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Ozone organosolv bleaching of radiata pine kraft pulp

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Summary The effect of organic solvents on the selectivity and brightness of high consistency ozone bleaching of radiata pine Kraft-oxygen pulp was investigated. Among several organic compounds, formic acid is the most attractive one, as this solvent improves ozone delignification and, efficiency and also prevents cellulose degradation. The selectivity at different ozone concentrations (1.1–1.7%) shows that formic acid increases the amount of ozone transferred and its accessibility to lignin. A peroxide stage (P) was carried out after ozonation (Z). The ZP sequence was used to reach high brightness (83.1%) pulp.

Introduction

Stricter environmental demands have increased the need not only to reduce chlorine charges in the bleaching of chemical pulps but also to replace altogether the chlorine base chemicals from bleaching sequences plants. Semibleached pulps have been obtained without chlorine chemicals, for example, by introducing an acid wash before the oxygen and peroxide bleaching stages or by treating the pulp with a chelating agent between oxygen delignification and peroxide bleaching. To achieve higher brightness, ozone bleaching included in a multiple stage non-chlorine bleaching sequence is an attractive possibility. Recent developments in mixing techniques made it possible to increase the "reactivity" between ozone and pulp at high (HC, 30–40%), low (LC, 1–3%) and medium (MC, 10–15%) consistency ranges (Byrd et al. 1992). More recently, the impetus for commercialization of ozone bleaching technology has been heightened environmental awareness, and the pressure to eliminate formation of chlorinated organic compounds in the bleaching plants. As a result, there has been a resurgence of ozone bleaching work, at pilot plant and mill scales. In the last three years a total of about 18 mills were put into operation using ozone bleaching technology. Several attempts have been made to enhance the selectivity of ozone bleaching. It is known that the decomposition of ozone in water is favored by hydroxyl ions (Patt et al. 1991). In particular, the decomposition is increased at pH values above 4. That is why best ozone delignification conditions can be achieved at pH 2–3.

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Thus, the pulp has to be acidified before ozone treatment. A pretreatment with different acids such as acetic acid, formic acid, oxalic acid and others, was found to significantly increase the selectivity of the ozone treatment (Kamishima et al. 1982).

Liebergott and van Lierop (1992) offered a comprehensive review of additive studies up to 1978. Takagi and Kayama (1980) bleached oak alkali-dioxane pulps with ozone and obtained reasonable pulp properties when optimum conditions were used and ozone consumption was kept under 3%. Osawa and Schuerch (1963) studied the effect of nitromethane, an organic solvent which preferentially wets lignin, on ozonation selectivity. They found that although the solvent did not increase the process selectivity, it markedly increased the reaction rate towards lignin. Kamishima et al. (1982) studied the effect of 27 organic acids and methanol as potential carbohydrate protectors for unbleached kraft pulp during ozonation. Nimz et al. (1991) showed how ozone bleaching could be applied to acetosolv pulps for pollution free production of bleached pulp. Mbachu and Manley (1981) found that pulps pretreated with acetic or formic acid consumed substantially less ozone to reach a given kappa number than pulps pretreated with water or sulfuric acid. Various other investigators (Lachenal and Bokström, 1986, Liebergott et al. 1992, Baeza et al. 1995) have examined the suitability of a wide variety of organic and inorganic substances as pretreatment and additives for viscosity and strength preservation during ozone bleaching with varying grades of success.

Even though the problem of AOX not longer exists when using chlorine free compounds in a bleaching sequence, care must be taken concerning the possible toxicity or pollution of the effluents of such sequences. In addition, chlorine-free bleaching allows the closure of the water cycle to a high extent by counter-current washing and using the filtrates for brownstock washing (Chirat and Lachenal, 1993). The main part of the filtrates is normally recycled within the stage for tower dilution and consistency adjustment. Thus, every bleaching stage runs mainly in its own filtrate (Annola et al. 1995). Indeed one disadvantage of the effluent free mill concept is that, when sending the bleaching effluent to the recovery system, the pulping capacity might decrease in those mills already limited at the recovery boiler. Then it may be preferable in a first step, not to recycle the whole effluent. The differences between using sulfuric acid to reach pH ozonization and formic acid-wet pulp ozonization may be even more pronounced, when the SO_2 emission in a closed water-flow is considered. This environmental emission is eliminated considering ozonization in formic-system. Therefore, the closure of the bleach plant's water cycle, which is a main objective of chlorine-free bleaching, is a bleaching process with minimum impact on the environment.

Material and methods

Raw material

Extended cooked oxygen-delignified softwood kraft pulp of *Pinus radiata* with Kappa number of 16.0, brightness 37.2% °Elrepho and viscosity 27.0 mPa.s was employed.

