

Improved Ozone Bleaching By Impregnation of Chemical Pulps With An Acidified Mixture of 1, 4-Dioxane And Water

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ABSTRACT

Ozone has become one of the alternative pulp bleaching chemicals to chlorine and chlorine dioxide in the Pulp and Paper Industry. However, ozone pulp bleaching is still limited by the severe cellulose degradation which occurs at higher ozone charges. In this paper, it will be described that 1, 4-dioxane, when present in the right proportion with water inside the pulp fibers, serves as an effective cellulose protector during ozone bleaching. When hemlock kraft pulp with a kappa number of 31.9 and viscosity of 35.8 mPa.s was impregnated with a 70% dioxane solution of pH 2.3, and subsequently was treated at about 40% consistency with a 2% ozone charge, a semi-bleached pulp with a kappa number of 4-5 and viscosity of about 28 mPa.s can be obtained after a standard oxidative extraction. This result shows a lignin-carbohydrate selectivity similar to that of chlorine dioxide bleaching. It is found that the presence of dioxane in the impregnation liquor does not affect the delignification efficiency. The effects of process parameters, such as pH, dioxane concentration and ozone charge, will be described.

In the remaining part of the paper, the underlying mechanism of the cellulose protection is examined. It is proposed that dioxane may scavenge the hydroxyl radicals generated in the ozone-lignin reactions. In addition, the dioxane containing impregnation liquor may deswell the carbohydrate-rich fractions while swell the lignin-rich fractions so that the accessibility of the carbohydrate-rich fractions relative to that of the lignin-rich fractions by ozone becomes smaller in dioxane containing solution than that in water.

INTRODUCTION

Chlorine based chemicals, such as chlorine and chlorine dioxide, have been used in pulp bleaching for several decades to achieve high brightnesses. However, in recent years there has been a growing concern about the environmental impact of chlorinated organic compounds present in bleached paper products and in pulp mill bleached effluents. One of the solutions to this problem is replacing chlorine with oxygen containing delignification reagents, such as

ozone and hydrogen peroxide. The drawbacks of ozone bleaching which delayed its industrial adoption include: the cost of ozone, the relative low solubility of ozone

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in water combined with its low concentration in air or oxygen as produced by commercial ozone generators, and the degradation of carbohydrates. Presently, the first two problems appear less important because of advances in ozone generation technology and the development appear less important because of advances in ozone generation technology and the development of medium consistency (MC) and high consistency (HC) ozone bleaching processes. However, the poor lignin-carbohydrate selectivity of ozone compared to other bleaching chemicals such as chlorine or chlorine dioxide, is presently still unresolved. It has been documented that the poorer selectivity leads to the production of less strong paper products (1). Therefore, for most full scale ozone installations, the charge of ozone is kept at a relatively low level of less than about 1% (on o.d. pulp) in order to keep the cellulose degradation within acceptable limits. The optimum pH for an ozone stage is between 2 and 3.

It is known that the presence of organic solvents, such as, methanol (2), ethanol (3), acetic acid (2) and DMSO (4), prevent the viscosity loss during ozone bleaching somewhat. Recently, it was reported (5, 6) that when pulp is impregnated with an acidified solution containing methanol during ozone bleaching, followed by a standard E_0 stage, a well delignified pulp with characteristic properties similar to those obtained by chlorine and chlorine dioxide bleaching was produced. Therefore, this technology represents an opportunity to produce full bleached TCF pulp with good strength properties starting from conventional kraft pulp.

In this paper, we will report that 1, 4-dioxane, when present in the right proportion with water inside the pulp fibers, improves the lignin-cellulose selectivity during ozone bleaching to a level comparable to that of chlorine bleaching. The effects of process variables, such as pH, 1, 4-dioxane concentration and ozone charge will be described. The underlying mechanism of the cellulose protection during this novel ozone bleaching technology will also be discussed.

EXPERIMENTAL

A kraft Hemlock pulp (kappa no. 31.9, viscosity 35.8 mPa.s) was used in this study. It was stored in a refrigerator at 4°C and pulp consistency of about 35% throughout this study.

