the bleached pulp, 15 mL of the sulphite liquor are collected to a beaker and 15 mL of 2% potassium iodide solution, KI, and 10 mL of 5 % sulphuric acid solution, H_2SO_4, were added. After remaining for 20 minutes in the dark, the free iodine, I_2, was titrated with a with 0.1 M sodium thiosulphate solution, $Na_2S_2O_3$, adding a few drops of 0.2 % starch indicator toward the end of the reaction.

The residual hydrogen peroxide content, in %, is given by:

Table 4. Physical analysis methods of pulps.

Physical characterization	Units	Standard method
Refining	—	NP EN 25264-2:1995
Drainability (Schöpper-Riegler)	°SR	ISO 5267-1:1999
Preparation of laboratory sheets	—	ISO 5269-1:1998
Grammage	g/m^2	NP EN ISO 536:1997
Density	g/cm^3	NP EN 20534:1994
Tensile strength	N.m/g	NP EN ISO 1924-2:1997
Bursting strength	kPa.m^2/g	NP 687:1989
Tearing resistance	mN.m^2/g	NP EN 21974:1995
Brightness	% ISO	ISO 3688:1977
Opacity	% ISO	ISO 2471:1998

$$H_2O_2 = \frac{\Delta V \times 0.0017}{15 \times 100}$$

Where ΔV is the volume, in mL, of the 0.1 M sodium thiosulphate solution, 0.0017 is the equivalents of hydrogen peroxide and 15 is the volume, in mL, of the sulphite liquor portion.

Kappa number of pulp, κ (Tappi 236CM-1985)

1 g of pulp in 200 mL distilled water is disintegrated and stirred. Pipet 25 mL of 0.02 M potassium permanganate solution, K_2MnO_4, and 25 mL of 2 M sulphuric acid solution, H_2SO_4, into a beaker and add this mixed solution to the disintegrated pulp and start timing. At the end of exactly 10 min, the reaction is stopped by adding 5 mL of 1 M potassium iodide solution, KI. Immediately after mixing, the free iodine, I_2, is titrated with 0.2 M sodium thiosulphate solution, $Na_2S_2O_3$, adding a few drops of 0.2 % starch indicator toward the end of the reaction.

The kappa number is given by:

$$\kappa = \frac{p \times f}{w} \quad \text{and} \quad p = \frac{(b-a) \times N}{0.1}$$

Where κ is the kappa number of pulp, f is the factor for correction to 50 % permanganate consumption (Table 5), w is the weight of humidity-free pulp (g), p is the amount of 0.02 M permanganate actually consumed by the pulp (mL), b is the amount of thiosulphate consumed in the blank determination (mL), and N is the normality of the thiosulphate.

Correction for reaction temperature – when a constant temperature bath is not available, the temperature of the reaction has to be determined after 5min the reaction has started. Then, the corrected kappa number is

$$\kappa = \frac{p \times f}{w} \times [1 + 0.013 \times (25 - T)]$$

Where T is the actual reaction temperature, in °C.

Table 5. Factors f to correct for different percentages of permanganate used.

f +	0	1	2	3	4	5	6	7	8	9
30	0.958	0.960	0.962	0.964	0.966	0.968	0.970	0.973	0.975	0.977
40	0.979	0.981	0.983	0.985	0.987	0.969	0.991	0.994	0.996	0.998
50	1.000	1.002	1.004	1.006	1.009	1.011	1.013	1.015	1.017	1.019
60	1.022	1.024	1.026	1.028	1.030	1.033	1.035	1.037	1.039	1.042
70	1.044									

Pulp viscosity [SCAN CM15:1988]

This standard describes the determination of the limiting viscosity number (η) of pulp in dilute cupri-ethylenediamine (CED) solution.

Weight 0.20 g of previously milled pulp and add 25.0 mL of distilled water using a pipette into a dissolving bottle (with an approximate volume of 52 mL). Add some pieces of copper wire. Close the bottle and shake it using a shaking device until the pulp is completely disintegrated. With a pipette, add 25.0 mL of the CED solution, expel all residual air by squeezing the bottle and then close it tightly. Shake the bottle again in the shaking device until the sample is completely dissolved.

Adjust the temperature of the test solution and the viscometer to 25.0 ± 0.1 ℃. Draw a portion of the solution into the viscometer by suction. Allow the solution to drain. When the meniscus is at the upper mark, start the timing device and measure, to an accuracy of ± 0.2 s, the efflux time, which is the time it takes for the meniscus to fall from the upper to the lower mark (Figure 18).
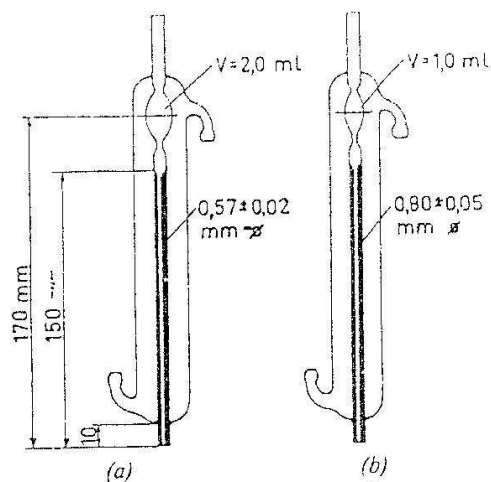
Figure 18. Capillary-tube viscometers: a) for calibration, and b) for the test solutions.

The viscosity ration η_{rel} is given by:

$$\eta_{rel} = h \times t_n$$

Where h is the viscometer constant obtained by calibration, in seconds, and t_n is the efflux time for the sample solution, in seconds.

In the table presented in the standard method SCAN CM15:1988, read the value of the product $[\eta]c$ that corresponds to the value obtained for η_{rel}. ($[\eta]$ is the limiting viscosity number and c is the concentration of the sample solution.)

Calculate from the sample weight and the dry matter content the concentration c. Divide $[\eta]c$ by c to obtain $[\eta]$.

If the product $[\eta]c$ is less than 2.6 or exceeds 3.4, the determination must be repeated.

For pulps with a value of $[\eta]$ above 1100 mL/g or below 400 mL/g special limitations apply. For pulps for which $[\eta]$ exceeds 1100 mL/g, the product $[\eta]c$ should be as near to 3.0 as possible and in no case outside the range 3.0 ± 0.1. When testing low-viscosity pulps, concentrations exceeding 0.005 g/mL should be avoided even if $[\eta]c$ is less than 2.6.

Calibration of the viscometers – Determine the efflux time as described above for distilled water, for a glycerol aqueous solution (650 g of glycerol per kilogram of solution) and for 0.5 mol/L CED solution (a volume of equal volumes of distilled water and of the 1 mol/L CED solution) in the calibration viscometer.

Measure the efflux time for the glycerol solution in the viscometer to be calibrated.

The viscometer factor f and the viscometer constant h are given by:

$$ f = \frac{t_{kg}}{t_{ng}} \quad \text{and} \quad h = \frac{f}{t_{CED}} $$

Where t_{kg} is the efflux time for the glycerol solution in the calibration viscometer , in seconds, t_{ng} is the efflux time for the glycerol solution in the viscometer to be calibrated, in seconds, and t_{CED} is the efflux time for the 0.5 mol/L CED solution in the calibration viscometer, in seconds.

Pentosans content [79]

20 mL of 13% of hydrochloride acid, *HCl*, is added to 0.10-0.15 g of milled pulp into a boiling flask. The sample is boiled and for each 5 mL of distillate that is recovered,

increments of 5 mL of 13% *HCl* are added to the boiling flask according to Figure 19. This operation is repeated until 50 mL of distillate is recovered. Then, the distillate is transferred to a 100 mL volumetric flask and diluted with 13% *HCl* until 100 mL. Three samples of 25 mL of this furfural solution are collected to three flasks with stoppers, to which 75 mL of distilled water and 5 mL of Br^-/BrO_3^- solution (5:1 molar proportion) are added. Bromine, Br_2, is formed and reacts with furfural giving rise to the liberation of bromide, Br^-. After 1 h in the dark, 20 mL of 10% potassium iodide, *KI*, are added. The flask is kept in the same conditions (in the dark at room temperature) during 10 min. After that, iodine, I_2, formed is titrated with 0.05 M of sodium thiosulphate, $Na_2S_2O_3$, adding a few drops of 0.2 % starch indicator toward the end of the reaction.
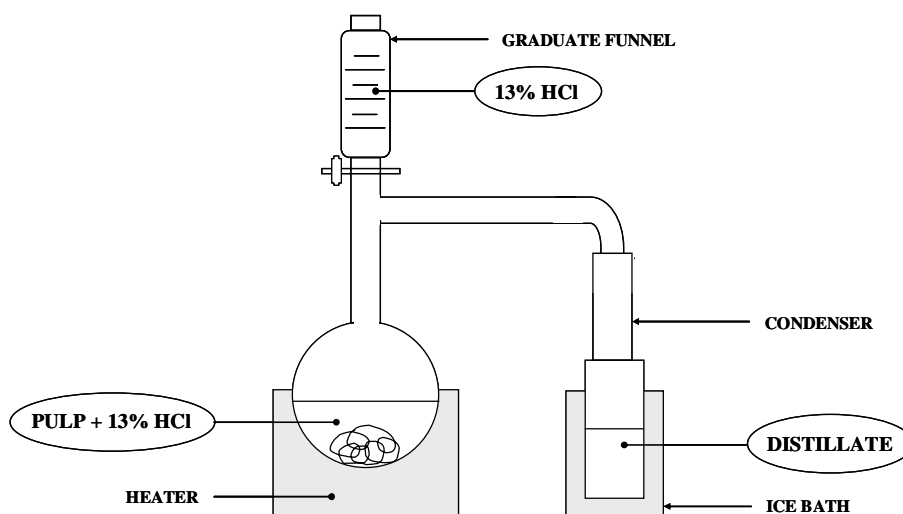
Figure 19. Distillation apparatus.

