

## EFFECT OF ADDING ADDITIVES ON THE SHAPE OF DRIFT SPECTRA ON THE OZONE BLEACHING

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### ABSTRACT

This work is aimed at quantification of performance of additives (1 % o.d. pulp) such as D-mannitol, salicylic acid, cationic potato starch, 2-tert-butyl-5-aminopyrimidine, zirconium (IV) propoxide, methylhydroxyethyl cellulose added ozone stage (Z) on the shape of diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), spectra of ozonized pulp. The Z stage was carried out at the following conditions: 50 g oven dry pulp mass pulp, the consistency 35 %, pH 3, temperature 40°C, 4.45 l O<sub>2</sub>.min<sup>-1</sup> oxygen flow rate, 7.563 mg O<sub>3</sub>.l<sup>-1</sup>O<sub>2</sub> ozone production and 0.3 % o.d. pulp ozone charge.

Studies of the effects of additives on the structural change are presented. The most conspicuous changes in the spectra of ozonized pulp were observed at wavenumbers 1655, 1508, 1458, 1375, 1248, 1043, 1092 and 899.cm<sup>-1</sup>.

KEYWORDS: Ozone bleaching, DRIFT, cellulose degradation.

### INTRODUCTION

FTIR (Hoang et al. 2005, Boeriu et al. 2004, Vazquez et al. 2002, Rodrigues et al. 2001, Meder et al. 1999, Faix and Böttcher 1992, Schultz et al. 1985) or DRIFT (Pandey and Pitman 2004, Vazquez et al. 2002, Rodrigues et al. 1998, Weinstock et al. 1998) spectra is a useful technique for studying wood decay chemistry (Pandey and Pitman 2004, Rodrigues et al. 1998) as well as an analytical technique for estimation of the chemical composition and functional properties of lignin (Hoang et al. 2005, Boeriu et al. 2004, Vazquez et al. 2002, Rodrigues et al. 1998, Faix and Böttcher 1992, Schultz et al. 1985) and polysaccharide (Vazquez et al. 2002, Rodrigues et al. 2001, Meder et al. 1999, Schultz et al. 1985).

Ozone as an individual oxidative reagent when compared with polysaccharides reacts

$10^5$  times faster with substances of the lignin type. The reason for degradation of a number of reactions is formation of hydroxyl (free) radicals (Ragnar et al. 1999). These radicals are the results of reactions with lignin. Free radicals in lignin are formed mainly by the cleavage of ether bonds leading to phenoxy radicals, but alkoxy radicals can also be produced when chemical bonds in the lignin-carbohydrate complex are broken (Hon 1983).

Destruction of aromatic ring of lignin has been recognized, while the process of ionization itself depends on the type of lignin as well as the environment in which the ozonization is performed. It has been proved that new compounds with active oxygen, peroxides, and hydroperoxides had incurred (Katušćák et al. 1971). These compounds are active and are capable of other reactions with the lignin structures, for example C=C fission reaction, radical reactions initiations (Katušćák et al. 1972).

In the oxidation of lignin it is possible to assume a similar oxidation mechanism has certain peculiarities, due to both the macromolecular character of lignin and to its complex structure. A relatively slowly moveable lignin macro matrix lowers the possibility of recombining the radicals formed during oxidation, to such an extent that a certain part remains alive even after the oxidation is completed (Katušćák et al. 1971). Considerable efforts have been devoted to research on identifying cellulose protectors (CP) able to prevent the degradation of cellulose during ozone bleaching (Jablonsky et al. 2004, Medwick et al. 1992, Liebergott et al. 1992a, b, Katušćák et al. 1972). The function of cellulose protectors is believed to lie in scavenging of free radicals, which consequently limits the carbohydrate degradation reactions (Liebergott et al. 1992b).

This work focuses on the influence of adding additives during ozonization of pulp on the shape of DRIFT spectra.

