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Sustainable bleaching of *Eucalyptus sp.* kraft pulp with hypochlorous acid, ozone and hydrogen peroxide



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ARTICLE INFO ABSTRACT Keywords: Eucalyptus sp. is the most important planted crop for the production of chemical pulp. This pulp is mostly Hypochlorite ion bleached with chlorine dioxide, which produces hypochlorous acid in situ when reacting with lignin. However, Hypochlorous acid applying hypochlorus acid directly is not practiced, even though it contributes significantly to the bleaching Tertiary amine reactions. Therefore, this article presents hypochlorous acid as the main bleaching chemical for oxygen Aerobic digestion delignified Eucalyptus sp. kraft pulp. The results showed that hypochlorous acid solely decreased the kappa AOX number of the pulp more efficiently than chlorine dioxide did, without increasing the content of adsorbable organic halogens (AOX) in the effluent. The bleaching sequence with hypochlorous acid, ozone and hydrogen peroxide produced fully bleached pulps, with low organically bound halogens (OX) and aerobically digestible effluents. The bleached pulps and digested effluents complied with international standards for the pulp industry. The hypochlorous acid bleaching sequence is appealing because it is short, uses mild conditions and requires less or similar energy to produce the bleaching chemicals than comparable ECF bleaching sequences from literature.

1. Introduction

Eucalyptus sp. is the most relevant planted crop for the pulp industry. It is a highly productive crop, reaching maturity in 10 years (De los Santos, 2016)(Töyssy and UPM Kymmene, 2016). Its plantations extend in more than 90 countries, and over 20 million hectares worldwide, especially in Brazil, India and China. (IUFRO, 2018). Currently, pulp industry produces ca. 190 million tons of pulp, with nearly a third corresponding to Eucalyptus sp. bleached pulp (CEPI (Confederation of European Paper Industries), 2019) (Carminati, 2017). Producing bleached pulp demands high amounts of energy. Bleaching alone represents 15-40 % of the carbon footprint for paper production (Jour et al., 2013)(Tomberlin et al., 2020). Eucalyptus sp. pulp bleaching usually employs bleaching sequences consisting of four or more alternating bleaching stages to eliminate the residual lignin and chromophores. Each bleaching stage uses elevated temperature for a long period of time, making the overall duration of the bleaching sequences several hours. Hence, an appealing alternative to make pulp and paper industry more sustainable is to design leaner bleaching processes, which use milder conditions and a smaller number of bleaching stages.

A great majority (90%) of the pulp mills use Elemental Chlorine Free (ECF) bleaching technology, (Sixta et al., 2006)(Jour et al., 2013), meaning that no elemental chlorine species, including chlorine (Cl₂) and sodium hypochlorite (NaOCl), are dosed into the bleaching sequence (Suhr et al., 2015). Instead, chlorine dioxide (ClO₂) is the main oxidant added in ECF sequences, which include 1-3 chlorine dioxide (D) bleaching stages (Suhr et al., 2015). Common ECF bleaching sequences for Eucalyptus sp. pulps are DEpDD and DhotEopD (Seco et al., 2008) (Ragnar, 2004), where the use of alternating oxidizing and alkaline stages produce fully bleached pulp. D stage oxidizes lignin structures, which are later solubilized during alkaline extraction (E) (Suess, 2010), and the residual chromophores are removed by a final peroxide bleaching stage (P) giving the pulp good brightness stability. (Suess, 2010) (Dence et al., 1996). Hydrogen peroxide or hydrogen peroxide and oxygen gas can be used to intensify the alkaline extraction (Ep and Eop stages, respectively).

During D stage, ClO_2 oxidizes lignin while producing hypochlorous acid (HOCl) and chlorite (ClO_2^-), which will react in a complex reaction

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Abbreviations: Act. Cl, active chlorine; AOX, adsorbable organic halogens; D, chlorine dioxide pulp bleaching; H_{cat} , catalytic pulp bleaching with HOCl and a tertiary amine; H_{mild} , pulp bleaching with HOCl; HexA, hexenuronic acid; KN, kappa number; ODT, Oven dry ton of pulp; OX, organically bound halogens.

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system forming chlorate (ClO_3^-), chloride (Cl^-) and regenerating ClO_2 (Dence et al., 1996)(Bergnor et al., 1987)(Kolar et al., 1983)(Bergnor et al., 1987)(Lehtimaa, 2010)(Tarvo, 2010). Here, nearly 40 % of the oxidation capacity of chlorine dioxide is transformed into HOCl (Kolar et al., 1983). Hence, an average ECF bleaching sequence which uses 18 kg ClO_2 /ODT (or 47 kg Act. Cl/ODT) (Meuller et al., 2003) (Mounteer et al., 2007), would produce nearly 20 kg of HOCl/ODT *in situ*. Most of this produced HOCl reacts with lignin and HexA, producing adsorbable organic halogen (AOX) and organically bound chlorine (OX) (Lehtimaa, 2010)(Tarvo et al., 2009). Hence, it is clear that HOCl has a significant role in ECF bleaching.

