WOOD RESEARCH
51 (4): 2006
55-68

APPLICATION OF ANTHRAQUINONE IN KRAFT PULPING OF BEECH WOOD

Mária Fišerová, Juraj Gigac
Pulp and Paper Research Institute, Bratislava, Slovak Republic

Peter Melník
Bukóza Holding, a.s. Hencovce, Slovak Republic

ABSTRACT

Influence of anthraquinone (AQ) on kraft pulping of beech wood was tested in laboratory scale. With increase AQ addition delignification is accelerated most markedly to an addition of 0.1% AQ on o. d. wood. At this addition level kappa number of pulp decreased by 4.5 units when compared with delignification without AQ. Pulp yield at same kappa number was by 2.2% higher and rejects content in pulp by 25% lower than in pulp prepared without AQ addition. Concentration of residual active alkali black liquor was higher with AQ addition which makes possible to reduce active alkali charge in the pulping process by 5% in order to achieve same results. Reduction of cooking liquor sulphidity from 18% to 10% in presence of AQ has no negative effect on pulping of beech wood and is resulting in reduction of sulphur compounds emission to atmosphere by 45%. Addition of AQ slightly reduced bleachability of kraft beech pulp by the OD(EOP)DD sequence as chlorine dioxide consumption increased by 8%. Addition of AQ and lower sulphidity of cooking liquor has no significant influence on physical and mechanical properties of bleached kraft beech pulp.

KEY WORDS: kraft pulping, beech wood, anthraquinone, bleachability, pulp properties

INTRODUCTION

Anthraquinone (AQ) is an important catalyst that has been used widely in alkaline wood pulping for its effectiveness in acceleration of delignification and preserving pulp yield. In 1975, the important discovery was made that unmodified AQ addition into the digester not only improved the resulting pulp yield, but also increases delignification rate of pulping (Holton 1977, Bach and Fiehn 1989). The combination of these two attributes made AQ a successful additive in kraft pulping. The mechanism of AQ has been studied in great detail (Blain 1992, Blain 1998, Brogdon and Dimmel 1994, Dimmel 1996). In spite of extensive research conducted on AQ pulping, AQ chemistry during the alkaline pulping process is not fully understood. Thus, the effectiveness of using AQ to improve pulping performance is limited. One of the main obstacles to research progress is the lack of an effective method for determination AQ in cooking liquors.

It is known that AQ behaves as a redox catalyst during alkaline pulping (Fig. 1), unlike alkali or hydrosulphide anions in the conventional kraft process, which are consumed during the chemical reactions. AQ reacts with reducing aldehyde end groups of the carbohydrates oxidizing them to carboxylic acids. This oxidation of aldehyde to carboxylic acid groups inhibits the stepwise alkaline depolymerization reaction that occurs with the reducing sugar end groups, resulting in increased yield. The oxidation of the aldehydes to carboxylic acids reduces AQ to anthrahydroquinone (AHQ), which is the second key component of the redox catalyst cycle. The ionized form of AHQ, AHQ^{2-}, is known to be the active species responsible for the enhanced delignification reaction (Fig. 1). AHQ^{2-} reacts with the end groups of lignin in wood resulting in the step-wise fragmentation reaction. In this process, AHQ^{2-} is reduced back to AQ thereby completing the overall redox catalyst cycle. The reactions of AHQ^{2-} in lignin fragmentation reactions is known to be much more effective than reactions of alkali or hydrosulphide anions, and operate by a significantly different delignification mechanism than hydrosulphide anions (Brogdon and Dimmel 1994, Dimmel 1996).