## MATERIAL AND METHODS

The kraft pulp after oxygen stage was used with the following characteristics: Kappa number 9.92, viscosity of  $876 \text{ ml}\cdot\text{g}^{-1}$  and brightness of 46.93 % ISO. The ozonization of the 50 g o.d. pulp in a rotating vessel with 250 ml volume was carried out at following conditions: the pulp consistency was 35 %, pH 3, temperature  $40^\circ\text{C}$ , oxygen flow rate was  $4.45 \text{ l O}_2\cdot\text{min}^{-1}$ , ozone production was  $7.563 \text{ mg O}_3\cdot\text{l}^{-1}\text{O}_2$  as determined by iodometric titration, ozone charge (0.3 % o. d. pulp). The ozonization 1 % additives on oven dry pulp (o.d.) as a cellulose protector were used. The following additives were used: methylhydroxyethyl cellulose (Tylose MH 300 P2, viscosity  $300 \text{ mPa}\cdot\text{s}$  ( $20^\circ\text{C}$ ), SE Tylose GmbH & Co.KG), zirconium (IV) propoxide solution (70 wt. % in 1-propanol, Lambda Life), 2-tert-butyl-5-aminopyrimidine (p.a.), ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , 81–83 % as  $\text{MoO}_3$ , Sigma), salicylic acid (Merck) and cationic potato starch derivate (Empresol NE 2 SE, degree of substitution 0.035, Emsland – Stärke GmbH.), D-mannitol (Sigma). The pulp was characterized by: kappa number (TAPPI T 236), viscosity (TAPPI T 230) and brightness (TAPPI T 452).

The pulp samples (approximately area of  $1\text{cm}^2$ ) were placed into a standard sample holder of Digilab Excalibur FTS 3000MX FTIR spectrometer. The FTIR spectra were recorded with the nominal resolution of  $4\cdot\text{cm}^{-1}$  using DRIFT technique. Spectra were recorded over the range  $600\text{--}1800\cdot\text{cm}^{-1}$ . Each spectrum is the average of 20 individual scans.

The mutual comparison of spectra requires their transformation from reflectance mode to absorption-dependent mode. All recorded spectra were mathematically converted to Kubelka - Munk intensity (KM intensity). The exact determination of individual spectral band height (intensity) requires the precise baseline-correction, held the same for each sample spectrum at the

same spectral region.

Spectral change at wavenumber on the ozone consumption was expected as following equation (1):

$$SC_w = \frac{X - X_0}{O_{3CON}} \quad (1)$$

Where:

$SC_w$  – spectral change at wavenumber on the ozone consumption

$X_0$  – band-height of initial sample

$X$  – band-height of sample after ozonization

$O_{3CON}$  – ozone consumption (%  $O_3$  on o.d. pulp)

Relative of spectral change at wavenumbers on the ozone consumption was expected as following equation (2):

$$SC_{w_1/w_2} = \frac{X_1 - X_{01}}{X_2 - X_{02}} \quad (2)$$

Where:

$SC_{w_1/w_2}$  – relative of spectral change at wavenumbers on the ozone consumption

$X_{01}$  – band-height of initial sample at wavenumber 1

$X$  – band-height of sample after ozonization at wavenumber 1

$X_{02}$  – band-height of initial sample at wavenumber 2

$X$  – band-height of sample after ozonization at wavenumber 2

$O_{3CON}$  – ozone consumption (%  $O_3$  on o.d. pulp)

The experimental DRIFT FTIR spectra were mathematically evaluated using OMNIC® (Thermo Nicolet Corp.) and MicroCal® Origin software.

## RESULTS AND DISCUSSION

The obtained experimental data summarized in the Tab. 1 shows the type of additives, ozone consumption, kappa number, viscosity and brightness after high consistency ozonization. As shown in Tab. 1, the presence of the methylhydroxyethyl cellulose and 2-tert-butyl-5-aminopyrimidine increases the ozone consumption. During the ozone bleaching with extra additives (magnesium ethoxide, D-mannitol) decrease of the Kappa number was observed (Tab. 1). The most negative effect on the change of Kappa number of ozone bleaching can be seen in substances such as 2-tert-butyl-5-aminopyrimidine, methylhydroxyethyl cellulose, zirconium (IV) propoxide. The presence of all additives enhanced brightness (Tab.1). During ozone bleaching at 0.3 % ozone charge with extra additives as D-mannitol and 2-tert-butyl-5-aminopyrimidine increase of the viscosity was measured.

Tab. 1: The influence of (1% on o.d. pulp) additives on the characteristic parameters of the ozonized pulp.

