EFFECT OF PH AND TEMPERATURE ON CELLULOSE CHAIN SCISSION NUMBER IN OZONIZATION OF OXYGEN DELIGNIFIED HARDWOOD KRAFT PULP

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ABSTRACT

Stemming from the absence of detailed kinetic description of the ozonization of oxygen delignified hardwood kraft pulps in the literature and based on its importance for optimizing the pulp treatment, we have focused our attention to evaluation of the following parameters characterizing the kinetic of ozonization: pH, temperature, and ozone consumption. To fulfil the goals, the ozone delignification of oxygen delignified hardwood kraft pulps was studied at various conditions. An influence of pH ranging from 0.3 to 9.6 at two temperatures, namely 20 °C and 40 °C in the process of ozone delignification were evaluated based on cellulose chain scission number. The conditions of the ozone stage were as follows: oxygen flow rate was 27 l O_2/h, the pulp consistency was 30%, and ozone production reached 56 ± 3 mg O_3/l O_2. The temperature and pH affected the progress of degradation at ozonization, but at the same time their influence depended also on the ozone consumption. At the ozonization, performed at the same pH ranging from 2.6 to 8.8 a substantial degradation of cellulose at 20 °C was observed when compared to that at 40 °C. At pH = 3.9 the lowest level of the cellulose chain at the both operational temperatures was determined.

KEY WORDS: degradation, ozonization, kinetics, cellulose chain scission number

INTRODUCTION

Ozone is a good alternative for use as a new bleaching agent in TCF sequences. However, its application will remain limited until the properties of the resulting pulp are improved, since ozone gives rise to extensive degradation of cellulose producing pulp with poor strength properties (Roncero, Colom, Vidal 2003). Within the first stage ozone attacks the aromatic rings of lignin. In addition to the 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, Rybarik, Paulinyova, Mahdalik, 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 minutes (Jablonsky and Vrska 2004). It is important to mention that the problem of ozone bleaching lies rather in the prevention of the cellulose chain destruction than in elimination of the lignin by its degradation. Within a reaction of glucose structures with ozone, direct cleavage of glycosidic bonds

appears. Hoigne´ and Bader (1983a, b), Nompex, Dore´, De Laat, Bawa, Legube (1991) and Ek, Gierer, Jansbo (1989) evaluated the kinetic constants of ozone and the ^oOH radical reactions with lignin and its carbohydrate models. The selectivity of the ozone is $10^5–10^6$, while the selectivity of the ^oOH radical is only 5−6, indicating that the hydroxyl radicals formed during ozonization of the pulp readily degrade carbohydrates. Thus in this paper, the effect of pH and temperature on ozone bleaching is examined and the performance of the reagents was analyzed through the monitoring of chain scission (CS) number in the cellulose chain.

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, brightness 48.1% ISO, degree of polymerization 1201, whiteness 83.04, a* coordinate 2.67, b* coordinate 15.13, yellowness 32.25%, zero span tensile strength index 57.97 N.m/g.

Conditions of ozone stage

The following conditions of the ozone stage were maintained: oxygen flow rate 7.5 ml O_2/s (27 l O_2/h), the consistency of the pulp 30% and ozone production 56 mg O_3/l O_2 as determined by iodometric titration.

The ozonization of the pulp was carried out at 40 ˚C and 20 ˚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 precision in ozone consumption and pH determinations are estimated to be ±3 mg and < ±0.1 units, respectively.

Viscosity

Viscosity was determined according to TAPPI T230. The data should be used primarily for relative comparisons within study. In order to estimate the amount of scissions, the degree of polymerization (DP) of the carbohydrates was calculated from intrinsic viscosity using Mark-Houwink equation, where ([η]) is the intrinsic viscosity (ml/g) of pulp.

Cellulose chain scission number (CS) was calculated applying the following equation (Lindholm, 1990):

$$CS = \frac{DP_0 - DP_t}{DP_t}$$

where CS is the cellulose chain scission number, DP_0 and DP_t are the degree of polymerization before and after scissions, respectively.

Statistical analysis

The experimental data were mathematically evaluated using the Origin software.

RESULTS AND DISCUSSION

The experimental data are gathered in Tables 1 and 2, and relations between individual quantities are illustrated in Figures 1 to 4. In Tables 1 and 2, the time of ozonization (t, s), ozone consumption ($O_{3\ CON}$, % O_3 on o.d. pulp), intrinsic viscosity ([η], ml/g) and degree of polymerization (DP) are listed. Figures 1 and 3 illustrate CS/time of ozonization dependences for individual pH at 40 ˚C and 20 ˚C, respectively, are presented. In Figures 2 and 4, the CS/ozone consumption plots at individual pH at the temperatures 40 ˚C and 20 ˚C, respectively, are shown.

