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Extended Oxygen Delignification of Birch Kraft Pulp

Abstract
We studied the effect of the conditions of the oxygen delignification of birch kraft pulp with kappa number 18 on pulp properties. The investigation refers in particular to the effect of the amount of NaOH added, as well as the time & temperature of oxygen delignification process on the kappa number, yield and strength properties of pulp, as well as what effect the pre-treatment of pulp with peracetic acid has on these indices. It has been stated that the oxygen delignification of birch kraft pulp with kappa number 18 with oxygen alone in aqueous alkali to a kappa number below 10 (the level of extended oxygen delignification) requires an increased amount of NaOH to be added, higher temperature and a longer process time, resulting in the deterioration of the pulp yield. The pre-treatment of pulp with peracetic acid in the amount of 0.33 or 0.66% A.O. (to oven-dried pulp) enables this pulp to be delignified to kappa number 7 and 5 with a higher yield than that of pulp delignified with oxygen alone. Pulp delignified with oxygen using the peracetic acid pre-treatment also restores higher viscosity and tear index, as well as higher fibre strength.

Key words: *birch kraft pulp, oxygen delignification, peracetic acid, pulp properties, fibre properties.*

Introduction

Extended oxygen delignification of conventional birch pulp (with a kappa number about 20) is not a widely used process in the pulp and paper industry. Such treatment of birch pulp prior to a bleaching process should result in a decreased consumption of bleaching agents, a reduced amount of detrimental effluents from the bleaching process, as well as a reduced cost of bleaching. The main reason why this process is not yet widely used in practice is the inability to decrease the residual lignin content in pulp to a level corresponding to a kappa number below 10, without excessive deterioration of pulp yield and strength. The effect of the decreased susceptibility of lignin on the delignifying action of oxygen results in all probability from the changes taking place in residual lignin, such as the accumulation of 5,5'-diphenyl, p-hydroxyphenyl units, which are hard to oxidise with oxygen, and the possibility that bonds between lignin and carbohydrates exist [2, 3]. Chemicals which can activate the residual lignin and make it more susceptible to the action of oxygen are peroxides [4 - 10]. Of these, persulphuric and peracetic acid will most probably be used in practice. According to literature, peracetic acid is characterised by a relatively high oxidising potential [11], but pulp when mixed with this compound is characterised by a high acid reaction (pH 1.8 - 2.8) [12, 13]. In most research works, pH was increased by up to 3.5 - 7 units during treatment with peracetic acid [14 - 19]. However, according to our results, in order to increase the pH of the medium to 3.5, or even higher during the pulp's treatment with this chemical, such a large amount of NaOH is needed that it does not seem possible to apply such a solution in practice [20, 21]. These reserch works showed that raising the pH of the pulp treatment with peracetic acid to 3.5 or 5.5 does not significantly increase the amount of removed lignin in the oxygen delignification process, compared to experiments in which the treatment of pulp with peracetic acid was carried out without raising the pH.

Aim of work

The aim of our work was to study the possibility of extending the delignification of birch kraft pulp with kappa number 18 in the oxygen delignification process with and without the application of peracetic acid pre-treatment, and to evaluate the fibrous semi-product thus obtained.

Methodology

Pulps

Industry birch kraft pulp of kappa number 18 was used for the tests.

Applied delignification and bleaching aids

Oxygen, EDTA, $MgSO_4$, distilled peracetic acid (CH_3COOOH).

Oxygen delignification

A 50 g weighed portion of oven-dried pulp (o.d. pulp) was placed in a polyethylene bag, and then the following substances were added in turn: 0.5% $MgSO_4$ to pulp o.d. pulp (as 1% solution) followed by the appropriate amount of sodium hydroxide. The content was mixed in a bag by squeezing, and then was transferred in quantity to a Jayme digester. The autoclave was closed, filled with oxygen to 8 MPa, the rotating mechanism was switched on, heated to a temperature of 100 °C or 110 °C within 30 minutes, and then heating was continued over the time given in Table 1. The pulp was delignified in a single-stage process of oxygen delignification. After the preset time lapse, the digester was degassed and emptied. After oxygen delignification, the pulp was pressed to obtain a liquor sample which was used to determine the final pH; then it was washed with distilled water, filtered and its dryness and yield were determined.

