

## THE CHANGE OF KINETICS RATE OF EXCITATION PURITY IN OZONIZATION OF OXYGEN DELIGNIFIED HARDWOOD KRAFT PULP

MICHAL JABLONSKÝ, LUCIA KUČERKOVÁ, MARTINA BOTKOVÁ  
SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA, FACULTY OF CHEMICAL AND FOOD  
TECHNOLOGY, DEPARTMENT OF CHEMICAL TECHNOLOGY OF WOOD PULP AND PAPER  
BRATISLAVA, SLOVAK REPUBLIC

(RECEIVED AUGUST 2012)

### ABSTRACT

The absence of detailed kinetic description of excitation purity of the ozonization of oxygen delignified hardwood kraft pulp in the literature was the reason to become interested in this topic. To fulfil the goals, the ozone delignification was studied at various conditions. Influence of pH in the range 0.3; 2.6; 3.9; 8.8 and 9.6 and the temperature of 20 and 40°C in ozonization process were studied according to excitation purity and its rate. The conditions of ozone bleaching process were: Oxygen flow rate 7.5 ml O<sub>2</sub>·s<sup>-1</sup> (27 l O<sub>2</sub>·h<sup>-1</sup>), the consistency of the pulp 30 % and ozone production of 56 mg O<sub>3</sub>·l<sup>-1</sup> O<sub>2</sub>.

It was found that temperature and pH affected the progress rate constants of excitation purity at the ozonization process. The most constant rate of excitation purity was observed at pH in acid range (pH = 2.6) and at temperature 20°C. The greatest decline of excitation purity was achieved at acidic pH range (0.3 and 2.6) in the ozone consumption 0.62-0.95 % O<sub>3</sub> on o.d. pulp at temperature 40°C. We found out that dominant wavelength is 578.93 ± 0.07 nm and is independent on temperature, pH and time of ozonization.

KEYWORDS: Ozonization, delignification, excitation purity, bleaching.

### INTRODUCTION

Ozone bleaching of pulp and effect of pH during ozonization on brightness, Kappa number and strength properties has been studied for many years and it is a subject of several publications. Some authors examined and discussed the impact of pH in the whole range of pH 1-12 (Godsay and Pearce 1985; Hosokawa and Kobayashi 1976a; Rutkowski and Szopinski 1984; Vrška et al. 2007a, b) on ozone bleaching results and general pulp properties. In other work, the effect of pH in a narrow range of pH 2-4 (Gunnar et al. 1975; Wade 1967; Wigren 1967; Vrška et al. 2007a, b),

pH 4-6 (Brabender et al. 1949; Kemf and Phillips 1978; Vrška et al. 2007a, b), pH 6-7.5 (Ancelle and Plancon 1969) or pH 7.5-10.5 (Hosokawa et al. 1976b; Vrška et al. 2007a, b) was studied. In the Brabender's et al. patent (1949) the optimum pH value in the range of 4 to 7 was marked. Significant effort was also devoted to the impact and effect of additives used in the process of ozone bleaching (Liebergott et al. 1992a, b; Liebergott and van Lierop 1978; Medwick et al. 1992; Jablonský et al. 2004, 2005a, b).

Lindholm (1987) showed that the type of acid (sulphuric, acetic, oxalic acid and water saturated by sulphur dioxide) are used to reduce pulp pH to around 3, at low ozone stage consistency does not affect the effectiveness of the lignin removal. At pH less than 2, oxalic acid removes lignin more effectively as pretreatment of pulps with sulphuric acid. This effect was much smaller at high consistency. By adjusting pH with acetic and formic acid was achieved a better removal of lignin at pH 2 and high consistency, as in the case of pH modification by sulphuric acid (Mbachu and Manley 1981). Jacobson et al. (1991) found out that the pulp with low content of lignin (Kappa number = 3) in comparison to pulp with high content of lignin, during the ozone bleaching, has a strange dependence of the reaction on pH.