Samples	Type of additive	Ozone consumption	Kappa No.	Viscosity	Brightness
		(% O <sub>3</sub> o.d. pulp)*	-	(ml.g <sup>-1</sup> )	(% ISO)
Original	-	0	9.92	876	46.9
A0	Without additive	0.185	6.39	763	47.9
A1	Methylhydroxyethyl cellulose	0.239	7.34	647	54.4
A2	Zirconium (IV) propoxide	0.154	8.41	723	49.4
A3	2-tert-butyl-5-aminopyrimidine	0.196	10.17	808	50.3
A4	Ammonium molybdate	0.131	6.99	745	54.2
A5	Salicylic acid	0.166	6.45	728	56.1
A6	Cationic potato starch	0.140	6.93	740	51.1
A7	D-mannitol	0.144	6.03	814	50.2

\* ozone charge is 0.3 % ozone on o.d. pulp.

Fig. 1 shows band intensities in the infrared spectra of oxygen delignified hardwood kraft pulp (original) and ozonization pulp without additive (A0) and with additives (A1 to A9) in the range from 1800 to 1400.cm<sup>-1</sup> and spectra of pulp in the range from 1400 to 800.cm<sup>-1</sup> can be seen on Fig. 2. The most conspicuous change is at wavenumbers 1655, 1458, 1375, 1248, 1043, 1092 and 899.cm<sup>-1</sup>. Peaks in the fingerprint are assigned (Pandey 2005, Pandey and Pitman 2004, Hinterstoisser et al. 2001, Maréchal and Chanzy 2000, Pandey and Theagarajan 1997, Gotwald and Wachter 1997, Collier et al. 1992, Fengel and Ludwig 1991, Faix 1991) 1734.cm<sup>-1</sup> for C=O valence vibration of acetyl- or COOH-groups, 1655.cm<sup>-1</sup> for C=O stretch, in conjugated ketons, carbonyls and in ester groups (frequently of carbohydrate origin) conjugated aldehydes and carboxylic acid, 1508.cm<sup>-1</sup> for aromatic skeletal vibrations in lignin, 1458.cm<sup>-1</sup> for asymmetric C-H bending from methoxyl groups, 1375.cm<sup>-1</sup> for absorbed O-H and conjugated C-O, 1248.cm<sup>-1</sup> for syringyl ring and C-O stretch in lignin and xylan, 1092.cm<sup>-1</sup> for C-O deformation in secondary alcohols and aliphatic ethers, 899.cm<sup>-1</sup> for anomere C-groups, C<sub>1</sub>-H deformation, ring valence vibration.

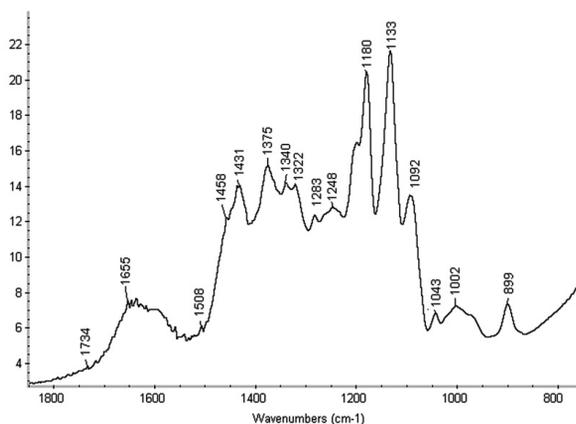


Fig. 1: FTIR DRIFT spectra of reference (original – oxygen delignified hardwood kraft pulp).

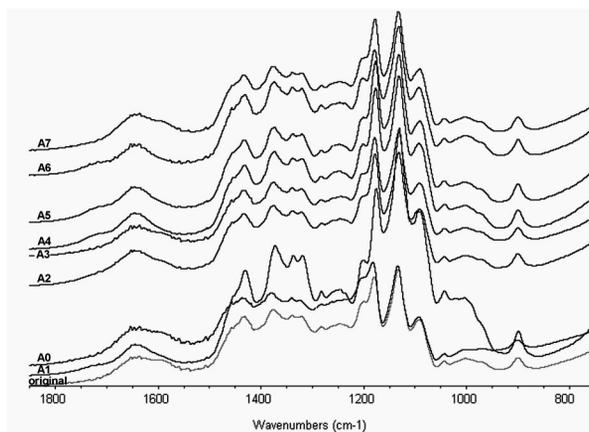


Fig. 2: FTIR DRIFT spectra of original, ozonized samples with and without additives. Spectra of pulp in the range 1800 to 800. $\text{cm}^{-1}$ . (original – oxygen delignified hardwood kraft pulp, A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 –ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

Fig. 3 up to Fig. 13 shows spectral change of characteristic band (1655, 899, 1734, 1508, 1375, 1508/1375, 1734/1375, 1458, 1043, 1248 and 1092. $\text{cm}^{-1}$ ) on ozone consumption, respectively.