The amount of furfural, in %, is given by:

$$furfural = \frac{(V_b - V_a) \times 0.001201 \times 4 \times f}{w} \times 100$$

Where V_b and V_a are the volumes of titrant, in mL, consumed during the blank and the assay experiment, respectively, 0.001201 is the furfural mass, in mg, related to the use of 1

mL of 0.05000 M $Na_2S_2O_3$ solution, 4 is the dilution factor, f is the correction factor for the concentration of $Na_2S_2O_3$ solution and w is the mass of the pulp sample, in g.

The percentage of xylans (pentosans) is given by:

$$xylan = 1.52 \times furfural$$

Lignin content in pulp [80]

25-30 mg of air-dried pulps with known humidity and previously milled are transferred into a 50 mL flask and dissolved in 15 mL of cadoxen with shaking over 1-3 h at 15-20ºC. The pulp solution obtained is diluted with 15 mL of distilled water and shaken for 10-15 min. The UV-Vis spectra of the pulp cadoxen solutions are recorded on a JASCO V-560 spectrophotometer in the range 205-500 nm against a cadoxen:water (1:1) solution and using 1 cm thickness quartz cells.

The content of residual lignin, in %, in the pulps is given by:

$$Lig = \frac{C_{Lig} \times 30}{G \times 10}$$

Where C_{Lig} is the concentration, in g/L, of the lignin in the cadoxen solution of the pulp (obtained from the Beer-Lambert Law $A = c \times \varepsilon \times l$) and, G is the weight of the o.d. pulp taken for the analysis, in g.

Preparation of cadoxen – 1 L of freshly prepared aqueous ethylenediamine (EDA) 28% (wt) solution ($\rho = 0.99$) is placed in a 2 L flask and cooled to 2ºC. The solution is cooled to -3ºC by placing the flask in an ice-bath containing sodium chloride. 80 g of cadmium oxide is added to the EDA solution at -3ºC with stirring. The complete dissolution of cadmium oxide occurs normally over 45-60 min. The mixture is kept into a dark bottle and kept at least 24 h at ~14ºC in order to precipitate the excess of cadmium hydroxide. The transparent cadoxen solution is decanted from the precipitate into a dark bottle and stored in the dark at ~14ºC. The control parameters for the cadoxen solution are: transparent colour; $\rho = 1.06-1.07$.

Carboxyl content in pulp (adapeted from T 237 om-1993)

In a 500 mL beaker, add 250 mL of 0.1 M hydrochloric acid, *HCl*, to 2.0-2.5 g of pulp, previously disintegrated and with known moisture, and stir with for 2 h. Filter the pulp on a filtering funnel and wash with distilled water to neutral pH. Transfer the pulp quantitatively to a tared 100 mL beaker and weight (take note of the water excess). Add 50 mL of a mixture of 0.01 M sodium bicarbonate, *NaHCO₃*, and 0.1 M sodium chloride, *NaCl*, stopper the flask and shake to obtain homogeneous slurry. Keep the beaker in the dark at room temperature for 24 h. Filter the slurry to a clean and dry flask. Pipet 25.0 mL of the filtrate into a flask and titrate with 0.01 M *HCl* using methyl red indicator. When the first change in colour occurs, boil the solution for 1 min to expel the carbon dioxide and continue the titration to the pink end point. Pipet 25.0 mL of the *NaHCO₃–NaCl* solution into a flask and titrate with 0.01 M *HCl* using methyl red indicator (this will be the blank assay).

The carboxyl content, in mmol/ g dry pulp, is given by:

$$COOH = \left(b - a - \frac{G \times a}{50} \right) \times \left(\frac{50}{25 \times w} \right)$$

Where *a* is the volume, in mL, of 0.01 M *HCl* consumed in the titration of the pulp filtrate, *b* is the volume, in mL, of 0.01 M *HCl* consumed in the titration of the blank, *G* is the weight, in g, of water in the pulp after the filtration, and *w* is the weight, in g, of the dry pulp.

Carbonyl content in pulp [79]

Weight 0.10-0.15 g of disintegrated pulp into a tube and add 0.5 mL of 0.2 M potassium hydroxide, *KOH*, solution and 0.5 mL of 0.2 % 2,3,5-triphenyl- (TTC). Stopper the tube and put it into a boiling water bath for 2-3 min (a maximum of 10 min), until the pulp turns reddish. Then, the tube is quickly cooled in an ice bath. The tube content is filtered under vacuum and, afterwards; the pulp is washed with 10 mL of ethanol until it turns white.

Finally the absorvance is red at 546 nm. In parallel, prepare the blank and read the absorvance at 546 nm. The coloured species formazan is photosensible and, therefore, the overall procedure has to be performed in a maximum time of 15 min.

The carbonyl content, in mmol/100g pulp, is determined from the calibration curve and is given by:

$$CHO = \frac{M \times 100}{G \times 29.018}$$

Where *M* is the weight, in mg, of *CHO* groups (from the calibration curve) and *G* is the weight, in mg, of the pulp.

Calibration curve – Transfer 50 µL of 0.1 % glucose solution into a tube and add 0.5 mL of 0.2 *KOH* solution and 0.5 mL of 0.2 % TCC solution. The mixture is heated in a boiling water bath for 2-3 min (maximum of 10 min). After the reaction is complete, the tube is quickly cooled in an ice bath and 10 mL of ethanol is added. The absorvance is red at 546 nm and this value corresponds to 0.05 mg of glucose or 0.0080536 mg of *CHO* groups. The calibration curve is based on the linear curve between the zero point and the glucose point, and the graph is the absorvance as a function of the *CHO* weight.

Neutral monosaccharides content [81]

Add 400 µL of 72 % sulphuric acid, H_2SO_4, to 10.0 mg of pulp into a tube and incubate at room temperature for 3 h. Then, add 4.4 mL of distilled water and incubate at 100 ºC for 2.5 hours. Cool the tube in an ice bath and add 200 µL of 2-deoxiglucose as the internal standard.

To 1 mL of the previous solution, keeping the tube in the ice bath, add (1) 0.2 mL of 25 % of NH_3 and (2) 0.1 mL of 3 M NH_3 with 150 mg/mL of sodium borohydride, $NaBH_4$. Incubate at 30 ºC for 1 hour. Afterwards, cool in the ice bath and add 2 times 50 µL of 100 % acetic acid, CH_3COOH. Cool in the ice bath.

To 0.3 mL of the previous solution add (1) 0.45 mL of 1-methylimidazole and (2) 3 mL of acetic anhydride, $(CH_3CO)_2O$. Incubate at 30 ºC for 30 minutes. Cool in the ice bath.

Add 3.8 mL of distilled water and 2.5 mL of dichlormethane, CH_2Cl_2. Stir using the vortex and centrifugate at low speed for 30 seconds. Gasp the aqueous solution. Add 3 mL of distilled water and 2 mL of CH_2Cl_2, stir in the vortex and centrifugate at low speed for 30 seconds, and gasp the aqueous solution. Repeat the previous step (adding of water and CH_2Cl_2, stirring and centrifugation, and gasping) two times more. Evaporate the CH_2Cl_2. Add 1 mL of acetone and evaporate. Repeat the adding of acetone and evaporation two times more.

Finally, perform the gas-chromatography (GC) analysis (conditions: DB 225 column, detector at 250 ºC, injector at 220 ºC and column at 220 ºC). Perform this methodology for the standards listed in Table 6, except for the two-steps hydrolysis. These will be used to determine the calibration curve.

Table 6. Standard monosaccharides used to determine the calibration curve.

Standard	A	B	C	D	E	F
Ramnose	50	100	150	200	300	400
Fucose	500	50	100	200	300	400
Ribose	400	500	50	100	200	300
Arabinose	200	300	400	50	100	150
Xylose	300	400	500	600	100	200
Manose	100	200	300	400	500	50
Galactose	500	100	200	300	400	50
Glucose	100	500	400	300	200	600

X-ray analysis of cellulosic pulp

X-ray diffraction analysis of pulps was performed in order to determine the crystallinity degree of pulps and to calculate the crystallite width.

The pulp samples were analysed by Philipps X'pert MPD diffractometer with *CuKa* radiation with $\lambda = 0.154$ nm, scanning rate of 0.05º/scan and 2θ in the order of 2-40º.
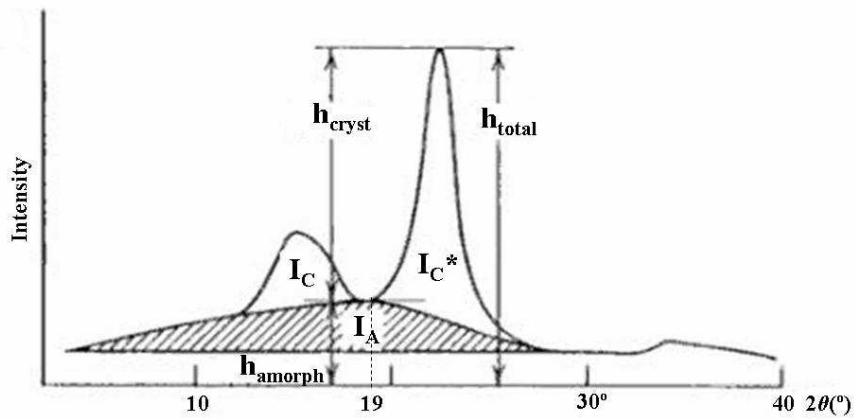
Figure 20. Method for the determination of the X-ray crystallinity of cellulose [8].

