THE REACTIVITY OF PREHYDROLYZED SOFTWOOD KRAFT PULPS AFTER PROLONGED COOKING FOLLOWED BY CHLORITE DELIGNIFICATION

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In a laboratory study high-quality spruce chips were prehydrolyzed to remove hemicelluloses and then kraft cooked to different kappa numbers by varying the cooking time. Each pulp sample was then chlorite delignified to selectively remove the remaining lignin. The reactivities of the pulp samples before and after chlorite delignification were determined by Fock's test, which is supposed to measure the pulp's reactivity in the conventional viscose process. A number of analyses were carried out to determine which parameters affected pulp reactivity, as, for example: intrinsic viscosity, kappa number, pulp yield, carbohydrate composition, levelling-off degree of polymerization (LODP), and alkali solubility. The results of the study showed that the pulp reactivity increased with decreasing kappa number, and the highest reactivity was obtained after total lignin removal using chlorite delignification. It was also found that the carbohydrate composition had no influence on the pulp reactivity, but lower intrinsic viscosity either obtained by prolonged cooking or chlorite delignification correlated with higher pulp reactivity. Finally, lower alkali solubility, i.e. higher R_{18}, reduced the reactivity.

Keywords: Alkali solubility; Carbohydrate composition; Chlorite delignification; Levelling-off degree of polymerization; Pulp reactivity; R_{18} *;* S_{18}

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INTRODUCTION

During the last decade there has been a substantial increase in interest in dissolving pulps, regenerated cellulose, and cellulose derivatives as part of the so-called biorefinery concept. There are several reasons for this new trend. First, there is growing awareness that the remaining oil resources are very limited and that oil prices will therefore increase significantly in the future. Thus, in the future petroleum may no longer be available as a basis for several products; therefore new raw materials have to be the low-cost source for various products. Secondly, cotton is a very important raw material for textiles, but cotton production cannot grow much above the present level to satisfy the future increased textile demand. The growing textile demand is due to global population increase and to the rapidly increasing GNP of many developing countries. The reasons for the limited growth potential of cotton production are mainly cotton's high demand for farming land, water, and pesticides. Farming land and water for irrigation will instead be needed for food production, and the high consumption of pesticides by the cotton farmers is a great environmental problem. Thus, the raw material for textiles has to switch to other sustainable and non-oil-based materials.

Cotton is basically pure cellulose, and it has been speculated that other cellulose materials therefore could take over as the raw material for future textile production. These arguments have led to the conclusion that the cellulose molecules found in trees and other plants could probably become a principal renewable resource for future textile manufacturing. However, in trees and most plants the cellulose molecules do not occur in isolation, but instead they are mixed in a complicated manner with other carbohydrates and lignin. Therefore, cellulose separation processes such as chemical pulping has to be used. By using this established fiber separation technique from the pulp industry, it is possible to obtain a cellulose-rich product called dissolving pulp. Yet, even after bleaching and hemicellulose extraction, such pulp still will contain between 5 and 10% of products other than cellulose. Thus, these components will affect the possibility to use the cellulose for production of textiles or other cellulose derivatives.

One product that is produced from dissolving pulp is viscose, and it is well known that the cellulose content in the dissolving pulp has to be high for the efficient preparation of viscose. The composition of a pulp with respect to cellulose and hemicellulose can be determined by performing a carbohydrate analysis based on the monomers in the sample or more approximately by performing a solubility test in strong alkali. Another way to determine if a pulp grade is suited to viscose preparation is by analyzing the filterability of the viscose solution prior to spinning, i.e. to determine the K_w value, where K_w is analyzed according to Treiber (1983).