The affected regions in the spectra of ozonized pulp with and without additives include those bands that are chiefly allocated to polysaccharides. These bands are in the fingerprint region (Fig. 1) such as those as  $\sim 1338$ , 1320, 1162 and 1110. $\text{cm}^{-1}$ , and in the range of C-O valence vibrations from 1060 to 1015. $\text{cm}^{-1}$ .

The application of additives in ozonization causes the change of formation of carboxylates (C=O stretch; in conjugated p-substituted aryl ketones) and decrease of band  $\sim 1655$ . $\text{cm}^{-1}$  was observed (Fig. 3). Ozonization by the addition of D-mannitol (A7) is causing increase of  $\text{SC}_{1655}$

(approximately to 8 % against ozonization without additives). At others additives was observed decrease of formation of carboxylates. The considerable decreased up to 103 % against ozone delignification without additive at methylhydroxyethyl cellulose (A1) and moderate decrease in the carboxylates was performed at ammonium molybdate (A4, approximately to 5 %) against ozone delignification without additive.

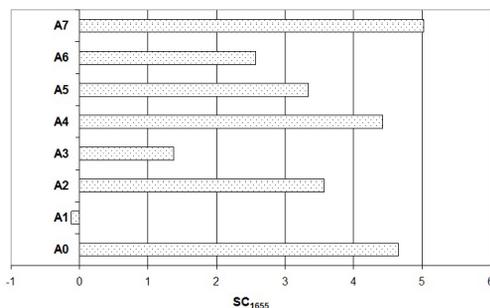


Fig. 3: Spectral change at  $1655.\text{cm}^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 – without additives, A1 – methylhydroxyethylcellulose, A2 – zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 – ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

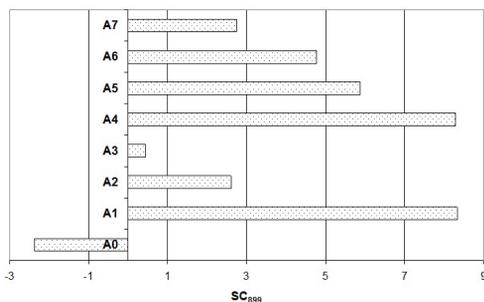


Fig. 4: Spectral change at  $899.\text{cm}^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 – without additives, A1 – methylhydroxyethylcellulose, A2 – zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 – ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

Peaks  $1375$ ,  $1158$  and  $898.\text{cm}^{-1}$  are mainly due to carbohydrates and have no significant contribution from lignin (Pandey 2005, Pandey and Pitman 2004). The spectral change at  $899.\text{cm}^{-1}$  on ozone consumption was increased at all additives against ozone delignification without additives (Fig. 4). The most considerable increase was in presence of additive methylhydroxyethylcellulose (A1) and ammonium molybdate (A4). The smallest change of  $\text{SC}_{899}$  was recognised at 2-tert-butyl-5-aminopyrimidine (A3) against the ozone bleaching without additives (A0) and this increase was moderate against the oxygen delignified hardwood kraft pulp. Increase of  $\text{SC}_{899}$  during the ozone delignification with additives indicated that degradation of carbohydrates is smaller than during at ozone bleaching without additives (A0).

At  $1734.\text{cm}^{-1}$  was observed the highest change of  $\text{SC}_{1734}$  at applied ammonium molybdate (A4), salicylic acid (A6), cationic potato starch (A5) in ozone delignification against the ozone bleaching without additive (Fig. 5). The moderate decrease ( $\sim 7\%$ ) of spectral change on the

ozone consumption at band of  $1734.\text{cm}^{-1}$  was observed at D-mannitol (A7) and slightly decrease ( $\sim 0.3\%$ ) at 2-tert-butyl-5-aminopyrimidine (A3), against the ozone delignification without additives.