Bleaching

Ozone bleaching of radiata pine kraft-oxygen pulp was carried out in different reaction media: formic acid, acetic acid, acetone, formic-acetone mixtures, acetic-acetone in different proportions and water, at high pulp consistency (HC-40%). The pulp was first impregnated with the corresponding solvent at 2% consistency for 1 hour, excess solvent was then pressed out and centrifugated to obtain the desired pulp consistency. For ozonation in water at HC, the pulp was first dispersed in deionized water to reach a pulp consistency of 1%, the pH was adjusted to 2.5 with 4N sulfuric acid. Excess water was pressed out after 1 hour to obtain the desired pulp consistency. These impregnated pulps were fluffed and ozonized in a rotating round-bottomed flask equiped with a gas inlet system.

The ozone consumption was calculated by the difference between charge and residual ozone. Ozone concentration was determined by UV absorption at 254 nm in a flow cell connected in series with the reactor. Ozonation was carried out by treating the pulp with a stream of ozone in oxygen at room temperature. Gas flow during ozonation was around 0.4 l/min. After ozonation in solvent system, the pulp was washed with the same solvent and then with deionized water.

The hydrogen peroxide stage was performed to 10% consistency in a polyethylene bag, at 70 °C during 180 min. The neccesary amount of NaOH 0.1 N was added to reach a pH of 11.5. H_2O_2, $MgSO_4$ and silicate concentrations were 1%, 0.5% and 1%, respectively.

The alkaline extraction stage was performed at 10% consistency in a polyethylene bag, at 60 °C, during 60 minutes, with a NaOH charge of 2%.

Pulp characterization

Kappa number, viscosity, and brightness were measured according to the Tappi standards. Brightness handsheets were formed according to Tappi Standard and, brightness was measured with a Zeiss Elrepho reflectance photometer.

Results and discussion[1]

The examination of the ozonation data presented in Table 1 shows that ozone selectivity is generally improved in organic acids and organic acid-acetone mixtures. Among the several solvents pretreatments, the 98% formic acid resulted in the highest ozone bleaching and delignification efficiencies and in the highest selectivity.

A great reduction in the Kappa number is observed after ozonation, independent of the solvent pretreatment but, viscosity in water at pH 2.5 decreased considerably (16.7 mPa.s) and a lower change is observed in the organic acid media. Enhancements of selectivity, brightness and efficiency were obtained in both cases.

Application of 1.1% ozone to the untreated pulp reduced the Kappa number from an initial value of 16.0 to 6.7, while, application to the formic acid (98%) and acetic acid (80%) pretreated ones reduced the Kappa numbers to 4.1 and 4.9, respectively. These results are in agreement with reports that the ozonization of lignin is enhanced under acid condition (Mbachu and Manley 1981). It was also observed that the lignin reactivity is not only a function of the pH but is also determined by the nature of the medium (Brolin et al. 1993).

Lowest kappa number and highest viscosity values were obtained at 70–90% acetic-acid-wet ozonization, while the selectivity was optimum at around 80% acid concentration. This higher selectivity as the acetic acid concentration increased may be explained by the swelling decrease of the pulps. This agrees with

[1] To facilitate the discussion of the experimental results, the following terms have been used in this work: *selectivity* is the degree of carbohydrate degradation and it is usually known as the reduction of pulp viscosity when pulp is bleached to a certain kappa number level and *efficiency* is the reduction in kappa number by % ozone consumed

Table 1. Influence of different pretreatments on ozone delignification (ozone consumed, 1.1%/b.d. pulp)

Pretreatment	Kappa number	Viscosity (mPa.s)	Selectivity	Brightness (Elrepho)
Acetic acid (%)				
96	6.9	18.9	1.90	58.6
90	5.4	18.1	2.00	60.5
80	4.9	18.3	2.15	63.8
70	4.9	18.0	2.08	64.0
48	5.7	18.0	1.93	59.4
Formic acid (98%)	4.1	18.1	2.25	64.7
Formic acid-water (V/V)				
1 : 1	5.9	18.5	2.00	59.3
Formic acid-acetone (V/V)				
7 : 3	5.6	18.8	2.14	61.3
1 : 1	5.1	17.9	2.02	62.3
3 : 7	5.7	18.8	2.12	61.5
Acetic acid-acetone (V/V)				
7 : 3	6.8	19.1	1.96	59.7
1 : 1	7.8	20.5	2.13	57.2
3 : 7	7.2	15.3	1.27	57.5
Acetone	11.7	16.6	0.70	47.4
Water, pH 2.5	6.7	16.7	1.52	57.9
Reference[a]	16.0	27.0	–	37.2

[a] Kraft pulp of *Pinus radiata* (extended cooked Kraft by oxygen stage)

the interpretation of the protection action of aqueous acetic acid during ozone bleaching proposed by Mbachu and Manley (1981). i.e, that ozone penetration into the carbohydrate matrix is limited by decreased swelling in the acid medium compared to water (Mantanis et al. 1994).

The selectivity of ozone treatment is largely dependent on the amount of hydroxyl radicals formed during the ozonation process (Brolin et al. 1993). Using organosolv-wet pulps as "model reaction media" to prevent, or at least minimize, the effect of hydroxyl radicals, the importance of selecting appropriate reaction conditions for ozonation has been demonstrated.