Ozone bleaching is not required at high temperature bath (Oltmann et al. 1992). Kobayashi et al. (1976a, b) found out that when the temperature was reduced within the range of 0-30°C, it decreased the consumption of ozone and the loss of the limit viscosity number, however the brightness increase was achieved by enhancing the consumption of ozone. In their work, this effect was confirmed by multistage ozonization. Liebergott and van Lierop (1978) observed that the temperature increase from 20 to 80°C enhances Kappa number and reduces the limit viscosity number. Oltmann et al. (1992) confirmed the influence of temperature on the pulp properties in MC and HC ozone bleaching. Kamishima et al. (1985a, b, c) found that the speed of delignification is reduced with the decreasing temperature. Singh (1982) showed that the clear degradation of cellulose is giving out at an ozonization temperature higher than 100°C. Allison (1985) confirmed the improvement of ozone bleaching to reduced temperature, which in turn decreases the ozone decomposition. A bleaching agent is a substance that can whiten or decolorize other substances. Coloured substances generally contain chromophores that can absorb visible light having specific, characteristic wavelengths, and reflect or transmit the part of light that is not absorbed (Edelstein and Sidney 1948). The specific objectives of this work were to determine the effect of ozone delignification conditions on the dominant wavelength changes. The purpose of this study was to describe the changes of excitation purity of pulp during the ozone delignification at various conditions T = 40 and 20°C and pH in the range of 0.3; 2.6; 3.9; 8.8 and 9.6.

## MATERIAL AND METHODS

### Raw material

Oxygen-delignified hardwood kraft pulp from an industrial source was used. Characteristics of the pulp are as follows: Kappa number 6.93, viscosity 817 ml.g<sup>-1</sup>, brightness 48.1 %ISO, degree of polymerization 1201, whiteness 83.04, a\* coordinate 2.67, b\* coordinate 15.13, yellowness 32.25 %, tensile strength 1034 m, zero span tensile strength index 57.97 N.m.g<sup>-1</sup>, tensile strength index 10.14 N.mg<sup>-1</sup>.

### Conditions of ozone stage

The following conditions of the ozone stage were maintained: Oxygen flow rate 7.5 ml

$\text{O}_2 \cdot \text{s}^{-1}$  ( $27 \text{ l O}_2 \cdot \text{h}^{-1}$ ), the consistency of the pulp 30 % and ozone production  $56 \text{ mg O}_3 \cdot \text{l}^{-1} \text{ O}_2$  as determined by iodometric titration. The ozonization of the pulp was carried out at 40 and  $20^\circ\text{C}$  in a rotating vessel (100 ml) at pH values 0.3; 2.6; 3.9; 8.8 and 9.6. The pH was adjusted with aqueous sulphuric acid and sodium hydroxide. The accuracy in ozone consumption and pH determinations are estimated to be  $\pm 3 \text{ mg}$  and  $< \pm 0.1$  units, respectively.

### Excitation purity

Excitation purity ( $P_e$ ) is the ratio of the distance from the point representing the achromatic stimulus ( $x_n, y_n$ ) to the colour stimulus considered ( $x_s, y_s$ ) to the distance from the point representing the achromatic stimulus ( $x_n, y_n$ ) to the point on the spectrum locus representing the dominant wavelength ( $x_D, y_D$ ) (CIE Publ. 17.4 1987).  $P_e$  is thus defined in terms of Fig. 1 as  $P_e = d_1 \cdot d_2^{-1}$ ,

where:  $d_1$  - the distance between ( $x_n, y_n$ ) and ( $x_s, y_s$ ),  
 $d_2$  - the distance between ( $x_n, y_n$ ) and ( $x_D, y_D$ ).

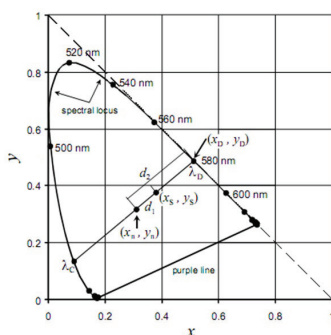


Fig. 1: CIE xy chromaticity diagram. In the diagram are shown the loci of CIE illuminant C ( $x_n, y_n$ ), a sample ( $x_s, y_s$ ), the dominant wavelength  $\lambda_D$  of the sample at the coordinates ( $x_D, y_D$ ) and the complementary wavelength  $\lambda_C$ .