The ozone bleaching experiments were performed in a standard rotovap equipment modified with a fritted glass gas dispersion tube inserted in the rotating

round bottom flask. Equivalent to 10 grams of oven-dried pulp was impregnated with a 1, 4-dioxane solution at a desired concentration. Subsequently, the pulp sample was squeezed to remove excess of the impregnation liquor, fluffed and transferred to the flask of the rotovap equipment. The fluffing was performed in a specially designed apparatus, with rotating cylinders having teflon-coated teeth about 25 cm apart. The residence time during fluffing is about 10 seconds. The resulting pulp mass could be described as well fluffed. Ozone bleaching was initiated by contacting pulp at approximately 40% consistency with a 3.83% (by weight) ozone in air mixture introduced through the gas dispersion tube at a flow rate of 1.04 l/min. The unreacted ozone leaving the flask was captured in a wash bottle filled with a KI solution. The ozone captured in this manner was determined by iodometric titration. The ozone consumption was then calculated from the difference between the charged and unreacted amounts. The ozone charge can be varied by changing the time that the ozone-air mixture flows through the pulp. In order to minimize agglomeration of the fluffed pulp into ball-shaped clumps, the rotational speed of the flask was kept at a low level of 4-5 rpm. The ozonation of pulp was performed at room temperature.

The oxidative extraction stage, E (O) was performed in a Parr bomb reactor with a teflon liner. The process conditions were as follows: 2.0% NaOH, oxygen pressure of 205 kPa, 10% pulp consistency, 70°C 1 hour. After the above treatments, the pulp was washed thoroughly, made into a handsheet and air-dried for further analysis. Viscosity and kappa tests were performed in accordance with Tappi standard T-230 om-89 and T-236 om-85 respectively.

A centrifugation technique (13) was used for the determination of the fiber swelling. About 1.5 grams pulp fibers were first mixed with the appropriate amount of 1, 4-dioxane and water so that the desired dioxane concentration was obtained, and then disintegrated with a hand blender at a fiber consistency of about 0.5%. The fiber slurry was then kept in a covered container for about 2 hours to ensure that equilibrium was reached. Subsequently, the fibers were filtered and then placed on a special screen made in accordance with the recommendations by Scallan and Carles (13). A centrifuge, model Eppendorf 5416 was used in this study. The centrifugal force and centrifugation time were 900 g and 30 minutes respectively. The swelling was calculated as the volume (ml) of liquid retained per gram of moisture-free fibers after centrifugation.

RESULTS AND DISCUSSION

The kraft Hemlock pulp was subjected to ozone bleaching. In one case the pulp was impregnated with water which was acidified by sulfuric acid, and in the other case, an acidified aqueous solution containing 70.5% 1, 4-dioxane was used. The pH of both solutions was 1.8.

The ozone bleaching response of pulp impregnated with the dioxane-water solution and that with water alone is shown in Figures 1 and 2 respectively in the form of the (lignin) ozone reaction efficiency (the kappa number versus ozone consumption) and the (lignin-cellulose) ozone selectivity (the pulp viscosity versus kappa number). Figure-1 shows that the delignification of the dioxane-water impregnated pulps is somewhat higher at the same ozone consumption than that of the water impregnated pulp. More importantly, however, is the substantially lower viscosity loss at the same kappa number shown in Figure-2 for the dioxane-water impregnated pulps after ozonations as compared to the water impregnated pulps. In other words, these results show that the presence of 1, 4-dioxane in the impregnation liquor of the pulp during ozone bleaching leads to a substantial improvement in the (lignin-cellulose) ozone selectivity.

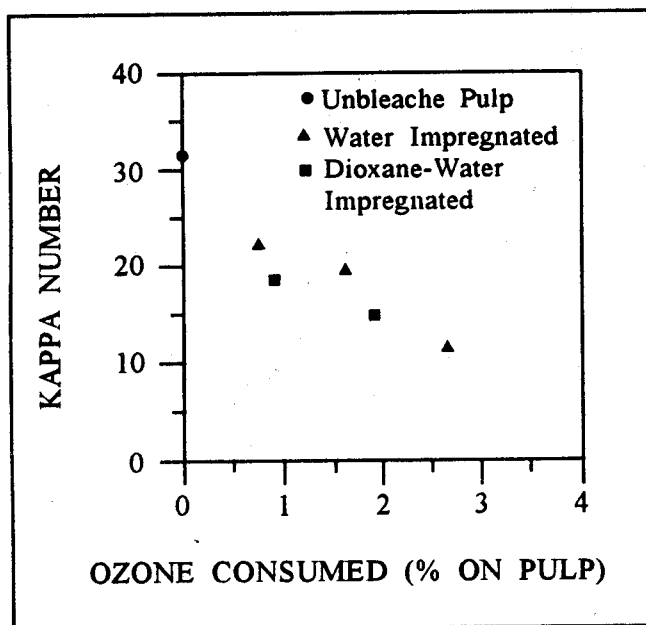


Fig.-1 Influence of the Presence of 1, 4-Dioxane in the Impregnation Solution on the (Lignin) Ozone Reaction Efficiency.