Nonetheless, HOCl is not a popular bleaching chemical in pulp industry, most likely due to unsatisfactory earlier bleaching experiments (Dence et al., 1996) and environmental concerns of using elemental chlorine chemicals (Cl₂, NaOCl and HOCl) (Suhr et al., 2015)(European Commission, 2001). Bleaching with Cl_2 (C stage) is known to generate remarkable amounts of AOX (Beeman et al., 1953) (Suess, 2010). While the use of NaOCl (H stage) produced pulp with poor brightness stability, low viscosity and effluents with of high chloroform content (Suess, 2010) (Iimori et al., 1999)(Sixta et al., 2006).(Prütz et al., 2001) (US Congress Office of Technology Assessment, 1989). Research on operating H stage at pH lower than 10, leading to an equilibrium between HOCl and ClO⁻, resulted in worse viscosity than regular H. Consequently, it was highly discouraged by several authors since the 1950's (Rapson, 1956) (Lyon and Salisbury, 1960) (Rapson, 1963). Only recently, a developed catalytic pulp bleaching (H_{cat}) used NaOCl and a tertiary amine, at mild pH. The dosed NaOCl becomes HOCl at pH 5-7, which reacts with the tertiary amine producing a chloroammonium cation (Chenna et al., 2013). The chloroammonium cation is a stronger oxidant than HOCl (Chenna et al., 2013). This catalytic stage was used in the bleaching sequence $H_{cat}ZP$ which provided fully bleached pulp with good viscosity, mechanical properties, and acceptable OX levels of 150 mg OX/ODT pulp, (Afsahi et al., 2019a, 2019b). However, there is little information available regarding the use of solely HOCl for delignification, and the questions regarding the catalyst efficiency and effluents digestibility still remain.

Nowadays, the reduction in energy consumption of pulp mills is particularly important because the European pulp and paper industry plans to reduce 80 % of their CO₂ emissions from the year 1990 by 2050 (CEPI (Confederation of European Paper Industries), 2011). However, achieving that goal requires breakthrough technologies using reagents produced with lower energy and shorter and leaner bleaching sequences.

On the other hand, ClO_2 is not an easy chemical to handle and it must be produced in the mill site due to its instability and transportation restrictions (Suhr et al., 2015). Hence, the reagents for ClO_2 production, often including sodium chlorate (NaClO₃) (OxyChem, 2018), are transported to the mill. There, they react in an acidic environment consuming energy produced by the pulp mill (OxyChem, 2018)(WHO et al., 2002) (Suhr et al., 2015). NaClO₃ is formed through electrolysis of NaCl with NaOCl as an intermediate. Hence, it would be highly appealing to apply NaOCl straight into the bleaching process, without its conversion first to NaClO₃ and then to ClO_2 , and to obtain pulps and effluents with similar properties to ECF processes.

This publication considers the scenario of having a bleaching system with HOCl, ozone (O_3) and hydrogen peroxide (H_2O_2) instead of a traditional ECF bleaching sequence. In this study the incoming *Eucalyptus sp.* oxygen delignified pulp is fully bleached in a much shorter and leaner bleaching sequence than in current bleaching practices. The final pulp properties are tested, and the effluents are analyzed and treated. The quality of the bleached pulp is estimated by brightness, viscosity, organically bound chlorine (OX) and extractive contents. The effluents are aerobically digested and characterized by their Adsorbable Organically bound Halogens (AOX), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Biological Oxygen Demand (BOD₇).

2. Materials and methods

2.1. Materials

Industrial oxygen-delignified *Eucalyptus sp.* kraft pulp with kappa number (KN) 11.9, 50.9 % ISO brightness and 1100 mL/g viscosity was used in the bleaching experiments. ECF bleached *Eucalyptus sp.* pulp from the same mill, with 89 % ISO brightness, 830 mL/g viscosity and KN < 1 was used as a reference pulp.

