

This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Using Oxone and TAED activator in non-chlorine bleaching of soda bagasse pulp

Zeinaly, Farhad; Gabov, Konstantin; Kanāni Sula, Hadi; Babavand, Arash; Fardim, Pedro

Published in:
Nordic Pulp and Paper Research Journal

DOI:
[10.1515/npprj-2019-0010](https://doi.org/10.1515/npprj-2019-0010)

Published: 01/01/2019

Document Version
Final published version

Document License
Publisher rights policy

[Link to publication](#)

Please cite the original version:
Zeinaly, F., Gabov, K., Kanāni Sula, H., Babavand, A., & Fardim, P. (2019). Using Oxone and TAED activator in non-chlorine bleaching of soda bagasse pulp. *Nordic Pulp and Paper Research Journal*, 34(4), 422–432. <https://doi.org/10.1515/npprj-2019-0010>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Bleaching

Farhad Zeinaly*, Konstantin Gabov, Hadi Kanāni Sula, Arash Babavand and Pedro Fardim

Using Oxone and TAED activator in non-chlorine bleaching of soda bagasse pulp

<https://doi.org/10.1515/npprj-2019-0010>

Received January 28, 2019; accepted July 8, 2019; previously published online September 12, 2019

Abstract: Bagasse fiber has been used in the production of bleached chemical pulp by the Pars Paper Company. In this company, a conventional three-stage sequence of hypochlorite, alkaline extraction and second hypochlorite (HEH) is applied in pulp bleaching. Pulp bleaching is one of the most important environmental pollutant stages in the pulp and paper industry. In this research, the bleaching of soda bagasse pulp by applying Oxone and TAED-activator in non-chlorine bleaching sequences has been investigated. The unbleached pulp, with kappa number of 20, 955 ml/g viscosity and 37 % brightness, was prepared from Pars Paper Company. Results indicated that, the TAED at the first and second stages were more effective than in the Oxone stages. Moreover, the sequences, which contained TAED- and Oxone-second-stage, could reach the minimum level of kappa (1.7), but the highest brightness (80 %) was attained by using only TAED with a comparatively high level of pulp viscosity (752).

Keywords: activated peroxide; oxone; peroxy acid; soda bagasse pulp; tetra acetyl ethylene di amine.

Introduction

The bleachability of lignocellulosic fiber rightly relates to the kind of fibers, bleaching process and the desirable

***Corresponding author: Farhad Zeinaly**, Young Researchers and Elite Club, Karaj Branch, Islamic Azad University, Karaj, Iran, e-mail: farhad.zeinaly@yahoo.com

Konstantin Gabov, Pedro Fardim, Laboratory of Fiber and Cellulose Technology, Department of Chemical Engineering, Faculty of Technology, Åbo Akademi University, Turku, Finland, e-mails: kgabov@abo.fi, pfardim@abo.fi

Hadi Kanāni Sula, Department of Wood and Paper Science and Technology, Faculty of Natural Resources, University of Tehran, Karaj, Iran, e-mail: hadi.kanani249@ut.ac.ir

Arash Babavand, Department of Pulp & Paper Technology, Faculty of Wood & Paper Engineering, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran, e-mail: a.babavand@yahoo.com

brightness. Therefore, changes to the pulping and bleaching process could be considered as a way to improve or substitute for the conventional process in a given pulp mill (Zeinaly et al. 2016a, Fang et al. 2017). The most important lignocellulosic fiber source in southern Iran is sugarcane bagasse. Pars Paper Company has been using bagasse fiber to produce bleached chemical pulp for several years (Zeinaly 2014). In this company, the soda process is applied in pulp production, and the three-stage sequence of hypochlorite, alkaline extraction and second hypochlorite (HEH) is used in the bleaching process to reach the target brightness of 80 %. Actually, the first hypochlorite stage substituted Cl_2 stage, in the primary bleaching sequence of CEH (Chlorination-Extraction-Hypochlorite), to minimize the amount of absorbable organic halides (AOX) that had been formed and discharged (Zeinaly 2014, Pars Paper Co. 2018). As the pulp and paper industry is regarded to be one of the main polluting industries in the world, in two recent decades, Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF) bleaching systems have been widely developed in pulp mills of North America and European countries (Boruah et al. 2016, Xiao et al. 2017). However, the conventional bleaching process, which uses chlorine (such as CEH or HEH sequences), is still alive in developing countries and regions, such as China, India, the Middle East and Southeast Asia (Rolf et al. 2009, Xiao et al. 2017). This conventional process generates enormous amounts of contaminants affecting ecology and health, which creates continuously growing environmental problems (Boruah et al. 2016).

The bleaching process requires a large amount of chemicals such as chlorine gas, chlorine dioxide, hypochlorite and sodium hypochlorite, and during this process a wide variety of chlorinated derivatives such as chlorinated aromatic compounds, polychlorinated dioxins, polychlorinated furans, carbon tetrachloride, dichloromethane are generated (Bajpai 2005, Sadhasivam et al. 2010, Boruah et al. 2016). The discharged effluent of the hypochlorite stage contains a significant level of chloroform, which is classified as carcinogens. Also, in this process a large amount of toxic and environmentally hazardous contaminants is generated, which is emitted into the soil and water (Boruah et al. 2016).

Oxygen delignification and TCF bleaching sequences are new environmentally friendly processes to produce bleached pulp, by which the problem of effluent pollution in the pulp bleaching process can be minimized (European Commission 2001, Jafari et al. 2014). Oxygen delignification plays a key role in the reduction of effluent pollution and waste water emission, because through the one-stage system the degree of further delignification is about 40–50 %, and the dissolved organic materials are piped to the recovery system with no major changes in the process. Oxygen delignification may also help to reduce the cost of bleached-pulp production by decreasing the consumption of chemicals and energy (European Commission 2001, Zeinaly et al. 2018). However, the negative aspect of this process is its poor selectivity, specifically at high delignification levels (Genco et al. 2012, Jafari et al. 2014). The use of acid pretreatment or the addition of carbohydrate protective compounds (namely magnesium sulfate) reduced the detrimental effects of transition metals on carbohydrate degradation; additionally, using activating agents (such as peroxy acids) may increase oxygen delignification selectivity (Jafari et al. 2014, Zeinaly et al. 2016a).

Hydrogen peroxide is one of the most important agents in TCF bleaching systems. The achievement of higher brightness in the chemical pulps by hydrogen peroxide requires two main functions: 1) eliminating cross-linked carbonyl groups in the lignin structures by hydroperoxide anions (nucleophilic attack); and 2) extended delignification through degradation and dissolution, by the reaction of hydroxyl radical ($\text{HO}\cdot$) and superoxide anionic radical ($\text{O}_2^-\cdot$). These radicals are electrophilic agents, which can attack aromatic structures of the residual lignin. The result is oxidative decomposition, which increases molecular hydrophilicity and solubility of lignin (Bajpai 2005, Zeinaly 2014). However, the reactivity of these radicals with lignin phenolic structures is slightly higher than with cellulose (primary and secondary alcohols). Therefore, when peroxide decomposition occurs at a high level, the concentration of radicals significantly intensifies; hence, the selectivity of delignification is reduced and cellulose destruction takes place, as in lignin dissolution (Bajpai 2005).