Figure 20 illustrates a typical X-ray diffractogram of cellulose where the amorphous and crystalline regions, I_A and I_K (which is the sum of $I_C + I_C{}^*$), respectively, are indicated. Based on the X-ray diffractogram, the degree of crystallinity is given by:

$$DC_0 = \frac{I_K \times 100}{I_K \times I_A}$$

$$DC = DC_0 \left[1 + 0.3 \left(w^{-1} - 1 \right) \right]$$

Where DC_0 is the apparent degree of crystallinity, I_K is the area corresponding to the crystalline region, I_A is the area corresponding to the amorphous region, DC is the corrected degree of crystallinity for 100% of cellulose, and w is the percentage of glucose (determined by the analysis of neutral monosaccharides).

The crystallite width is given by:

$$CL = \frac{1}{\sqrt{\left[\left(\frac{\beta \cos \theta}{\lambda} \right)^2 - 0.0162 \right]}}$$

Where CL is the crystallite width, in nm, β is the width at half the height of the I_C^* peak, θ is the position of the maximum intensity of the I_C^* peak, and $\lambda = 0.154$ nm (which corresponds to the wavelength of the X-ray analysis).

3. RESULTS AND DISCUSSION

According to established industrial practice in Portugal, the acid sulphite eucalypt pulp is bleached by a two-stage E(O)P-EP TCF bleaching sequence allowing a final pulp brightness of 88.5-89.0% ISO. This pulp is used for the production of viscose, tissue and printing papers among others. The further market tendencies request the improvement of magnesium-based acid sulphite eucalypt pulp brightness to 90-91% ISO, which implies the implementation of radical changes (introduction of new stages) or modification/ optimisation of conventional E(O)P-EP bleaching sequence. The advantage of the latter approach is the possibility to reach the final target without significant increase of the pulp price and with minimal investments to the existing bleaching facilities. Hence in this work, an effort was done to improve the sulphite eucalypt pulp brightness in the E(O)P-EP sequence by the optimisation of bleaching conditions (temperature, alkali load, hydrogen peroxide profile, etc.) in each stage, by the addition of different hydrogen peroxide activators and by the implementation of final reduction stage. The last stage was proposed to degrade the chromophoric structures that are difficult to eliminate in stages with hydrogen peroxide. The implementation of a pressurized peroxide-reinforced oxygen pre-bleaching stage (O(P)) before the E(O)P-EP sequence suggest the probability of increasing the pulp brightness to 92 % ISO.

3.1. THE E(O)P-EP BLEACHING SEQUENCE OPTIMIZATION

At *CAIMA* industry, the TCF bleaching sequence is composed by two stages: the first one consists of a combined delignification/bleaching with oxygen reinforced with hydrogen peroxide in alkaline medium – E(O)P, followed by a bleaching stage with hydrogen peroxide in an alkaline medium – EP (Figure 21).
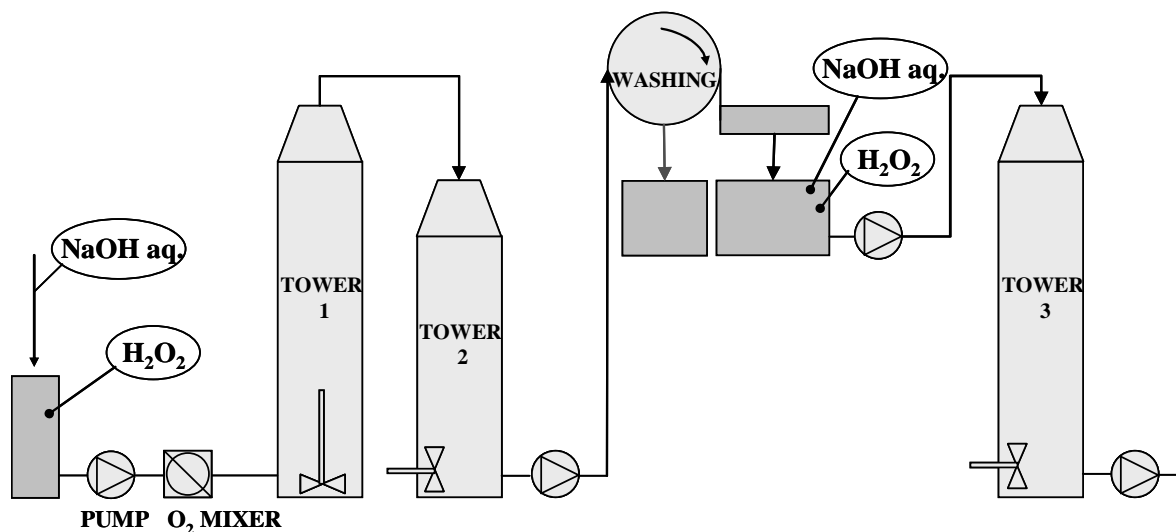
Figure 21. E(O)P-EP bleaching sequence used at CAIMA.

3.1.1. Chemical characterization of the industrial bleached pulp

Following the industrial practice the bleaching sequence was carried out in the laboratory under industrial conditions in order to obtain a bleached sulphite eucalypt pulp. This bleached pulp including its chemical analysis was used as a reference for future experiments. After bleaching, the industrial unbleached sulphite pulp with a kappa number of 18.8 gave rise to a bleached pulp with 88.0% ISO brightness (similar to the brightness obtained at industrial scale) (Table 7).

Chemical analysis of bleached eucalypt pulps supplied from CAIMA (sulphite) and from PORTUCEL (kraft) was performed. The kraft pulp was used for comparison reasons as possessing the reference mechanical strength. According to the listed results in Table 8, sulphite pulp has a higher viscosity than kraft, which implies a higher degree of polymerization of cellulose. On the other hand, kraft pulp contains twice the pentosans content, which is in agreement with monosaccharide analysis, and almost twice carboxyl content. Sulphite pulp has considerably high residual lignin and carbonyl contents, which can be sources of chromophoric structures that may not be easily accessible to the

bleaching chemicals. This fact determines the potential difficulties in the sulphite pulp bleaching to high brightness. The values of the crystallinity degree and the crystallite length obtained by X-ray analysis are very similar for both types of pulps.

Table 7. Industrial conditions for the E(O)P-EP bleaching sequence and chemical analysis of the laboratory bleached pulp according to these conditions.

	E(O)P	EP
Consistency (%)	11.2	11.5
T (ºC)	80	80
H_2O_2 (%)	0.84	1.53
NaOH (%)	2.1	0.83
P (O_2) (bar)	2	-
Time (h)	3	2.5
H_2O_2 res.(g/L)	0.003	0.33
Kappa number	9.7	8.2
η (mL/g)	1190	1175
Pentosans (%)	-	6.7
Lignin (%)	-	1.1
Brightness ISO (%)	81.3	88.0

3.1.2. Optimization of the E(O)P-EP bleaching sequence

As a first approach to improve sulphite pulp brightness in the E(O)P-EP bleaching sequence, the optimisation of bleaching conditions (temperature, oxygen pressure, alkali charge and hydrogen peroxide charge) in both stages was carried out.

The increase of the alkali charge from 2.1% (pH 11) to 2.5% (pH 13) in the E(O)P stage turned out to be ineffective since a loss of the final pulp brightness of 0.9% ISO was observed (and 0.8% ISO in the final bleached pulp), when compared to the reference pulp (Table 9). Additionally, the viscosity of bleached pulp and the pentosans content decreased

and the amount of residual lignin increased significantly. For these reasons, in all further experiments the alkali charge was maintained at 2.1% in the first stage and 0.83% in the second stage.

Table 8. Chemical analysis of bleached eucalypt pulps.

	Pulps	
	Sulphite	**Kraft**
Viscosity (mL/g)	1160	1075
Pentosans (%)	7.2	16.8
Lignin (%)	0.96	0.18
Carbonyl groups (mmol/100g)	3.7	0.9
Carboxyl groups (mmol/100g)	4.7	7.3
Extractives (%)	0.36	0.36
Cristallinity degree (%)	70.0	71.1
Cristalite length (nm)	5.0	5.4
Monosacharides (% w/w)		
Ramnose	0.4	0.4
Fucose	0.0	0.0
Arabinose	0.1	0.1
Xylose	5.9	18.3
Manose	1.3	0.2
Galactose	0.1	0.3
Glucose	92.2	80.7

The delignification stage with oxygen is more effective at temperatures between 100ºC and 120ºC and pressures of 5-7 bar [42], higher than those used in the mill. On the other hand, the hydrogen peroxide decomposition rate increases above 90ºC [59,60]. Therefore, as a compromise, in further experiments the temperature was increased to 90ºC in both stages and the oxygen pressure increased up to 6 bar (Table 10).

Table 9. Chemical analysis of the sulphite pulp after increasing the alkali charge to 2.5 %.