Ozone was produced in a Wedeco GSO 30 reactor by oxygen electrolysis at an estimated rate of 0.117 ± 0.01 g/ min. Chlorine dioxide (ClO₂) was produced by mixing 265 g of potassium chlorate (Sigma Aldrich) with 1000 g of oxalic acid (Merck) and 1000 mL of distilled water in a Denzo reactor at 65 °C. The produced ClO₂ gas was trapped in water and stored as solution (18 g Act. Cl/l). Commercial pure sodium thiosulfate, potassium iodide, 1 M sodium hydroxide, 1 M sulfuric acid, 37 % hydrochloric acid, 12 % hydrogen peroxide (H_2O_2), 99.8 % acetone and 10 % sodium hypochlorite (NaOCI) were purchased from VWR. The NaOCI contained 1.17 M ClO⁻ and 0.27 M ClO⁻₃. Analytical grade toluene, chloroform (CHCl₃), sodium sulfate, glacial acetic acid, \geq 97.5 % sulfuric acid and 12 % titanium (II) chloride solution were bought from Sigma-Aldrich.

This study uses CEM-DABCO (1-carboethoxymethyl-1-azonia-4-azabicyclo[2.2.2]octane chloride) as catalyst for H_{cat} experiments, since it was proven to be stable and active with *HOCl* (Isaza Ferro et al., 2020). This tertiary amine catalyst, CEM-DABCO, was synthetized following the procedure proposed by (Engel et al., 2009), as described in (Isaza Ferro et al., 2020), obtaining pure CEM-DABCO as a white solid (1.9 g, 74 % yield). ¹H NMR (400 MHz, D₂O): δ H 1.20 (3H, t, ³J_{HH} = 7.2, COOCH₂CH₃); 3.16 (6H, t, ³J_{HH} = 7.6, (CH₂)₃N⁺); 3.59, (6H, t, ³J_{HH} = 7.6, (CH₂)₃N); 4.17 (2H, s, N⁺CH₂COOEt); 4.21 (2H, q, ³J_{HH} = 7.2, COOCH₂CH₃). ¹³C NMR (400 MHz, D₂O): 13.10, 43.97, 52.79, 61.67, 63.42, 164.70.

2.2. Bleaching experiments

Chlorine dioxide stage (D), catalytic bleaching with tertiary amine and hypochlorous acid (H_{cat}) and hydrogen peroxide bleaching (P) were performed in sealed plastic bags at 10 % consistency inside a water bath, with manual mixing. Ozone stage (Z) was carried out in 30 % consistency at room temperature (20 °C) using a glass balloon flask with constant agitation. The NaOCl, ClO₂, O₃ and H₂O₂ were titrated daily before the experiments to determine their actual concentration. The chlorine species were titrated following the procedure described by Wartiovaara (1982). The effluent was collected after every bleaching stage and frozen for latter effluent characterization. The pulp was washed thoroughly with deionized water, centrifuged and homogenized before continuing to the next bleaching stage or storage in the fridge.

Two main sets of bleaching experiments were done. The first set was bleaching experiments H_{cat} and its control stage with no catalyst (H_{mild}), using 2–10 min residence time, 1% Act. Cl, at 18 °C or 60 °C. D stage at pH 3 was used as reference stage. The second set of experiments consisted of bleaching sequences that include H_{cat} and the newly introduced H_{mild} stage. The conditions for the bleaching sequences $H_{mild}ZP$ and $H_{cat}ZP$, are presented in Table 1.

Further experiments on the use of NaOCl at different end pH levels (2.2, 4, 5.5, 7 and 10) are included in the Appendix A: Supplementary information (Fig. A.1 and A.2).

Table 1

Operation conditions for	D stage, H _{cat} ZP an	d H _{mild} ZP bleaching sequences.
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Parameter	D	H _{cat}	H _{mild}	Z	Р
Dosage (%) *					
NaOCl (Act. Cl)	-	1	1	-	-
CEM – DABCO	-	0.1	-	-	-
ClO ₂ (Act. Cl)	1.8	-	-	-	-
H_2SO_4	-	0.5	0.5	-	_
O ₃	-	-	-	0.5	_
NaOH	-	-	-	-	1.6
H_2O_2	-	-	-	-	1.1
Temperature (°C)	70	60	60	20	85
Time (min)	30	10	10	2	60
Consistency (%)	10	10	10	30	10
pH	3	5 - 5.5	5 - 5.5	2.9	10.5

w% on dry weight of pulp.

2.3. Pulp characterization

Hand sheets were made according to the standard method SCAN-CM 11:95 and their ISO Brightness measured following the SCAN-CM 11:75. The kappa number (KN) and viscosity of the pulps were determined according to SCAN-CM 1:00 and SCAN-CM 15:99 respectively. The acetone extractives of the bleached pulps were measured according to SCAN-CM 49:03. The Ultraviolet Resonance Raman (UVRR) spectra were measured according to (Jääskeläinen et al., 2005).

The OX was determined according to ISO 11480 using a Trace Elemental Instruments Xplorer with duplicates. The standard error was \pm 30 g OX/ODT.