Actually, hydrogen peroxide under alkaline condition is not able to attack lignin phenols (aromatic rings), and so lignin removal is limited by using this bleaching agent. The hydroperoxide anion acts as a nucleophile; it would not be capable of oxidizing electron-rich lignin aromatic rings, but it adds to the quinone structures and eliminates side chains from lignin. The peroxide bleaching of chemical pulps must be conducted in an intense condi-

tion and the reaction temperature must be set at about 90 °C in non-pressurized systems. In this situation, the residual lignin degradation and depolymerization and carboxylic group formation occur (Walker 2006, Suess 2010, Zeinaly et al. 2016b). Hydrogen peroxide decomposition is extremely affected by temperature, and thermal decomposition takes place through homolytic cleavage. Alkaline peroxide bleaching has also been conducted at 120 °C, but the results have indicated that temperatures of about 90 °C are optimal for this process, because lignin removal occurs at a sufficient level and carbohydrate degradation is not high; and also, there is no requirement of pressurized equipment (Walker 2006, Suess 2010).

The peroxide bleaching process can be performed at higher pressures and temperatures by the use of oxygen gas as a reinforcement factor. Released radicals from the peroxide self-decomposition cause carbohydrate chains' degradation and hence reduce pulp viscosity; in pressurized systems, the peroxide consumption and viscosity lessening are reduced, and the process selectivity is improved (Nishimura et al. 1996, Zeinaly 2014).

Using peroxide activators is a way to increase peroxide process efficiency. These components produce new bleaching agents with higher oxidative capacity, which improve the bleaching process in lower retention times and temperatures (Khristova et al. 2003). Peroxide activators include ammonium molybdate, sodium nonanoxyl oxy benzene sulfonate (NOBS), polypyridines, peracids, oxone and tetra acetyl ethylene diamine (TAED) (Khristova et al. 2003, Zeinaly et al. 2013, Jafari et al. 2014, Miri et al. 2015).

Hydrogen peroxide efficiency as a lignin remover agent is limited in low temperatures, neutral pH, absence of transition metals, and low amount of residual lignin. On the other hand, hydroperoxide anion is a nucleophilic agent and could not attack the electron-rich aromatic rings of the residual lignin (Bajpai 2005, Suess 2010). Therefore, with the use of peracids (e. g., oxone) or peroxide activators (e. g., TAED), lignin removal can be improved and retained, via creating new active agents that have electrophilic characteristics (like peracetic acid and peracetate anion) (Zeinaly et al. 2013, Miri et al. 2015).

In this study, the best condition and sequences were achieved via improving the soda bagasse bleaching process by the use of oxygen-reinforced peroxide, oxone and TAED activator stages in the non-chlorine bleaching system. The condition of each stage and their interaction were evaluated to reach the best properties of the pulp. The properties of bagasse pulp were determined after each stage, and the interactions of bleaching stages were evaluated.

Material and Methods

Material

Unbleached soda bagasse pulp, with kappa number of 20.2, viscosity of 955 ml/g, hexenuronic acid (HexA) content of 7.70 $\mu\text{mol/g}$ and initial ISO brightness of 36.7 %, was prepared from Pars Paper Industries Co, headquartered in Hoseynabad Rural District, in the Central District of Shush County, Khuzestan Province, Iran.

TAED (Tetra Acetyl Ethylene Di-amine) with the empirical formula of $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_4$ and Oxone (potassium mono-persulfate triple salt) with the linear formula of $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ were purchased from Sigma-Aldrich Company. All using chemicals were analytical grade. Distilled water was used in all experiments for washing or dilution.

Methods

Bleaching

The TCF bleaching sequences used, as applied in soda bagasse pulp bleaching, were OQPQP, OQPoQP, OQPPa, OQPpaQP, OQOxQP, OQPoPa, and OQPoOx. Table 1 indicated the condition of each stage. Q stages (chelation stages) were performed by using DTPA (diethylene triamine pentaacetic acid) charge of 0.3 % (based on o. d. pulp), at a controlled pH of 4–5. Peroxide activation in the Pa stage was conducted by applying TAED with the constant molar ratio of 0.3 to peroxide (the molar mass of the TAED activator is $228.25 \text{ g mol}^{-1}$). Pulp consistency of all stages was 10 % and all chemicals were used based on oven dried pulp.

Measurements

After the completion of each stage a sample was collected to analyze the kappa number (Standard of SCAN-C 1:00), viscosity (Standard of ISO/FDIS 5351:2009), and brightness (Standard of SCAN-CM 11:95 and ISO 2470). Hexenuronic acid (HexA) content of pulp samples was determined as per the Tappi Test Method T 282 pm-07 based on the procedure developed by Chai et al. (2001). The metal contents (Fe, Mg, Mn, and Cu) of the pulp samples were determined by the method of flame atomic absorption spectrophotometry (Shimadzo AA-7000).

The yield of each stage was measured by weighing the resulted air-dried pulp and determining its moisture content (Standard of TAPPI T 412 OM-94).

Selectivity values were calculated as a function of both the Kappa number drop and the loss of viscosity, according to the equation 1 (Zeinaly 2014).

$$S = \frac{1 - (K_f/K_i)}{1 - (\eta_f/\eta_i)} \quad (1)$$

S: Process selectivity

K_i : Initial kappa number

K_f : Final kappa number

η_i : Initial viscosity

η_f : Final viscosity

At the completion of the bleaching time, the pulp sample was diluted to 4 % suspension with deionized water. The well-mixed pulp suspension was then filtered by a 200-mesh Teflon screen in a Büchner funnel, after that, the thin layer of pulp was washed with deionized water in a constant ratio of 1 liter per 100 g of pulp. The resultant filtrate was further filtered with a Whatman medium-fast filter paper to remove the residual fines, and then used for determining the COD (Standard Method 5220 D).

All treatments and measurements were carried out thrice. ANOVA test at a 95 % ($\alpha = 0.05$) confidence interval was applied to analyze the results, and the Duncan test was used to categorize acquired means of the results. The means with the same letter (mentioned lower cases in tables and figures) are not significantly different at the confidence level of 95 %.