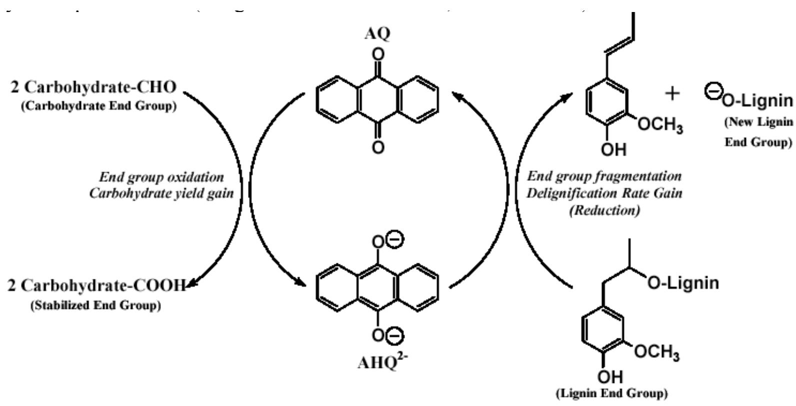

Fig. 1: Catalytic redox reactions involving AQ and AHQ^{2-} species participating in carbohydrate stabilization and lignin fragmentation reactions (Blain 1992, Blain 1998, Brogdon and Dimmel 1994, Dimmel 1996)

The improved pulp yield due to AQ (at a given kappa number) results in decreased organic solids loading to the recovery boiler due to less carbohydrates being dissolved in the spent liquor. The catalytic action of AQ on delignification can be used to extend the delignification, to lower the required active alkali charge, to lower digester cooking temperatures, or to shorten the cooking times. Besides decreased cooking temperatures and reduced alkali charge, an added benefit is reduced scaling that has also been observed in the digester and heat exchangers (Holton 1977, Bach and Fiehn 1989, Katz et al. 1995). These benefits of AQ addition to the kraft process can assist mills faced with production bottlenecks either in digester throughput or chemical recovery, or can assist mills in achieving higher yield per unit of wood resulting in lower wood costs. One of the attractive features of AQ addition to the kraft process is its ability to achieve these benefits without expensive capital-intensive equipment. Several investigators have developed computer programs to determine the appropriate economic applications of AQ to assist these various bottlenecks or to assist achievement of environmental goals with low capital investments (Katz et al. 1995, Parthasarathy 1995, Parthasarathy 1998).

The objective of laboratory experiments were to find out effects of AQ and low sulphidity on kraft delignification rate of beech wood, yield of pulp, bleachability, physical and mechanical properties of bleached kraft pulps.

MATERIAL AND METHODS

Material

Beech wood (*Fagus silvatica* L.) chips from mill were used in this study. The natural dirt was removed (Tappi test method T 265 om-93) and the chips with dimensions of 20x20x3 mm were used for the laboratory experiments. Kraft cooking liquors were prepared and analysed according to TAPPI test method T 624 cm-85.

Laboratory kraft pulping

Pulping studies were performed in a laboratory series digester consisting of six autoclaves, each of 0,75 L volume. The autoclaves were filled with 100 g of o.d. screened beech wood chips. The liquor/wood ratio was 4:1, the sulphidity (S) of cooking liquors were 18% and 10% respectively, total active alkali charge of 16% Na_2O. The time to maximum pulping temperature at 168 °C was constantly 120 min and the dwell time at this temperature was in range of 0 to 120 min. AQ addition was in a range 0.05 to 0.3% on o. d. wood chips. Control experiments were performed simultaneously.

Laboratory bleaching with OD(EOP)DD sequence

Oxygen delignification (O) of beech kraft pulps was carried out in steel autoclave at 95 °C, 60 min, 10% consistency, pressure 0.6 MPa O_2, 1.5% NaOH and 0.3% $MgSO_4$ added to pulp.

D_0 stage: 0.8 % ClO_2, initial pH 2.5 (adjusted with H_2SO_4), 10% consistency, 70 min, 60 °C.

EOP stage: 1.3% NaOH, 0.3% H_2O_2, 10% consistency, pressure 0.5 MPa O_2 (20 min)/0.1 MPa (110 min), 75 °C.

D_1 stage: 0.5% ClO_2, initial pH 3.5 (adjusted with H_2SO_4), 10% consistency, 180 min, 80 °C.

D_2 stage: 0.2, 0.3, 0.4 and 0.5% ClO_2, initial pH 4.0 (adjusted with H_2SO_4), 10% consistency, 180 min, 75 °C.