2.4. Effluent characterization and aerobic digestion

2.4.1. Chloroform quantification

The quantification of chloroform in the effluent was carried out by the GC-MS headspace (HS) method using a Thermo Fisher GC Trace 13000 coupled with a MS-ISQ and a Triplus-RSH autosampler. The headspace incubation time of the vials in the Triplus-RSH autosampler was 10 min at 90 $^\circ \rm C$ with intermittent agitation (5 s on and 5 s off). The GC conditions were 1:10 split ratio, 1 mL/min of He carrier gas, and the column temperature of 40 $^\circ$ C for 3 min with a later elevation of 30 $^\circ$ C/ min up to 150 °C. The used column was Thermo Scientific TG-200MS, 30 \times 0.25 mm X 0.25 mm. The mass transfer line temperature was 280 °C. The ion source temperature was 250 °C, electron impact ionization 70 eV with scan range from 45 to 250 amu. A set of solutions with different CHCl₃ concentrations (0–1000 μ g/L) was used to generate the calibration line. The chosen internal standard (IS) was toluene (1 ppm). Each vial contained 3 g of Na₂SO₄, 8 mL of sample and 0.020 mL of toluene. All the samples were measured in duplicates. The standard error was ± 1 g CHCl₃ /ODT.

2.4.2. Aerobic digestion of bleaching effluents (AOX, COD, TOC and BOD₇ measurements)

The digestibility of the bleaching effluents was assessed in batch laboratory scale aerobic digesters with constant aeration, a Mass/Fed ratio of 0.2 and temperature of 31–37 °C for 24 h. The aerobic bacteria were provided by a Finnish pulp mill. AOX, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Biological Oxygen Demand (BOD₇) were measured before and after the aerobic digestion. The sludge contribution to AOX, COD, TOC and BOD₇ was subtracted from initial and digested samples. The AOX was measured according to the ISO 9562, using a Trace Elemental Instruments Xplorer with duplicates, the standard error was \pm 30 g AOX. The Chemical Oxygen Demand (COD) was measured according to ISO 6060, using HACH LKC-114 test tubes, the HACH oven LT 200 and the UV–vis spectrophotometer HACH DR 6000. The Total Organic Carbon (TOC) was measured according to EN1484 using a Shimadzu TOC-VCPH analyzer. The Biological Oxygen Demand (BOD₇) was obtained following the ISO 9408 using a closed respirometer OxiTop WTW.

3. Results and discussion

3.1. Bleaching experiments with HOCl

This section compares the bleaching stages that use HOCl as the main bleaching chemical with D stage (Fig. 1), and it also presents an optimization for the HOCl bleaching stages (Fig. 2) (Table 2). The bleaching stages that used HOCl as main bleaching chemical were: H_{cat} , (1% Act. Cl, 0.1 % CEM-DABCO) and its control stage without the use of the catalyst, which will be referred as H_{mild} from this point onwards.

The bleaching experiments H_{cat} and H_{mild} were carefully performed at pH 5–5.5, proposed operating pH for the H_{cat} stage (Afsahi et al., 2015). At this pH probability for the formation of the chloroammonium cation is high (Dawson, 2018)(Isaza Ferro et al., 2020). Furthermore, H_{cat} and H_{mild} at pH 5 produced the pulps with lowest kappa number within all pH range experiments at same Act. Cl dosage (Appendix A: Supplementary information, Fig. A.1).

 $\rm H_{cat}$ and $\rm H_{mild}$ (1% Act. Cl) were more efficient than D stage for the decrease of KN (Fig. 1A). $\rm H_{cat}$ and $\rm H_{mild}$ decreased the KN of the Eucalyptus sp. oxygen delignified pulp from KN 11.9 to 4.6 and 4.9, respectively. In contrast, D stage even with higher active Cl dosage (1.8 % Act. Cl), only decreased KN to 6.6. This implies that the D pulp had more residual unsaturated lignin structures than the HOCl treated pulps. However, D stage was superior in terms of ISO brightness, producing pulp with almost 10 units higher in brightness than HOCl stages (Fig. 1B)

The pulps' viscosity after $H_{cat},\,H_{mild}$ and D stage were comparable, 1000 ± 60 mL/g (Fig. 1C). These high viscosity values for H_{cat} and H_{mild} are consistent with previous H_{cat} experiments, which reported low carbonyl group content in the treated pulps (5 μ mol/g) (Afsahi et al., 2019b). Therefore, the similar high viscosity values of the pulps bleached with HOCl could be explained by the low Act. Cl dosage in these stages.