	E(O)P	EP
H$_2$O$_2$ res.(g/L)	0.003	0.08
Kappa number	9.1	8.5
η (mL/g)	1150	1120
Pentosans (%)	-	5.8
Lignin (%)	-	1.8
Brightness ISO (%)	80.4	87.2

In general the increase of the temperature and the oxygen pressure in E(O)P stage favoured the pulp delignification and brightness increase without significant loss of viscosity. The best brightness was achieved when the temperature rise in E(O)P stage up to 100ºC. However, in our further experiments the oxygen pressure was maintained of 2.0 bar taking into account the particular industrial facilities of CAIMA pulp mill.

Table 10. Study of the P(O$_2$) and T(ºC) at the E(O)P stage and chemical analysis of the semi- and bleached pulps.

	E(O)P				EP			
Assay	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
P(O$_2$) (bar)	2	4	6	6	—	—	—	—
T (ºC)	90	90	90	100	90	90	90	90
H$_2$O$_2$ res.(g/L)	0.004	0.003	0.004	0.004	—	—	—	—
Kappa number	9.8	9.0	9.6	8.4	—	—	—	—
η (mL/g)	1100	1200	1140	1135	1060	1095	1065	1060
Brightness ISO (%)	79.3	80.9	81.7	84.5	87.4	87.9	88.5	88.8

Finally, the hydrogen peroxide charge was optimised at 90ºC in both stages (Table 11). The best results were obtained with a peroxide charge of 1.2% in the E(O)P stage and 1.4% in the EP stage, which gave rise to higher brightness without affecting pulp viscosity. From these values, a relevant decrease in the pulp viscosity is observed leading to a loss of the pulp yield due to the degradation of the hemicelluloses and cellulose.

Table 11. Variation of the peroxide charge in the E(O)P stage and chemical analysis of the pulps.

	E(O)P					EP*				
H_2O_2 (%)	**0,9**	**1,0**	**1,2**	**1,5**	**2,0**	**1,2**	**1,4**	**1,53**	**1,8**	**2,0**
H_2O_2 res.(g/L)	0.01	0.04	0.05	0.04	0.05	0.12	0.13	0.19	0.19	0.20
Kappa number	9.1	7.7	7.7	8.2	8.6	7.0	6.6	7.4	6.9	7.2
η (mL/g)	1150	1150	1150	1130	1055	1065	1050	1040	995	925
Pentosans (%)	—	—	—	—	—	—	6.8	5.7	—	—
Lignin (%)	—	—	—	—	—	—	1.7	1.3	—	—
Brightness ISO (%)	83.8	86.0	86.3	86.0	86.1	89.5	89.9	89.7	89.5	89.2

* EP stage performed after E(O)P stage experiment with 1.2% H_2O_2 load (highest brightness of 86.3%)

The optimisation of the bleaching conditions allowed the pulp brightness increase of 1.5-1.9% ISO comparing with industrially applied conditions, reaching practically 90% ISO without significant extra charge of hydrogen peroxide (Table 12) [82,83]. However, the brightness higher than 90% was impossible to obtain even with 50% extra charge of hydrogen peroxide. In the latter case, remarkable pulp polysaccharides degradation has been detected.

Table 12. Laboratory bleaching results on sulphite eucalypt pulp.

	Mill conditions		Proposal conditions	
	E(O)P	EP	E(O)P	EP
Consistency (%)	8.0	8.0	8.0	8.0
T (ºC)	80	80	90	90
H$_2$O$_2$ (%)	0.85	1.55	1.20	1.40
NaOH (%)	2.1	0.83	2.1	0.83
P (O$_2$) (bar)	2.0	-	2.0	-
Time (h)	3.0	2.5	3.0	2.5
Brightness ISO (%)	81.3	88.6	86.3	89.9

3.1.3. The optimized E(O)P-EP bleaching sequence at industrial scale

At laboratory scale it is not possible to get the same experiments conditions as in the mill such as the reactor itself, the mechanical stirring (which is much efficient at the mill improving pulp-reagents contact), the pulp consistency (which is higher at the mill – 11.5% instead of 8% – and allows to get a higher reagents concentration) and the oxygen pressure (which is not at 2 bar at the mill where there is a gradient of oxygen from 2 bar at the bottom of the tower to atmospheric pressure at the top).

The bleaching ability of unbleached pulps can be defined for a given bleaching sequence, by the amount of chemicals needed to reach a target brightness value, divided by the initial kappa number. The oxidation equivalents (OXE) are used to compare different sequences (1 OXE is equal to the quantity of substance which receives 1 mol of electrons when the substance is reduced). For example, when hydrogen peroxide is used in the sequence, one kg of hydrogen peroxide represents 58.79 OXE/kg (Table 13).

The improved E(O)P-EP sequence was carried out at industrial scale. The amount of hydrogen peroxide to be used in this situation was calculated according to the OXE used in the laboratory experiments (Table 14).

Table 13. Conversion factors to OXE (adapted from [33]).

Species	Formula weight	e^-/molecule	Equivalent weight	OXE/kg
	(g/mol)		(g/mol e^-)	
O_2	32.00	4	8.00	125.00
H_2O_2	34.018	2	17.01	58.79

Some adjustments have to be done since the unbleached pulp exhibited a kappa number of 19.6 different from the one used in the laboratory. These adjustments regarding the increase of the temperature and the variation of hydrogen peroxide amount in each bleaching stage were done in a gradual way in order to stabilize the system until a pulp ISO brightness of 90% was reached (similar to the one obtained in the laboratory). The initial unbleached pulp, the bleached pulp after the E(O)P stage and the bleached pulp after the EP stage were characterized by their kappa number, superficial brightness, ISO brightness, COD and OXE. Initially, the mill was operating at 80ºC in both stages with a hydrogen peroxide feed of 230L/h in the first stage and 410L/h in the second stage. Therefore, the first step consisted in the increase of the temperature from 80ºC to 90ºC in the first stage and after that the hydrogen peroxide feed in this stage was increased from 230L/h to 290L/h. Then, changes in the second stage were performed: first the hydrogen peroxide was shifted from 410L/h to 340L/h and second the temperature was increased from 80ºC to 90ºC. Finally, the hydrogen peroxide charge was increased to 380L/h in the second stage. The adjustments that have to be done were partially due to: (1) the values of the COD, which contribute to the hydrogen peroxide charge since this is a measure of the organic matter in the effluents/washing water that has to be removed – as a consequence, if the COD values increase, the hydrogen peroxide charge will also increase; and (2) the unbleached pulps showed different kappa number varying between 16 and 25, implying new OXE calculations, therefore changes regarding the hydrogen peroxide charge in each bleaching stage.

Table 14. Processing conditions and results.

Day	Production	Analysis	Samples			EP(O) stage		EP stage	
Time	(ton pulp o.d./h)		DPA	EP(O)	EP	T (ºC)	H$_2$O$_2$ (L/h)	T (ºC)	H$_2$O$_2$ (L/h)
Laboratory results		Kappa number	18.8	8,0	6.6	90	—	90	—
		Bright. ISO (%)	64.4	86.4	89.9				
		OXE/(ton*Kappa)	—	65.4	588.2				
1 8:00 a.m.	12.2	Kappa number	21.9	10.1	7.4	90	230	82	410
		Bright. ISO (%)	62.2	80.2	89.6				
		OXE/(ton*Kappa)	—	47,0	383.9				
		COD (kg/ton)	12.4	—	—				
1 4:00 p.m.	12.2	Kappa number	20,0	9.2	7.2	90	290	82	410
		Bright. ISO (%)	64.2	82.6	89.2				
		OXE/(ton*Kappa)	—	51.3	518.3				
		COD (kg/ton)	12.4	—	—				
2 0:00	12.0	Kappa number	21.2	9.2	6.6	90	290	82	340
		Bright. ISO (%)	63.7	82.7	89.7				
		OXE/(ton*Kappa)	—	59.2	405.4				
		COD (kg/ton)	11.8	—	—				
2 8:00 a.m.	12.0	Kappa number	20.7	11.8	8.7	90	290	90	340
		Bright. ISO (%)	63.7	80.6	88.5				
		OXE/(ton*Kappa)	—	79.9	268.8				
		COD (kg/ton)	11.6	—	—				
2 4:00 p.m.	12.0	Kappa number	21.2	10.5	8.3	90	330	90	380
		Bright. ISO (%)	61.3	79.2	88.6				
		OXE/(ton*Kappa)	—	75.6	378.8				
		COD (kg/ton)	No	—	—				
3 8:00 a.m.	12.1	Kappa number	20.3	9.5	7.3	90	330	90	380
		Bright. ISO (%)	63.5	2,0	89.3				
		OXE/(ton*Kappa)	—	74.3	419.9				
		COD (kg/ton)	15,0	—	—				
3 4:00 p.m.	12.1	Kappa number	19.6	8.6	6.2	90	330	90	380
		Bright. ISO (%)	64.7	82.8	90.3				
		OXE/(ton*Kappa)	—	72.9	384.9				
		COD (kg/ton)	17.7	—	—				

DPA - unbleached pulp

Finally, the hydrogen peroxide charge was increased to 1.3% (330L/h) instead of 1.2% in the E(O)P stage and to 1.5% (380L/h) instead of 1.4% in the EP stage, both occurring at

90ºC. With these conditions, it was possible to obtain a pulp with a kappa number of 6.2 and brightness of 90.4% ISO. This experiment provided better results than in the laboratory due to the higher pulp consistency and the better mechanical stirring.