Results and discussion

In bagasse fibers, the main hemicellulose is composed of a backbone of xylose, branched with glucose and arabinose units (Sun et al. 2004, Walford 2008, Zeinaly et al. 2017a) (Figure 1). Hexenuronic acid groups are formed as a result of base-catalyzed elimination of methanol from 4-O-methyl-D-glucurnoxylans, in the alkaline condition, but in the mild acidic condition there is no formation of these groups and also deformation of 4-O-methylglucuronic acid groups (Jiang et al. 2000).

Hence, the HexA groups' content in unbleached soda bagasse pulp was slight (7.70 $\mu\text{mol/g}$), the further treatments to remove HexA (like hot acid pretreatment) were not necessary and pulp bleachability by all bleaching agents, especially electrophilic reagents, would not have any problem. Actually, these unsaturated sugars are the active consumers of electrophilic reagents such as ozone, peracetic acid and chlorine dioxide; however, they are relatively inert to nucleophilic reagents like alkaline peroxide and oxygen (Vuorinen et al. 1996, Nie et al. 2015). Among

Table 1: Bleaching stages condition.

Stage	Time (min)	Temp. (°C)	H ₂ O ₂ (%)	NaOH (%)	Oxone (%)	DTPA (%)	O ₂ Pressure (bar)	MgSO ₄ (%)
O ₉₀	60	90	–	2.5	–	–	5	0.3
O ₁₀₀	60	100	–	2.5	–	–	5	0.3
O ₁₁₀	60	110	–	2.5	–	–	5	0.3
Q	60	70	–	–	–	0.3	–	–
P	60	90	2.0	2.0	–	0.1	–	0.1
P	120	90	2.0	2.0	–	0.1	–	0.1
P	180	90	2.0	2.0	–	0.1	–	0.1
P	240	90	2.0	2.0	–	0.1	–	0.1
P	180	90	2.0	1.5	–	0.1	–	0.1
P	180	90	2.0	2.5	–	0.1	–	0.1
Po	45	100	2.0	2.0	–	0.1	5	0.1
Po	60	100	2.0	2.0	–	0.1	5	0.1
Po	75	100	2.0	2.0	–	0.1	5	0.1
Po	90	100	2.0	2.0	–	0.1	5	0.1
Po	60	90	2.0	2.0	–	0.1	5	0.1
Po	60	110	2.0	2.0	–	0.1	5	0.1
Pa	60	70	2.0	2.0	–	0.1	–	0.1
Pa	90	70	2.0	2.0	–	0.1	–	0.1
Pa	120	70	2.0	2.0	–	0.1	–	0.1
Pa	150	70	2.0	2.0	–	0.1	–	0.1
Pa	90	60	2.0	2.0	–	0.1	–	0.1
Pa	90	80	2.0	2.0	–	0.1	–	0.1
Pa	90	90	2.0	2.0	–	0.1	–	0.1
Ox	60	70	–	2.5	5	0.1	–	0.1
Ox	90	70	–	2.5	5	0.1	–	0.1
Ox	120	70	–	2.5	5	0.1	–	0.1
Ox	150	70	–	2.5	5	0.1	–	0.1
Ox	90	60	–	2.5	5	0.1	–	0.1
Ox	90	80	–	2.5	5	0.1	–	0.1
Ox	90	90	–	2.5	5	0.1	–	0.1

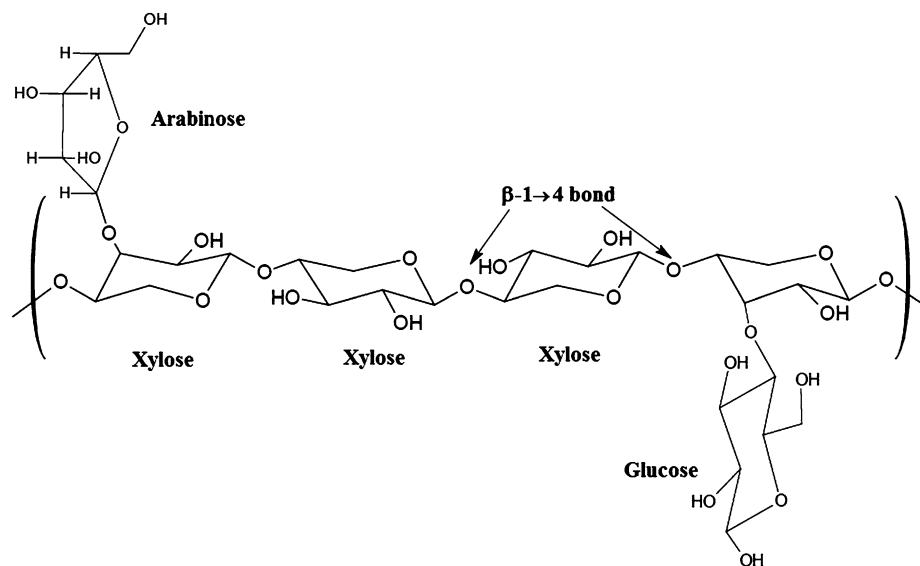


Figure 1: Simplified structure of bagasse main hemicellulose (Zeinaly 2014).

Table 2: Oxygen delignified pulp properties.

Reaction temp. (°C)	Kappa number	Yield (%)	HexA ($\mu\text{mol/g}$)	Viscosity (ml/g)	Brightness (%)	COD (g/kg-odp)
90	11.27 ^[a]	96.3 ^[a]	7.16 ^[a]	1007 ^[a]	41.51 ^[b]	31.72 ^[c]
100	9.81 ^[b]	94.8 ^[b]	6.41 ^[b]	999 ^[a]	41.93 ^[a-b]	48.63 ^[b]
110	8.55 ^[c]	93.6 ^[c]	6.25 ^[b]	997 ^[a]	42.47 ^[a]	59.83 ^[a]

different alkaline pulping processes, the lowest amount of HexA belongs to the soda process (Jiang et al. 2000); in some research, it has been reported that the increase in selective lignin removal leads to the creation of many HexA groups (Buchert et al. 1996, Lindström and Larsson 2005, Ek et al. 2009), since the hexenuronic acid groups are known as xylan chain protectors toward the alkali peeling reaction (Jiang et al. 2000). In addition, the viscosity of the soda pulp was comparable to that of other reports (Mohta et al. 1998a, Mohta et al. 1998b, Hostachy 2009) and it was in an appropriate level for the pulp bleaching.

Results of the oxygen delignification process are shown in Table 2. As it was expected, the oxygen delignification at the higher reaction temperature (110 °C) had the greatest effect on the chemical composition of the delignified pulp. Kappa number reductions of the delignified pulps were, respectively, 47, 54 and 60 % at the three different reaction temperatures of 90, 100 and 110 °C. Results indicated that the oxygen delignification was an efficient process to delignify soda bagasse pulp selectively, because the pulp viscosity had not been reduced by this process. Additionally, the 60 % decrease in the kappa number at the reaction temperature of 110 °C showed the high performance of this process, since normally the kappa number reduction in single-stage oxygen delignification has been reported in the range of 35–50 % (Bajpai 2005). Therefore, in all of the bleaching sequences, 110 °C was the applied temperature for the oxygen delignifying treatment. Moreover, results showed that with the rise in the reaction temperature in oxygen delignification treatment, the selective lignin removal also increased, and so the process selectivity rose up.