Dominant wavelength and excitation purity were determined using TAPPI standard T 527 om-94 (1996). The excitation purity of pulp samples was measured by Elrepho 2000. The obtained formal rate constant  $k_{P_e}$  represents the rate of excitation purity increase and can be well expressed by the formal first-order kinetic model.

$$P_e = a + b \cdot \exp(-k_{P_e} \cdot t)$$

where:  $P_e$  - excitation purity of colour (%),  
 $k_{P_e}$  - formal first-order rate constant ( $\text{s}^{-1}$ ),  
 $t$  - time of ozonization (s).

Excitation purity is an indication of saturation. Saturation depends on the amount of white light mixed with the hue. A pure hue is fully saturated, i. e. no white light mixed in.

### Statistical analysis

The experimental data were mathematically evaluated using the Matlab and Origin software.

## RESULTS AND DISCUSSION

The activation energy of ozone bleaching is known to be very low compared to bleaching with other chemicals. Ozone bleaching does not require high temperature because increased temperature contributes to decomposition of ozone. In ozone bleaching, adjustment of pH below 3 enhances delignification significantly as it has been proven by several authors (Liebergott and van Lierop 1978; Lindholm 1987; Allison 1985; Oltmann et al. 1992). On the other hand the delignification pH decreasing leads to improved selectivity. Corresponding to the lower Kappa number, brightness increases with the decreasing pH (Oltmann et al. 1992). A reaction of ozone with lignocellulosic materials depends on pH conditions (Vrška et al. 2007a, b). Ozone decomposition is a significant parameter; it would strongly affect the cellulose because of the reactive and unselective radicals generation.

In this work it was found out that the temperature, pH and time of ozonization or charge of ozone don't have an effect to dominant wavelength. The average value of the dominant wavelength for ozonization was  $578.93 \pm 0.07$  nm. The relations between individual quantities are illustrated in Figs. 2 to 5. In Figs. 2 and 3, the excitation purity/ozone consumption plots for individual pH, and temperatures 40 and 20°C, respectively, are shown. Figs. 4 and 5 illustrate excitation purity/time of ozonization dependences for individual pH at 40 and 20°C, respectively, are presented.

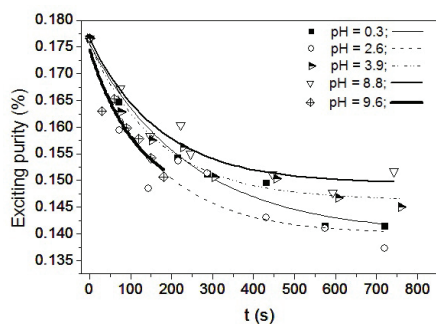


Fig. 2: Evolution time of excitation purity at the temperature 40°C in the systems with applied pH values.

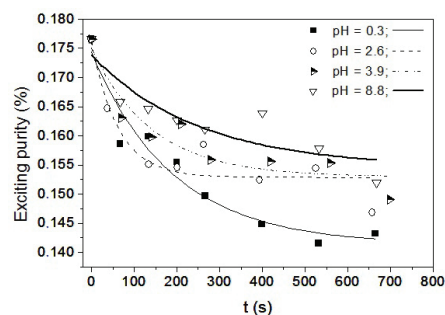


Fig. 3: Evolution time of excitation purity at the temperature 20°C in the systems with applied pH values.

Ozone delignification occurring at the temperature 40°C the lowest excitation purity is achieved at pH = 2.61 (Fig. 2). This dependence can be formulated in mathematical terms of regression in the following way:  $P_e = (0.140 \pm 0.003) + (0.036 \pm 0.004) \cdot \exp(-5.98 \pm 2.18) \cdot 10^{-3} \cdot t$ ,  $r = 0.9892$ . At pH = 8.86 (Fig. 2) there is the smallest decrease of excitation purity and the corresponding function is in the form:  $P_e = (0.149 \pm 0.002) + (0.027 \pm 0.003) \cdot \exp(-5.83 \pm 1.39) \cdot 10^{-3} \cdot t$ ,  $r = 0.9763$ . We can also see that excitation purity decrease with prolonged time of ozonization at pH in acid range from the highest value 0.175 to the smallest 0.135.