The fact that the kappa number of the unbleached pulps strongly vary makes the results difficult to control in particular the pulps brightness and the kappa numbers of the bleached pulps, since and as already mentioned, the bleaching parameters were optimized for an unbleached pulp with kappa number of 18.8 and no prediction was made regarding the initial kappa numbers. So, it was crucial to determine an equation to predict the peroxide charge to use according to the kappa number before and after the bleaching stage and as a function of the obtained OXE values (Table 15).

Table 15. Average values of OXE for each stage.

	E(O)P	EP
OXE/(ton*κ)_average	72.9	384.9

An equation was suggested in order to calculate the peroxide charge to use in a certain stage:

$$H_2O_2(L/h) = OXE_i \times 2 \times 0.017 \times A \times (\kappa_{i-1} - \kappa_i)$$

where OXE_i is the peroxide OXE at stage i, A is the o.d. pulp weight (ton/h), 2 is the coefficient for the correction of H_2O_2 concentration (50%) in solution, 0.017 is the number of equivalents of H_2O_2 (kg/mol e$^-$) and κ is the kappa number at stage i.

For example, assuming that the production of o.d. pulp is 12 ton/h, the kappa number of the unbleached pulp is $\kappa_0 = 22$ and one whish to obtain after the first bleaching stage a pulp with a kappa number $\kappa_1 = 8$, then the peroxide charge to be used in that stage is:

$$H_2O_2\left(L/h\right)=72.9\times2\times0.017\times12\times\left(22-8\right)\approx416$$

For the second stage, it will be:

$$H_2O_2\left(L/h\right)=384.9\times2\times0.017\times12\times\left(8-6.5\right)\approx236$$

The mechanical tests for the bleached pulp before and after applying the new bleaching conditions were performed. The results obtained are similar except for the brightness that improved 1% as expected (Table 16 and Table 17). Comparing the opacity values, one can observed that the optimized bleached pulp has higher opacity value than the standard bleached pulp, therefore, it is the most suitable to be applied for the printing papers. Comparing the other physical properties, there are very similar therefore suggesting that both pulps have similar strength, which means that the optimized bleaching sequence allows obtaining a bleached pulp with similar properties to the standard pulp but with an improved ISO brightness.

Table 16. Mechanical tests for the standard bleached pulp (60 g/m^2) with 89% ISO brightness.

	Revolutions				Interpolation	
	0	**700**	**1000**	**2000**	**1273**	**1727**
Drainability (ºSR)	17	25	27	38	30	35
Density (g/cm^3)	0.55	0.66	0.69	0.74	0.7	0.73
Bursting strength (kPa.m^2/g)	0.5	1.8	2.2	3.0	2.4	2.8
Tearing resistance (mN.m^2/g)	1.9	2.6	4.7	5.4	4.9	5.2
Tensile strength (N.m/g)	14.5	32.0	37.5	40.0	38.2	39.3
Stretch (%)	0.8	2.0	2.4	2.9	2.5	2.7
Opacity (%)	78.1	74.3	73.4	71.3	72.8	71.9

Table 17. Mechanical tests for the optimized bleached pulps (60 g/m^2) with 90.3% ISO brightness.

	Revolutions				Interpolation	
	0	**700**	**1000**	**2000**	**1182**	**1636**
Drainability (ºSR)	19	25	28	39	30	35
Density (g/cm^3)	0.54	0.65	0.68	0.74	0.69	0.72
Bursting strength (kPa.m^2/g)	0.5	1.6	2.0	2.9	2.2	2.6
Tearing resistance (mN.m^2/g)	1.8	4.2	4.5	5.5	4.7	5.1
Tensile strength (N.m/g)	13.0	28.5	33.6	44.3	35.5	40.4
Stretch (%)	1.0	1.9	2.6	3.2	2.7	3.0
Opacity (%)	79.7	76.1	75.8	72.7	75.2	73.8

3.2. THE USE OF PEROXIDE ACTIVATORS/CATALYSTS IN THE EP STAGE

Although the results obtained from the new proposed conditions are satisfactory, it is not possible to reach a sulphite pulp brightness of 91% ISO or higher. Furthermore, the bleached pulp obtained have a relatively high lignin content (up to 1%), so it was decided to carry out with new experiments with the addition of hydrogen peroxide catalysts/activators (0.1% o.d. pulp) such as cyanamide (CyA) , tetraacetylethylenediamine (TAED) , pentaacetylglucose (PAG) and peracetic acid (PA, 0.5-1.0% o.d. pulp) (Figure 22).

Using the newly optimized conditions for the E(O)P-EP sequence presented in Table 12, the activators/catalysts chosen were added at the EP stage using the proportions above. According to published results, improved brightness was expected; but the use of these activators showed only 0.3-0.4 % brightness improvements (Table 18). Furthermore, it was expected that peracetic acid would provide some of the best results; however and surprisingly, brightness reversion occurred perhaps due to the formation of new chromophoric structures giving rise to a decrease in pulp brightness.
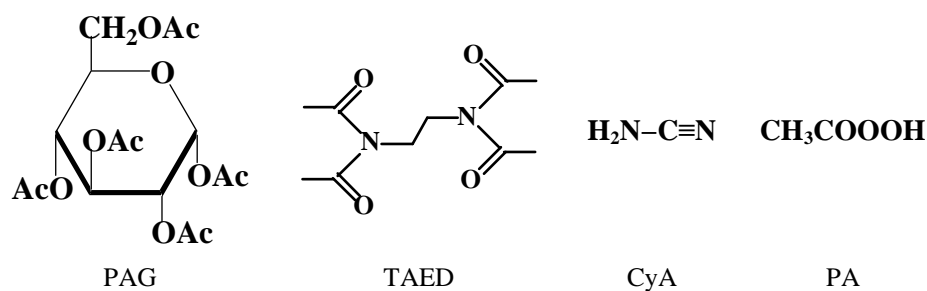
Figure 22. Peroxide activators/catalysts used.

Table 18. Activation of the EP stage and analysis of the pulps.

	Optimized E(O)P-EP	Activator/catalyst			
		TAED	CyA	PAG	PA
H_2O_2 res. (g/L)	0.05	0.09	0.10	0.11	0.42
Kappa number	7.0	7.3	7.0	6.5	7.3
Viscosity (mL/g)	980	1050	1000	970	940
Brightness ISO (%)	89.8	90.1	90.2	90.2	89.4

3.3. NEW BLEACHING SEQUENCES FOR BRIGHTNESS IMPROVEMENT

The basic goal of this work was to improve the sulphite pulp brightness up to 91% and this was not possible by performing the previous experiments, *i.e.*, by optimizing the E(O)P-EP sequence or by using peroxide activators/catalysts in the EP stage. Therefore, it was necessary to find new solution to improve the existing bleaching sequence. The strategy was limited to the following conditions: (1) a three-stage bleaching sequence by introducing a complementary terminal stage to improve E(O)P-EP sequence using other bleaching chemicals than oxygen and hydrogen peroxide, such as chlorine dioxide, hypochlorite, ozone and sodium dithionite, and (2) a three-stage bleaching sequence by

introducing a peroxide-reinforced oxygen pre-stage to the improved E(O)P-EP sequence (O-E(O)P-EP).

3.3.1. Complementary stage to the E(O)P-EP sequence

A complementary post stage to the conventional E(O)P-EP sequence have been proposed employing four bleaching chemicals such as chlorine dioxide, hypochlorite, ozone and sodium dithionite. According to the bleach plant used at *CAIMA* industry, there is a dilution tank available between the bleaching line and the pressing step that could be used for these purposes. This reserve tank is indicated in the scheme as reservoir (Figure 23). Alternatively, the addition of some reagents reinforcing the pulp bleaching can be done during the EP stage. Therefore, the implementation of the complementary stage is possible under suitable conditions using conventional *CAIMA*'s bleach plant facilities without significant investment.
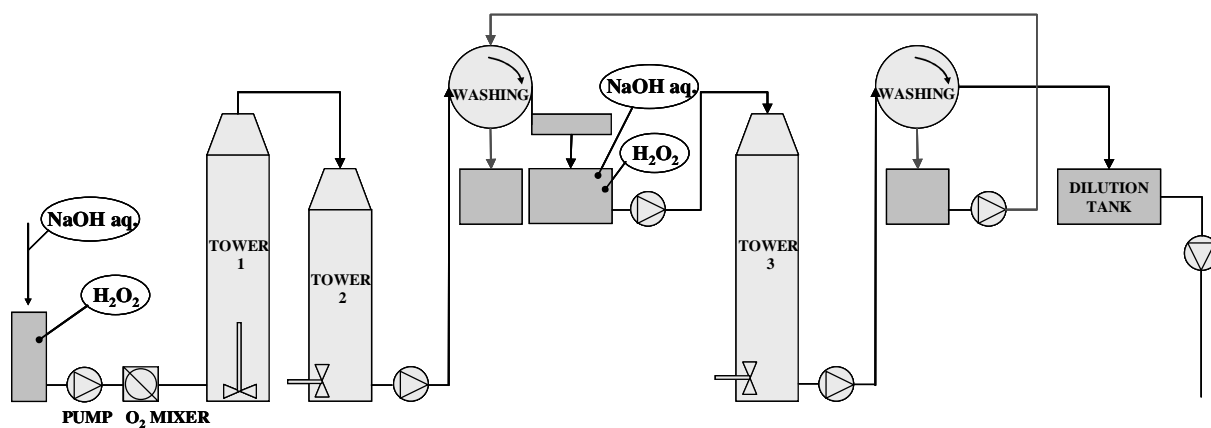
Figure 23. E(O)P-EP bleaching sequence followed by a dilution tank used at CAIMA.

