**WOOD RESEARCH**
**54 (2): 2009**
**73-82**

# OPTIMIZATION OF OZONE BLEACHING CONDITIONS OF OXYGEN DELIGNIFIED HARDWOOD KRAFT PULP WITH D-MANNITOL

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## ABSTRACT

The influence of ozone charge (0 – 1.2 % $O_3$ on oven dry pulp), temperature (20 – 60 °C) and charge of D-mannitol (0 – 1 % D-mannitol on oven dry pulp) on the kappa number, viscosity and brightness in oxygen delignified hardwood kraft pulp, was studied.

The central composite factorial design in order to identify the optimum operating conditions, equations relating the dependent variables of the operational variables of the ozone bleaching process were derived that reproduced the former with errors lower than 8 %, was used.

On the basis of optimum values of factorial design was determined that the D-mannitol at the ozone consumption 0.05 % $O_3$ on oven dry pulp at 20 °C and 1 % charge of D-mannitol on oven dry pulp prevent the most marked decrease degree of polymerization (ΔDP about 39 unit). The maximum the of lignin removal (Δkappa number ≈ 2.6) was achieved at ozone consumption 0.54 % of $O_3$ on oven dry pulp at temperature 21 °C and 0.87 % charge of D-mannitol on oven dry pulp. The maximum increase of brightness (ΔB about 10.27 % ISO) was achieved at temperature 60 °C, ozone consumption 0.167 % of $O_3$ on oven dry pulp and charge of D-mannitol 0 % on oven dry pulp.

KEY WORDS: ozone bleaching, cellulose protectors, statistical modelling

## INTRODUCTION

Ozone represents a very effective bleaching agent. However, ozone is not selective in its attack on lignin as carbohydrates are also degraded, leading to a lower viscosity (Mbachu and Manley 1981). Within the first minutes, ozone attacks the aromatic rings of lignin. In addition to primary oxidation reactions, secondary ones proceed on a remarkable scale, giving rise to carbonyl products and causing a gradual decrease in the average molecular weight (Katuscak et al. 1971). The same has been proved in the effect of ozone in kraft pulp bleaching. Due to a high ozonization reaction rate the effects can be seen during the first minute (Jablonsky and Vrska 2004, Jablonsky et al. 2004). A remarkable decrease in viscosity (up to 200 $ml.g^{-1}$) was found with the ozone consumption higher than 3 $kg.t^{-1}$ oven dry pulp. It is important to mention that the problem of ozone bleaching

is not as much elimination of the lignin by degradation as it is the prevention of the cellulose chain destruction. Within a reaction of glucose structures with ozone, direct cleavage of glycosidic bonds appears. This reaction is about the same as the formation of carbonyl groups, providing a further support that the cellulose degradation is caused by the radical attack (Zhang et al. 2000). The kinetic point of view is as important well. The selectivity ratio of these species indicates that ozone is $10^5$ to $10^6$ times more selective than hydroxyl radicals towards lignin (Hoigne and Bader 1983a, 1983b; Bouchard et al. 1995). The hydroxyl and hydroperoxy radicals formed at ozone decomposition are more reactive and far less selective than ozone itself (Ragnar et al. 1997, Zhang et al. 2000). When investigation lignin model compounds, the selectivity of the hydroxyl radicals seems to be only about 5-6 (Ek et al. 1989), causing unwanted carbohydrate degradation.

Considerable efforts have been devoted to research on identifying cellulose protectors (CP) able to prevent the degradation of cellulose during ozone bleaching (Lachenal and Bokstrom 1986). A lot of organic compounds have been found to effectively improve selectivity (Liebergott et al. 1992a and 1992b, Medwick et al. 1992, Jablonsky et al. 2004b).

A lot of articles has been dedicated to finding an additive or a pretreatment that would protect the cellulose and make the ozone react more preferentially with the lignin in the fiber. These substances are expected to decrease or completely eliminate the degradative reactions that affect the decrease of selectivity and efficiency of ozone bleaching. The main task of additives is to prevent the degradation of polysaccharides. Besides the cellulose protection, we have also tried to increase the brightness and the amount of eliminated lignin. Some additives are able to prevent the degradation of polysaccharides, but on the other side, their application to the system of ozone bleaching lacks the required elimination of lignin or brightness rise, or both.