Analyses

The kappa number was determined according to ISO standard 302 and brightness according ISO standard 2470.

Beating degree of pulps was determined according ISO 5267-1 standard, hand sheets prepared on a Rapid Köthen sheet former according ISO 5269-2 standard and mechanical properties determined according ISO 5270 standard.

RESULTS AND DISCUSION

Laboratory kraft pulping with and without AQ addition

Laboratory scale experiments were performed with 0.05% up to 0.3 of AQ on wood in order to establish an optimal AQ addition in kraft pulping of beech wood. On Fig. 2 the dependence of kappa number on AQ addition to cooking liquor at constant 60 min cooking time at maximum temperature is shown. The kraft delignification of beech wood is significantly accelerated by increase of AQ addition up to 0.1 % on o. d. wood. Further increase of AQ addition has no marked increase on delignification rate therefore in laboratory cooking experiments an addition of 0. 1 % AQ on o. d wood was applied.

The influence of AQ on stabilisation of the polysaccharide component and kraft delignification rate of beech wood was investigated. On Fig. 3 the delignification curves of beech wood in the kraft pulping process at 18% sulphidity with and without addition of 0.1 % AQ are compared. The screened yield of kraft pulps prepared with AQ addition in the evaluated range of kappa number (12 to 23.5) was by 2 to 2.4% higher. At kappa number 17 the screened yield of pulp prepared with 0.1% AQ addition was 52.5% i.e. by 2.2% higher than without AQ addition.

Comparison of kappa number dependence on cooking time at maximum temperature in kraft pulping (sulphidity 18%) with and without AQ addition is shown on Fig. 4. AQ significantly increased delignification rate. At same cooking time the kappa number of pulps prepared with AQ was by 4 to 6 numbers lower.

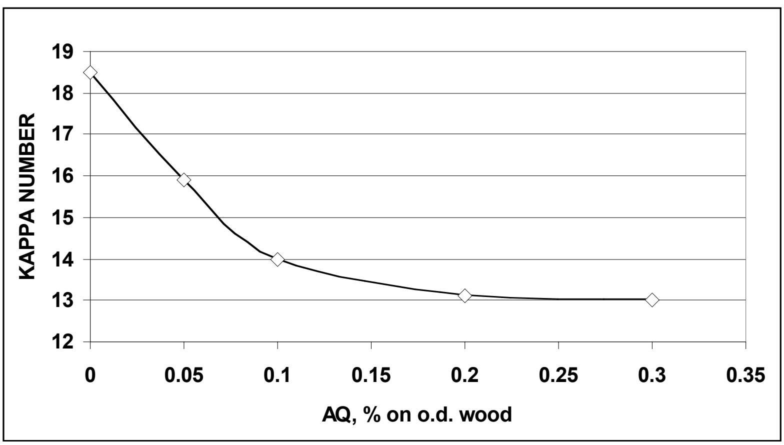

Fig. 2: Effect of AQ addition to kraft pulping (18% S) of beech wood on kappa number of unbleached pulp (dwell time at maximum temperature 60 min)

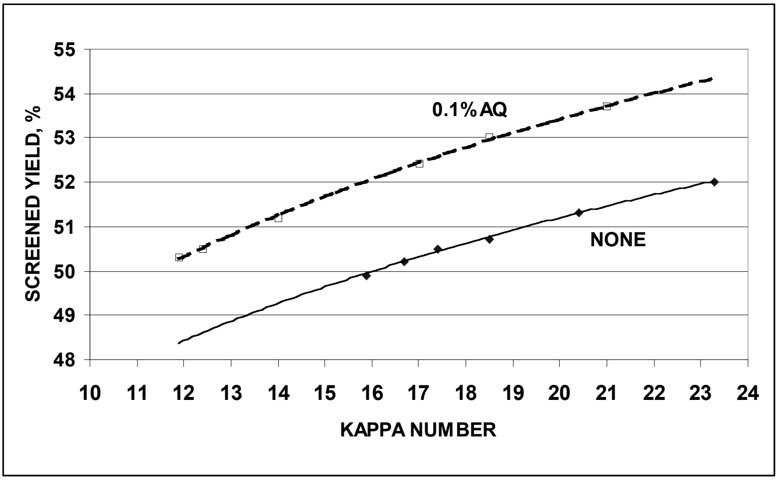

Fig. 3: Screened pulp yield as a function of kappa number in kraft pulping (18% S) of beech wood without and with addition of AQ