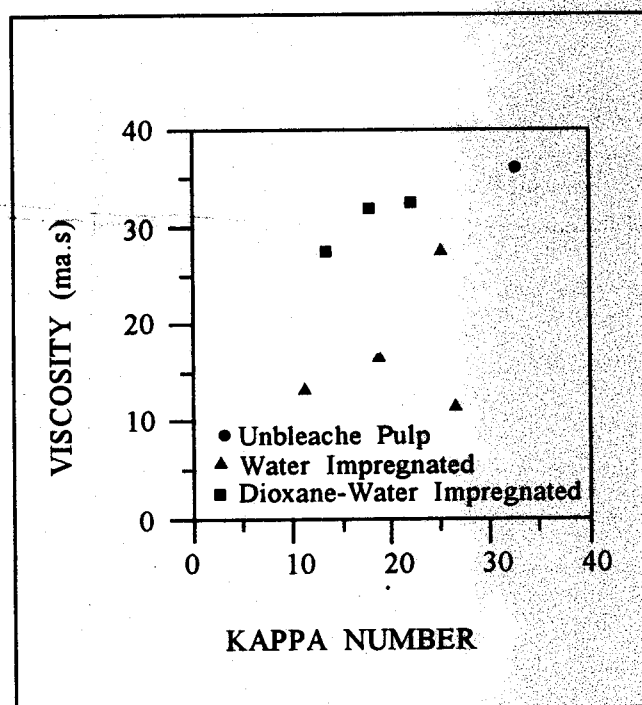


Fig.-2 Influence of the Presence of 1, 4-Dioxane in the Impregnation Solution on the (Lignin Cellulose) Ozone Selectivity.

EFFECT OF 1, 4-DIOXANE CONCENTRATION

The dioxane concentration in the impregnation liquor during ozone treatment was varied. Seven solutions with a weight percentage of 1, 4-dioxane of respectively 0, 4.8%, 9.8%, 25.4%, 48.2%, 70.6% and 100% were used. Neither acid nor alkali were added to the dioxane solution for pH adjustment. The results are summarized in Table-1. The bleaching efficiency is defined as the decrease in kappa units per 1% ozone consumed during the course of the reaction.

Table-1 shows that as the weight percentage of dioxane in the dioxane-water impregnation liquor increases, the viscosity of the ozone-bleached pulp increases until a plateau is reached at about 70% dioxane concentration. Since 100% dioxane as impregnation liquor is not favourable in terms of delignifications, it can be concluded that the presence of water is necessary to maximize the delignification during ozone bleaching. Comparison of the results obtained with 0% and 70.6% dioxane shows that in the former case the viscosity decreases from 35.8 mPa.s to 22.4 while in the latter a similar delignified

Table-1

Influence of the Dioxane Concentration in the Impregnation Liquid on the Ozonation Response of Pulp

Dioxane Concentration (Weight %)	Ozone (% on o.d. pulp)		Kappa no.	Viscosity (mPa.s)	Bleaching Efficiency
	Supplied	Consumed			
0	1.96	1.60	21.8	22.4	6.31
4.8	2.16	1.59	22.0	24.4	6.23
9.8	2.16	1.70	20.0	24.1	7.00
25.4	2.16	1.68	19.1	27.3	7.02
48.2	2.16	1.71	18.4	29.9	7.89
70.6	2.16	1.73	19.4	32.3	7.22
100	2.96	2.41	21.5	32.2	4.32

pulp with a viscosity of 32.2 mPa.s was obtained at a slightly higher ozone consumption (1.60% versus 1.73%). This again confirms that the presence of 1, 4-dioxane in the impregnation liquor during ozone bleaching protects the cellulose from degradation by ozone.

EFFECT OF THE pH OF DIOXANE CONTAINING SOLUTIONS

It is well known that the best efficiency of ozone

bleaching in water is achieved at a pH of about 2-3 (7, 8). Higher pH will increase the ozone decomposition, and as a result, will lead to less efficient ozone bleaching, although it was found that the ozone to (lignin-carbohydrate) selectivity is not affected by pH between about 7 to 1.8 (9). Therefore, additional experiments were performed to investigate the combined effect of pH and dioxane concentration of the impregnation liquor on the ozone bleaching response of the kraft Hemlock pulp. In two series of tests the pH of the impregnation liquor was adjusted

Table-2

Influence of pH and the Dioxane Concentration of the Impregnation Solution on the Ozonation Response of Pulp