A greater degree of residual lignin structure accessibility in bagasse soda pulp for oxygen-delignifying agents, predominant elimination of xylan hemicelluloses by soda pulping process, and so, the slight amount of pulp HexA content, which is a waster of chemicals, were reasons of high efficiency of the oxygen delignification process.

Due to relatively low solubility of oxygen to the alkaline liquor, the delignification reactor is pressurized and the temperature is elevated to about 100 °C. The additional evaporator steam requirements are from 4–10 %

Table 3: Pulp metal contents.

Pulp sample	Fe (ppm)	Mn (ppm)	Cu (ppm)	Mg (ppm)
Unbleached	5.71 ^[a]	0.15 ^[a]	0.03 ^[a]	2.60 ^[c]
Before Q ₁	5.32 ^[a]	0.17 ^[a]	0.03 ^[a]	195.12 ^[a]
After Q ₁	4.51 ^[b]	0.08 ^[b]	<0.01	84.23 ^[b]

for medium consistency system. Its operating costs are 2.5–3.0 MEuro/a. However, the oxygen delignification will decrease the chemical consumption in bleaching (European Commission 2001).

The second applied stage in all of the sequences was the chelation (Q) stage; its goal had been to prevent the adverse effects of metal ions on oxidizing agents in the subsequent bleaching stages. The acidic condition of the Q stage and further pulp washing caused a reduction in the metal contents of the pulp (Table 3). Except in HexA content, the pulp properties did not change after the Q stage; also, COD load of the filtrate was placed in its lowest amount, because of the established mild condition and no decomposition of the organic compounds in this stage. Furthermore, there was a slight decrease in HexA content affected by the acidic condition of the Q₁ stage (Table 4).

Decomposition of peroxide under alkaline conditions is greatly influenced by the presence of certain inorganic compounds, which, depending on their effect, can be termed peroxide decomposition “catalysts” (transition metals as Fe, Mn and Cu) or “stabilizers” (like alkali-earth metal Mg) (Basta et al. 1991). The cause of the increase in magnesium level in the pulp after oxygen delignification can be referred to the use of magnesium sulfate as a stabilizer in the oxygen delignification process (Table 3).

The optimum conditions of every used stage in examined sequences were obtained by conducting several treatments at variable conditions (Table 1). Primary results showed the effect of processing time on the properties of the single stage-treated pulps (Figures 2–5). As shown in Figure 2, in P₁ stage, the extension of reaction time from 60 to 180 min had a relatively considerable effect on the kappa reduction, as well as a mild impact on the reduction of pulp viscosity and process selectivity. Extending the reaction time to 240 min led to an intense fall in the

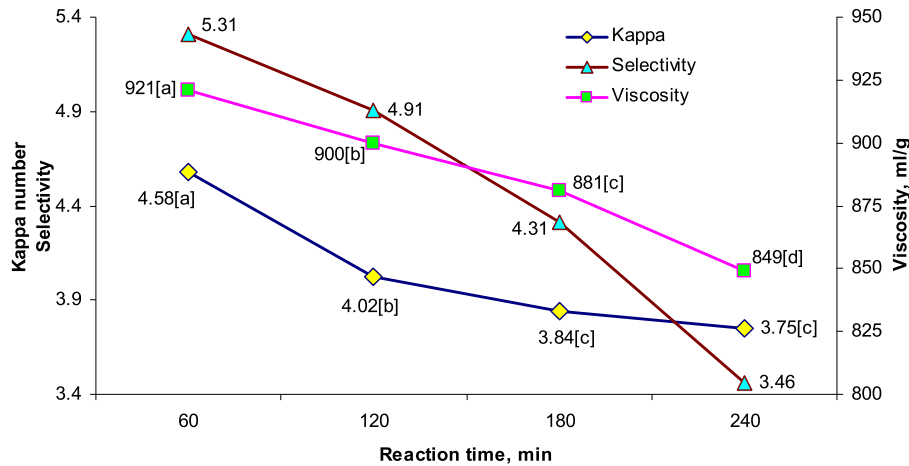


Figure 2: The effect of reaction time on pulp properties in P_1 stage (90 °C).

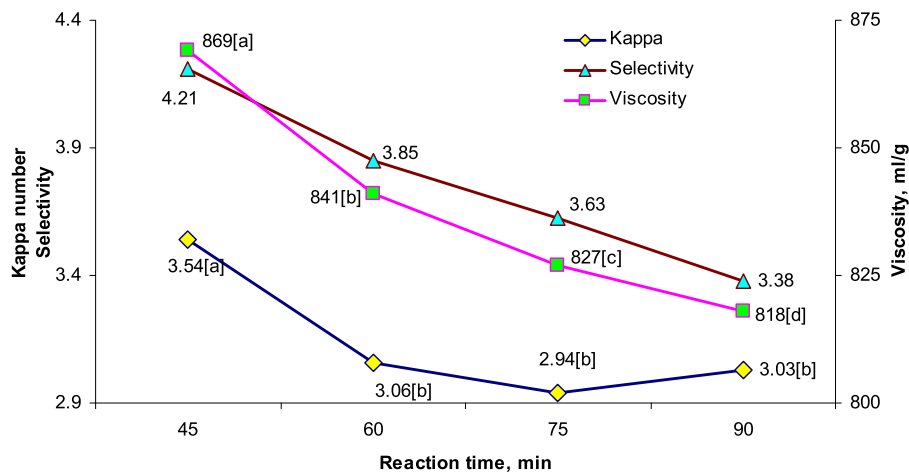


Figure 3: The effect of reaction time on pulp properties in P_0 stage (100 °C).

process selectivity, while the kappa number had a negligible change.

In P_0 stage, the reaction time extension of more than 60 min did not have any meaningful result in the reduction of kappa number, while the pulp viscosity and process selectivity decreased (Figure 3).

In P_1 stage, the process selectivity did not decrease during the first 120 min of reaction time, but further retention time caused process selectivity and pulp viscosity to decrease. Moreover, the kappa number reduction trend had almost stopped after 120 min (Figure 4). Finally, in Ox_1 stage, the most efficient bleaching was achieved at the 90 min-reaction time, after which the process selectivity was intensely reduced, while the kappa number remained almost constant (Figure 5).

In Figure 6, the constant peroxide charge (2%) of P_1 stage, the effect of different levels of alkali charge on

bleaching process is shown. Results indicated that the high level of alkali charge (2.5 %) led to an intense reduction of the selectivity and the pulp viscosity but had no significant influence on the kappa reduction trend.