Tab. 1: Experimental data obtained within the study of the ozone bleaching kinetics in the oxygen delignified hardwood kraft pulp at temperature 40 ˚C

Exp.	pH	$O_{3\ CON}$ (% O_3 on o.d. pulp)	t (s)	[η] (ml/g)	DP
0		0.00	0	817	1201
1		0.10	72	720	1046
2		0.20	216	702	1017
3	0.3	0.31	288	679	980
4		0.41	432	677	977
5		0.51	576	672	968
6		0.62	720	667	961
0		0.00	0	817	1201
7		0.05	72	763	1115
8		0.28	144	723	1050
9	2.6	0.37	216	706	1023
10		0.44	287	691	999
11		0.76	431	705	1021
12		0.95	575	660	949
13		0.90	719	630	902
0		0.00	0	817	1201
14		0.14	76	783	1146
15		0.26	152	757	1104
16	3.9	0.41	228	754	1100
17		0.51	304	746	1087
18		0.68	456	729	1060
19		0.80	607	710	1029
20		0.85	759	698	1010
0		0.00	0	817	1201
21		0.15	74	752	1096
22		0.35	148	723	1050
23	8.8	0.36	222	703	1019
24		0.60	247	693	1003
25		0.88	445	702	1017
26		1.14	593	668	962
27		1.45	742	615	878
0		0.00	0	817	1201
28		0.07	60	781	1144
29		0.11	30	763	1115
30	9.6	0.20	90	727	1057
31		0.21	120	718	1043
32		0.29	150	702	1016
33		0.32	180	712	1032

Tab. 2: Experimental data obtained within the study of the ozone bleaching kinetics in the oxygen delignified hardwood kraft pulp at temperature 20 ˚C

Exp.	pH	$O_{3\,CON}$ (% O_3 on o.d. pulp)	t (s)	[η] (ml/g)	DP
0		0.00	0	817	1201
34		0.06	67	753	1098
35		0.15	133	739	1076
36	0.3	0.20	200	730	1061
37		0.22	266	697	1009
38		0.32	399	696	1006
39		0.39	532	697	1009
40		0.54	665	682	984
0		0.00	0	817	1201
41		0.19	37	750	1093
42		0.24	134	709	1028
43	2.6	0.32	201	709	1027
44		0.43	263	706	1023
45		0.56	394	687	992
46		0.67	525	648	931
47		0.82	657	652	937
0		0.00	0	817	1201
48		0.12	70	771	1128
49		0.29	140	751	1095
50	3.9	0.38	209	752	1097
51		0.47	279	729	1060
52		0.62	419	705	1020
53		0.81	559	689	996
54		0.87	698	658	947
0		0.00	0	817	1201
55		0.04	67	708	1027
56		0.28	133	728	1058
57	8.8	0.39	200	703	1018
58		0.46	266	691	999
59		0.59	400	681	983
60		0.71	533	663	954
61		1.09	667	644	924

At the ozone delignification occurring at the temperature 40 ˚C the lowest CS is achieved at pH = 3.9 (Fig. 1.). This dependence can be formulated in mathematical terms of regression in the following way: $CS = (0.189 \pm 0) + (-0.185 \pm 0.001).e^{(-t/(321.397 \pm 34.695))}$, $R^2 = 0.9661$. Ozonization running at pH = 0.3 ($CS = (0.25 \pm 0) + (-0.238 \pm 0.020).e^{(-t/(124.357 \pm 23.122))}$, $R^2 = 0.9550$) causes the most expressive degradation of cellulose chain, most increase of CS was up to 420 s (CS = 0.24). With the increasing time of ozonization at pH = 0.3, process of degradation reactions on cellulose chain is being muted. In alkaline system (pH = 8.8, $CS = (0.368 \pm 0) + (-0.343 \pm 0.033).e^{(-t/(426.030 \pm 90.345))}$, $R^2 = 0.8628$) and also in acidic one (pH = 2.6, $CS = (0.331 \pm 0) + (-0.317 \pm 0.026).e^{(-t/(345.316 \pm 59.024))}$, $R^2 = 0.9112$) there are the highest degree of cellulose chain degradation. The degree of degradation increases with prolonged time of ozonization.