D stage produced the expected AOX level of 313 g AOX/ODT (Alen et al., 2011), which is similar to the AOX amounts produced by HOCl stages (385 \pm 30 g AOX /ODT) (Fig. 1D). The low AOX production from H_{cat} and H_{mild} stages is striking, taking into consideration the poor reputation that elemental chlorine has regarding AOX formation. However, the chloroform (CHCl₃) amounts produced by HOCl stages were nearly 3 times higher than the quantities produced by D stage (8.4 and 2.5 g CHCl₃/ODT respectively) (Fig. 1E). CHCl₃ amounts from HOCl stages are consistent with limori, Iwase and Tsuji (1999) for this same pH. The CHCl₃ produced by D seems a little high, since 3–5 g CHCl₃/ODT is the expected chloroform formation for a full bleaching



Fig. 1. Pulps' properties (KN, Brightness, viscosity, OX) and effluent characteristics (AOX and CHCl₃) of Eucalyptus sp. oxygen delignified pulp treated with H_{mild} (1%Act. Cl, 18 °C, 10 min), H_{cat} (1% Act. Cl, 0.1 % CEM DABCO, 18 °C, 10 min) or D stage (1.8 % Act. Cl, 70 °C, 30 min).



Fig. 2. Fast H_{cat} and H_{mild} experiments with 1% Act. Cl at 18°C. A) KN decrease on time, B) Residual Act. Cl on time, and C) UVRR of the produced samples after 10 min.

Table 2

H_{cat} and H_{mild} bleaching stages after 2 min.

HOCl stages (60°C at 2 min)	CEM DABCO (%)	Kappa Number	Residual Act. Cl (kg/ ODT)	Brightness (%ISO)	Viscosity (ml/g)
H _{mild}	- 0.1	5.1	0	56.0	1065
H _{cat}		5.1	0	55.8	1127

sequence of type DEpD (Nakamata et al., 2004). Relating CHCl₃ and AOX amounts, it is possible to say that even if D, H_{cat} and H_{mild} stages have similar AOX levels, the composition of their AOX is obviously different.

On the other hand OX, or organically bound chlorine, present in the pulp from HOCl stages is higher than from D stage (Fig. 1F). Therefore, to make H_{cat} and H_{mild} stages more appealing, the OX should be removed from the pulp with subsequent bleaching stages, and additionally, the effluent should be digested to a similar degree than D stage effluents.

It is interesting that H_{cat} and H_{mild} presented similar results for most of the previously mentioned parameters (Fig. 1). This is explained by the catalyst speeding up the already fast oxidization reactions of HOCl with HexA and lignin. In H_{mild} stage, the dosed HOCl (1% Act. Cl) was consumed completely in 10 min, and hence, it is expected that the use of the catalyst in H_{cat} would decrease this reaction time. Fig. 2 proves this hypothesis, where H_{cat} decreased the KN (Fig. 2A) and consumed the HOCl faster than H_{mild} (Fig. 2B). On the other hand, the UVRR intensity of HexA from H_{cat} stage was lower than from H_{mild} stage (Fig. 2C), suggesting a more efficient reaction of HexA's C—C double bond through chlorination and/or cleavage of HexA. This could relate also to the slightly lower KN, OX and AOX from H_{cat} stage.

These results (Fig. 2) showed that H_{cat} stage is a highly efficient bleaching stage and that it can be performed in 5 min or less, at room temperature. However, this mild temperature is not energetically feasible for industrial pulp bleaching applications because cooling is also energetically expensive and most of the stages are carried out at minimum 60 °C. Hence, H_{cat} and H_{mild} stages were also performed at 60 °C (Table 2). At this temperature, the reaction time was decreased to 2 min, or less, for both stages, consuming all Act. Cl and producing pulps with KN 5.1, 56 % ISO brightness and a viscosity of 1100 ± 30 mL/g

(Table 2). However, efficient hand mixing in less than 2 min is challenging, and hence further treatments were carried out using 10 min duration at 60 $^{\circ}$ C with 1% Act. Cl.

3.2. Bleaching sequences with hypochlorous acid, ozone and hydrogen peroxide

Bleaching sequences $H_{mild}ZP$ and $H_{cat}ZP$ were performed, and the produced pulps and effluents characterized. As expected, $H_{mild}ZP$ and $H_{cat}ZP$ bleaching sequences behaved almost identically, which is consistent with H_{cat} and H_{mild} producing pulps and effluents with extremely similar characteristics (Table 2). Hence, for clarity, from this point onwards only $H_{mild}ZP$ will be discussed. This bleaching sequence is also cheaper since it does not use the tertiary amine. The results for $H_{cat}ZP$ can be found in the Appendix A: Supplementary information (Table A.1).