The smallest decrease of excitation purity expressed as a dependence of  $P_e$  at pH = 8.8 (T = 20°C) on ozonization time is shown in Fig. 3 and their relation is expressed as  $P_e = (0.155 \pm 0.005) + (0.019 \pm 0.005) \cdot \exp(-3.99 \pm 2.8) \cdot 10^{-3} \cdot t$ ,  $r = 0.8974$ . The most considerable decrease of excitation purity is seen at pH = 0.3 and corresponding function is in the following form:

$P_e = (0.141 \pm 0.003) + (0.033 \pm 0.004) \cdot \exp(-5.26 \pm 1.61) \cdot 10^{-3} \cdot t$ ,  $r = 0.9697$ . In moderate

acidity range (pH = 3.9) the dependence of excitation purity/time of ozonization can be formulated in the mathematical terms of regression in the following way:  $P_e = (0.153 \pm 0.002) + (0.022 \pm 0.004) * \exp(-(7.05 \pm 2.73) * 10^{-3} * t)$ ,  $r = 0.9409$ .

Ozonization running at pH = 2.6 ( $P_e = (0.153 \pm 0.002) + (0.023 \pm 0.004) * \exp(- (16.8 \pm 7.73) * 10^{-3} * t)$ ,  $r = 0.9382$ ) causes the most expressive decrease of excitation purity on the outset of ozonization. The most decrease of excitation purity was up to 273 s ( $P_e = 0.153$ ). With the increase of ozonization time at pH = 2.6, the decrease of excitation purity is being muted.

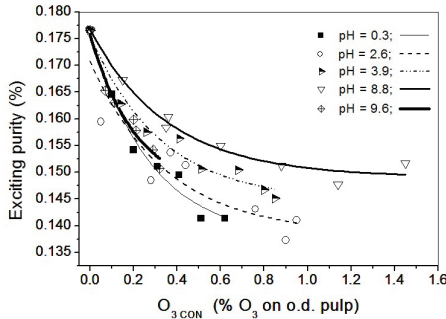


Fig. 4: The excitation purity/ozone consumption plots at individual pH at the temperature 40°C.

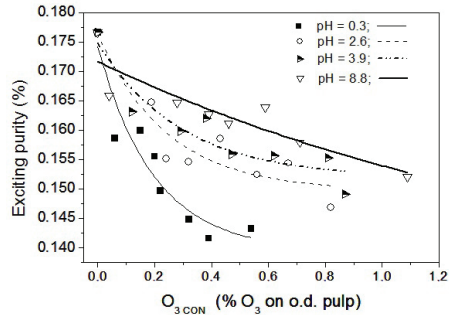


Fig. 5: The excitation purity/ozone consumption plots at individual pH at 20°C.

The dependence of excitation purity from the ozone consumption at 40°C is shown in Fig. 4. The greatest decline is achieved at acidic pH range in the ozone consumption 0.62 - 0.95 % O<sub>3</sub> on o.d. pulp. At alkaline pH range excitation purity has a decline to 0.150 value, but at pH 9.6, 0.32 % of O<sub>3</sub> was consumed on o.d. pulp and at pH 8.8, it was dependent on 1.45 % O<sub>3</sub> on o.d. pulp. The excitation purity decreased with regressed pH of the ozonization system.

Fig. 5 shows a dependence of excitation purity on ozone consumption at the temperature 20°C. The most significant decrease of excitation purity is recorded at pH = 0.3 in the ozone consumption of 0.54 % O<sub>3</sub> on o.d. pulp. The excitation purity develops with rising pH value.

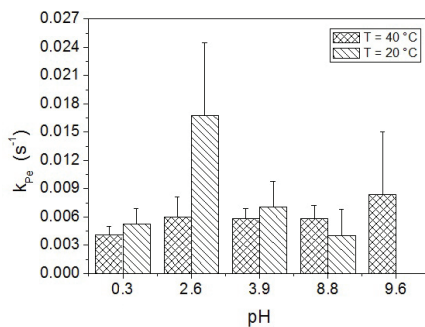


Fig. 6: Rate of excitation purity at individual pH at the temperatures 20 and 40°C.

At 20 and 40°C there is no considerable difference in the kinetic constant of excitation purity between ozonized pulp. It means that the pH treatment does not rise to a higher rate

of excitation purity rate during the ozone bleaching at pH 0.3; 3.9 and 8.8 (Fig. 6). However, the highest change of rate constant of excitation purity was observed at pH in acid range (pH = 2.6) and at temperature 20°C, where value of  $k_{P_c}$  in ozonization was 0.016 s<sup>-1</sup>. The most rate of  $P_c$  in evaluated range of pH from 0.3 to 8.8 at temperature 20°C was achieved at pH = 2.6. At temperature 40°C was reached the highest rate of  $P_c$  at pH in alkaline level (pH = 9.6). This means that the pH treatment at pH = 2.6 and temperature 20°C has a beneficial effect on the kinetic of excitation purity during ozone bleaching.