Pulp treatment by peracetic acid

A sample of the disintegrated pulp was placed in a polyethylene bag. Heated distilled water, in the amount necessary to ensure the assumed concentration of fibrous slurry, and the appropriate amount of peracetic acid as active oxygen (A.O.) relative to o.d. pulp were added to a beaker. After thoroughly mixing up the ingredients, the solution was poured into a polyethylene bag containing heated pulp. The content was mixed by squeezing and heated in a water bath for 30 minutes at 50 °C, and then for 90 minutes at 70 °C. After the preset time lapse, the pulp slurry was squezed in a Büchner funnel, washed with distilled water, and stored in polyethylene bags in a fridge for further work. We analysed the active oxygen concentration (A.O.) in a solution of peracetic acid by means of the titration method described by Amini & Webster [22].

Determining the pulp's properties

Standard methods were used to measure the kappa number (PN-70/P50095), viscosity (SCAN – C 15:62, SCAN-C 16: 62), and the tear index [23]. For determining the percentage of lignin content in pulp on the basis of the kappa number, a conversion index 0.152 was assumed. Pulp brightness was determined according to standard ISO 2470 (ISO brightness). The fibre strength factor (FS-factor) was determined with a TroubleShooter tester TS-100 (Pulmac) [24].

Results and discussion

Birch kraft pulp with kappa number 18 was delignified by an O_2-single-stage delignification, at medium pulp consistency (8%), in order to decrease the content of residual lignin in it to the level of the conventional (kappa number 10 - 13) and extended delignification of pulp (kappa number < 10). The possibility of producing pulp with a very low lignin content with and without the application of peroxide chemicals (peracetic acid and hydrogen peroxide) was investigated. Peroxide chemicals increase the susceptibility of residual lignin to the delignifying action of oxygen. All the experiments are specified in Table 1 which contains in columns the process sequence, the total amount of alkali added, the process temperature, the time, the amount of peracetic acid and hydrogen peroxide used in the Pa and O stages, as well as the pH of the liquor after the O_2-stage.

Our earlier research indicated that the pH of the treatment of pulp with peracetic acid does not have a significant effect on the results of the oxygen delignification, and a relatively large amount of NaOH is required to settle it to the values 3.5 and 5.5 [20, 21]. For these reasons, the treatment of pulp with peracetic acid was performed at pH 2.6, i.e. with no NaOH added.

Table 1 shows that the performed pulp delignification experiments differed from each other by:

- the amount of NaOH added, which amounted to 1, 2 and 3% to o.d. pulp, respectively;
- process time – 60, 120 or 180 minutes;
- temperature – 100 or 110 °C;
- the application of peracetic acid pre-treatment and the amount of distilled CH_3COOOH used – 0.33 or 0.66% A.O. to o.d. pulp;
- application of the addition of hydrogen peroxide.

Table 1. List of performed experiments.

Exp. number	Process sequence	Total amount of NaOH	Temp., °C	Time, min	Amount of peracetic acid used, % to o.d. pulp	Amount of hydrogen peroxide used, % to o.d. pulp	pH of liquor after O_2-stage
1	QO	1	100	60	-	-	9.5
2	QO	2	100	60	-	-	11.2
3	QO	2	100	120	-	-	10.7
4	QO	3	100	180	-	-	11.1
5	QO	1	110	60	-	-	9.3
6	QO	2	110	60	-	-	10.7
7	QO	2	110	120	-	-	9.8
8	QO	3	110	180	-	-	10.2
9	QOp	1	100	60	-	1.5% H_2O_2	9.8
10	QOp	2	100	60	-	1.5% H_2O_2	10.6
11	QPaO	1	100	60	0.33 % A.O.	-	9.4
12	QPaO	2	100	60	0.33 % A.O.	-	10.6
13	QPaO	2	100	120	0.33 % A.O.	-	9.6
14	QPaO	3	100	180	0.33 % A.O.	-	9.7
15	QPaO	1	110	60	0.33 % A.O.	-	9.3
16	QPaOp	1	100	60	0.33 % A.O.	1.5% H_2O_2	9.1
17	QPaOp	2	100	120	0.33 % A.O.	1.5% H_2O_2	9.9
18	QPaO	2	110	120	0.33 % A.O.	-	9.7
19	QPaO	1	100	60	0.66 % A.O.	-	9.4
20	QPaO	2	100	60	0.66 % A.O.	-	10.7
21	QPaO	2	100	120	0.66 % A.O.	-	10.0
22	QPaO	3	100	180	0.66 % A.O.	-	10.5