Dioxane Conc. (% W)	pH 1.8				pH 2.3			
	O ₃ consumed (% on pulp)	Kappa no.	Viscosity (mPa)	Bleaching Efficiency	O ₃ consumed (% on pulp)	Kappa no.	Viscosity (mPa)	Bleaching Efficiency
0	0.87	22.3	25.9	11.04	0.86	20.6	23.9	13.14
10	0.88	20.2	24.7	13.30	0.87	20.2	26.7	12.76
25	0.86	20.3	27.1	13.49	0.86	20.3	28.0	13.60
50	0.88	20.4	29.8	13.07	0.86	20.4	31.7	14.53
70.6	0.93	19.3	31.8	13.55	0.90	19.3	33.4	12.67

to respectively 1.8 and 2.3 by the addition of sulfuric acid. In each experiment, a single ozone charge of 1.08% was applied. The results thus obtained are listed in Table-2. It is again apparent from Table-2 that the viscosity of the ozonated pulp increases with increasing dioxane concentration in the impregnation liquor.

Comparison of the results obtained at the two pH levels shows that a higher pulp viscosity is obtained at a pH of 2.3 than that at a pH of 1.8, while the kappa number of the corresponding pulps at the two pH levels are approximately the same. This may be due to increased acid hydrolysis of cellulose at the stronger acidity of pH 1.8. When comparing the results in Table-1 and Table-2, one can see that the bleaching efficiency without acidification is about one half of that in the other two cases with pH adjustment. Therefore, these experiments show that a pH of about 2 to 3 during ozone bleaching of chemical pulp is very beneficial to achieve a high (lignin) ozone reaction efficiency. This is in agreement with the findings reported for conventional ozone bleaching (7, 8). Furthermore, these experiments show that a large improvement in the (lignin-cellulose) ozone selectivity is obtained when an aqueous solution containing about 70-75% 1, 4-dioxane is used as impregnation liquor.

RESPONSE OF THE OZONATED PULP IN THE SUBSEQUENT E₀ STAGE

Fluffed unbleached kraft Hemlock pulp at approximately 40% pulp consistency was contacted with 3.83% ozone in air at a flow rate of 1.0 l/min in a specially designed rotating vessel which can handle 150 g oven dried pulp. A 70% 1, 4-dioxane solution acidified with H₂SO₄ to pH of 2.3 was used as impregnation liquor during ozone bleaching. At an ozone charge of 2% it was found that more than 95% of the ozone was consumed during the course of the reaction. The resulting pulp had a kappa number of 10.8 and viscosity of 27.9 mPa.s. Subsequently, the ozonated pulp was subjected to an E₀ stage under the following conditions: sodium hydroxide charge of 2.0%, oxygen pressure of 405 kPa, 10% pulp consistency, 70°C, 1 hour. The thus obtained pulp had a kappa number of 4.8 and a viscosity of 27.8 mPa.s. This compares favourably to a semi-bleached pulp of kappa number 4.2 and a viscosity of 23.4 mPa.s obtained from the same furnish by a (D₅₀ C₅₀) E sequence. The above results indicate that the (lignin-carbohydrate) selectivity achieved during ozone bleaching of pulp impregnated with a pH 2.3, 70%

dioxane solution is comparable to, if not better, than that obtained during conventional chlorine based bleaching.

POSSIBLE MECHANISMS OF CELLULOSE PROTECTION IN THE PRESENCE OF 1, 4-DIOXANE

Two possible mechanisms may account for the much improved ozone (lignin-carbohydrate) selectivity when a dioxane containing solution rather than pure water was used as impregnation liquor. Since there seems to be a consensus that hydroxyl radicals are mainly responsible for the carbohydrate degradation during ozone bleaching, it might be that 1, 4-dioxane scavenges these highly reactive radical species, which can be formed ozone decomposition and by ozone-lignin reactions. Alternatively, the protective effect of 1, 4-dioxane may be the result of reduced accessibility of ozone in cellulose-rich regions, and of enhanced accessibility of ozone in lignin-rich regions of the fiber.

In an earlier paper on the effect of ozone treatment of cellulose and lignin model compounds in homogeneous aqueous systems [10], it was found that the consumption of the cellulose model compound increased when phenolic lignin model compounds, such as creosol, were present during the ozone treatment. The increase was explained by the generation of reactive radical species by the ozone-lignin model reactions. Therefore, it is logical to propose that the reactive radical species are also produced during ozone bleaching of wood fibers which contain both lignin and carbohydrates. It is well known that the highly reactive radical species are unselective and degrade both lignin and cellulose. Many of the organic solvents are good radical scavengers. Therefore, with 1, 4-dioxane present in the fiber wall during ozone bleaching, the generated radical species could be scavenged in-situ, and thus protect cellulose from degradation.