The aim of this work was to study the protective effects of cellulose protector which performed function such as hydroxyl radical scavenger. In this work was used cellulose protector D-mannitol becasuse D-mannitol is a *OH scavenger (Yamazaki and Piette 1991, Yamazaki et al. 2001, Tsou et al. 1999). Effect of the D-mannitol on the properties of pulp during the ozonization was evaluated in another works (Jablonsky et al. 2005, 2006).

In this work, a central composite factorial design was used to study the influence of independent variables in the ozone bleaching of oxygen delignified hardwood kraft pulp (viz. ozone charge, temperature and charge of D-mannitol) on the kappa number, degree of depolymerization and brightness, with the aim of identifying the optimum operating conditions.

## MATERIAL AND METHODS

### Raw material

Hardwood oxygen-delignified kraft pulp from an industrial source was used. Characteristics of the pulp are as follows: kappa number 6.93, viscosity 817 $ml.g^{-1}$, brightness 48.1 % ISO, degree of polymerization 1201.

### Conditions of ozone stage

Fig. 1 shows the pulp ozonization procedure. The pH 2.6 and consistency of the pulp 30 % was adjusted with aqueous sulphuric acid and required amount of D-mannitol according to central composite factorial design was added. Ozone was produced in oxygen gas (about 3.92 wt %) at a constant flow rate (27 L $O_2$/h) by passing oxygen through an ozone generator. The outflow was directed into a laboratory reactor consisting of a rotating glass evaporator. The gas inlet was on the bottom of the vessel. The vessel was under constant rotation during the ozonization. Varying the flow time of ozone gas through the reactor controlled the ozone charge and vessel was tempered

on the required temperature by constant-temperature circulator and temperature the pulp inlet was determined by multimeters for measuring temperature with the accuracy ± 2 °C. The precision in ozone consumption and pH determinations are estimated to be ±3 mg and < ±0.1 units, respectively. The reactivity of ozone bleaching to formulated according Lindholm (1987).

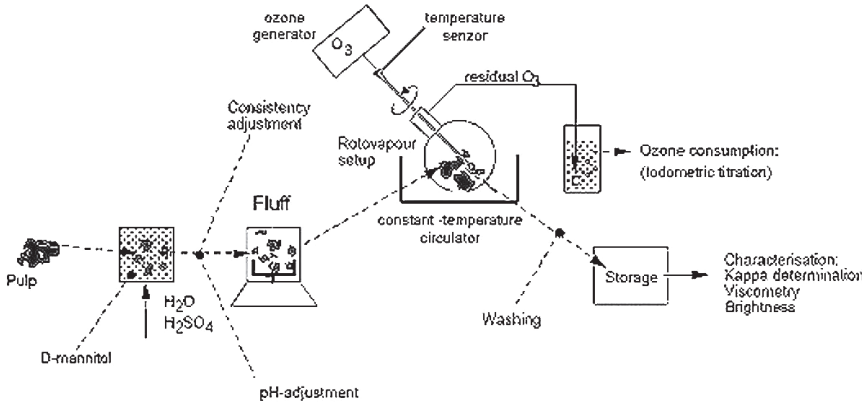


*Fig. 1: Experimental set-up. High consistency pulp ozonization*

The efficiency of ozone bleaching in this respect can be described by the reactivity (1):

$$\text{Re}\,activity = \frac{O_{3\,CON}}{O_{3\,in}}.100\% \quad (1)$$

where, $O_{3\,CON} = O_{3\,IN} = O_{3\,OUT}$ (2)

$O_{3\,CON}$ - consumption of ozone in reaction with pulp (% $O_3$ on oven dry pulp (o.d.p.))
$O_{3\,IN}$ - ozone charge (% $O_3$ o.d.p.)
$O_{3\,OUT}$ - residual ozone (% $O_3$ o.d.p.)
2.3. Characterization of the raw material and ozonized pulp