The results of the delignification obtained in the experiments performed according to the conditions compiled in Table 1 are presented in Figure 1. The Figure shows that oxygen delignification of birch kraft pulp with kappa number 18, with oxygen alone, to the kappa number of conventionally delignified birch pulp (i.e. 10 - 13) can be obtained using 1 - 2% of NaOH in the oxygen delignification, and during a process time of about 60 minutes. The addition of hydrogen peroxide in the amount of 1.5% to the o.d. pulp or raising the temperature of the process to 110 °C, enables the pulp with kappa number lower by 0.8-1.5 units to be obtained for the specific amount of NaOH used. As the result, the kappa number of the delignified pulp approaches the lower border of the range to which this pulp is conventionally delignified.

However, the aim of extended oxygen delignification should be a lower level of the residual lignin content in pulp, so in the next experiments we investigated what the best conditions are for obtaining birch pulp with a kappa number <10.

As seen in Figure 1, after extending the process time and increasing the amount of added NaOH to 3% to o.d. pulp, it is possible to obtain pulp with a kappa number of only 8-10. In this case, however, it should be noted that the conditions of the process are such that they probably could not be applied in industry. On the one hand, the reason for this is the long retention time of the pulp in the oxygen reactor, while on the other it is due to the low kappa number reduction obtained in comparison with the amount of NaOH added.

Thus, in the next experiments the effect of applying the peracetic acid pre-treatment on reducing the kappa number was studied. As shown in Figure 1, in comparison with the conventional oxygen delignification experiments, after pre-treatment of pulp with peracetic acid in the amount of 0.33 or 0.66% A.O. (to o.d. pulp), the kappa number was reduced to about 9 and 6 respectively at 1% of NaOH used and a process time of 60 min. So, the pre-treatment of pulp with peracetic acid enabled us to easily obtain a pulp which is characterised by extended delignification without any increase of the amount of alkali or extension of the process time. As can be further seen in Figure 1, extending the oxygen delignification process time to 120 or 180 minutes and increasing the amount of alkali added in it to 2 or 3% leads to a very low kappa number for pulp (around 4-7).

The degree of delignification obtained as a result of changing the conditions of

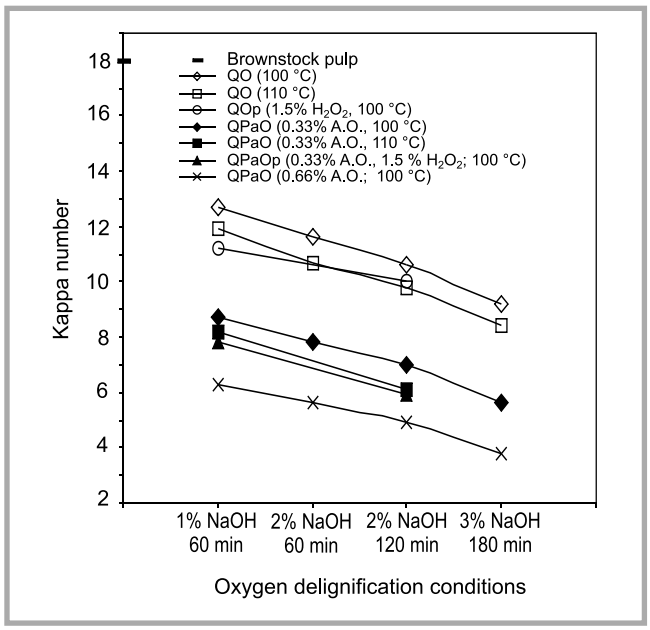

Figure 1. *Kappa number values obtained in different variants of the oxygen delignification of birch kraft pulp.*