The effect of reaction temperature on the kappa number, the pulp viscosity and the process selectivity in P_0 , P_1 and Ox_1 stages is reported in Figure 6. Results show that the increase of the temperature to 100 °C had relatively positive effects on the process results of P_0 stage; on the other hand, applying more heat caused a severe drop in the process selectivity.

According to the results displayed in Figure 6, the ideal reactive temperature, in both P_0 and Ox_1 stages, was 70 °C. At this temperature, the process selectivity was at its highest amount and the kappa number significantly decreased, while the decline of the pulp viscosity was not so severe.

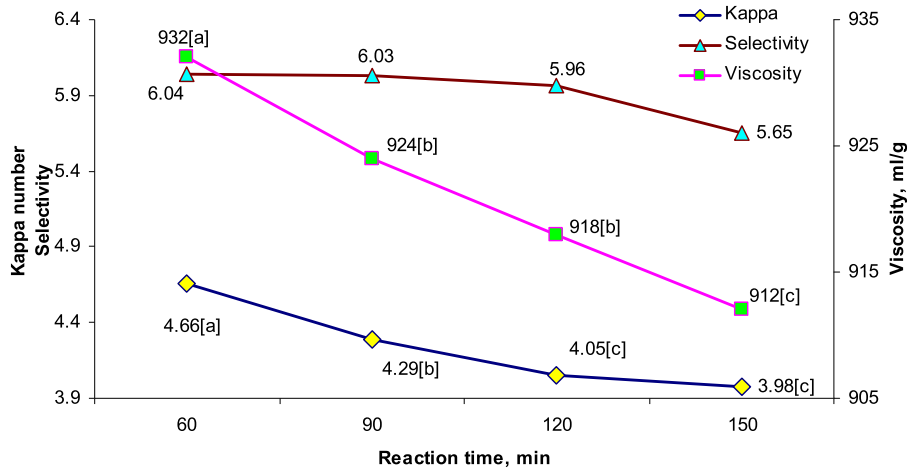


Figure 4: The effect of reaction time on pulp properties in Pa₁ stage (70 °C).

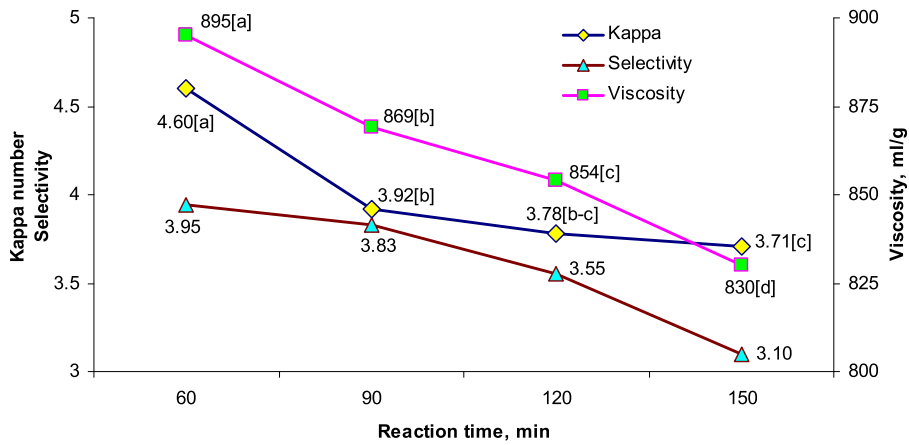


Figure 5: The effect of reaction time on pulp properties in Ox₁ stage (70 °C).

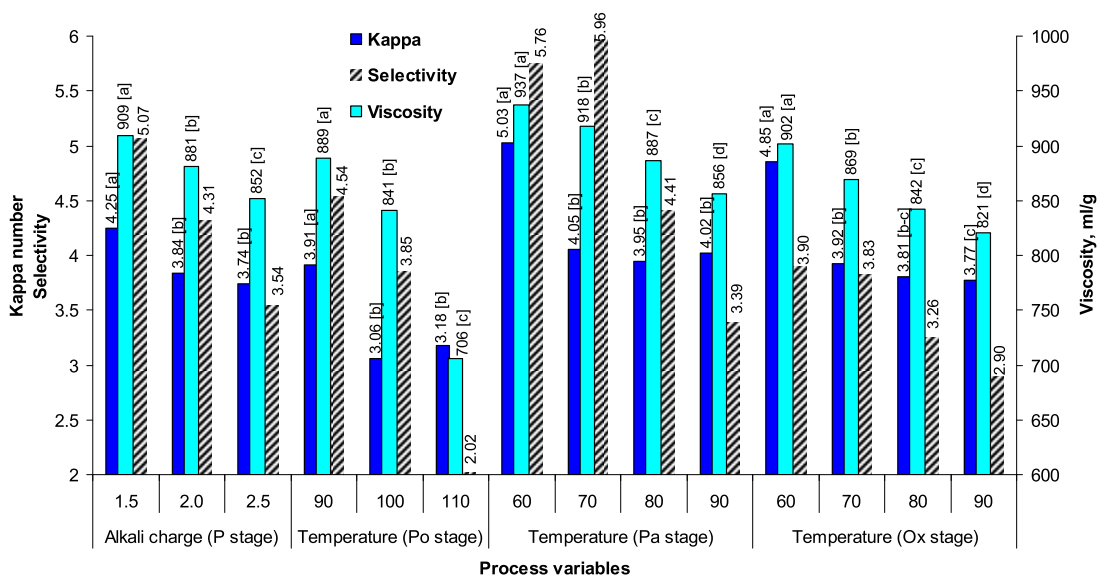


Figure 6: The effect of the process variables on pulp properties in P₁ (90 °C, 180 min), Po (60 min), Pa₁ (90 min) and Ox₁ (90 min) stages.

Table 4: Pulp properties at each stage of sequences.