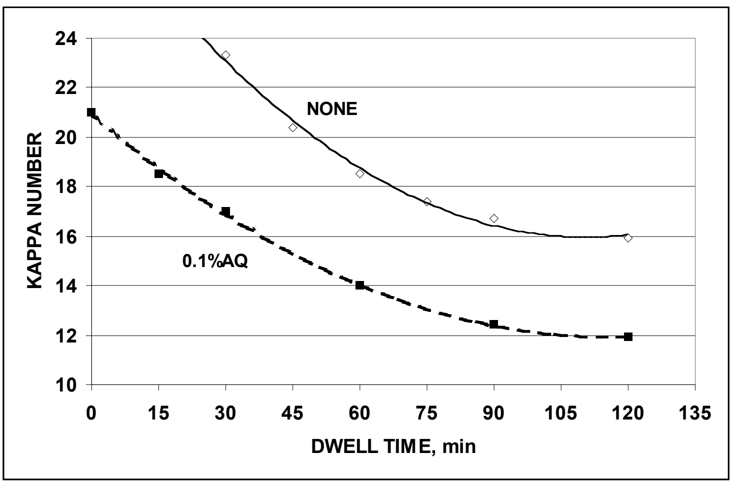

Fig. 4: Kappa number as a function of dwell time at maximum temperature in kraft pulping (18% S) of beech wood without and with addition of AQ

AQ in the kraft pulping process improves the uniformity of delignification resulting in decreased amount of rejects as shown by the dependence of rejects on kappa number (Fig. 5). With decrease of kappa number rejects content in pulp decreases but the difference in rejects content in pulp prepared without and with AQ addition is approximately same and represents 0.025% rejects in o. d. pulp at same kappa number. When compared pulps with kappa number 17 the difference in rejects content is approximately 50%. On base of these laboratory experiments it can be assumed that in mill conditions a more marked decrease of rejects in pulp prepared by AQ addition can be achieved.

As AQ stabilises the polysaccharide component of wood it can be expected that at same kappa number of pulp less active alkalis will be consumed. This was confirmed by higher residual alkali content in black liquor at equal pulping conditions. From the residual alkali concentration vs. kappa number of kraft pulp relationship it follows that at 0.1% AQ addition concentration of residual active alkali in black liquor is higher at same kappa number (Fig. 6). Same results in kraft pulping of beech wood with AQ addition can be achieved with a lower active alkali charge. With addition of 0.1% AQ active alkali charge can be reduced from 16% to 15.2% representing a saving of 5% active alkali.

In order to reduce gaseous sulphur emissions influence of AQ in kraft delignification of beech wood at reduced sulphidity of cooking liquor was investigated. Beech wood delignification curves with cooking liquor of 18% sulphidity and 10% sulphidity with addition of 0.1% AQ on o. d. wood were compared (Fig. 7) resulting in 45% reduction of gaseous sulphur emissions. In the presence of AQ selectivity of delignification was improved resulting at same kappa number in an increased screened yield by 2% in spite of lower sulphidity of cooking liquor. Accelerating effect of AQ on kraft delignification of beech wood is manifested also at lower sulphidity of cooking liquor as shown by the relationship on Fig. 8. The kappa number of pulp prepared with 0.1% addition of AQ was at same cooking time lower by 3.5 to 5.5 points than of the pulp prepared without AQ addition. It can be concluded from laboratory experiments that AQ accelerates delignification of beech wood at both levels of sulphidity (10% and 18%) (Fig. 4 and 8).