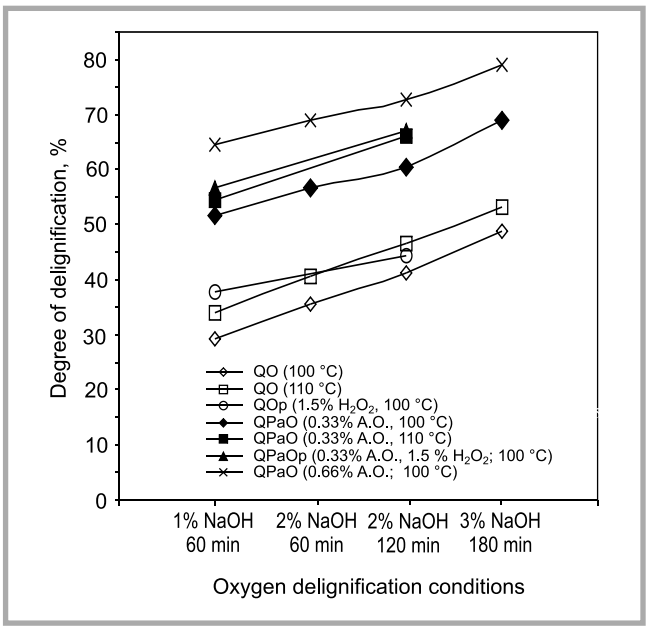

Figure 2. *Degree of delignification of birch kraft pulp in different variants of oxygen delignification.*

oxygen delignification and the application of the peracetic acid pre-treatment is shown in Figure 2. The data presented also enables us to establish how much we may increase the amount of lignin removed from the pulp as a result of the peracetic acid pre-treatment, and how much more lignin can be removed upon a twofold and threefold increase of the amount of NaOH added, and by extending the process time to 120 and 180 minutes.

As seen therein, the increase in the amount of the removed lignin obtained with peracetic acid at 0.33% A.O. (to o.d. pulp) was 20-22% rel., while at a twofold dose the figure was 30-35% rel., in comparison with experiments in which the pre-treatment of pulp with this chemical was not applied.

As for how much more lignin can be removed upon a twofold and threefold increase of the amount of added NaOH and extension of the process time, Figure 2 shows that increasing the amount of added NaOH at the beginning of the process to 2% and simultaneously extending its time up to 120 min. makes it possible to remove from the pulp 8-12% more of lignin than at 1% of NaOH added and a process time of 60 min. In turn, by increasing the amount of NaOH added up to 3% with simultaneous extension of the process time to 180 minutes, it is possible to remove from pulp 15-20% more of lignin than at 1% of NaOH and duration time 60 min., and only 6-8% of lignin more than at 2% of added NaOH and 120 min.

Thus, in the case of the oxygen delignification of birch kraft pulp, as in the case of pine kraft pulp [21], after removing a definite part of the lignin, the remainder is far less susceptible to the delignifying action of oxygen. Difficulties in effectively removing this part of the lignin from pulp are attributable to the accumulation of residual lignin structures 5,5'-diphenyl and p-hydroxyphenyl units in pulp, which are relatively hard to oxidise under oxygen delignification conditions.

The studies performed clearly show that peracetic acid has a pronounced activating effect toward the part of lignin mentioned-above which is hard to oxidise with oxygen.

An important reason why oxygen delignification of birch kraft pulp to a kappa number below 10 - 13 is not commonly used is the significant decrease in the yield of the pulp. Figure 3 shows the relationship between yield and kappa number in different variants of oxygen delignification of birch kraft pulp with kappa number 18, as well as the simulation of changes to this index in a process

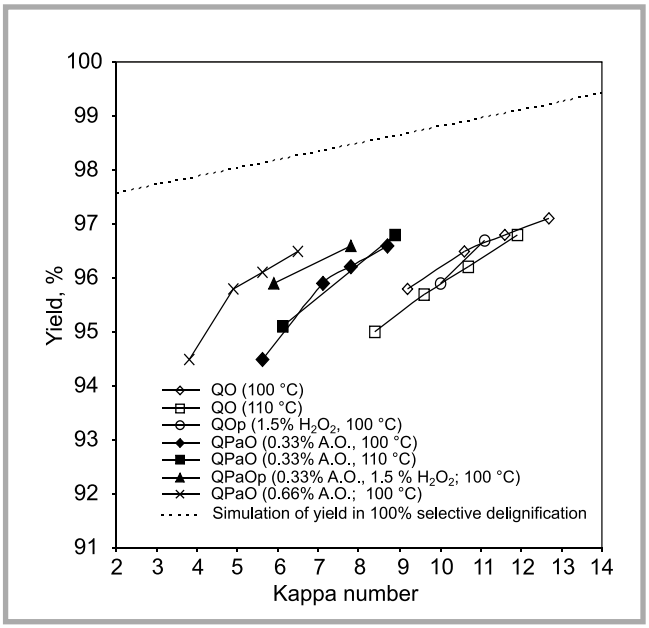

Figure 3. *Relationship between yield and kappa number of birch kraft pulp in different variants of oxygen delignification; (standard deviation of yield amounted to 0.14%).*

of 100% selective delignification of this pulp.