Process position	Stages	Kappa	Yield (%)	Hex.A ($\mu\text{mol/g}$)	Viscosity (ml/g)	Selectivity factor	Brightness (%)	COD (g/kg-odp)
After Pulping	O ₁₁₀	8.55 ^[a]	93.6	6.25	997 ^[a]	–	42.47 ^[i]	59.83
Before Bleaching	Q ₁	7.76 ^[b]	98.9	2.71	998 ^[a]	–	44.09 ^[h]	6.41
Primary Stages	P ₁	3.84 ^[d]	97.4	1.63	881 ^[c]	4.46	71.98 ^[e]	20.37
	Po	3.06 ^[e]	96.7	2.67	841 ^[e]	3.85	72.27 ^[e]	31.68
	Pa ₁	4.05 ^[c]	98.2	1.74	918 ^[b]	5.96	69.7 ^[f]	19.34
	Ox ₁	3.92 ^[c-d]	98.2	2.09	869 ^[d]	3.83	64.45 ^[g]	20.41
Seq. Mid	P ₁ Q ₂	3.81 ^[d]	99.4	1.95	889 ^[c]	–	72.23 ^[e]	6.10
	PoQ ₂	3.00 ^[e]	99.2	1.75	840 ^[e]	–	72.79 ^[e]	6.00
	Pa ₁ Q ₂	4.00 ^[c]	99.5	–	920 ^[b]	–	70.55 ^[f]	–
	Ox ₁ Q ₂	3.94 ^[c-d]	99.4	–	871 ^[d]	–	65.08 ^[g]	–
Secondary Stages	P ₁ Q ₂ P ₂	2.63 ^[f]	97.2	1.64	713 ^[h]	1.56	75.81 ^[d]	23.65
	PoQ ₂ P ₂	2.26 ^[h]	97.8	2.58	684 ^[i]	1.33	76.96 ^[c]	20.81
	P ₁ Pa ₂	2.50 ^[g]	98.1	0.35	775 ^[f]	2.90	77.66 ^[c]	18.58
	Pa ₁ Q ₂ P ₂	2.44 ^[g]	97.8	1.24	750 ^[g]	2.11	77.82 ^[b-c]	20.02
	Ox ₁ Q ₂ P ₂	2.38 ^[g-h]	97.9	1.33	706 ^[h]	2.09	77.02 ^[c]	19.84
	PoPa ₂	1.78 ^[i]	98.0	0.28	752 ^[g]	3.95	79.96 ^[a]	18.83
	PoOx ₂	1.75 ^[i]	98.0	–	710 ^[h]	2.75	78.51 ^[b]	19.02

The bleaching sequence of OQPQP had a target brightness of 75.81 and a kappa number of 2.63. In this sequence, the first peroxide stage (P₁) was more effective in lignin removal and brightness increase than the second peroxide stage (P₂); also, the pulp viscosity drop was higher in the P₂ stage than the P₁ stage (Table 4). The reason was the existence of a high level of lignin in the pulp, and so, an efficient accessibility for the selective removal of the lignin by oxidative agents at the first stage (P₁). In addition, the high number of phenolic groups in the P₁ stage made the lignin more reactive towards the alkaline peroxide (Suess 2010). Actually, the main bleaching agent at the peroxide process is hydroperoxide ion (HOO⁻) and the bleaching reaction is attributed to the oxidative action of this nucleophilic agent, which is produced by the dissociation of hydrogen peroxide in alkaline conditions (Singh 1991, Sixta 2006, Zeinaly et al. 2013). The principal action of the hydroperoxide ion is a nucleophilic attack on the quinone structures and conjugated side chains; it does not have any considerable effect on the lignin aromatic rings (Bajpai 2005, Suess 2010). Thus, the hydroperoxide ion is actually more of a brightening agent than an extensive lignin remover.

However, the creation of hydroxyl radical (HO•) and anionic superoxide radical (O₂⁻•) caused an extensive lignin elimination through the polymer decomposition and dissolution. Certain transition metals (e. g., manganese, copper and iron) catalyze peroxide decomposition and contribute to the formation of hydroxyl radicals and superoxide anion radicals (Singh 1991, Suess 2010). The above-mentioned radicals electrophilically attack the

lignin aromatic rings (electron-rich areas), resulting in an oxidative decomposition and an increase in molecular hydrophilicity and solubility of the lignin. However, the reactivity of HO• and O₂⁻• towards the aromatic lignin (phenolic structures) is only slightly higher than towards cellulose (primary and secondary alcohols). Therefore, in high concentrations of such radicals (HO• and O₂⁻•), process selectivity is lost, and cellulose degradation occurs along with the lignin degradation (Bajpai 2005, Zeinaly 2014).

Thus, it is common practice to add magnesium sulfate and sodium silicate to the bleach liquor as stabilizing, buffering agents and carbohydrate protectors (Zeinaly et al. 2016b). Mg²⁺ and SiO₃²⁻ make complexes with harmful transition metals through oxy or hydroxy bridges that change the catalytic activity of the transition metals with regard to H₂O₂ decomposition (Bajpai 2005).

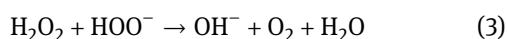
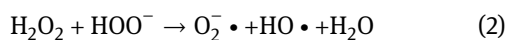
Figure 2 shows that the lignin elimination was at its highest level in the primary phase of the P₁ stage, and it was reduced during the process. The reason for the limited turnover of hydrogen peroxide is the reduction of reactive sites in the remaining lignin during the process time (Suess 2010, Zeinaly 2014). Also, the ratio of carbohydrate decomposition to the lignin removal increased during the process time. In fact, while the accessibility of the lignin reaction sites and its depolymerization were decreasing, it was expected for the carbohydrate degradation to increase, and the process selectivity to decrease (Figure 2).

The formation of the sequence OQPQP via substitution of the P₁ stage with Po improved the bleaching process, owing to the fact that the final brightness of the pulp rose to 76.96 and the kappa number reduced to 2.26, while

the viscosity loss increased slightly (684) (Table 4). Results showed that the Po stage had extended lignin elimination in less process time (60 min) compared to that of the P₁ stage (180 min) and the kappa number reduction value was 60 %. The process selectivity was relatively satisfactory (Table 4).

The use of pressurized oxygen (5 bar O₂) and the existence of a more intense condition (higher temperature) at the Po stage, increased the peroxide capability of removing lignin and decreased the needed reaction time. This improvement in the bleaching process is the result of: 1) reducing the self-decomposition of peroxide (Equations 2–4); 2) occurrence of more permeation of bleaching agents into the cellulosic fibers and 3) the act of bleaching and lignin removal by further oxygen charge (Nishimura et al. 1996). In fact, in pressurized systems, the reduction of peroxide self-decomposition, and so the resulting radicals occur, even without the presence of oxygen; thus, the destruction of carbohydrates by these radicals is decreased and the process selectivity is promoted (Nishimura et al. 1996, Zeinaly 2014).

Furthermore, in the oxygen-reinforced peroxide bleaching system, both nucleophile (e. g., hydroperoxide anion) and electrophile (e. g., oxygen biradical) bleaching agents could cooperatively participate in the degradation of chromophores, phenolic structures and conjugated aromatic structures in the residual lignin (Asgari and Argyropoulos 1998, Bajpai 2005).