The hardwood oxygen delignified kraft pulp and ozonized pulp was characterized kappa number (TAPPI T236), brightness (TAPPI T452) and viscosity was determined according to TAPPI T230. In order to estimate the degree of polymerization (DP) of the carbohydrates was calculated from intrinsic viscosity using Mark-Houwink equation (3), where ([η]) is the intrinsic viscosity (ml/g) of pulp (Rydholm 1965):

$$DP^{0.905} = 0.75\,[\eta] \quad (3)$$

## Experimental design

The proposed model used a series of experiments based a central composite design: 2^3 + star design which will study effects of 3 factors. The total number of testes required for our three independent variables [viz. ozone charge ($x_1$), temperature ($x_2$) and charge of D-mannitol ($x_3$)] was 19. The design has to be run in a single block. The present work aims to be a study for the optimization of coprocessing conditions. The effects of ozone charge (% $O_3$ o.d.p., $x_1$),

temperature (°C; $x_2$), and charge of D-mannitol (% D-mannitol o.d.p., $x_3$) were investigated. Each of the parameters was coded at five levels: -1.682, -1, 0, 1 and 1.682. The range and the levels of the variables investigated in this research are given in Tab. 1. For this study, a $2^3$ factorial design with six star points and five replicates at the central points were employed to fit the second-order polynomial model, which indicated that 19 experiments were required for this procedure. "Statgraphic Plus v7.1" software was used for regression and graphical analysis of the data obtained.

*Tab. 1: The experimental domain*

| Factor | Symbol | Range and levels | | | | |
|---|---|---|---|---|---|---|
| | | - 1.682 | - 1 | 0 | + 1 | + 1.682 |
| Ozone charge (% $O_3$ o.d.p.) | $x_1$ | 0 | 0.3 | 0.6 | 0.9 | 1.2 |
| Temperature (°C) | $x_2$ | 20 | 30 | 40 | 50 | 60 |
| Charge of D-mannitol (% D-mannitol o.d.p.) | $x_3$ | 0 | 0.15 | 0.5 | 0.85 | 1 |

## RESULTS AND DISCUSSION

Tab. 2 shows the values obtained for the independent variables in the 19 tests required to construct the model.

*Tab. 2: Absolute and normalized values of the operational variables used in the ozone bleaching of oxygen delignified hardwood kraft pulp*

| Experiment number | Range and levels | | | $O_{3\,CON}$ (% $O_3$ o.d.p.) | $\kappa$ | $[\eta]$ (ml/g) | $B$ (% ISO) |
|---|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | | | | |
| 1 | 0 | 0 | 0 | 0.29 | 5.00 | 728 | 55.98 |
| 2 | 0 | 0 | 0 | 0.29 | 5.00 | 719 | 55.57 |
| 3 | 0 | 0 | 0 | 0.28 | 4.90 | 734 | 55.36 |
| 4 | 0 | 0 | 0 | 0.29 | 5.21 | 711 | 55.62 |
| 5 | 0 | 0 | 0 | 0.28 | 4.91 | 734 | 54.91 |
| 6 | + 1.682 | 0 | 0 | 0.49 | 4.43 | 679 | 57.80 |
| 7 | 0 | + 1.682 | 0 | 0.26 | 4.88 | 691 | 54.03 |
| 8 | 0 | 0 | + 1.682 | 0.34 | 4.94 | 724 | 54.25 |
| 9 | - 1.682 | 0 | 0 | 0.00 | 5.53 | 774 | 50.81 |
| 10 | 0 | - 1.682 | 0 | 0.26 | 5.31 | 737 | 54.05 |
| 11 | 0 | 0 | - 1.682 | 0.21 | 5.47 | 724 | 55.70 |
| 12 | + 1 | + 1 | + 1 | 0.47 | 5.17 | 678 | 56.88 |
| 13 | + 1 | - 1 | + 1 | 0.37 | 4.82 | 722 | 55.24 |
| 14 | + 1 | + 1 | - 1 | 0.29 | 5.72 | 724 | 55.83 |
| 15 | - 1 | + 1 | + 1 | 0.21 | 5.50 | 746 | 54.48 |
| 16 | - 1 | + 1 | - 1 | 0.13 | 5.40 | 731 | 55.17 |
| 17 | + 1 | - 1 | - 1 | 0.28 | 4.95 | 688 | 56.95 |
| 18 | - 1 | - 1 | + 1 | 0.14 | 4.96 | 744 | 54.97 |
| 19 | - 1 | - 1 | - 1 | 0.14 | 5.80 | 738 | 54.08 |

Tab. 3 shows the values obtained the significance contrast, as well as the $R^2$ values in the both cases.