As shown in Figure 3, the yield of birch pulp delignified to kappa number 13 was about 97.1%. At the same time, it can also be seen that the share of carbohydrates in the yield decrease is already high, i.e. 2.3%. The oxygen delignification of birch pulp to kappa number 8.4 by increasing the amount of added alkali and the extension of the process time leads to a decrease in yield to 95%. The share of carbohydrates in the yield reduction increases to about 3.5%. Thus, it is not a good way to extend the delignification of normal birch kraft pulp.

Considering the yield of pulp, the oxygen delignification of birch pulp with peracetic acid pre-treatment brings better results. As shown in Figure 1, the pre-treatment of pulp with 0.33% A.O. of peracetic acid can lower the kappa number of birch kraft pulp to 8.4 with a pulp yield of 96.5%. The share of carbohydrates in yield reduction in this case was about 2.1%. Thus the pulp yield was higher and the share of carbohydrates in yield reduction lower than the values of these indices in the case of pulp delignified only with oxygen to the same kappa number.

The data from Figure 3 concerning the experiments in which the peracetic acid pre-treatment of pulp in the amount of 0.66% A.O. to o.d. pulp was applied indicate that it is possible to obtain pulp with a kappa number 6.5 with much lower yield reduction. The yield of oxygen-delignified pulp to a kappa number of 6.5 using peracetic acid pre-treatment in this amount is the same as the yield of pulp delignified with peracetic acid pre-treatment in the amount of 0.33% A.O. to kappa number 8.4, and the yield of pulp delignified without the application of peracetic acid to kappa number 10.6. Based on the results obtained, it can be stated that the peracetic acid pre-treatment stabilises polysaccharides (cellulose and hemicelluloses), and as a result they are more resistant to the alkali hydrolysis occurring under the oxygen delignification conditions.

Moreover, Figure 3 shows that in the case of peracetic acid pre-treated pulp, the addition of hydrogen peroxide to the oxygen delignification process can bring some additional protective effect for carbohydrates, which leads to the production of a fibrous semi-product characterised by a somewhat higher yield.

To achieve a better image of the changes taking place in birch pulp during the extended oxygen delignification, the tear index and intrinsic viscosity of the pulps were determined. The effect of the conditions of the oxygen delignification on the fibres' strength was evaluated by determining the zero-span fibre strength factor in a Pulmac tester. These results are presented in Figures 4, 5 and 6.

As shown in Figure 4, the tear index of pulp delignified with oxygen to kappa number 4-9 using pre-treatment with peracetic acid was 8.5 to 9.5 mN·m^2/g. Thus it was higher than that of pulp delignified only with oxygen to kappa number 8-13, which was 8 to 8.7 mN·m^2/g. Comparing the result of these two variants of the oxygen delignification at kappa number 8.4 (Figure 4, dotted line), it can be stated that the values of tear index of the pulp delignified with the peracetic acid pre-treatment should be higher by about 10% than those obtained in experiments in which the birch pulp was delignified with oxygen alone. Similar tendencies can be observed for viscosity (Figure 5) and fibre strength factor (Figure 6). By comparing the values of these indices at kappa number 8.4 (Figures 5 and 6, dotted lines), it can be stated that the values of viscosity and fibre strength factor of the pulp delignified with peracetic acid pre-treatment should be higher than those indices obtained in experiments in which the birch pulp was delignified only with oxygen by about 17 and 8% rel., respectively.