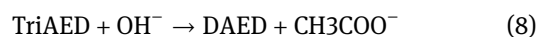
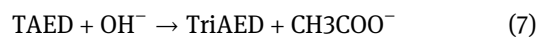
In the sequences of OQPoQP, the final P stage was more effective than the P₂ stage in the OQPQP sequence, and the kappa number reduction and the brightness-gain of this stage were respectively 2.26 and 76.96 (Table 4); its main reason for this efficacy was the increase in the reactive sites and the accessibility of the residual lignin, acquired by the previous intense bleaching stage (Po).

In the sequences of OQOxQP and OQPaQP, the main reactive agents in the Ox and Pa stages are the electrophilic bleaching agents. Therefore, the electrophilic attack was the dominant reaction for the lignin elimination. Oxone is a triple salt with the formula 2KHSO₅•KHSO₄•K₂SO₄, in which the active part is potassium peroxydisulfate (KHSO₅) and its bleaching activity is grouped in the peroxy acids function (Miri et al. 2015).

Results showed that the use of the Ox stage at the first stage of bleaching sequence caused the bleachability of the pulp to improve during the further bleaching

stage (P₂), as the final brightness of the bleached pulp and sequence selectivity factor were respectively increased to 77.02 and 2.09 (Table 4). The oxidation and hydroxylation reactions in the lignin aromatic rings took place by the function of potassium peroxydisulfate, which caused an increase in the number of free phenolic groups in the residual lignin and so an increase in the reactive sites in the remaining lignin during the next bleaching stage (Suess and Helmling 1987, Yaqoob et al. 2010).

The obtained results of the OQPaQP sequence indicated that the activated peroxide stage (Pa) in the first stage of the bleaching process was more efficient than the Ox stage, and the final brightness value and process selectivity in OQPaQP sequence were higher than in the OQOxQP sequence (Table 4). Bleaching improvement in the sequence of OQPaQP was related to the changing nature of reactive agents and also higher bleachability of Pa stage at the milder condition (lower temperature, alkalinity and remain-time). In the activated peroxide stage, electrophilic agents, peracetic acid (CH₃COOOH) or peracetate anion (CH₃COO⁻), are produced by the reaction of TAED activator with hydroperoxide anion (HOO⁻) in the alkaline environment (Equations 5–8) and have more oxidation properties compare to nucleophilic hydroperoxide anion. They can attack the electron-saturated aromatic rings in the residual lignin and destroy them. The formation of acetic acid through the reaction of TAED with hydroxyl anion (HO⁻) in the alkaline environment assists in the delignification of the pulp (Couchariere et al. 2002, Zeinaly et al. 2017b).



In the sequences of OQPoPa and OQPoOx, the forceful primary stage of Po was used, and the extensive delignification was performed on the pulp. The second Q stage was removed from these sequences, because the Q treatment lacks any important effect on the pulp bleachability in the activated peroxide and peroxy acids stages (Zeinaly et al. 2013, Miri et al. 2015). In these stages, the pH falls to neutral and slightly acidic and the undesirable effects of transition metal ions often occur at high pH levels. Furthermore, the predominant bleaching agents in these stages are peroxy acids, such as peracetic acid or peracetate anion, which are insensitive to heavy metal ions (Zeinaly et al. 2013).

Results indicated that the use of activated peroxide (Pa) in the second stage was efficient and the brightness

gain was at the highest amount, 79.96 %. Moreover, the Pa stage was conducted in nearly neutral condition; thus, in this condition the D.P of carbohydrate chains does not significantly reduce compared to other stages (Table 4).

Conclusions

Results indicated that the O₂ treatment at the reaction temperature of 110 °C was an efficient process to reduce lignin content of soda bagasse pulp, selectively (about 60 %), while the pulp viscosity did not decline. As the O₂-stage effluent is usually sent to the recovery boiler, the 60 % reduction of lignin content results in the reduction of bleaching effluent volume and its COD content that is piped to the wastewater treatment plant.

Obtained results from the first stage experiments showed that the lowest kappa number and highest selectivity were, respectively, achieved by the Po and Pa stages. The TAED-activated peroxide at the first and second stages were more effective than in the Ox stages, because the selectivity factor amounts in the Pa stages were greater than those of the Ox stages, while the kappa number levels of the Ox stages were slightly lower than those of the Pa stages.

Moreover, results showed that both sequences of OQPoPa and OQPoOx could reach the minimum level of kappa number (about 1.7), but the target brightness (80 %) was reached only by the sequence of OQPoPa with a comparatively high level of final pulp viscosity (752 ml/g).

Acknowledgments: The authors are grateful to Åbo Akademi University, Pars Paper Company, Gorgan University of Agricultural Sciences and Natural Resources and Karaj Azad University for technical, materials and chemicals preparation support. We also appreciate Nooshin Zeinaly for her help during this research. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Conflict of interest: The authors declare no conflicts of interest.

References

- Asgari, F., Argyropoulos, D.S. (1998) Fundamentals of oxygen delignification. Part II. Functional group formation/elimination in residual kraft lignin. *Can. J. Chem.* 76:1606–1615.
- Bajpai, P. (2005) Environmentally benign approaches for pulp bleaching. In: *Developments in Environmental Management*, first ed. Elsevier, Amsterdam, Netherlands.