*Tab. 3: Parameters of model signification tests*

| | $\kappa$ | *DP* | *B* (% ISO) |
|---|---|---|---|
| $b_0$ | 4.99659 | 1053.39 | 55.4464 |
| $b_1$ | -0.208684* | -36.1221* | 1.31478* |
| $b_2$ | 0.0393085 | -10.7237 | 0.0795473 |
| $b_3$ | -0.169245* | 1.14827 | -0.212245 |
| $b_{11}$ | 0.0322934 | 0.781088 | -0.189342 |
| $b_{12}$ | 0.1225* | -0.75 | -0.01 |
| $b_{13}$ | 0.0075 | -6.75 | -0.1075 |
| $b_{22}$ | 0.0729522 | -6.11323 | -0.283034 |
| $b_{23}$ | 0.065 | -14.0 | 0.1475 |
| $b_{33}$ | 0.111843* | -0.63313 | 0.0475396 |
| $R^2$ | 0.6279 | 0.7995 | 0.6711 |

* p-value < 0.05

The values estimated using the previous equations reproduced the experimental values for the different dependent variables with errors less than 8 %, 2.8 % and 3.7 % for kappa number, degree of polymerization and brightness.

On the basis of parameters of the model tests and p-value is possible to say that the calculated regression parameters $b_1$; $b_3$; $b_{12}$; $b_{33}$ are with a confidence level of 95% and this parameters significantly affect the obtained value kappa number. At values DP and B was statistically important ozone charge with a confidence level of 95 %.

On the basis of regression coefficients (Tab. 3) was found, that Kappa number value negatively affects linear parameters of regression $b_1$, $b_3$ and combination of linear coefficient $b_{12}$ and quadratic term of $b_{33}$. In the quest of decrease the kappa number is effect of these linear terms positive and effect of their linear combination on the decrease of kappa number in process is negative. At DP on the basis minus regression term of $b_1$ this effect on the degree of polymerization is negative which corresponding with experience from the field of ozonization. On the other side in the case of the brightness the effect of ozone charge is positive.

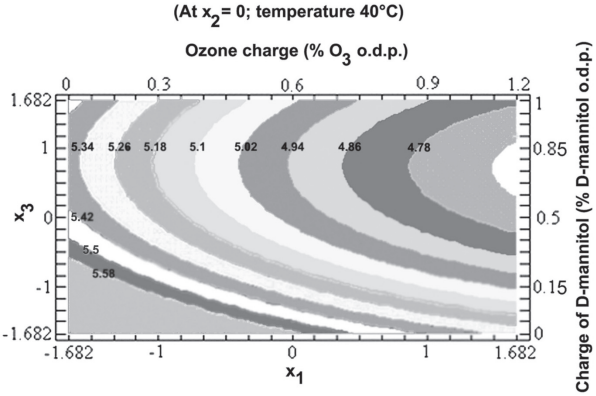


*Fig. 2: Predicted contour levels for kappa number as a function of ozone charge (% $O_3$ on oven dry pulp) and charge of D-mannitol (% D-mannitol on oven dry pulp) at a constant temperature 40 °C*

Fig. 2 shows the change of lignin content formulated by the kappa number. Values measured value kappa number for different constant level represents contour line on the figure. The contour lines on the figure point out on the function directed into the minimum. The behaviour of this function has typical shape of the rising ridge. On the basis of contour line, it may be observed that at constant temperature (40 °C) kappa number depends on the charge of D-mannitol and ozone.

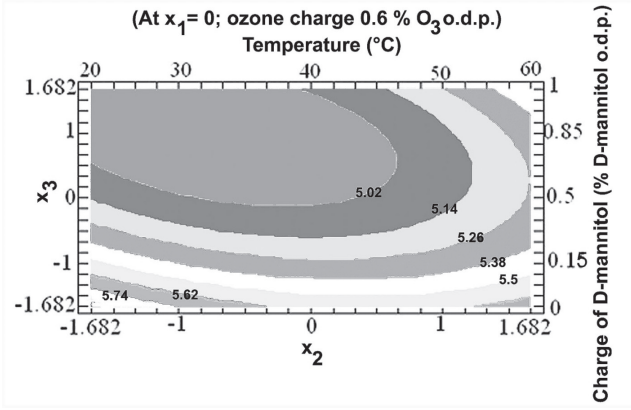


*Fig. 3: Predicted contour levels for kappa number as a function of temperature (°C) and charge of D-mannitol (% D-mannitol on oven dry pulp) at constant ozone charge 0.6 % $O_3$ on oven dry pulp*