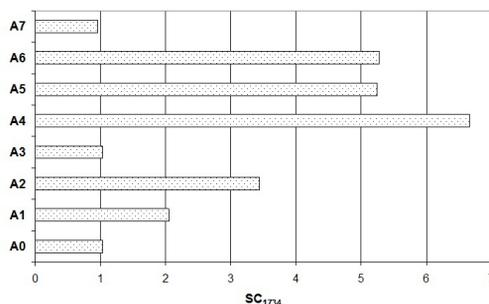


Fig. 5: Spectral change at  $1734.\text{cm}^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 –ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

Fig. 6 shows the effect of additives on the spectral change at  $1508.\text{cm}^{-1}$  (aromatic skeletal vibrations of lignin) on ozone consumption. A comparison of spectral change of ozonized pulp with additives against that without additive shows significant change of lignin. All additives cause the spectral change at  $1508.\text{cm}^{-1}$  and the most considerable effect on the change (decrease) was achieved at D-mannitol (A7) and the smallest change of  $\text{SC}_{1508}$  was at salicylic acid (A5).

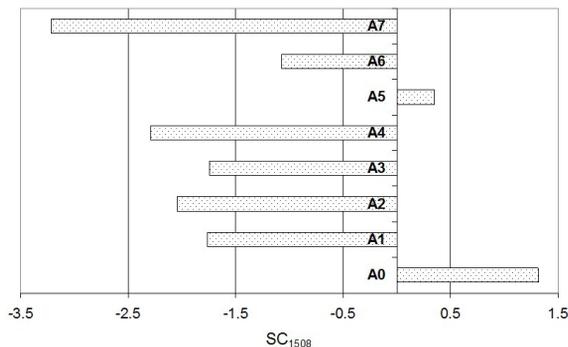


Fig. 6: Spectral change at  $1508.\text{cm}^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 –ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

At ozone delignification at all ozonized pulps with additives was observed increase of  $\text{SC}_{1375}$ , which is characteristic for CH deformation vibration.

Fig. 7 shows that the highest change of  $\text{SC}_{1375}$  was achieved at additive methylhydroxyethyl cellulose (A1) and the considerable change of  $\text{SC}_{1375}$  was found at additives such as ammonium molybdate (A4), cationic potato starch (A6) and salicylic acid (A5). The smallest change of  $\text{SC}_{1375}$

against original pulp was observed at additives such as zirconium (IV) propoxide (increase) and 2-tert-butyl-5-aminopyrimidine (A3).

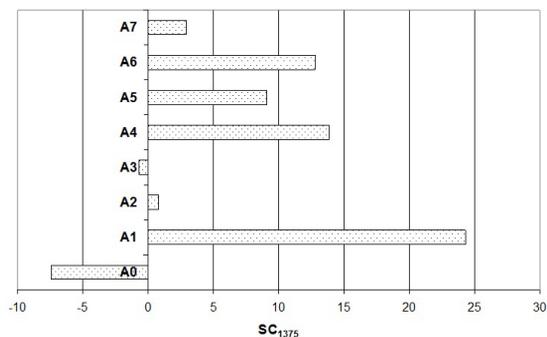


Fig. 7: Spectral change at  $1375.\text{cm}^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 –ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

The relative change in ratio of lignin/carbohydrate peaks at applied different additives on ozone delignification was calculated by taking ratio of intensity of lignin reference band at  $1508.\text{cm}^{-1}$  against carbohydrate reference bands  $1375.\text{cm}^{-1}$ . The variations of lignin/ carbohydrate spectral change on ozone consumption ( $\text{SC}_{1508/1375}$ ) are plotted on Fig. 8.

After ozone delignification with additives the spectral change of the lignin ( $\text{SC}_{1508/1375}$  ratio) markedly decrease at 2-tert-butyl-5-aminopyrimidine (A2) and in case of additive D-mannitol was noticed decreases of spectral change of the lignin. At applied additive such as methylhydroxyethyl cellulose was achieved evident increase of ratio  $\text{SC}_{1508/1375}$  against ozonization without additive and oxygen delignified hardwood kraft pulp. At the rest additives slight increase of carbonyl content was observed.