3.3.1.1. Implementation of ozone stage

The application of this final stage is attractive in the *CAIMA*'s bleach plant due to the presence of the dilution tank following the E(O)P-EP sequence as already mentioned. According to recently published results [73,74], using diluted ozone solution in water for the pulp treatment after the bleaching sequence permits to improve the final pulp brightness. Therefore, similar experiments have been performed with our E(O)P-EP bleached pulp using ozone in the final washing step of the bleached pulp in order to improve the final pulp brightness. All experiments were carried out at room temperature during 30 min (Table 19). Two ozone-containing aqueous solutions were prepared with two different ozone concentrations, 0.32 and 0.64 mg O_3/g bleached pulp o.d. Treatments were carried out at 4 % pulp consistency in a flask under stirring at different pH in order to confirm the most feasible conditions.

Table 19. Results on pulp brightness after ozone treatment (T = 25ºC, 30 min).

	pH							
	2		**3**		**4**		**5.5**	
O_3 (mg/g pulp o.d.)	0.32	0.64	0.32	0.64	0.32	0.64	0.32	0.64
Brightness ISO (%)	87.6	87.1	87.5	87.9	87.9	87.5	87.0	88.1

Pulp brightness before the treatment with O_3 was 88.6 % ISO.

In the applied pH range and ozone concentrations, sulphite bleached pulp did not show brightness improvement (Table 19). At pH 5.5 the ozone decomposition was rather significant, which explained the less decrease of pulp brightness. Overall, according to the obtained results, the post-treatment of bleached pulp with ozonated aqueous solution was not efficient to improve pulp brightness since brightness reversion occurred due to the probable formation of new chromophoric structures. Therefore, other attempts for a complementary stage were done using chlorine-based chemicals.

3.3.1.2. Hypochlorite stage

Sodium hypochlorite is a known bleaching reagent to improve pulp brightness, which is usually used under weak alkaline conditions. Two different kinds of experiments were performed using 1% load (g NaOCl/g Pulp o.d.) of sodium hypochlorite : (1) hypochlorite was added into the EP stage 15 min before it finishing, and (2) hypochlorite was used as the bleaching chemical in a separate complementary stage to the E(O)P-EP sequence at 50ºC during 45 min and 60 min.

Table 20. Bleaching experiments with 1% load of NaOCl.

	EP stage	Complementary stage	
		45 min	**60 min**
Brightness ISO (%)	88.6	86.3	85.4

E(O)P-EP pulp brightness was 88.7 %ISO

According to the results obtained (Table 20), hypochlorite was not efficient to improve pulp brightness since: (1) adding hypochlorite into the EP stage did not change the pulp brightness, and (2) using hypochlorite in a complementary stage caused brightness reversion due to the formation of new chromophoric structures. When the complementary stage is increased from 45 min to 60 min, brightness reversion was even more accentuated because of the longer time exposure of pulp to hypochlorite leading to the formation of a higher concentration of chromophoric structures. Hence, hypochlorite treatment was probably mostly efficient for the pulp delignification rather than for the brightness improvement.

After these experiments, it was decided to use chlorine dioxide in the complementary stage.

3.3.1.3. Chlorine dioxide stage

Chlorine dioxide was the other chlorine-based chemical employed beside hypochlorite. A complementary stage to the E(O)P-EP sequence was performed using 1% load (g ClO_2/g pulp o.d.) of chlorine dioxide at 70ºC during 180 min. the final pulp brightness obtained was 82.2 % ISO. Comparing with the E(O)P-EP pulp brightness, which was 88.5 % ISO, chlorine dioxide was not efficient to improve pulp brightness causing brightness reversion due to the formation of new chromophoric structures.

3.3.1.4. Dithionite stage

As the efforts on the degradation of minor chromophoric groups in pulp using different oxidation reagents/catalysts failed and the implementation of a complementary oxidative stage also were unsuccessful; then, a reductive complementary stage was proposed. This stage would be easily implemented at CAIMA industry since no new tower bleaching installations are required being used the dilution tank.

Improved E(O)P-EP bleached pulps were treated with sodium borohydride (*$NaBH_4$*, 0.5% o.d. pulp, pH 10), sodium dithionite (*$Na_2S_2O_4$*, 1% o.d. pulp, pH 6), sodium thiosulphates (*$Na_2S_2O_3$*, 1% o.d. pulp, pH 6) and sodium pirosulphite (*$Na_2S_2O_5$*, 1% o.d. pulp, pH 6) at moderate conditions (60ºC, 40 min) [84] (Table 21). All reductive reagents showed a positive effect on pulp brightness. The best brightness improvement occurred in the case of addition of sodium borohydride, which improved the final pulp brightness to 91.3% ISO, and sodium dithionite, which improved the final pulp brightness to 90.9% ISO, as shown in Table 22. The response of the bleaching efficiency of these reductive reagents is proportional to the reduction potential of each one. It is not clear that there was additional delignification since all kappa numbers that were determined were similar. Besides, viscosity results suggest that no further cellulose degradation occurred, confirming that these reagents reduce chromophoric structures in lignin without degrading lignin backbone.

Table 21. Conditions of the Y stage.

	Y stage
Consistency (%)	8
T (ºC)	60
Reductor (%)	1 *
pH	5.5-6
Time (min)	40

* In the case of $NaBH_4$ it was 0.5 % at pH 11

Table 22. Reductive stage results and pulp analysis.

	New proposal	Reductive reagents		
		$NaBH_4$	$Na_2S_2O_4$	$Na_2S_2O_3$	$Na_2S_2O_5$
Eº (V)	-	-1.9	-0.53	0.08	0.12
Kappa number	7.1	7.4	7.1	8.2	7.1
η (mL/g)	1040	1050	1025	1070	1035
Brightness ISO (%)	89.9	91.2	90.7	90.3	90.2

Since sodium borohydride needs special security cares and is very expensive, it was decided to optimise this reductive stage by using sodium dithionite, which is the bleaching chemical usually used for the bleaching of semi-chemical and thermo-mechanical pulps. The final sulphite pulp brightness obtained was 90.8-90.9% ISO. The optimized conditions for the reductive Y stage using sodium dithionite were proposed in separate set of experiments and are presented in Table 23. Hence, the performance of the reduction stage at the end of E(O)P-EP bleaching sequence was suggested to be one of the effectiveness ways to improve the brightness of the acid sulphite eucalypt pulp [82,83].

Table 23. Optimized conditions for the Y stage by using Na$_2$S$_2$O$_4$.

	Y stage
Consistency (%)	8
T (ºC)	60
Reductor (%)	1-2
pH	6.5
Time (min)	40

Subsequently, aiming to evaluate the practical feasibility of the Y stage, the preliminary work was carried out in collaboration with *BASF* laboratories (*BASF The Chemical Company*) using sulphite bleached pulp and washing waters from *CAIMA* industry and commercial dithionite chemicals supplied by *BASF*, namely Blankit MF, Blankit B, Blankit S, Hydrosulphite PF and Liquid Hydrosulphite. Blankit grades are fine, white, crystalline powders with sodium dithionite content of at least 58% (w/w); Hydrosulphite P grades are fine, white, crystalline powders with sodium dithionite content of at least 88% (w/w); and Liquid Hydrosulphite is a stabilized aqueous solution with sodium dithionite content of at least 150 g/L [85]. The conditions of the reductive stage were similar to those employed in the laboratory (Table 24) [86].

According to the lab trials results, bleaching with sodium dithionite can increase pulp brightness approximately three percent over the bleached CAIMA pulp brightness when Blankit grades and Hydrosulphite PF are used. The optimized dithionite dosage is between 0.4 and 0.8% (w/w pulp o.d.) and Blankit MF provided the best performance. On the other hand, Liquid Hydrosulphite was also efficient to increase bleached pulp brightness but only by two percent [86]. It was suggested to perform an industrial-scale experiment by using Blankit MF.

Table 24. Conditions for the reductive stage at *BASF* laboratories.

	Y stage
Consistency (%)	3.5
T (ºC)	55
pH	6.7-6.9
Time (min)	60

Afterwards, in order to confirm the promising laboratory results obtained and later at *BASF* laboratories, which provided final pulp brightness up to 91% ISO, it was decided to perform an industrial-scale experiment. For this purpose, the reserve tank was used to perform this complementary stage after the E(O)P-EP bleach plant and Blankit MF was used as the commercial dithionite chemical, considered by *BASF* laboratories. Figure 24 shows the results where "brightness filter" refers to the pulp brightness entering the reserve tank (*i.e*. after the E(O)P-EP sequence), "brightness after tank" refers to the pulp brightness after the reductive stage, "dosage [kg/t]otro" refers to the dithionite charge used during the stage, "delta brightness" refers to the difference between the pulp brightness after and before the stage corresponding to the gain on brightness percent, and "pH" corresponds to the medium pH of the stage.