Fig. 3 shows predicted contour levels for kappa number as a function of temperature (°C) and charge of D-mannitol (% D-mannitol on oven dry pulp) at constant ozone charge 0.6 % $O_3$ on oven dry pulp. Kappa number leads to the minimum with increasing charge of

D-mannitol and decreasing temperature. On the basis of the contour line can be said that in scale of temperature from 20 to 40 °C at ozone charge 0.6 % $O_3$ o.d.p. is necessary to apply 0.675 % D-mannitol o.d.p. in order to achieve of minimum kappa number.

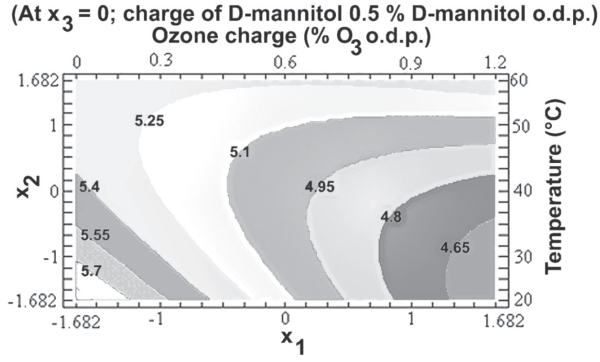


*Fig. 4: Predicted contour levels for kappa number as a function of temperature (°C) and ozone charge (% $O_3$ on oven dry pulp) at a constant charge of D-mannitol 0.5 % D-mannitol on oven dry pulp*

By the constant charge of D-mannitol (0.5 % D-mannitol o.d.p.) value of the kappa number were running to the minimum. This behaviour is possible to achieve at increasing charge of ozone and decreasing temperature. The effect is show in Fig. 4.

Values of parameters obtained for degree of polymerization (DP) show, that the ozone charge had the most important effect in the process. Predicted contour levels for (DP) as a function of ozone charge (% $O_3$ o.d.p.) and charge of D-mannitol (% D-mannitol o.d.p.) at a constant temperature 40 °C is shown on Fig. 5. At ozone charge in scale from 0-0.55 % $O_3$ o.d.p. and at a constant temperature 40 °C it was possible to increase positive effect of the charge of D-mannitol on suppress drop of DP.

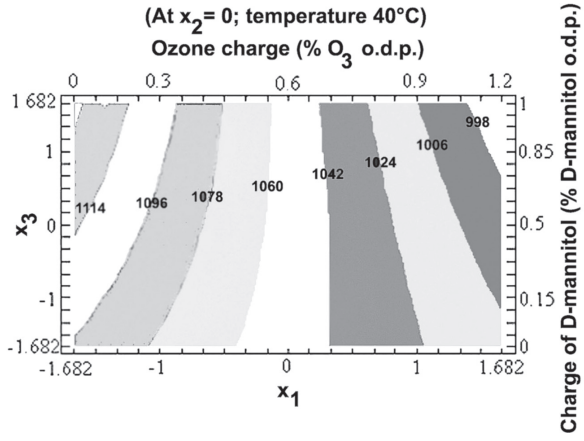


*Fig. 5: Predicted contour levels for Degree of polymerization (DP) as a function of ozone charge (% $O_3$ on oven dry pulp) and charge of D-mannitol (% D-mannitol on oven dry pulp) at a constant temperature 40 °C*