It is well accepted [11] that the fiber wall consists of cellulose and lignin gels, which are separated by polyoses. Since cellulose gels swell extremely well in water, it is possible that the observed severe carbohydrate degradation during ozone bleaching is due to the improved accessibility of cellulose by ozone. However, it is also known [12] that the swelling of cellulose gels is much less in 1, 4-dioxane than in water. Therefore, one would expect that the cellulose portion of the fibers is less accessible by ozone when the pulp fibers are

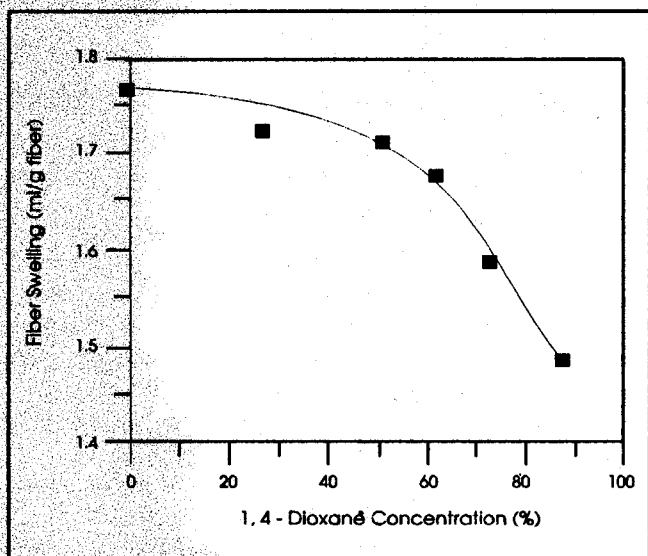


Fig.-3 Effect of 1, 4-Dioxane Concentration on the Fiber Swelling Determined by the Centrifugation Technique.

impregnated with a 1, 4-dioxane solution. Consequently, the decreased carbohydrate degradation observed when ozone bleaching takes place in dioxane-water might be attributed to the decreased swelling of the cellulose gel when dioxane is present.

Further experiments were undertaken to determine the degree of fiber swelling as a function of the 1, 4-dioxane concentration. The centrifugation technique [13] was used. In this study, the fiber swelling was determined at a centrifugal force of 900 g and 30 minutes, and expressed as the volume (ml) liquid retained per gram of moisture-free fiber after centrifugation. The results are shown in Figure-3. The maximum pulp fiber swelling of 1.78 ml/g fiber is obtained in pure water. Figure-3 also shows that as the 1, 4-dioxane concentration increases, the fiber swelling continues to decrease. Therefore, it is confirmed that the swelling of pulp fibers is reduced in the presence of 1, 4-dioxane as compared to that in pure water.

In addition, it is known [14] that the lignin gels swell much more in the presence of organic solvents such as 1, 4-dioxane, than in pure water. Therefore, it is logical to propose that lignin gels are much more accessible towards ozone when a 1, 4-dioxane containing solution is used as impregnation liquor during ozone bleaching. Since 1, 4-dioxane is a much better solvent for lignin than water, the degree of lignin degradation needed for its dissolution

in 1, 4-dioxane may not be as high as that in pure water. This may also contribute to the observed improved (lignin-cellulose) selectivity when ozone bleaching takes place in the presence of 1, 4-dioxane rather than in water.

CONCLUSION

In this study, it was found that 1, 4-dioxane is a very effective cellulose protector during ozone bleaching when present in the right proportion with water inside the pulp fibers. The delignification efficiency, however, is not affected by the presence of 1, 4-dioxane in the impregnation liquor. The ozone selectivity increases with increasing 1, 4-dioxane concentration. At a 1, 4-dioxane concentration of about 70%, the (lignin-cellulose) selectivity achieved during ozone bleaching is equivalent or better than that obtained during conventional chlorine based bleaching processes. Possible mechanisms explaining the cellulose protection were examined. It is proposed that 1, 4-dioxane may scavenge the reactive radical species generated by the ozone-lignin reactions. Alternatively, the protective effect of 1, 4-dioxane in the impregnation solution may be the result of the reduced accessibility of ozone in the cellulose-rich regions and of enhanced accessibility of ozone in the lignin-rich regions of the fiber. In addition, the better solubility of lignin in a 1, 4-dioxane containing solution may contribute to the better selectivity of this novel ozone bleaching technology.

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