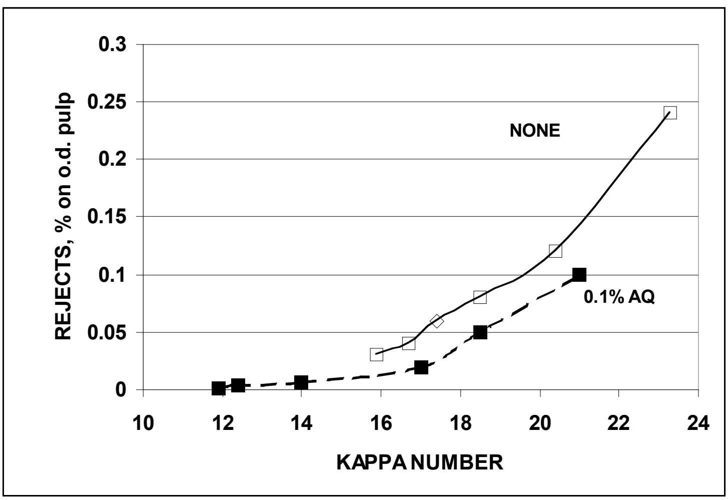

Fig. 5: Rejects content as a function of beech kraft pulp kappa number

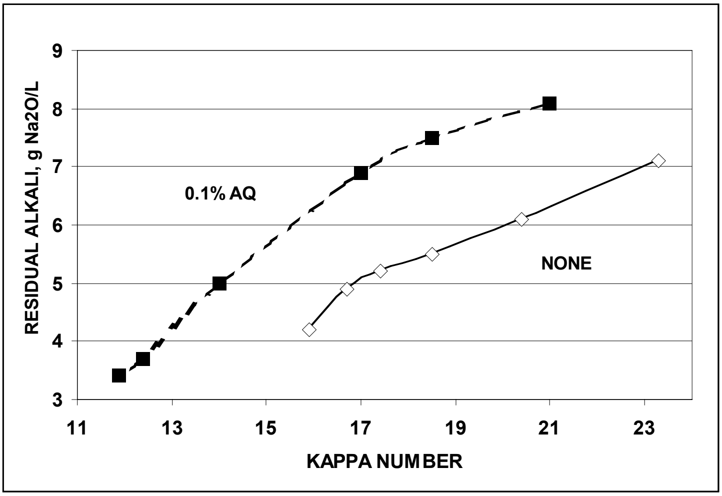

Fig. 6: Residual alkali content as a function of beech kraft pulp kappa number

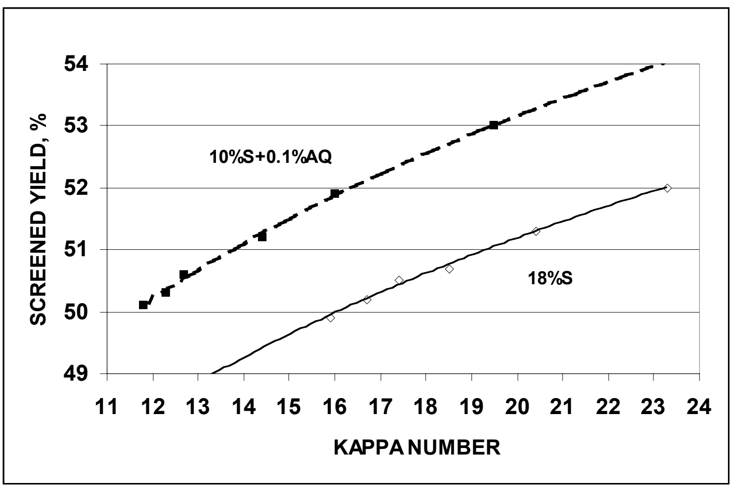

Fig. 7: Screened yield as a function of beech kraft pulp kappa number prepared without (18% S) and with addition of AQ (10% S)