Effect of formic acid on ozonation

In order to evaluate the effect of ozone charge in a formic acid media, the pulp was brought to 40–45% consistency in formic acid 98%, and ozonated with various ozone charge (Table 2). It can be seen that for the same concentration of acid, the Kappa number and selectivity decreased when the ozone charge was increased. The selectivity drop (1.92–1.93) was less marked at the highest ozone charges (1.4 and 1.7%). This can be explained by the drop in efficiency (10.7 at 7.6) at this low level of kappa number (Table 2).

Bleaching of the ozone-delignified pulp with hydrogen peroxide

When using proper conditions of temperature, pH, ozone charge and control of metal ions, it is possible to minimize pulp degradation during ozonation. But in most cases the nondegrading OZ or OPZ bleaching treatments proposed nowa-

Table 2. Effect of the amount of ozone consumed by kraft-oxygen pulp pretreated with formic acid (98%) on delignification efficiency and selectivity

% Ozone consumed	Kappa number	Viscosity (mPa.s)	Selectivity	Brightness (Elrepho)	Efficiency
Reference	16.0	27.0	–	37.2	–
0.9	6.6	18.1	1.78	50.8	10.5
1.1	4.2	17.6	2.12	62.6	10.7
1.4	3.5	16.0	1.92	67.5	8.9
1.7	3.1	15.7	1.93	70.3	7.6

days as total chlorine free alternatives do not give the brightness level required for most printing and writing papers (Chirat et al. 1993, Chirat and Lachenal, 1993).

Thus some other bleaching stages have to be implemented after Z. Hydrogen peroxide (P) is known to be a good brightening agent. Unfortunately P must be carried out under alkaline conditions, which is known to severely degrade cellulose molecules containing carbonyl groups (Chirat and Lachenal 1994). The next logical step was to try a ZP bleach. As shown in Table 3 this sequence resulted in brightnesses of 76 to 83 Elrepho, depending upon ozone dosage.

In Table 4 the bleaching results are shown by the sequence ZP for 0.9% ozone dosage in different media. The sequence ZP at pH 2.5 water-medium was less efficient than formic-acid 98%-medium. The effect can be due to the formic acid carbohydrates protection, but does not affect significantly the delignification rate (6.6 and 7.5 kappa number, for "formic-medium" and "water-medium previous formic-wet pulp" respectively). As a result, the selectivity of ozone bleaching decreased (1.78 to 1.02), but the efficiency was not affected.

Conclusions

The ozone delignification efficiency is significantly improved when the pulps were pretreated with formic acid 98%. This implies that a lower ozone charge will be required to reach a certain degree of delignification, with consequent enhancement in progress selectivity and bleached pulp production.

Among the pulp treatments with solvents prior to ozone bleaching, the most effective to improve delignification efficiency and selectivity was that with formic

Table 3. Bleaching sequences investigated for final bleaching of the ozone-delignified pulp pretreated with formic acid 98% (1% hydrogen peroxide (P))

Stage	Kappa number	Viscosity (mPa.s)	Selectivity	Brightness (Elrepho)
Z: 1.1% Ozone consumed				
Z	4.2	17.6	2.12	62.6
P	1.7	15.1	–	76.3
Z: 1.4% Ozone consumed				
Z	3.5	16.0	1.92	67.5
P	1.1	14.7	–	80.7
Z: 1.7% Ozone consumed				
Z	3.1	15.7	1.93	70.3
P	0.9	13.9	–	83.1

Unbleached pulp: Kappa number 16.0, viscosity 27.0, brightness 37.2

Table 4. Bleaching sequences investigated for final bleaching of the ozone-delignified pulp on different pretreatments, at 0.9% ozone (Z)

Stage	Kappa number	Viscosity (mPa.s)	Selectivity	Brightness (Elrepho)
Formic medium				
Z	6.6	18.1	1.78	57.6
P	2.2	16.1	-	72.0
pH 2.5, water-medium, formic-wet pulp[a]				
Z	7.5	13.0	1.02	57.5
P	2.8	11.8	-	72.2
pH 2.5 water-medium				
Z	9.9	14.1	0.80	50.8
P	4.2	12.5	-	67.6

[a] Before ozonation, the pulp was first impregnated with formic-acid 98%, as described in material and methods section, then washing exhaustively with water and finally the pH was adjusted to 2.5 with 4N sulfuric acid

acid 98% followed by acetic acid 80%. The ozonation of pulp pretreated with pure acetone resulted in the poorest delignification efficiency and selectivity among the evaluated pretreatments.

Extensive delignification of the pulp is possible with the ozone without a devastating decrease in viscosity. Brightness levels of 80–83%, starting with *Pinus radiata* kraft pulp of kappa number 16.0, were obtained in a two bleaching sequence steps, 1.1–1.7% ozone (Z) and 1% hydrogen peroxide (P).

The effect of formic-acid-wet pulp pretreatment on bleaching (0.9% ozone charge) appears clearly. 72.0% brightness was reached with ZP sequence, whereas water-wet pulp only reached 67.6% brightness with the same sequence.

Evaluation of strength properties is now in progress.

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