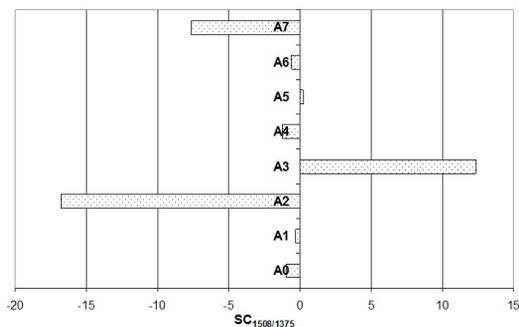


Fig. 8: Relative of spectral change at wavenumbers of lignin (C=C) peak at  $1508.\text{cm}^{-1}$  to carbonyl (C=O) peak at  $1375.\text{cm}^{-1}$  on ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 –ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

The relative change in the proportion of carbonyl groups spectral change at  $1734.\text{cm}^{-1}$  on ozone consumption against carbohydrates  $\text{SC}_{1375}$  was calculated. The relative changes in the concentration of carbonyl groups ( $\text{SC}_{1734/1375}$ ) as a function of adding additive are plotted in Fig. 9.  $\text{SC}_{1734}$  are affected while adding additives on ozone delignification (Fig. 5). The relative concentration of carbonyl groups was increased in presence of all additives in ozonized pulp, except for additive 2-tert-butyl-5-aminopyrimidine (A3). At zirconium (IV) propoxide was attained the highest increase of relative concentration of carbonyl groups.

The increase of asymmetric C-H bending from methoxyl groups at  $1458.\text{cm}^{-1}$  (Faix 1991) in the presence of all additives except for 2-tert-butyl-5-aminopyrimidine (A3) in ozonized pulp was observed (Fig. 10). The most considerable increase  $\text{SC}_{1458}$  was carried out at adding cationic potato starch (A6), methylhydroxyethyl cellulose (A1) and ammonium molybdate (A4).

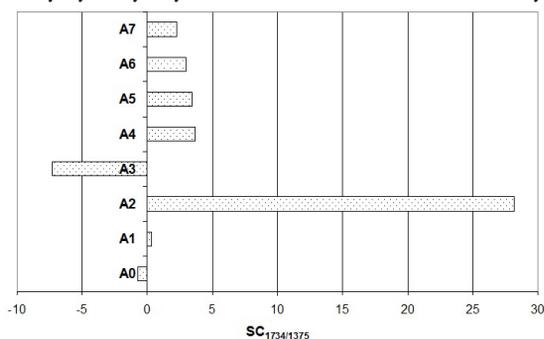


Fig. 9: Relative of spectral change at wavenumbers of carbonyl (C=O) peak at  $1734.\text{cm}^{-1}$  to carbohydrate (C=O) peak at  $1375.\text{cm}^{-1}$  on ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 –ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

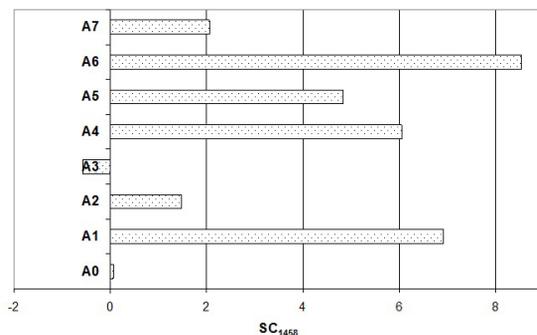


Fig. 10: Spectral change at  $1458.\text{cm}^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 –ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

In lignin, the most important are  $\text{C}_{\text{alkyl}}-\text{O}$  ether vibrations, methoxyl and  $\beta\text{-O-4}$  were assigned to the  $1047\text{-}1004.\text{cm}^{-1}$  region and the  $\text{C}_{\text{alkyl}}-\text{O}$  vibrations to the  $1262\text{-}1224.\text{cm}^{-1}$

region (Gotwald and Wachter 1997, Collier et al. 1992). Change of  $C_{alkyl}-O$  ether vibrations, methoxyl and  $\beta-O-4$  (Faix 1991) due to addition of additives on ozonized pulp are shown in Fig. 11. The influence of all additives was observed as an increase of band at  $1043.cm^{-1}$ . The highest spectral change on the ozone consumption at methylhydroxyethyl cellulose (A1) was observed at  $1043.cm^{-1}$  band. At zirconium (IV) propoxide (A2) and 2-tert-butyl-5-aminopyrimidine (A3) the smallest change against to other additives at  $1043.cm^{-1}$  band was achieved.