Fig. 3 presents the ISO brightness, KN, OX and AOX development of the H_{mild} ZP bleaching sequence. H_{mild} ZP produced fully bleached pulps with 89 % ISO Brightness within 71 min overall reaction time (Fig. 3). The pulp's OX after H_{mild} stage was 540 g/ODT, and it was further degraded during the following Z and P stages producing pulps with a final OX content of 147 g OX/ODT (Fig. 3). This OX level is in the accepted range for ECF pulps of 100–250 g OX/ODT, and in the OX limits for ECF Ecolabeled pulps of maximum 150 g OX/ODT (Suess, 2010) (Afsahi et al., 2019a, 2019b) (Dodd et al., 2013). The AOX content of H_{mild} stage's effluent was 376 g AOX/ODT (Fig. 3), and later aerobical digestion lowered the content further. An interesting fact about using ozone and hydrogen peroxide is that the OX removed during Z and P stages was degraded instead of just passed to the effluent as AOX.

 $H_{mild}ZP$ is a fast bleaching sequence compared to bleaching sequences from literature DEpDD (Seco et al., 2008) and D_{hot}EopD (Ragnar, 2004). DEpDD required 520 min (Seco et al., 2008) and D_{hot}EopD took 360 min (Ragnar, 2004) to obtain fully bleached pulps, from initial similar Eucalyptus sp. pulps with initial KN between 11 and 13. Whereas $H_{mild}ZP$ only required 71 min.

On the other hand, it is possible to compare the AOX production from $H_{mild}ZP$ with the theoretical AOX production from DEpDD (Seco et al., 2008) and $D_{hot}EopD$ (Ragnar, 2004). (D stages produce 20 g AOX/kg Act. Cl (Alen et al., 2011) and D_{hot} produces nearly half of the AOX than regular D stages, at same reagent dose (Gomes et al., 2007)). Hence, DEpDD (55 kg Act. Cl/ODT) would theoretically produce 1100 g AOX /ODT. Whereas, $D_{hot}EopD$ (25.3 Act. Cl/ODT) would produce nearly 340 g AOX/ODT, which is similar to the AOX levels (376 g AOX/ODT) measured in $H_{mild}ZP$ bleaching sequence.

The final viscosity of $H_{mild}ZP$ pulp was 615 mL/g (Appendix A: Supplementary information, Fig. A.3). This final viscosity value could be increased by optimizing the bleaching sequence (reducing the ozone and hydrogen peroxide dosage as well as lowering the temperature in P stage). However, this is not the objective of this study and it has been proved previously that the final viscosity of $H_{cat}ZP$ Eucalyptus pulps can be as high as 1080 mL/g (Afsahi et al., 2019a, 2019b).

Another aspect to take into consideration for the HOCl bleaching



Fig. 3. Bleaching of Eucalyptus oxygen delignified pulp with H_{mild}ZP sequence. Kappa number, ISO brightness and OX development, as well as AOX in the effluent of each bleaching stage.

sequence is the amount of extractives present in the bleached pulp. Extractives are mostly removed during kraft pulping and oxygen delignification (Freire et al., 2006). However, the bleaching process should eliminate residual extractives since they can cause "pitch" problems, or undesired odors and black spots, in the final pulp (Freire et al., 2002). The *Eucalyptus sp.* bleached H_{mild}ZP pulp and the commercial *Eucalyptus sp.* ECF bleached pulp from a Brazilian pulp mill presented low values of extractives, 0.05 and 0.1 % in mass of acetone soluble matter. This suggests that the H_{mild}ZP sequence was as efficient as the industrial sequence in removing this type of extractives.

In general, the bleaching sequence $H_{mild}ZP$ proved that it is possible to deliver fully bleached *Eucalyptus sp.* pulp with acceptable OX levels in very short time. However, for this bleaching sequence to be competitive the quality of its effluent also needs to be assessed.

3.3. Environmental assessment of H_{mild} stage effluent

As stated before, AOX was only formed during H_{mild} stage in the $H_{mild}ZP$ bleaching sequence, hence only the filtrate from H_{mild} stage was characterized and digested. This section includes the digestibility of its AOX, COD, TOC and BOD₇ as well as presence of ClO_3^- ion in this effluent's stage. The results are compared with the digestibility of a traditional D stage with 1.8 % Act. Cl.

3.3.1. Digestibility of the H_{mild} effluent (AOX, COD, TOC and BOD₇)

The H_{mild} and D effluents were digested with aerobic bacterial sludge from a Finnish pulp mill for 24 h at 31-37 °C. The digestibility of their AOX during those 24 h was monitored (Fig. 4) and the TOC, COD and BOD₇ measured at the start and end of the treatment (Fig. 5).