According to the results, the initial dithionite charge used was 8 kg/t [otro] giving rise to an increase in pulp brightness from 89% to 91%. These results confirmed the efficiency of this complementary stage to the E(O)P-EP bleaching sequence since the brightness gain was 2 %. During the experiment, the pH was sustained between 5.5 and 6.5. Afterwards, and in order to verify the possibility to increase the final pulp brightness more than 91%, the dithionite charge was increased but no satisfactory results were obtained since the E(O)P-EP bleached pulp had a high brightness of 90%.
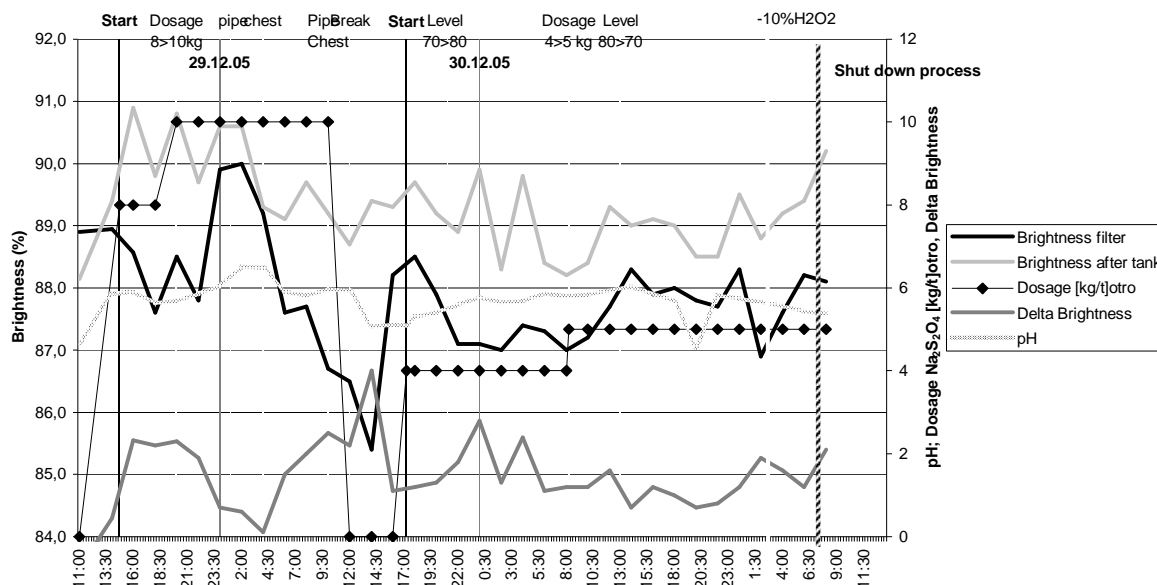
Figure 24. Industrial results of the Y stage following the E(O)P-EP sequence.

Because no further brightness improvements were possible to achieve, it was decided to verify the minimum dithionite charge necessary to satisfactorily improve the pulp brightness. Therefore, no dithionite was added in order to clean the reserve tank ensuring that no interference would occur due to the presence of residual dithionite. After that, 4 kg/t[otro] of dithionite, which is half the initial dosage, were added. This dosage gave rise to a pulp brightness improvement from 87% to 89-90% that corresponds to about 3 % of brightness increment.

The implementation of a complementary reductive stage to the E(O)-EP bleaching sequence has been proven to be efficient to improve the final pulp brightness up to 91% ISO, perhaps due to the presence of carbonyl group-containing chromophores that may undergo the reduction. In fact, and according to Table 8, sulphite bleached pulps have a high carbonyl content comparing to kraft bleached pulps. On the other hand, it was confirmed that there is a limit dithionite dosage to employ in order to reach a maximum pulp brightness improvement. Above this certain dosage value dithionite is in excess and does not access to some chromophoric structures and, consequently, no further brightness improvement occurs.

3.3.2. Pre-bleaching stage to the E(O)P-EP sequence

Another possibility to radically improve the pulp brightness to 91 % ISO or higher is the implementation of oxygen pre-bleaching stage prior to the E(O)P-EP bleaching sequence. The basic idea was to delignify the pulp with oxygen under alkaline conditions thus saving the peroxide in the consecutive stages.

Table 25 presents the results obtained for the pressurized oxygen pre-stages. The first attempt was to perform a single oxygen delignification pre-stage. Comparing with the unbleached pulp, extensive delignification took place since kappa number decreased from 18.8 to 11.2, which is around 40 %. However, the brightness development was rather small, which is unacceptable from a point of view of general bleaching strategy. Therefore, it was found advantageous to combine delignification and bleaching effects. For this reason, the oxygen delignification pre-stage was reinforced with hydrogen peroxide. Some parameters were studied, such as time, temperature, hydrogen peroxide charge and the base to be used.

Pre-bleaching stage experiments from **2** to **6** (Table 25) were performed by employing 0.5 % hydrogen peroxide and 2.1 % sodium hydroxide (O(P) stage) as the base. Hydrogen peroxide addition showed a very positive effect on pulp brightness without loss of the pulp viscosity. Consequently, brightness was about 10 % higher with addition of 0.5 % of H_2O_2 to the pressurized oxygen reactor when compared to pure oxygen delignification at the same conditions. Probably due to the limited oxygen reactivity at 90 ºC, the time increase did not favour the delignification extent. As already mentioned, oxygen is more efficient at temperatures between 100º and 120ºC; however, above 100ºC, hydrogen peroxide degradation is significant. This statement is confirmed in view of the fact that at 100ºC delignification was not as effective as at 90ºC with the same hydrogen peroxide charge and time (pre-bleaching stages **2** and **3**).

Since the higher brightness was gained at 100ºC than at 90 ºC, the pre-bleaching stage with the same conditions was performed for only 30 minutes (pre-bleaching stage **4**) in order to enhance the delignification efficiency of oxygen at 100ºC and to avoid extensive hydrogen peroxide degradation. However, no improvements were achieved and, for that reason, it was decided to perform the further experiments at 90ºC.

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Table 25. Results on oxygen pre-bleaching stage ($P(O_2)$ = 6 bar). (Unbleached pulp: k = 18.8, h = 1055, brightness = 64.4 % ISO)

Pre-stage	H$_2$O$_2$	T	Time	NaOH	Kappa number	Viscosity	Brightness
	(%)	(ºC)	(min)	(%)		(mL/g)	(% ISO)
1	-	90	60	2,1	11.2	1050	66.8
2	0.5	90	60	2.1	9.9	1080	77.1
3	0.5	100	60	2.1	11.4	1155	77.8
4	0.5	100	30	2.1	11.4	1125	77.2
5	0.5	90	30	2.1	9.7	1020	78.0
6	0.5	90	90	2.1	10.3	1030	80.3
7	1	90	60	2.1	9.3	1050	83.4
8	1	90	60	6*	14.8	930	64.4

* NH$_4$OH was used instead of NaOH.

The pre-bleaching stage time was optimized and, according to the results obtained, the best reaction time was 60 minutes. Above a reaction time of 60 minutes, delignification did not develop significantly. Hydrogen peroxide charge was studied at 1 % giving rise to enhanced bleaching and delignification improvements comparing when only 0.5 % H$_2$O$_2$ pre-bleaching stage were used under the same reaction conditions. All these experiments did not affect the pulp viscosity. A last pre-bleaching stage (assay **8**) was performed using ammonium hydroxide as the base instead of sodium hydroxide. This experiment was carried out in order to estimate the consequences of possible substitution of non-renewable base (sodium hydroxide) with a base that does not need to be regenerated (ammonium hydroxide). This last one can be used in industrial streams without limits. However, the pulp brightness after oxygen stage with ammonium hydroxide was similar to the unbleached pulp brightness. One of the reasons was a low delignification degree reached (kappa number of 14.8) in this trial. At the same time, a decrease in pulp viscosity occurred indicating potential loss of pulp strength. Finally, the optimized pre-bleaching stage conditions were selected according to the delignification and bleaching improvements without affecting pulp viscosity (Table 26).

Table 26. Conditions for the pre-bleaching stage to the E(O)P-EP sequence.

	Pre-stage
Consistency (%)	8
T (ºC)	90
H_2O_2 (%)	1
NaOH (%)	2.1
$P(O_2)$ (bar)	6
Time (min)	60

Afterwards, the complete O(P)-E(O)P-EP bleaching sequence was performed in order to verify the contribution of the O(P) on final pulp brightness. The total hydrogen peroxide dosage was redistributed in order to optimize and minimize the dosage increment and consequently to avoid a significant additional reagent cost (Table 27). In the previously optimized E(O)P-EP bleaching sequence, the total amount of hydrogen peroxide employed was 2.6 % and according to the previous results of the pre-bleaching stage O(P) it is necessary to use additional 1 % hydrogen peroxide. Therefore, using the same operating conditions, *i.e.*, temperature, time, alkali charge according to Table 12 and Table 23, and employing 1 % hydrogen peroxide in the pre-bleaching stage O(P), the effect of hydrogen peroxide charge distribution in the E(O)P and EP stages was studied.

Table 27. O(P)-E(O)P-EP sequence and pulp analysis.