## CONCLUSIONS

The dominant wavelength of ozonized pulp reached 578.93 ± 0.07 nm. This value does not change with different ozonization conditions. Temperature and pH affected the progress rate constants of excitation purity at the ozonization process. The most rate constant of excitation purity was observed at pH in acid range (pH = 2.6) and at temperature 20°C. The greatest decline of excitation purity is reached at acidic pH range (0.3 and 2.6) in the ozone consumption 0.62-0.95 % O<sub>3</sub> on o.d. pulp at 40°C.

## ACKNOWLEDGMENT

This study is a result of the project implementation: APVV 0850-11 supported by the Slovak Research and Development Agency (SRDA), Slovakia and Finalization of Infrastructure of the National Center for Research and Application of Renewable Energy Sources (ITMS: 26240120028), supported by the Research & Development Operational Programme funded by the ERDF.

## REFERENCES

1. Allison, R.W., 1985: Effects of temperature and chemical pretreatment on pulp bleaching with ozone. CPPA/TAPPI Int. Pulp Bleaching Conf. (Quebec City) Proc.. Pp 47-53.
2. Ancelle, B., Plancon, M., 1969: U.S. pat. 3 451 888.
3. Brabender, G.J., Bard, J.W., Daily, J.M., 1949: U. S. pat. 2 466 633.
4. CIE Publication 17.4, 1987: CIE International lighting vocabulary. 4<sup>th</sup> Ed. Geneva 1987.
5. Edelstein, S.M., 1948: The role of chemistry in the development of dyeing and bleaching. *Journal of Chemical Education* 25(3): 144-149.
6. Godsay, M.P., Pearce, E.M., 1985: Mechanism of inhibition & retardation of ozone – lignocellulose reactions. In: Book 2. Proc. Pulping Conference. TAPPI 1985. Pp 245-262.
7. Gunnar, K.C., Isacson, P.U., Hultman, B.G., Johan, P.H.O., 1975: German pat. 2 448 731.
8. Hosokawa, J., Kobayashi, T., 1976a: Effects of thickness and pH pulp sheets on the properties of pulp bleached with ozone. *Japan Tappi* 30(4): 226-230 (in Japanese).
9. Hosokawa, J., Kobayashi, T., Kubo, T., Kimura, Y., 1976b: Studies on colour reversion of ozone – bleached KP. Part I. Properties of ozone – bleached KP in colour reversion. *Mokuzai Gakkaishi* 22(12): 683-685.
10. Jablonský, M., Vrška, M., Szeiffóvá, G., Šutý, Š., 2005a: Influence of new cellulose protectors in ozone bleaching. *Chemické listy* 99(S): 571-573, electronic (web) version ISSN 1213-7103.