Fock's reactivity method is a quick and simple way of indicating how well a pulp is suited as raw material for viscose production (Fock 1959). In recent years this method has been used by several researchers (Agnemo 2009; Köpcke el al. 2008; Engström et al. 2006; Kvarnlöf et al. 2006; Elg Christoffersson et al. 2002) for assessing the reactivity of different pulps, especially for viscose preparation. It has also been shown that there is no correlation between Fock reactivity and the degree of xanthate substitution on the cellulose backbone in the viscose preparation process (Östberg et al. 2011). Thus, the objectives were: 1) to assess the relevance of Fock's method as a tool for determining the reactivity of a given pulp, and 2) to determine which parameters and components in the dissolving pulp have an influence on Fock reactivity.

MATERIAL AND METHODS

Prehydrolysis

Commercial spruce chips were taken from a local pulp mill and dried, screened to a thickness of 3 to 7 mm, and manually inspected. Bark and oversized chips were removed, and the rest was used in the cooking experiments. 200 g of oven-dry wood chips (spruce) were then charged into each 2.5 L steel autoclave. The six autoclaves were then steamed for 10 min at 2 bars to heat up the chips and to remove air from them. After closing the bottom valve, deionised water was added to a liquor-to-wood ratio of 4:1. A nitrogen pressure of 10 bars was then added to each autoclave to improve the impregnation of the chips. The autoclaves were then rotated in a PEG bath for 30 min at

90 ^{o}C. The nitrogen pressure was then released, the top valve was closed, and the temperature was increased to 160 ^{o}C at a rate of 1.17 ^{o}C/min. The chips were then kept in the PEG bath for 1 h at 160 ^{o}C, after which the autoclaves were taken out and cooled in cold water. The lids were removed and the free liquor phase was drained off prior to the addition of white liquor and water. The lids were then put back on the autoclaves and the kraft cook started.

Kraft Cooking

Kraft pulping was carried out at 30% sulphidity and 27% effective alkali. Thus, 210 g NaOH and 180 g Na_2S were added to each autoclave, after which water was added to a liquid-to-wood ratio of 4:1. Nitrogen gas of 10 bars was then added to facilitate the impregnation of the chips and to check that there were no leaks between the lid and the autoclave. After 10 min the nitrogen gas pressure was released. The autoclaves were then rotated in the PEG bath and kept at 90 °C for 30 min. The temperature was raised to 160 °C at a rate of 1.17 °C/min. The kraft cooking times at 160 °C was 50, 70, 90, and 150 min, respectively.

Chlorite Delignification

The sodium chlorite and acetic acid used in this study were of puris p.a. quality (Sigma Aldrich). The chlorite delignification method used was the same as used by Germgård (2010), which is a modified version of the Canadian method (Anon. 2005). Thus, 30 g of oven-dry pulp was put in a plastic bag made of polyethylene with an exterior layer of aluminium. 0.5 g $NaClO_2$/g oven-dry pulp and 1% buffer (diluting 10 mL of glacial acetic acid to 1 L with distilled water) was added up to 8% pulp consistency, properly mixed, and sealed. The plastic bag was put in a water bath at 60 ^{o}C for 6 h. Then it was washed with 1.5 L of distilled water and thickened on a filter paper in a Buchner funnel. The filtrate was re-circulated to recover the fiber. The pulp sample was then air dried and stored in a refrigerated room prior to further analysis.

Kappa Number

Kappa no was measured according to ISO 302:2004(E).

Intrinsic Viscosity

Intrinsic viscosity was determined according to ISO 5351:2004(E).

Levelling-off Degree of Polymerization (LOPD)

H_2SO_4 (puris grade, Merck) was used for hydrolysis. The hydrolysis was done according to the method described in the literature (Battista 1956). Thus, 2 g of the oven-dry pulp and 200 mL of H_2SO_4 (1.5 M) were added to a flask. The flask was then put in a water bath at 80 ^{o}C with a loosely-fitted glass stopper so that pressure could be released, and the flask was shaken throughout hydrolysis. Each pulp sample was split in two subsamples, which were treated with the acid for 1 or 2 h. If the same intrinsic viscosity later was obtained for both samples, it was decided that LODP had been reached already after 1 hour. Then the acid treatment each sample was filtered with a glass filter (porosity 4) and washed with deionised water until the filtrate became neutral with respect to pH.