The amount of chemicals used in the process of bleaching kraft pulps to a brightness level of 88-90% ISO is not

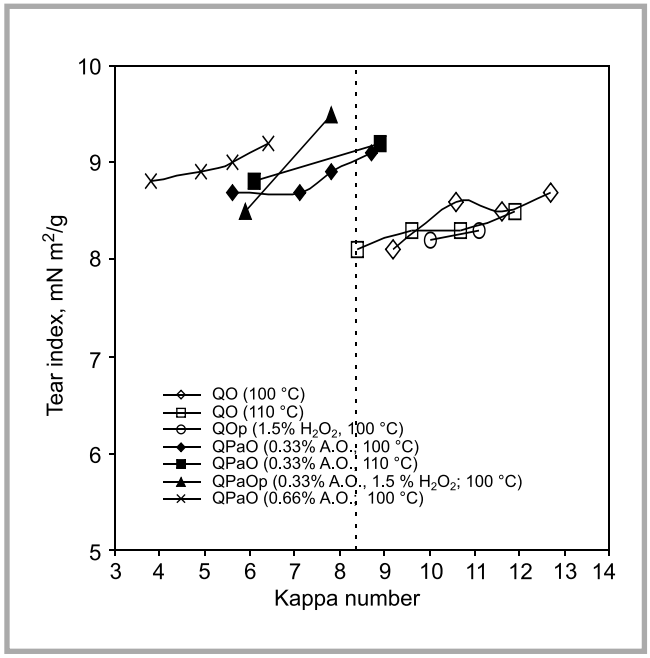

Figure 4. *Relationship between tear index and kappa number of oxygen-delignified birch kraft pulp in different variants of process (after beating in Jokro mill to a freeness of 22°SR for 12 min.); (standard deviation of tear index was 0.2 mN·m^2/g).*

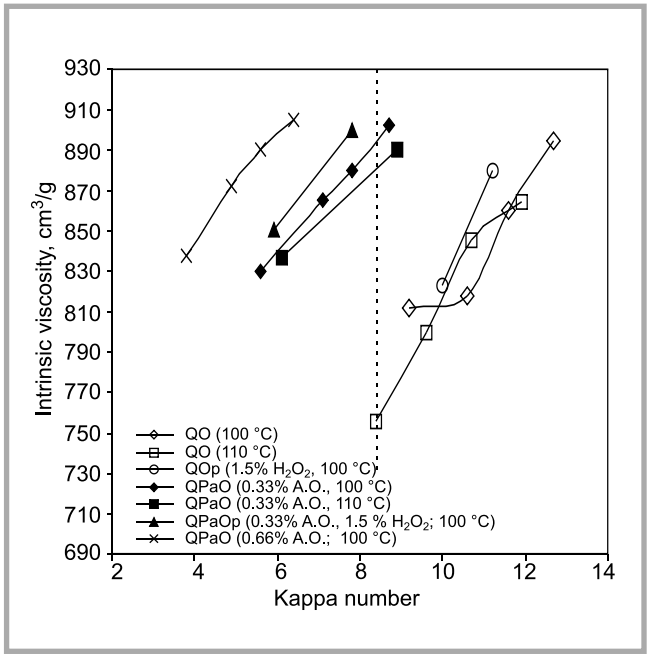

Figure 5. *Relationship between intrinsic viscosity and the kappa number of oxygen-delignified birch kraft pulp in different variants of process; (standard deviation of viscosity measurements was 8 cm^3/g).*

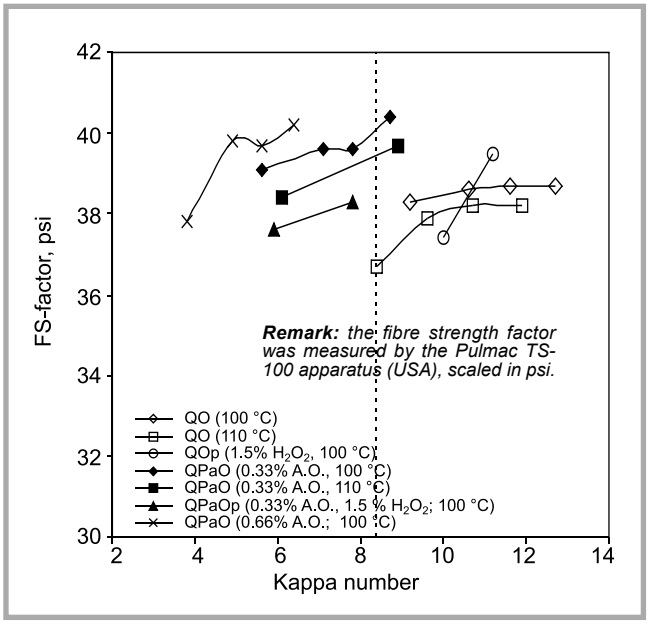

Figure 6. *Relationship between fibre strength factor and the kappa number of oxygen-delignified birch kraft pulp in different variants of the process; after beating in Jokro mill to freeness 22°SR ; (standard deviation of FS-factor was 1.1).*