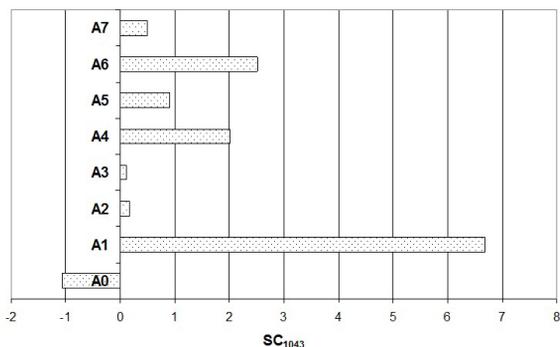


Fig. 11: Spectral change at  $1043.cm^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 – ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

At band  $1248.cm^{-1}$  increase of spectral change on the ozone consumption by all additives was observed. At the same band, the highest spectral change on ozone consumption was attained at ammonium molybdates (A4) and the smallest increase of bands was accomplished at 2-tert-butyl-5-aminopyrimidine (A3) as can be seen on Fig. 12.

Fig. 13 shows the spectral change of C-O deformation in secondary alcohols and aliphatic ethers on the ozone consumption at band  $1092.cm^{-1}$  which was attained at all additives (increase of  $SC_{1092}$  against ozonization without additives).

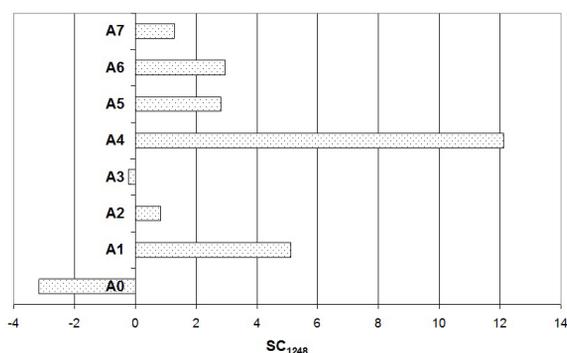


Fig. 12: Spectral change at  $1248.cm^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyethylcellulose, A2 –zirconium (IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 – ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

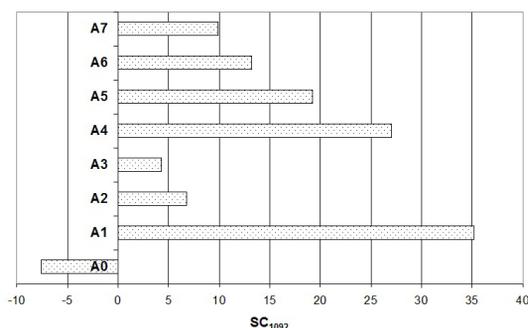


Fig. 13: Spectral change at  $1092.\text{cm}^{-1}$  on the ozone consumption in ozone delignification with and without additives (A0 –without additives, A1 – methylhydroxyetylcellulose, A2 –zirconium(IV) propoxide, A3 – 2-tert-butyl-5-aminopyrimidine, A4 –ammonium molybdate, A5 – salicylic acid, A6 – cationic potato starch, A7 – D-mannitol).

Results show that DRIFT FTIR spectroscopy can be used for evaluation of structural changes in ozonized pulp in general. Presence of methylhydroxyetyl cellulose (A1) and ammonium molybdate (A4) in ozonized pulp has increased spectral change on the ozone consumption against investigated additives and ozonized pulp without additive (A0) at all examined wavenumbers.

## CONCLUSIONS

This study describes how the addition of additives in ozone delignification can be evaluated by DRIFT FTIR spectrum in  $1800 - 600.\text{cm}^{-1}$ .

The most conspicuous changes in the spectra of ozonized pulp with additives were observed at wavenumbers 1655, 1458, 1375, 1248, 1043, 1092 and  $899.\text{cm}^{-1}$ .

In the presence of additive such as methylhydroxyetyl cellulose and ammonium molybdate there was increased spectral change at wavenumber on ozone consumption in general.

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