The residue was air dried, and the intrinsic viscosity was determined according to the SCAN-CM 15:88 methods.

Alkali Solubility (S_{18})

Alkali solubility at 18% sodium hydroxide (S_{18}) was determined according to SCAN-C 2:61 methods. Thus, 100 mL of an 18% NaOH solution was transferred to a 200 mL beaker and 1.5 g oven-dry pulp was added. After 2 min it was stirred with a magnetic stirrer for 3 min. The mixture was kept at room temperature for 60 min. It was then stirred with a glass rod and sucked through a glass filter (porosity 4). The first 10 to 20 mL of the filtrate was discarded and the next 30 to 40 mL were taken for analysis. 10 mL of the filtrate, 10 mL $K_2Cr_2O_7$ (20 g $K_2Cr_2O_7$, and 150 mL H_2SO_4 (conc. 95%) in 1 l deionised water) was added to a 250 mL flask and cooled to room temperature. The solution was then transferred to a 1 L volumetric flask with 500 mL of deionised water, and 2 g KI was added for 5 min, before it was titrated against $Na_2S_2O_3$ (0.1 N) by adding 5 mL starch as an indicator. The S_{18} numbers were used to calculate the corresponding residual quantity, here denoted as R_{18}, according to the equation $R_{18} = 100\% - S_{18}$.

Fock's Method

Fock's method was used to measure the cellulose reactivity ((Fock 1959). The method involves mixing a significant surplus of sodium hydroxide and carbon disulfide with a pulp sample. The following procedure was used: 0.5 g oven-dry pulp was added to a 100 ml Erlenmeyer flask. 1 mL CS_2 and 50 mL NaOH (9% w/w) were added, and the mixture was stirred for 3 h with a magnetic stirrer. The mixture was then diluted to 100 g with deionised water and transferred equally to two tubes with stopcocks. These tubes were shaken vigorously and then centrifuged for 5 min at 6000 rpm to separate the undissolved fibres. A sample of 5 mL of the liquid phase was then taken from each tube and transferred to 100 mL Erlenmeyer flasks. The mixture was neutralized with 3 mL H_2SO_4 (20% w/w) to decompose the xanthate complexes thus leading to the regeneration of the cellulose and left to react for 15 to 20 h. A volume of 20 mL of H_2SO_4 (68% w/w) was added to the regenerated cellulose, and the mixture was stirred for 1 h with a magnetic stirrer. The mixture was then transferred to a flask and 10 mL $K_2Cr_2O_7$ (1/6 M) was added. It was then re-boiled for 1 h to oxidize the regenerated cellulose. In this reaction Cr^{6+} ions are reduced to Cr^{3+} when the organic material in the sample is oxidized. When the sample had cooled to ambient temperature, it was transferred to a 100 mL volumetric flask and diluted to 100 mL with deionised water. Finally, 40 mL of the solution was transferred to a 250 mL Erlenmeyer flask to react with 5 ml KI (10% w/v) to determine the remaining Cr^{6+} amount. It was then titrated with $Na_2S_2O_3$ (0.1 M), using starch as an indicator.

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of cooking time on the kappa number of the pulp samples before and after chlorite delignification. As can be expected, a longer cooking time resulted in a lower kappa number. The kappa number after chlorite delignification was almost zero, which indicated that approximately all the lignin had been removed by the chlorite delignification method.

The corresponding intrinsic viscosities are shown in Fig. 2. It is seen that the intrinsic viscosity was reduced by increased cooking time, but also by the chlorite delignification treatment. Thus, at the temperature used (60°C) the chlorite treatment was not only affecting the lignin as is commonly assumed, but reactions also took place with the cellulose. These cellulose reactions resulted in shorter cellulose chains and thus lower intrinsic viscosity. That a cellulose reaction takes place in a chlorite delignification stage and especially if the temperature is raised above room temperature had earlier been shown by Germgård (2010).