In alkaline system with pH = 9.6 there is also present a high degree of degradation of cellulose chain, but it is more moderate than in a strongly acidic system (pH = 0.3) where $CS = (0.182 \pm 0) + (-0.184 \pm 0.024).e^{(-t/(75.762 \pm 17.821))}$, $R^2 = 0.8708$.
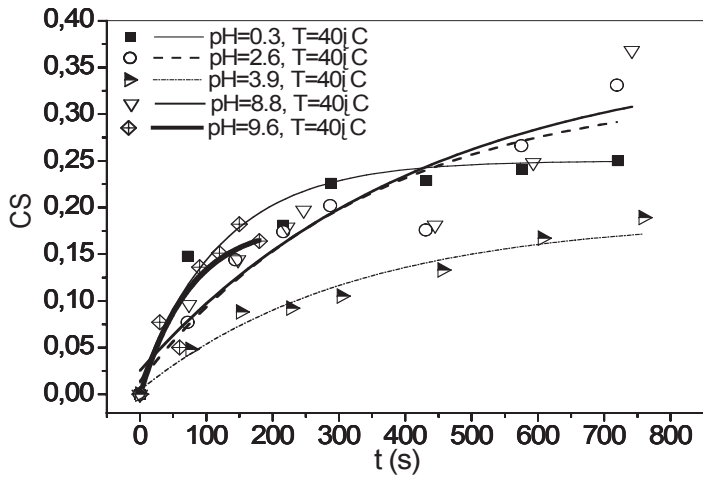
Fig. 1: Time evolution of cellulose chain scission number (CS) at the temperature 40˚C in the systems with applied pH values
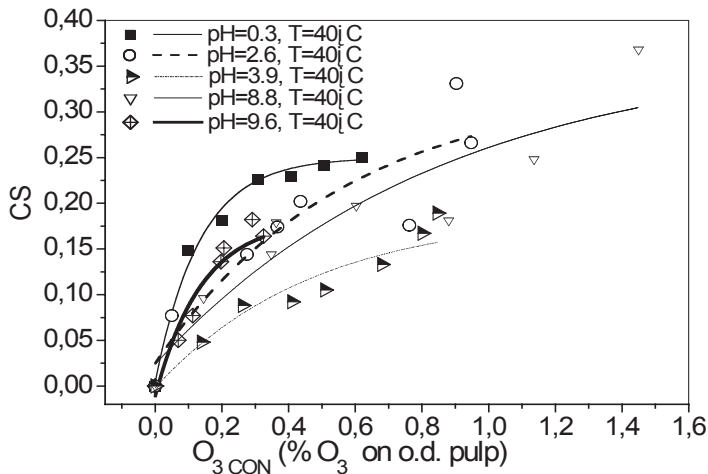

Fig. 2: The effect pH on cellulose chain scission number (CS) at temperature 40 ˚C on the ozone consumption ($O_{3\ CON}$, % O_3 on o.d. pulp)

At pH = 0.3 (Fig. 2.) there is a considerable degradation of cellulose chains at the beginning of the ozonization process. By the ozone consumption over 0.5% O_3 on o.d. pulp degradation of cellulose becomes much more gentle and subsequent increase in ozone consumption does not affect cellulose chain degradation.

In the range of applied pH at 40 ˚C it is possible to follow saddle backed form of CS of cellulose chain with the minimum achieved at pH = 3.9.
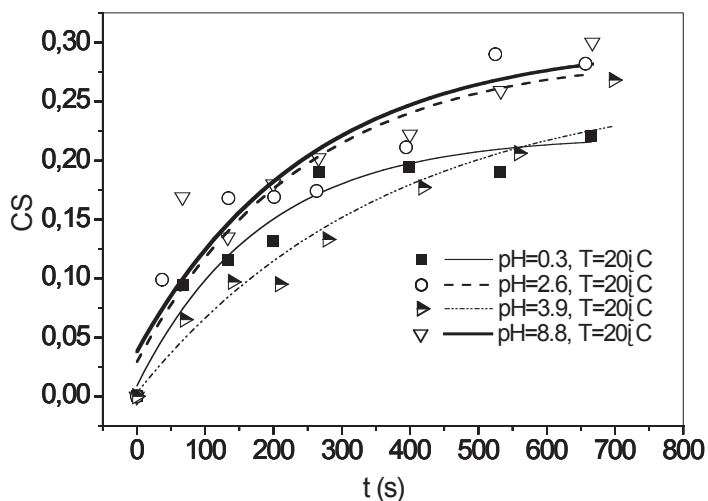
Fig. 3: Time evolution of cellulose chain scission number (CS) at the temperature 20°C in the systems with applied pH values
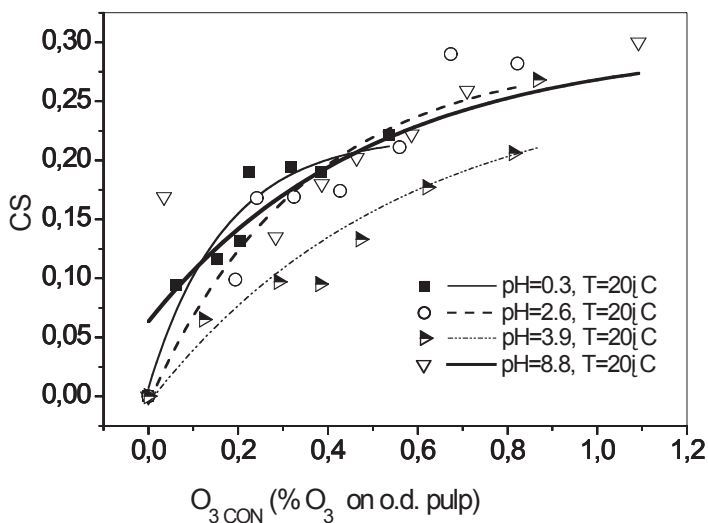