- Basta, J., Holtinger, L., Hook, J. (1991) Controlling the profile of metals in the pulp before hydrogen peroxide treatment. In: *Proceedings, 6th Int. Symposium Wood and Pulping Chemistry*. Appita, Melbourne, Australia.
- Boruah, P., Dowarah, P., Hazarika, R., Yadav, A., Barkakati, P., Goswami, T. (2016) Xylanase from *Penicillium meleagrinum* var. *viridiflavum* – a potential source for bamboo pulp bleaching. *J. Clean. Prod.* 116:259–267.
- Buchert, J., Tenkanen, M., Ek, M., Teleman, A., Viikari, L., Vuorinen, T. (1996) Effects of pulping and bleaching on pulp carbohydrates and technical properties. In: *Proceedings, Int. Pulp Bleaching Conf.*, Washington DC., USA.
- Chai, X.S., Zhu, J.Y., Li, J. (2001) A simple and rapid method to determine hexenuronic acid groups in chemical pulps. *J. Pulp Pap. Sci.* 27(5):165–170.
- Couchariere, C., Mortha, G., Lachenal, D., Briois, L., Larnicol, P. (2002) Rationalization of the use of TAED during activated peroxide delignification and bleaching. Part I: kinetic model. *J. Pulp Pap. Sci.* 28(10):332–340.
- Ek, M., Gellerstedt, G., Henriksson, G. *Pulp and Paper Chemistry and Technology*, Volume 2, first ed. Walter de Gruyter GmbH & Co, Berlin, Germany, 2009.
- EUROPEAN COMMISSION (2001) *Integrated Pollution Prevention and Control (IPPC). Reference Document on Best Available Techniques in the Pulp and Paper Industry*.
- Fang, L., Zheng, M., Liu, G., Zhao, Y., Liu, W., Huang, L., Guo, L. (2017) Unexpected promotion of PCDD/F formation by enzyme-aided Cl₂ bleaching in non-wood pulp and paper mill. *Chemosphere* 168:523–528.
- Genco, J.M., Heiningen, A.R.P.V., Miller, W. (2012) Oxygen delignification. In: *The Bleaching of Pulp*, fifth ed. Eds. Hart, P.W., Rudie, A.W. Tappi Press, Atlanta, USA.
- Hostachy, J.C. (2009) Bagasse pulp bleaching with ozone: it's time to implement green bleaching practices. In: *Proceedings, Int. Technical Conf.*, New Delhi, India.
- Jafari, V., Sixta, H., Heiningen, A.V. (2014) Multi stage oxygen delignification of high-kappa pine kraft pulp with peroxymonosulfuric acid (Px). *Holzforschung* 68(5):497–504.
- Jiang, Z.H., Lierop, B.V., Berry, R. (2000) Hexenuronic acid groups in pulping and bleaching chemistry. *Tappi J.* 83(1):167–175.
- Khristova, P., Tomkinson, J., Lloyd Jones, G. (2003) Multi stage peroxide bleaching of French hemp. *Ind. Crop. Prod.* 18:101–110.
- Lindström, L.A., Larsson, P.E. (2005) Fiber lines for bleached eucalyptus kraft pulps – Impact on bleachability and pulp properties. *Metso Paper's Fiber Technology Center*, Sundsvall, Sweden.
- Miri, M., Ghasemian, A., Resalati, H., Zeinaly, F. (2015) Total chlorine-free bleaching of *Populus deltoides* kraft pulp by oxone. *Int. J. Carbohydr. Chem.* 15:1–8.
- Mohta, D., Kapoor, S.K., Ray, A.K. (1998a) Environmentally Friendly Pulping and Bleaching of Bagasse. University of Roorkee, Saharanpur-247 001, U.P., India.
- Mohta, D., Upadhyaya, J.S., Kapoor, S.K., Ray, A.K., Roy, D.N. (1998b) Oxygen delignification of soda and soda-AQ bagasse pulps. *Tappi J.* 81(6):184–187.
- Nie, S., Wang, S., Qin, C., Yao, S., Ebonka, J.F., Song, X., Li, K. (2015) Removal of hexenuronic acid by xylanase to reduce adsorbable organic halides formation in chlorine dioxide bleaching of bagasse pulp. *Bioresour. Technol.* 196:413–417.

- Nishimura, T., Hamaguchi, K., Iwasaki, M., Yamamoto, T. (1996) Application of pressurized hydrogen peroxide bleaching to TCF pulp production. In: Proceedings, Int. Pulp Bleaching Con., Washington DC., USA.
- Pars Paper Co. (2018) Pulping and bleaching process. Overall Report. Ahvaz, Iran.
- Rolf, B., Christina, J., Ke, L.L., Yngve, L. (2009) Non-wood pulping technology present status and future. *Ippta J.* 21:115–120.
- Sadhasivam, S., Savitha, S., Swaminathan, K. (2010) Deployment of *Trichoderma harzianum* WL1 laccase in pulp bleaching and paper industry effluent treatment. *J. Clean. Prod.* 18:799–806.
- Singh, R.P. *The Bleaching of Pulp*, first ed. TAPPI Press, Atlanta, USA, 1991.
- Sixta, H. *Handbook of Pulp*, first ed. Strauss GmbH, Morlenbach, Germany, 2006.
- Suess, H.U. *Pulp Bleaching Today*, first ed. Walter de Gruyter GmbH & Co. KG, Berlin, Germany, 2010.
- Suess, H.U., Helmling, O. (1987) Acid hydrogen peroxide/oxygen treatment of kraft pulp prior to oxygen delignification. In: Proceedings, Int. Oxygen Delignification Conf., San Diego, USA.
- Sun, J.X., Sun, X.F., Sun, R.C., Su, Y.Q. (2004) Fractional extraction and structural characterization of sugarcane bagasse hemicelluloses. *Carbohydr. Polym.* 56:195–204.
- Vuorinen, T., Buchert, J., Teleman, A., Fagerstrom, P. (1996) Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of Kraft pulps. In: Proceedings, Int. Pulp Bleaching Conf., Atlanta, USA.
- Walford, S.N. (2008) Sugarcane bagasse: how easy is it to measure its constituents. In: Proceedings, South African Sugar Technologists Association, Durban, South African.
- Walker, J.C.F. *Primary Wood Processing: Principles And Practice*, second ed. Springer, Dordrecht, Netherlands, 2006.
- Xiao, Q., Song, X., Li, W., Zhang, Y., Wang, H. (2017) A primary estimation of PCDD/Fs release reduction from non-wood pulp and paper industry in China based on the investigation of pulp bleaching with chlorine converting to chlorine dioxide. *Chemosphere* 185:329–335.
- Yaqoob, N., Stack, K., Nguyen, K.L. (2010) TCF bleaching of eucalypt kraft pulp with oxone. *Appita J.* 63(5):381–386.
- Zeinaly, F. (2014) Investigating the Effects of Open and Semi Closed Loop Systems in Totally Chlorine Free (TCF) Bleaching on Bagasse Soda Bleached Pulp Properties. PhD thesis, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran.
- Zeinaly, F., Karimi, M., Shakhes, J., Mohammadi, H. (2016b) Improving the bleaching process of hardwood chemi-mechanical pulp. *Cellul. Chem. Technol. J.* 50(2):285–292.
- Zeinaly, F., Kazemi Tabrizi, A., Einollahi, Y., Asadi Malek Jahan, F. (2018) Investigating the effect of using oxygen delignification process on kenaf bast kraft pulp properties. *Iran. J. Wood Pap. Sci. Res.* 33(3):367–377.
- Zeinaly, F., Kazemi Tabrizi, A., Shakhes, J., Zeinali, N. (2017b) The use of TAED in the last phase of CMP peroxide bleaching. *Nord. Pulp Pap. Res. J.* 32(2):189–194.
- Zeinaly, F., Saraeian, A.R., Aryaie Monfared, M.H., Kazemi Tabrizi, A. (2016a) Investigating the effect of using oxygen delignification process on bagasse soda pulp properties. *Iran. J. Wood Pap. Sci. Res.* 26(2):339–351.
- Zeinaly, F., Saraeian, A.R., Gabov, K., Fardim, P. (2017a) Determination of carbohydrates in sugarcane bagasse pulp in different TCF bleaching sequences. *Cellul. Chem. Technol. J.* 50(1–2):45–53.
- Zeinaly, F., Shakhes, J., Zeinali, N. (2013) Multi stage peroxide and activated peroxide bleaching of kenaf bast pulp. *Carbohydr. Polym.* 92:976–981.