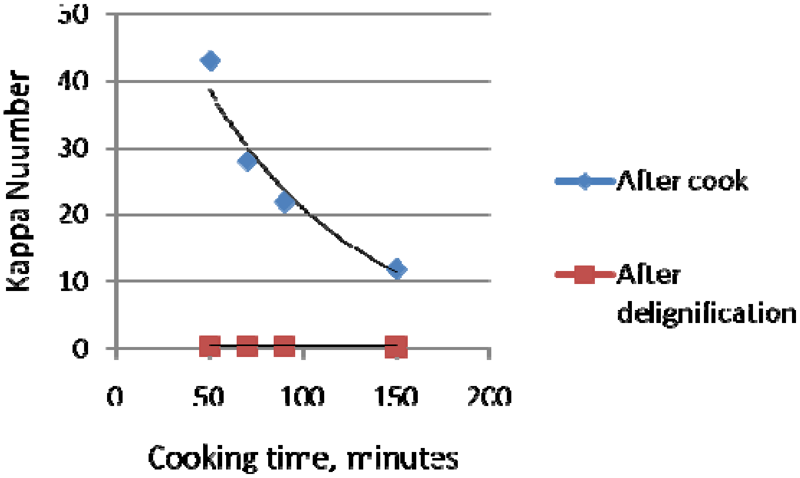

Fig. 1. Kappa number of the pulps studied as a function of cooking time analyzed before and after chlorite delignification

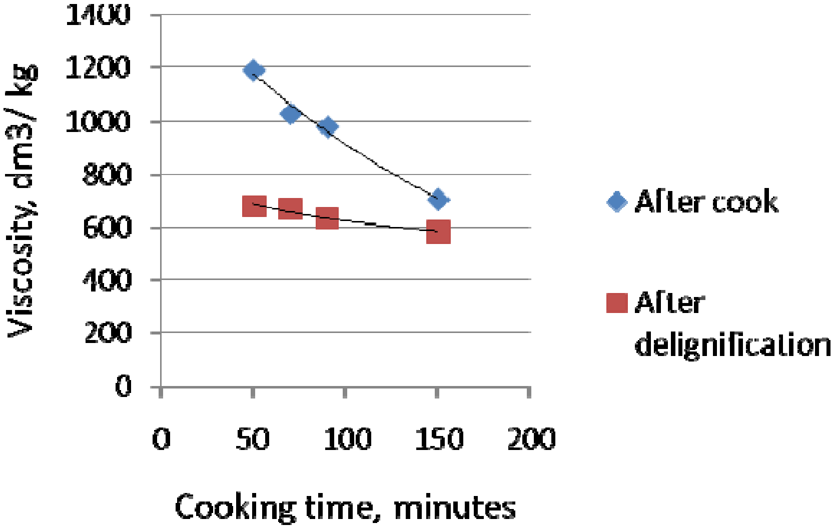

Fig. 2. Intrinsic viscosity of the pulps studied as a function of cooking time analyzed before and after chlorite delignification

In this study reactivity was measured using Fock's test (Fock 1959), as this method has been used in a number of studies both at our university and at other universities. This test simulates the chemical conditions used in a viscose plant in a simplified manner. Fig. 3 shows that the reactivity of the pulp samples increased with decreasing kappa number. The reactivity increased particularly if the pulps had been chlorite delignified, i.e. when the lignin content was almost zero.

Thus, lignin seems to have a negative effect on the reactivity, which could be due to a lignin blocking effect of the cellulose molecules in the fiber wall, making them less susceptible to chemical reactions. Also note that the chlorite delignified pulps had a higher reactivity if the kappa number directly after the kraft cook was lower, i.e. if the pulps had been pulped longer. Prolonged cooking leads to lower lignin content, but also to more decomposed lignin. The decomposed lignin is not only more readily available to chemical reactions, but is also easier to remove from the fiber wall. Thus, the lignin amount after the chlorite treatment was most probably slightly lower if the kappa number of the starting pulp was low. Therefore even the low lignin content that was available after the chlorite delignification seems to have a negative influence on the reactivity. Simply put, the influence of the kappa number prior to the chlorite treatment on the reactivity after chlorite delignification treatment, may be described as a memory of earlier treatment stages retained by the pulp. Such a memory effect is well known in pulping and bleaching of pulps, for example when studying the kinetics of the kraft cook (Gustavsson et al 1997) and may be due to reaction mechanisms in earlier stages that influence the reactivity during later stages of the process.