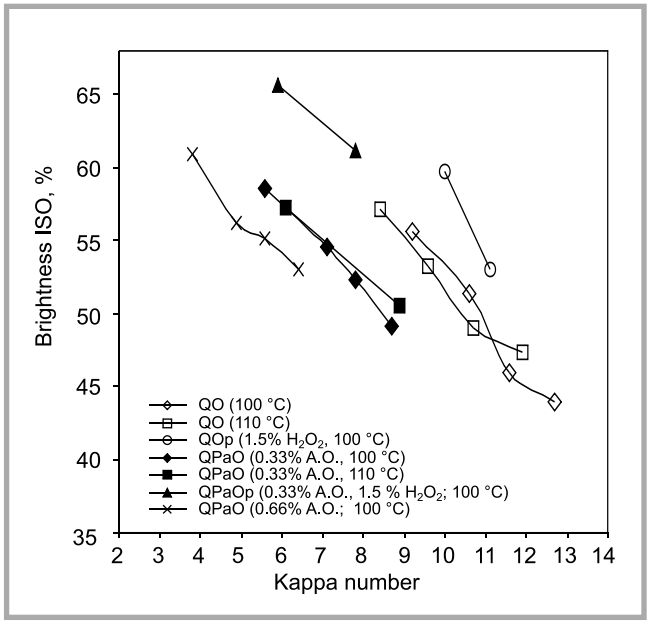

Figure 7. *Relationship between kappa number and ISO brightness in different variants of oxygen delignification of birch kraft pulp; (standard deviation of ISO brightness measurements was 0.5%).*

only dependent on the lower lignin content in these pulps. Their higher brightness level before bleaching (i.e. after the oxygen delignification process) may also have a significant effect.

Figure 7 shows that the brightness ISO of pulp delignified with oxygen alone increases from about 30 to about 57%, with a decrease in the kappa number to about 8 - 9. The temperature does not affect the brightness level of pulp delignified with oxygen. The higher brightness of birch pulp can be obtained by the addition of hydrogen peroxide to the oxygen delignification. The addition of hydrogen peroxide in the amount of 1.5% to o.d. pulp increases the brightness of the pulp by 3 - 5%.

The data in Figure 7 also shows that at a specific kappa number, the level of brightness of oxygen delignified pulp with peracetic acid pre-treatment can be lower (by about 5%) than the brightness of pulp delignified with oxygen alone. In this case, the brightness of the birch pulp can be significantly raised by the addition of hydrogen peroxide to the oxygen delignification (Figure 7).

Conclusions

1. The oxygen delignification of birch kraft pulp with kappa number 18 with oxygen alone to kappa number <10 (i.e. to within the range of extended delignification) requires the use of a larger amount of alkali and an extension of the process time, and results in the decreased yield and deterioration of the pulp's strength characteristics. The application of the pre-treatment of pulp with peracetic acid in the amount of 0.33 or 0.66% A.O. (to o.d. pulp) increases the susceptibility of the residual lignin to the delignification action of oxygen, and allows the pulp to be delignified to kappa number 5 and 7, with a clearly higher yield than that of pulp delignified with oxygen alone.

2. The increase in the amount of lignin removed in the oxygen delignification of the birch pulp obtained after pre-treatment with peracetic acid in the amount of 0.33 and 0.66% A.O. was higher by 20-22% and 30-35% rel. respectively, in comparison with pulp delignified with oxygen alone.

3. In the case of birch pulp delignification with oxygen alone and also using peracetic acid pre-treatment, it is most effective to remove part of the lignin which accounts for 29-64% of its content in pulp. Upon a twofold and threefold increase of the amount of NaOH added and an extension of the process time, the amount of lignin removed from them pulp increases by only 8-12 and 15-20% rel. respectively.

4. The pre-treatment of birch pulp with peracetic acid prior to the oxygen delignification allowed the tear index, viscosity and zero-span fibre strength factors to be maintained at a higher level than when the pulp was delignified with oxygen alone, by 10, 17 and 8% rel. respectively.

Acknowledgment

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