Fig. 4: The effect pH on cellulose chain scission number (CS) at temperature 20 °C on the ozone consumption ($O_{3\ CON}$, % O_3 on o.d. pulp)

The smallest degree of degradation of cellulose chain expressed as a dependence of CS at pH = 3.9 (T = 20 °C) on time of ozonization t = 568 s (CS = 0.21) and it is shown in Fig. 3., their relation is expressed as CS = $(0.268 \pm 0) + (-0.265 \pm 0.016).e^{(-t/(364.598 \pm 47.367))}$, R^2 = 0.9477. With longer times of ozonization less degradation of cellulose can be achieved at pH = 0.3 and the corresponding function is of the form of CS = $(0.221 \pm 0) + (-0.212 \pm 0.144).e^{(-t/(181.885 \pm 23.438))}$,

$R^2 = 0.9573$. The most considerable degradation comes up at pH = 8.8 and function in this case is $CS = (0.3 \pm 0) + (-0.262 \pm 0.030).e^{(-t/(250.204 \pm 55.430))}$, $R^2 = 0.8691$, however at pH = 2.6 there is also apparent strong degradation approximated by $CS = (0.29 \pm 0) + (-0.261 \pm 0.023).e^{(-t/(241.601 \pm 44.158))}$, $R^2 = 0.9152$.

Fig. 4 shows a dependence of CS on ozone consumption at the temperature 20 °C. The least pronounced degradation of cellulose was observed at pH = 3.9. Other applied pH values (0.3; 2.6; 8.8) led to a more distinctive degradation of cellulose chain.

Temperature and pH affected the progress of degradation reactions at the ozonization, but at the same time their influence depends also on the ozone consumption. At the ozonization, carried out at the same pH conditions ranging from 2.6 to 8.8, a more substantial degradation of cellulose was observed at 20 °C in comparison to that at 40 °C (the effect of the temperature is reverse at pH = 0.3). In the case of ozonization carried out at pH = 3.9, the least rate of degradation of cellulose chain was observed. This can be explicitly expressed as a CS at both observed temperatures (40 °C and 20 °C). At 40 °C and pH = 3.9 the least decrease of CS was observed, even in comparison with ozonization carried out at 20 °C and the same pH. It can be concluded that a higher temperature can prevent cellulose chain against degradation reactions in the range of pH with lower acidity (pH = 3.9). The most considerable degradation of cellulose chain was achieved at pH = 0.3, T = 40 °C and ozone consumption 0.6% O_3 on o.d. pulp. If the ozonization is carried out deeper, then the strongest effect of degradation on cellulose chain was determined at pH = 2.6, but on the other hand also in alkaline range at pH = 8.8 at both observed temperatures.

CONCLUSIONS

Temperature and pH affected the progress of degradation reactions at the ozonization process, but at the same time their influence depends also on the ozone consumption. At the ozonization performed at the same pH conditions varying from 2.6 to 8.8 a substantial degradation of cellulose at 20°C was observed when compared to that determined at 40 °C (the effect of the temperature is reverse at pH = 0.3). At pH = 3.9 the smallest degradation of the cellulose chain occurs at the both applied temperatures. Up to ozone consumption 0.6% O_3 on o.d. pulp, the highest degradation of cellulose chain occurs at pH = 0.3 and temperature 40 °C. Above 0.6% O_3 on o.d. pulp, accelerated degradation of cellulose is most substantive at pH = 2.6, and also at pH = 8.8.

ACKNOWLEDGEMENTS

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