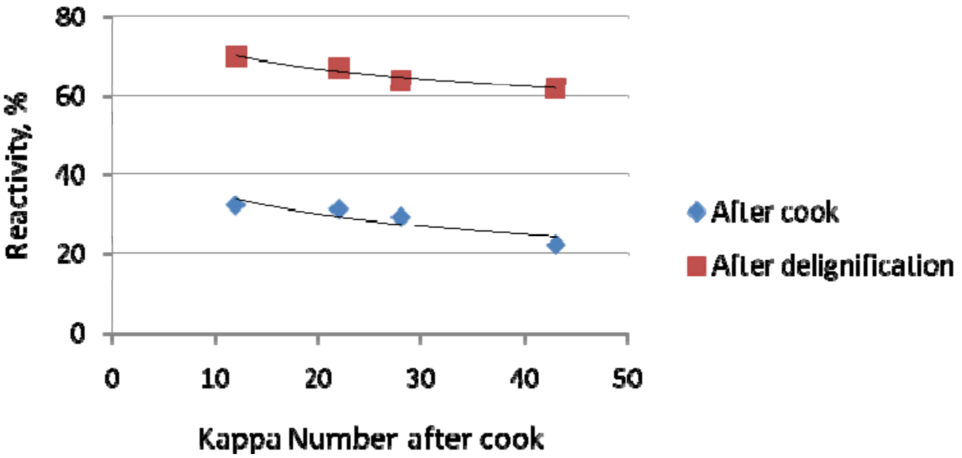

Fig. 3. Reactivity according to Fock's test versus the kappa number of the samples measured before chlorite delignification

Figure 4 shows a negative correlation between the reactivity and the pulp yield, calculated on wood. The same type of correlation between increasing reactivity and decreasing intrinsic viscosity has earlier been reported by Ibarra et al. (2008). In this case there was also one correlation for unbleached pulps and another for chlorite delignified pulps. It is also the case that the reactivity was highest for pulp samples that were chlorite delignified, but it was also higher for pulp samples with the lowest kappa numbers.

It is seen that the reactivity increased with decreased pulp yield, but decreased pulp yield is the same as decreased content of hemicellulose, cellulose and/or lignin compared with the starting wood. However, a lower pulp yield obtained via prehydrolysis, kraft pulping or chlorite delignification also means that the relative cellulose content is higher than that of lignin or hemicellulose. Thus, the reactivity increased directly with decreasing pulp yield or indirectly by the decreasing lignin content or increasing fraction of cellulose in the pulp samples. Most probably the important parameter is not the pulp yield, but instead the lignin and cellulose content. It can therefore be expected that Figs. 3 and 4 should be relatively similar in shape.

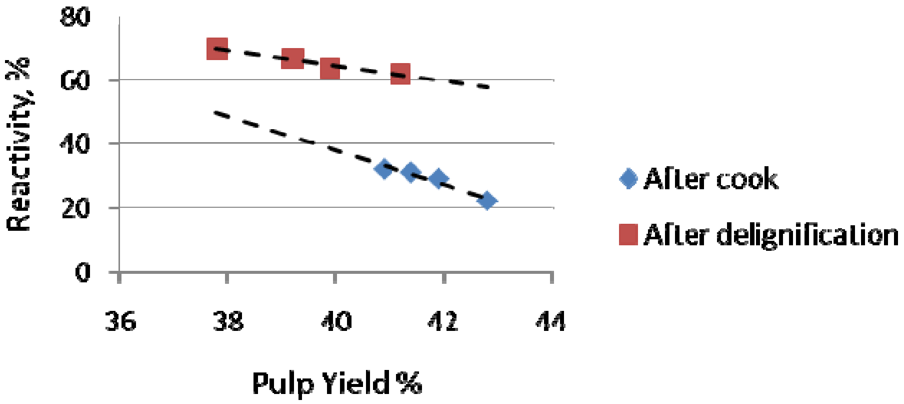

Fig. 4. The reactivity of the pulps studied versus the pulp yield for the pulps after the cook and after chlorite delignification