11. Jablonský, M., Vrška, M., Štefan, Š., Szeiffová, G., 2005b: Ozone bleaching of kraft pulp of beech in the presence of peracetic acid as cellulose protector. *Wood Research* 50(4): 51-60.
12. Jablonský, M., Vrška, M., Katuščák, S., 2004: Cellulose protectors for improving ozone bleaching – review. *Wood Research* 49(4): 71-86.
13. Jacobson, B., Lindblad, P.O., Nilvebrant, N.O., 1991: Lignin reactions affect the attack of ozone in carbohydrate. In: *Proc. Int. Pulp Bleaching Conference, SPCI Stockholm, Sweden, Vol. 2: 45-58.*
14. Kamishima, H., Fujii, T., Akamatsu, I., 1985a: Protective agents for carbohydrates in ozone bleaching of unbleached kraft pulps. II. Screening of protective agents for carbohydrates in ozone bleaching. *Shikoku Kogyo Gijutsu Shikensho Kenkyu Hokoku* (9): 15-30.
15. Kamishima, H., Fujii, T., Akamatsu, I., 1985b: Protective agents for carbohydrates in ozone bleaching of unbleached kraft pulps. III. Effect of protection agents for carbohydrates on properties of ozone bleached pulps. *Shikoku Kogyo Gijutsu Shikensho Kenkyu Hokoku* 17(9): 31-39.
16. Kamishima, H., Fujii, T., Akamatsu, I., 1985c: Protective agents for carbohydrates in ozone bleaching of unbleached kraft pulps. IV. Protection mechanism of methanol and oxalic acid for carbohydrates in ozone bleaching. *Shikoku Kogyo Gijutsu Shikensho Kenkyu Hokoku* 17(9): 40-62.
17. Kemf, A.W., Phillips, R.B., 1978: S. pat. 4 080 249.
18. Kobayashi, T., Hosokawa, K., Kubo, T., Kimura, Y., 1976a: Effect of ozone concentration and bleaching temperature on the properties of pulp bleached with ozone. *Japan Tappi* 30(3): 159-164 (in Japanese).
19. Kobayashi, T., Hosokawa, J., Kubo, T., Kimura, Y., 1976b: Effects of multistage ozone bleaching of pulps. *Japan Tappi* 30(6): 330-335 (in Japanese).
20. Liebergot, N., van Lierop, B., Skothos, A., 1992a: A survey of use of ozone in bleaching pulps. Part 1. *Tappi J.* 75(1): 145-152.
21. Liebergot, N., van Lierop, B., Skothos, A., 1992b: A survey of use of ozone in bleaching pulps. Part 2. *Tappi J.* 75(2): 117-124.
22. Liebergott, N., van Lierop, B., 1978: The use of ozone bleaching and brightening wood pulp. Part I. Chemicals pulps. *TAPPI Seminar Notes oxygen/ozone/peroxide pulping bleaching seminar, New Orleans, 90 pp.*
23. Lindholm, C.A., 1987: Effect of pulp consistency and pH in ozone bleaching. Part 1. General aspects. *Paperi ja Puu* 69(3): 211-218.
24. Mbachu, R.A.D., Manley, R.St.J., 1981: The effect of acetic and formic acid pretreatment on pulp bleaching with ozone. *Tappi J.* 64(1): 67-70.
25. Medwick, V.B.Jr., Gratzl, J.S., Singh, R.P., 1992: Delignification and bleaching of chemical pulps with ozone: A literature review. *Tappi J.* 77(3): 207-213.
26. Oltmann, E., Gause, E., Kordsachia, O., Patt, R., 1992: Ozone bleaching technology: A comparison between high and medium consistency. Part I. *Das Papier* 7: 341-350.
27. Rutkowski, J., Szopinski, R., 1984: Investigations on bleaching of sulfate pine with pulp ozone. *Cellulose Chem. Technol.* 18(3): 323-333.
28. Singh, R.P., 1982: Ozone replaces chlorine in the first bleaching stage. *Tappi J.* 65(2): 45-52.
29. T527 om-94, 1996: Color of paper and paperboard (d/0° geometry). *TAPPI Test Methods 1996-1997*, TAPPI Press, Atlanta.
30. Vrška, M., Jablonský, M., Tiño, R., 2007a: Effect of pH on the kinetics of cellulose degradation and delignification in ozonization oxygen delignified hardwood kraft pulp. *Wood Research* 52(1): 47-56.

31. Vrška, M., Jablonský, M., Tiňo, R., Katuščák, S., 2007b: Effect of pH and temperature on cellulose chain scission number in ozonization of oxygen delignified hardwood kraft pulp. Wood research 52(2): 49-56.
32. Wade, R.C., 1967: U. S. pat. 3 318 657.
33. Wigren, G.A., 1967: Can. pat. 769 631.

JABLONSKÝ MICHAL, LUCIA KUČERKOVÁ, MARTINA BOTKOVÁ  
SLOVAK UNIVERSITY OF TECHNOLOGY  
FACULTY OF CHEMICAL AND FOOD TECHNOLOGY  
DEPARTMENT OF CHEMICAL TECHNOLOGY OF WOOD, PULP AND PAPER  
RADLINSKÉHO 9  
812 37 BRATISLAVA  
SLOVAK REPUBLIC  
Corresponding author: [michal.jablonsky@stuba.sk](mailto:michal.jablonsky@stuba.sk)