The aerobic digestibility of the AOX from H_{mild} stage (1% Act. Cl) was compared to the aerobic digestibility of the AOX from a reference D stage (1.8 % Act. Cl) (Fig. 4). The AOX from H_{mild} and D stage presented similar aerobic degradation. During the first 5 h, the AOX of both stages was rapidly degraded to approx. 30 % of the original AOX load. After 24 h, most of the AOX from H_{mild} and D stages was degraded, leaving only 38 g AOX/ODT in the effluent, which is a remanent of approximately 10 % of the initial AOX in both stages (Fig. 5). This residual amount of AOX from H_{mild} is low enough to meet the AOX European Commission requirements for Ecolabeled products <170 g AOX/ODT (Kowalska et al., 2019). The aerobic biodigestibility of the AOX experiments had a big variation between duplicate samples caused by the use of aerobic sludge from different seasons and use of fresh and frozen bleaching effluents. Nevertheless, the behavior of the AOX degradation and its final values were consistent.

The biodigestibility of the COD, TOC and BOD₇ from H_{mild} and D effluents was also measured (Fig. 5). The COD and TOC are parameters that indirectly measure the amount of organic matter in the effluent from H_{mild} and D stages. The COD of H_{mild} and D stage, before and after the aerobic digestion, complied with the BREF range of 5–42 kg COD/ODT for liquid discharges of pulp mills (with bleaching units after



Fig. 4. Digestibility of the AOX from $H_{\rm mild}$ and D stages with aerobic bacteria for 24 h at 31-37°C.



Fig. 5. $H_{\rm mild}$ and D effluents' characteristics before and after their aerobic digestion. Degradation % are represented by arrows.

aerobic treatment) (Suhr et al., 2015) (Fig. 5). This is expected because wastewaters of pulp mills are mixtures of effluents from debarking, cooking, washing and bleaching stages, with the highest contribution to COD coming from the initial stages of the pulping process. The initial and final TOC values after digestion for H_{mild} and D effluents, were between the typical ranges for pulp mills: 20–30 g TOC/ODT for effluents before digestion, and 2.6–3.9 g TOC/ODT for digested effluents (Suhr et al., 2015). The initial Biological Oxygen Demand (BOD₇) of H_{mild} effluent was lower than the initial BOD₇ from D stage, 59 and 123 mg/l respectively. However, after aerobic digestion both effluents had similar BOD₇ values (approx. 20 mg/l), which is similar to the average BOD₇ production of EU pulp mills according to the BREF (Suhr et al., 2015).

In general, H_{mild} and D stage effluents presented similar biodegradability represented by close degradation percentages of their AOX, COD, TOC and BOD₇ (Fig. 5). Approximately 90 % of the AOX from both stages was degraded, which might suggest that H_{mild} and D produced predominantly low molecular weight (LMW) AOX (Costa and Colodette, 2007). The COD, TOC and BOD₇ of both stages was degraded in similar percentages (approx. 20, 65 and 75 % respectively).

On the other hand, it is known that toxicity has an impact in the biodigestibility of the effluents and that highly toxic compounds can hinder this degradation process. Therefore, the previous results could suggest that the effluents from H_{mild} and D stage might have a similar toxicity. However, more specific tests should be performed to prove this hypothesis since effluent biodigestibility does not relate with some types of toxicity (Mounteer et al., 2002) (Müller, 2003).

Digestibility of *CHCl*₃ was not assessed since it evaporates in the aerobic reactor at 34 °C, and its real degradation cannot be quantified precisely. However, several authors have stated that nearly 95 % of the *CHCl*₃ will be eliminated by aerobic lagoon either by digestion or evaporation and only a 5% would remain in the final effluent (EPA and U.S.E.P.A., 1990) (Institut National de l'Environnement Industriel et des Risques (Institut National de l'Environnement Industriel et des Risques (INERIS), 2007). Therefore, the expected *CHCl*₃ amounts in the aerobically digested H_{mild} effluent would be approximately 0.5 g/ODT *HCl*₃. This *CHCl*₃ value would comply with the EPA restrictions for *CHCl*₃ discharge from pulp mills in water sources of 6.92 g/ODT and monthly average of 4.42 g/ODT (United States of America EPA, 2000). The European BREF does not present a limit in *CHCl*₃ probably because by restricting the use of hypochlorite it has been assumed that the production of *CHCl*₃ in European Pulp industry is negligible.

3.3.2. Chlorate levels

Chlorate ion (ClO_3^-) is one of the main toxic compounds produced in chlorine-containing bleaching stages but it is not currently measured in

ECF pulp mill effluents (van Wijk and Hutchinson, 1995)(Bergnor et al., 1987)(Tarvo et al., 2009). This subsection presents the initial and produced amounts of ClO_3^- in H_{mild} and D stages were measured *via* titration according to Wartiovaara (1982).