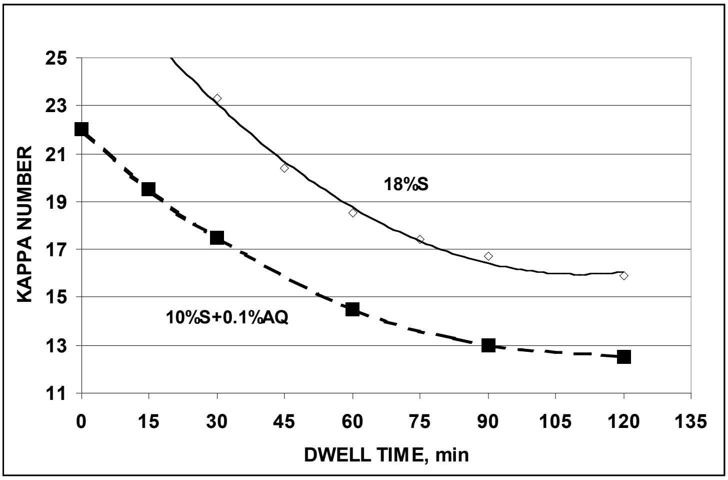

Fig. 8: Kappa number as a function of dwell time at maximum temperature in kraft pulping of beech wood without and with addition of AQ (10% S)

Influence of cooking liquor sulphidity on screened yield of beech kraft pulp prepared in the presence of AQ is illustrated on Fig. 9 on which delignification curves of beech kraft cooking at 10% sulphidity and 18% sulphidity with addition of 0.1% AQ are compared. The screened yield of pulp prepared with a cooking liquor of higher sulphidity was at same kappa number by 0.2% higher. From comparison with results presented on Fig. 3 it follows that at the same sulphidity of cooking liquor 18% with application of 0.1% AQ was the yield of pulp at same kappa number by 2.2% higher. Reduction of sulphidity by 45% is causing decrease of screened yield by 0.2% while addition of AQ increases yield up to 2%.

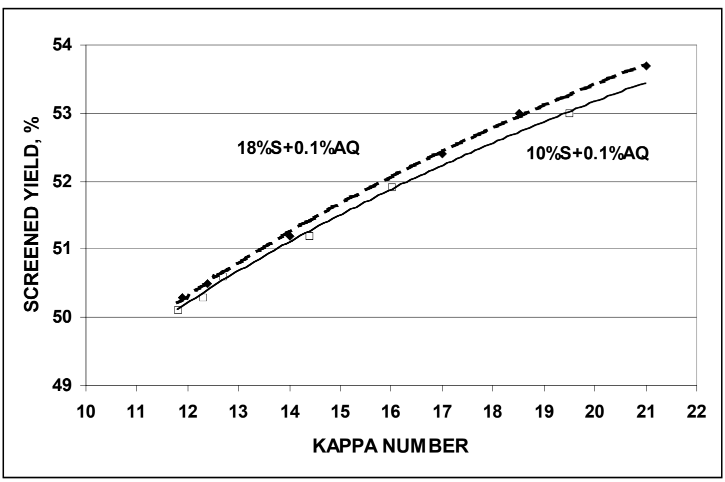

Fig. 9: Screened yield versus kappa number of beech kraft pulps prepared with addition of AQ at 10% and 18% sulfidity of cooking liquor

Tab. 1: Physical and mechanical properties of bleached beech kraft pulps prepared without AQ (18% S)

Beating degree, °SR	14	20	30	41	50
Beating time, min	0	15	34	52	59
Apparent density, g/cm^3	0.50	0.63	0.69	0.74	0.76
Tensile index, N.m/g	24.0	56.5	62.0	63.0	64.5
Breaking lenght, km	2.45	5.76	6.32	6.42	6.58
Tear index, $mN.m^2/g$	3.40	8.70	7.60	7.40	7.05
Burst index, $kPa.m^2/g$	0.90	2.85	3.15	3.20	3.25
Stretch, %	0.9	2.2	2.3	2.4	2.5
Air permeability (Gurley), s	0.7	1.8	5.9	21.8	38.3

Tab. 2: Physical and mechanical properties of bleached beech kraft pulps prepared with addition of 0.1% AQ (10% S)