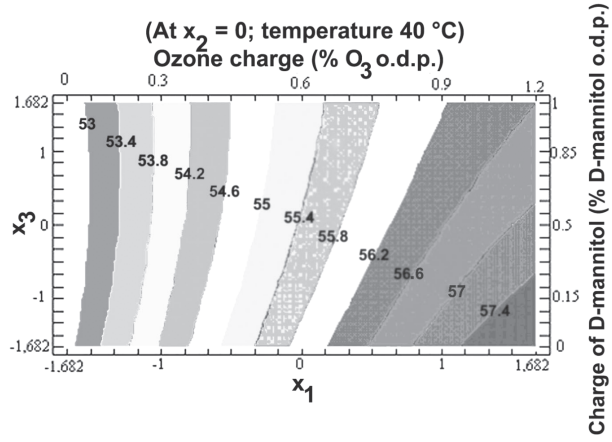


*Fig. 6: Predicted contour levels for brightness (B, % ISO) as a function of ozone charge (% $O_3$ on oven dry pulp) and charge of D-mannitol (% D-mannitol on oven dry pulp) at a constant temperature 40 °C*

It is also possible to say that at a constant temperature 40 °C the ozone charge significantly affects the brightness. This effect is shown in Fig. 6.

Tab. 4 shows the operational variables in ozone bleaching of oxygen delignified hardwood kraft pulp which has to be obtained to reach the optimum of dependent variables (viz. kappa number, degree of polymerization and brightness) at pH = 2.6. The reactivity of ozone stage for the ozone charge as the independent variable was 45 %.

*Tab. 4: Variables of the operational variables in the ozone bleaching of oxygen delignified hardwood kraft pulp required to obtain the optimum values of dependent variables for the ozone bleaching at pH = 2.6*

| Independent variables / Dependent variables | $x_1$ Ozone charge (% $O_3$ o.d.p.) | $x_2$ Temperature (°C) | $x_3$ Charge of the D-mannitol (% D-mannitol o.d.p.) | Optimum value of dependent variable (maximum or minimum*) |
|---|---|---|---|---|
| Degree of polymerization | - 1.441 | - 1.682 | + 1.682 | 1162 |
| | (0.107) | (20) | (1) | |
| Kappa number | + 1.682 | - 1.677 | + 1.184 | 4.37* |
| | (1.2) | (20.9) | (0.868) | |
| Brightness (% ISO) | - 0.668 | + 1.682 | - 1.682 | 58.37 |
| | (0.372) | (60) | (0) | |

On the basis of optimum values of factorial design was determined that D-mannitol at the ozone charge 0.107 % $O_3$ o.d.p. at 20 °C (ozone consumption 0.05 % $O_3$ o.d.p.) and 1 % charge of D-mannitol o.d.p. most significantly prevents decrease of degree of polymerization (ΔDP about 39 unit). The maximum of the lignin removal (Δkappa number ≈ 2.6) was achieved at ozone charge 1.2 % $O_3$ o.d.p. (ozone consumption 0.54 % of $O_3$ o.d.p.) at temperature 21 °C and 0.87 % charge of D-mannitol o.d.p. The maximum increase of brightness (ΔB about 10.27 % ISO) was achieved at 60 °C, ozone charge 0.372 % $O_3$ o.d.p. (ozone consumption 0.167 % of $O_3$ o.d.p.) and charge of D-mannitol 0 % o.d.p.

## CONCLUSIONS

Using the central composite factorial design in order to identify the optimum operating conditions (ozone charge, temperature and charge of D-mannitol), equations relating the dependent variables (kappa number, degree of polymerization and brightness) on the operational variables of the ozone bleaching process were derived that reproduced the former with errors lower than 8 %.

On the basis of optimum values of factorial design was determined that the D-mannitol at the ozone consumption 0.05 % $O_3$ o.d.p. (ozone charge 0.107 % $O_3$ o.d.p.) at 20 °C and 1 % charge of D-mannitol o.d.p. the most significantly prevents the decrease of degree of polymerization (ΔDP about 39 unit). The maximum of the lignin removal (Δkappa number ≈ 2.6) was achieved at ozone consumption 0.54 % of $O_3$ o.d.p. (ozone charge 1.2 % $O_3$ o.d.p.) at temperature 21 °C and 0.87 %

charge of D-mannitol o.d.p. The maximum increase of brightness (ΔB about 10.27 % ISO) was observed at 60 °C, ozone consumption 0.167 % of $O_3$ o.d.p. (ozone charge 0.372 % $O_3$ o.d.p.) and charge of D-mannitol 0 % o.d.p.

## ACKNOWLEDGEMENTS

The authors express their thanks the Ministry of Education of the Slovak Republic – project KNIHA.SK 2003 SP/028 03 01.

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