Figure 5 shows the correlation between the reactivity of the pulps and intrinsic viscosity. As shown, there was a relatively good correlation between the pulp reactivity and the intrinsic viscosity. This correlation was roughly the same for the pulp samples, both before and after chlorite delignification. Thus, it seemed that a high reactivity was obtained if the intrinsic viscosity was low. This correlation between increasing reactivity and decreasing intrinsic viscosity in the starting pulp could be due to a higher accessibility for cellulose reactions when the cellulose chain length is short. However, it could also be an indirect effect of the harsher chemical attack on the pulps at a prolonged cooking time, which indirectly resulted in lower intrinsic viscosity. A prolonged cook could be expected to yield a more open structure and thus a higher susceptibility to chemical reactions. Thus, irrespective of the reason, it appeared to be important that the intrinsic pulp viscosity was low in order to obtain a good cellulose reactivity.

The intrinsic viscosity at LODP is a measure of the part of the cellulose that is intact after a strong acidic treatment, which indicates that this is a very crystalline fraction of the cellulose (Håkansson et al 2005). A higher LODP number suggests that the crystalline fraction of the cellulose fibrils in the pulp are larger and thus more intact. As can be seen in Fig. 6, the reactivity of the pulps was increased with a decreasing LODP number. Thus, the reactivity increased if the crystalline fraction of the cellulose decreased. Or, stated in another way: it is beneficial for the reactivity if the amorphus fraction of the cellulose is increasing. For the chlorite delignified pulps the reactivity was higher than for unbleached pulps compared at a given LODP value, therefore showing that the presence of lignin decreased the reactivity of the pulps.

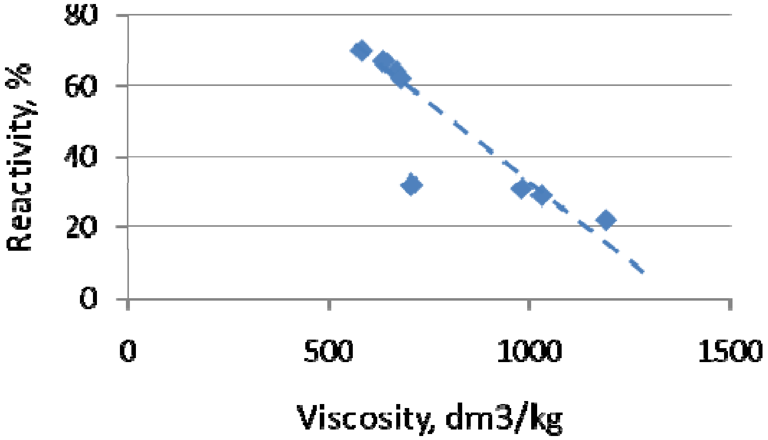

Fig. 5. The reactivity of all the pulps studied versus their intrinsic viscosities. It seems that all pulp samples, except for one, follow the same linear correlation