Beating degree, °SR	14	20	30	40	50
Beating time, min	0	18	40	58	65
Apparent density, g/cm^3	0.50	0.64	0.69	0.73	0.74
Tensile index, N.m/g	25.0	57.0	58.0	63.0	63.0
Breaking lenght, km	2.55	5.81	5.91	6.42	6.42
Tear index, $mN.m^2/g$	4.95	8.10	8.25	8.00	7.65
Burst index, $kPa.m^2/g$	1.15	3.25	3.35	3.55	3.60
Stretch, %	1.1	2.2	2.3	2.4	2.4
Air permeability (Gurley), s	0.7	1.8	4.6	19.6	28.6

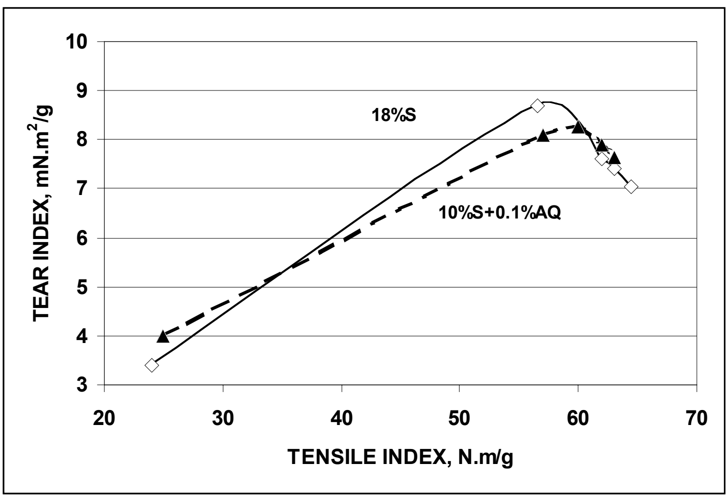

Fig. 12: Tear-tensile relationship for beech kraft pulps (18% S) prepared without and with addition of AQ

On Fig. 12 dependence of tear index on tensile index of bleached beech kraft pulps is shown. It is obvious from this relationship that at same tensile index pulp prepared using a cooking liquor of 18% sulphidity has a slightly higher tear index. These differences are very small and are at the level of measurement errors. It can be therefore concluded that mechanical properties of bleached kraft beech pulp are not significantly influenced by sulphidity of cooking liquor and AQ addition.

CONCLUSIONS

Laboratory scale cooking confirmed that AQ increases kraft delignification selectivity resulting in accelerated delignification of beech wood, stabilisation of the polysaccharides component and, consequently, the yield of pulp increased by 2% and 2.2% respectively depending on sulphidity of cooking liquor. Catalytic effect of AQ is observed even at low sulphidity (10%) of cooking liquor. Addition of AQ into the kraft pulping makes thus possible to reduce sodium sulphide charge by 45% without a significant influence on course of delignification, bleachability as well as on physical and mechanical properties of bleached pulp. Kraft pulping of beech wood with AQ addition is more uniform. Consequently, at same kappa number the pulp contains less rejects. By AQ application consumption of alkali in kraft pulping is lower which makes possible to reduce active alkali charge by 5%. The kraft pulping process with AQ addition is advantageous mainly from ecological point of view as it makes possible to reduce sulphur emissions to atmosphere without additional investment.

AKNOWLEDGEMENTS

This research was supported by Ministry of Economy of the Slovak Republic and Bukóza Holding, a.s. Hencovce, Slovak Republic under Grant No. 2003 SP 26 028 0C 03 „Processing of Surplus Wood Raw Material of Lowest Quality in Pulp and Paper Production to New Products“ for which authors are thankful.

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Ing. Mária Fišerová, PhD.
Pulp and Paper Institute
Lamačská cesta 3
841 04 Bratislava
Slovak Republic
E-mail: fiserova@vupc.sk

Ing. Juraj Gigac, PhD.
Pulp and Paper Institute
Lamačská cesta 3
841 04 Bratislava
Slovak Republic
E-mail: gigac@vupc.sk

Ing. Peter Melník
Bukóza Holding, a.s.
Hencovská 2073
093 02 Hencovce
Slovak Republic
E-mail: melnik@bukoza.sk