	O(P) +	H_2O_2 (%)		Kappa number	Viscosity	Brightness
		E(O)P	EP		(mL/g)	(% ISO)
1	**E(O)P-EP**	1.0	0.8	6.3	960	90.1
2	**E(O)P-EP**	1.1	1.1	6.2	940	90.9
3	**E(O)P-EP**	1.2	1.2	6.0	915	91.4
4	**E(O)P-EP-Y***	1.2	1.2	6.0	905	91.3

The highest pulp brightness was of 91.4 % when using 1 % in the pre-bleaching stage O(P), 1.2 % in E(O)P and 1.2 % in EP stages. Comparing to the optimized E(O)P-EP sequence where the total amount of hydrogen peroxide was 2.6 %, this new O(P)-E(O)P-EP sequence implies an increase of 130 % of H_2O_2 load. On the other hand, comparing to the *CAIMA*'s operating conditions, it implies an increase of 140 % of H_2O_2 load. However, the final pulp brightness up to 91 % was achieved beings the main goal of *CAIMA*'s mill. Based on these preliminary results, it has been proposed that if peroxide charge would be increased to 1.3 % in the E(O)P stage and to 1.3 % in the EP stage, the pulp brightness could increase even more and possibly reach 92 % ISO brightness. However this would imply considerably high costs to *CAIMA*'s mill and, therefore, no advantages were find to proceed with this experiment test to confirm this assumption.

In order to confirm the possibility to reach a final pulp brightness of 92%, the complementary reductive stage was used after the three-stages bleaching sequence (using the experiment **3** conditions) (Table 27). Nevertheless, similar pulp brightness (91.3 %, experiment **4**) was achieved possibly due to the presence of chromophoric structures that were not accessible to dithionite.

Table 28. Physical analysis of the unbleached pulp (60 g/m^2).

	Revolutions		Interpolation	
	0	**1000**	**429**	**667**
Drainability (ºSR)	21	42	30	35
Density (g/cm^3)	0.62	0.78	0.69	0.73
Bursting strength (kPa.m^2/g)	1.6	2.9	2.2	2.5
Tearing resistance (mN.m^2/g)	3.2	3.2	3.2	3.2
Tensile strength (N.m/g)	39.0	57.5	46.9	51.3
Stretch (%)	1.4	2.1	1.7	1.88
Opacity (%)	87.1	82.2	85.0	83.8

Because of the satisfactory brightness gain achieved, physical tests of the unbleached pulp (Table 28), bleached *CAIMA*'s pulp (Table 29) and O(P)-E(O)P-EP bleached pulp (Table 30) were performed. Most of the strength properties are very similar, so the three most important, which are tensile strength, tear resistance and burst strength, were plotted into a single graph to compare each other (Figure 25).

Table 29. Physical analysis of the E(O)P-EP bleached pulp (60 g/m^2).

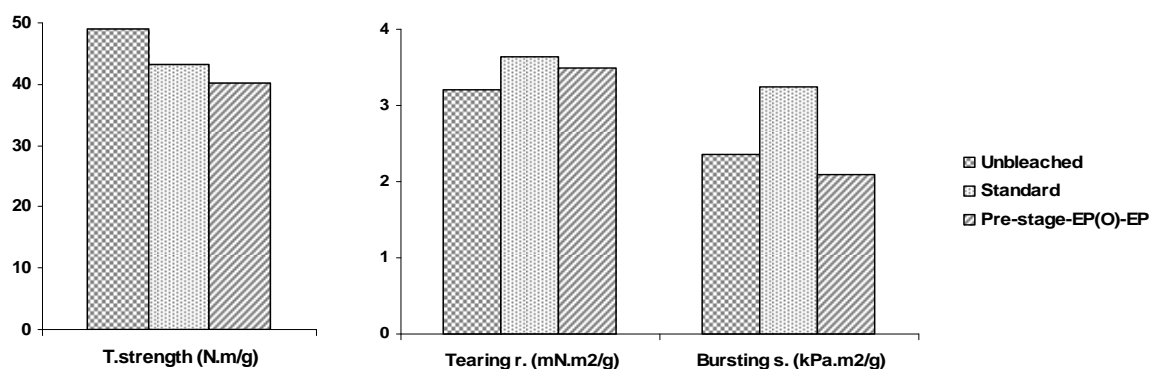|	Revolutions		Interpolation	
	0	**1000**	**333**	**750**
Drainability (ºSR)	26	38	30	35
Density (g/cm^3)	0.64	0.75	0.68	0.72
Bursting strength (kPa.m^2/g)	1.7	2.7	2.0	2.5
Tearing resistance (mN.m^2/g)	3.5	3.7	3.6	3.7
Tensile strength (N.m/g)	37.0	48.5	40.8	45.6
Stretch (%)	1.7	2.6	2.0	2.4
Opacity (%)	74.9	71.0	73.6	72.0

Figure 25. Comparison of physical properties of pulps.

The similarity of physical properties of bleached pulps indicated that this new bleaching sequence, where a pressurized pre-bleaching stage O(P) is implemented to the E(O)P-EP sequence, is a feasible tool for the production of a pulp with final brightness of 91.5-92 %. However, this brightness improvement implies additional costs to *CAIMA*'s mill related to the installation of a new oxygen stage and the increased consumption of hydrogen peroxide (about 30 %).

Table 30. Physical analysis of the O(P)-E(O)P-EP bleached pulp (60 g/m^2).

	Revolutions		Interpolation	
	0	**1000**	**429**	**786**
Drainability (ºSR)	24	38	30	35
Density (g/cm^3)	0.61	0.76	0.67	0.73
Bursting strength (kPa.m^2/g)	1.4	2.5	1.9	2.3
Tearing resistance (mN.m^2/g)	3.2	3.7	3.4	3.6
Tensile strength (N.m/g)	31.0	46.0	37.4	42.8
Stretch (%)	1.5	2.7	2.0	2.4
Opacity (%)	74.2	69.4	72.1	70.4

4. CONCLUSIONS

1.   In order to improve the sulphite pulp brightness from 88 % to 90 % ISO, the E(O)P-EP bleaching sequence conditions were optimised and some modifications were suggested. These included the increase of the temperature to 90ºC in both stages and the redistribution of the hydrogen peroxide charge (1.2% in the E(O)P stage and 1.4% in the EP stage instead of 0.9 % and 1.5 %, respectively, according to conventional practice). After the changes of bleaching conditions, it was possible to reach a pulp brightness of 89.9% ISO and pulp kappa number of 6.6.

The results of the experiments done at industrial scale confirmed the main conclusions obtained during the laboratory study on the improvement of E(O)P-EP bleaching sequence. The industrial scale experiment revealed also to be more efficient than the experiment performed at laboratory scale since it was possible to obtain a bleached pulp with a kappa number of 6.2 and brightness 90.3% (ISO) while at laboratory scale it was obtained a bleached pulp with kappa number of 6.6 and brightness of 89.9% (ISO). This fact was explained by a higher pulp consistency and reagents concentration, and due to a better mechanical stirring under industrial trials. On the other hand, the initial kappa number of the pulp before bleaching revealed to be a crucial factor to control the bleaching sequence. Based on the results, an equation was developed to calculate the peroxide charge to apply in each bleaching stage based on pulp brightness and kappa number requirements. Consequently it was estimated that for the E(O)P stage 1 kappa number unit takes to the consumption of 72.9 OXE (ton*Kappa) of hydrogen peroxide in the industrial pulp stream. On the hand, for the EP stage, for the E(O)P and the consumption 1 kappa number unit takes to the consumption of 384.9 OXE (ton*Kappa) of hydrogen peroxide in the industrial pulp stream.

The addition of peroxide catalysts/activators to the EP stage, namely TAED, cyanamide and pentaacetylglucose, gave rise only to a slight increase of pulp brightness of 0.3-0.4 % and was not considered as a reliable tool for the radical pulp brightness increment.

2.   In order to improve pulp brightness up to 91 %, the implementation of complementary stage to the optimized E(O)P-EP bleaching sequence was applied using

ozone, sodium hypochlorite, chlorine dioxide, or sodium dithionite. In all of post-treatment stages, further delignification occurred with the deterioration of brightness showing that the new chromophoric structures were formed. Therefore, the use of these oxidative chemicals in a complementary stage was suggested to be not feasible. On the other hand, by using dithionite in a complementary reductive stage, it was possible to get an additional increase of pulp brightness gain of 1-3 %. This effect was suggested to be due to the presence of a large amount quinone-type structures (since a high amount of carbonyl groups in the bleached sulphite pulp has been detected), which can be reduced giving rise to a final pulp brightness up to 91 % ISO or even higher. This was confirmed in the industrial scale experiment, which was performed applying the reduction stage (Y) after the E(O)P-EP sequence (Figure 23) using Blankit MF, as the dithionite source. This experiment demonstrated the final pulp brightness increase (similar, or even higher than that obtained in the laboratory) as well as the feasibility of using the E(O)P-EP-Y bleaching sequence at *CAIMA*'s mill.

3.   An attempt was done to increase the final sulphite pulp brightness by implementing a pressurized peroxide-reinforced oxygen pre-bleaching stage (O(P)) before the E(O)P-EP sequence. The best operating conditions of O(P) (oxygen at 6 bar, 1 % peroxide, 2.1 % alkaline charge, at 90ºC for 1 h) with a peroxide charge distribution (1.0 % in the O(P), 1.2 % in the E(O)P and 1.2 % in the EP stages) gave rise to a final pulp brightness of 91.4 %. These results suggest that using an even higher peroxide distribution would probably increase the pulp brightness to 92 % ISO. The pulp properties were evaluated and it was found that no relevant differences were obtained comparing laboratory bleached pulps with standard bleached pulp from *CAIMA*. The use of the complementary reductive stage did not affect the pulp brightness. Even though the use of this pressurized pre-bleaching stage (O(P)) allows achieving the goal of *CAIMA*'s industry, which is final pulp brightness higher than 91 %, it implies enormous additional costs including supplementary equipment and extra chemicals.

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