 H_{mild} and D bleaching stages produced small amounts of $ClO_3^$ compared to the initial amounts in the bleaching chemicals. However, D stage had a higher starting and produced ClO_3^- than H_{mild} . D stage started with 3.31 mM ClO_3^-/g Act. Cl and produced a net amount of 0.99 mM ClO_3^-/g Act. Cl. In contrast, H_{mild} started with 2.58 mM ClO_3^-/g Act. Cl and generated a net amount of 0.17 mM ClO_3^-/g Act. Cl. (The higher amounts of ClO_3^- correlate with previous literature on the D stage (Tarvo et al., 2009)). The error for these measurements was ± 0.1 mM ClO_3^-/g Act. Cl.

3.4. Energy consumption for the production of the bleaching chemicals

This section presents an analysis of the energy required to produce the bleaching chemicals for $H_{mild}ZP$ and for ECF bleaching sequences from literature (DEpDD and $D_{hot}EopD$) (Fig. 6). Presenting a full energy balance for the bleaching sequences with hypochlorous acid is beyond the scope of this publication. The energy values for the production of the bleaching chemicals were taken from Folke et al., 1996 and Franzén et al.,1997, and the chemicals dosage for DEpDD from Seco et al., 2008 and for $D_{hot}EopD$ from Ragnar, 2004.

This analysis reveals that producing the chemicals for $H_{mild}ZP$ bleaching sequence requires nearly half of the energy to produce the chemicals used in ECF bleaching sequence DE_pDD (Seco et al., 2008) (Fig. 6, "Accumulated Energy (E) for the production of bleaching chemicals"). $H_{mild}ZP$ requires only 146 kW h/ODT, whereas DEpDD employs 264 kW h/ODT for similar results. In contrast, $D_{hot}EopD$ (Ragnar, 2004) is competitive in terms of energy required for the production of the bleaching chemicals, requiring only 130 kW h/ODT. (Detailed calculation in Appendix A: Supplementary information, Table A.2).

In general, it is possible to conclude that $H_{mild}ZP$ bleaching sequence might consume less energy than traditional ECF bleaching sequences (DEpDD and $D_{hot}EopD$) because these ECF sequences use higher temperatures and they require at least 5 times the residence time than $H_{mild}ZP$ bleaching sequence. Furthermore, $H_{mild}ZP$ bleaching sequence can still be optimized for lower ozone and peroxide dosage, but HOCI must never be dosed in excess since it will impact on the OX, AOX and chloroform levels of overall bleaching sequence.

4. Conclusions

This article revealed that bleaching stages with hypochlorus acid delignified *Eucalyptus sp.* pulp more efficiently than chlorine dioxide bleaching stage. It also showed that the bleaching sequence $H_{mild}ZP$ produced fully bleached pulp with acceptable OX and extractive levels, even without the use of the catalyst. Also, the most critical filtrate from the bleaching sequence, produced during H_{mild} stage, complied with international regulations after its aerobic digestion. Hence, the $H_{mild}ZP$ is highly competitive in terms of its delay, produced pulp properties and digested effluents quality. Furthermore, considering that it uses lower energy to produce its bleaching chemicals, $H_{mild}ZP$ is superior to current ECF bleaching sequence DEpDD and competitive against $D_{hot}EopD$. This is particularly important since pulp and paper industry plans a massive carbon footprint reduction by the year 2050.

In the future, the technical quality of the produced pulp and the environmental impact of the $H_{mild}ZP$ bleaching sequence should be evaluated in more detail. A full energy balance and a thorough study of the treated effluents, including their chloroform levels, could provide significant information for the environmental viability of the sequence and its possible scale up.

Finally, this article fulfils the aim to start a discussion regarding the



Fig. 6. Energy required to produce the chemicals used in the bleaching sequences for Eucalyptus sp. kraft pulps. (All sequences consider oxygen delignified Eucalyptus pulps, with initial KN between 9 and 11, and achieved final ISO brightness values of 89 %).

use of hypochlorous acid in pulp industry. Hopefully, it will bring interest to this topic and encourage other studies to solve the remaining environmental questions of pulp bleaching with hypochlorus acid.

CRediT authorship contribution statement

Estefania Isaza Ferro: Writing - original draft, Conceptualization, Methodology, Visualization, Investigation. **Kyösti Ruuttunen:** Writing review & editing, Conceptualization. **Jordan Perrin:** Conceptualization. **Tapani Vuorinen:** Supervision, Writing - review & editing, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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