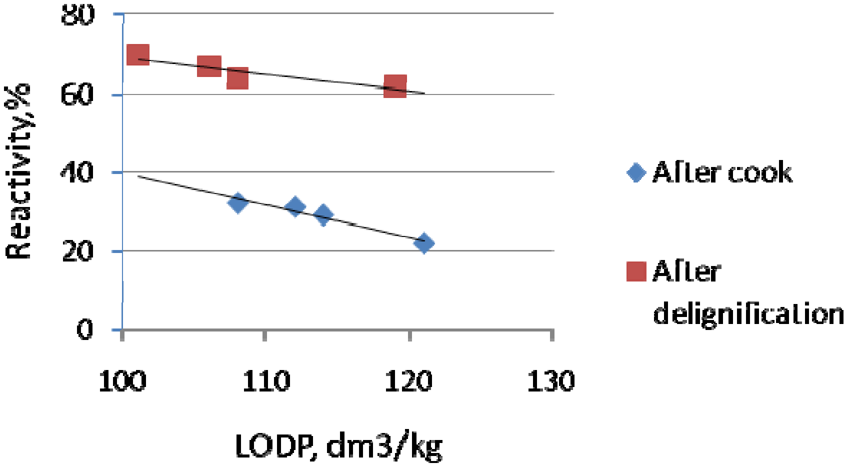

Fig. 6. Reactivity according to Fock's test versus LODP of the samples after the cook and chlorite delignification

The solubility of a pulp sample in an 18% sodium hydroxide solution can be used as a measure of the amount of material in the pulp that possibly could be dissolved under these conditions. Amorphous material like hemicelluloses and amorphous cellulose will be dissolved (S_{18}) while the more crystalline cellulose will stay as a residual (R_{18}). These two parameters are correlated according to $R_{18} + S_{18} = 100\%$. When plotting the reactivity of the pulps versus the R_{18} value, two correlations were obtained, i.e. one for the pulp samples that had not been chlorite delignified and another correlation for the pulps that had been delignified with chlorite (Fig. 7). Thus, for each group there was a correlation showing that if the R_{18} value increased the reactivity went down. Therefore, a certain amount of amorphous material, either of cellulose or hemicellulose origin, was needed in the pulps to obtain a good reactivity. It is interesting to note that chlorite delignification increased the reactivity substantially and it seemed that a very high reactivity required more or less lignin-free pulp samples.

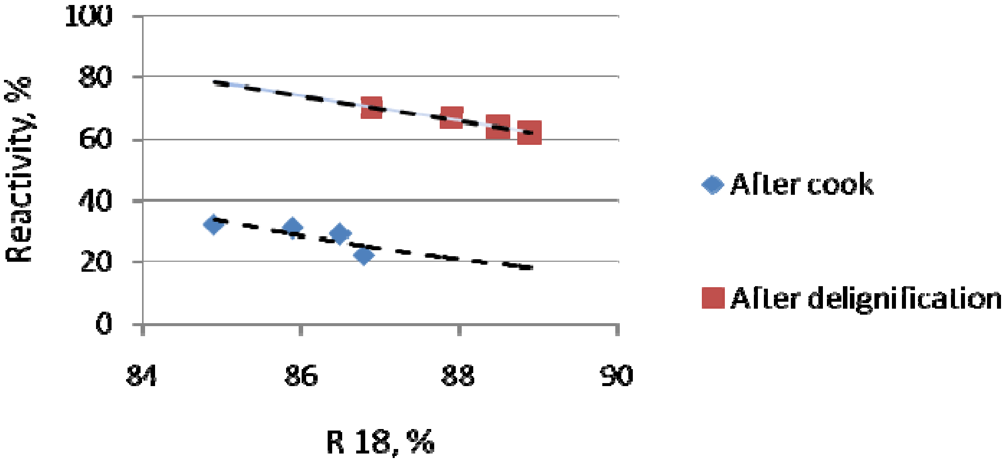

Fig. 7. Pulp reactivity as a function of R_{18}, for pulp samples before and after chlorite delignification

In Figure 8 the relative fractions of cellulose, glucomannan, xylan, and lignin are plotted against the reactivity of the pulps. On the one hand it is shown that for the studied pulp samples, there were no differences in the cellulose, glucomannan, or xylan contents. Accordingly, it could be interpreted as meaning that the carbohydrate composition in the pulps was not a variable that could explain the variation in reactivity. On the other hand, there was a significant difference in the lignin content and lower lignin fraction correlated strongly with higher reactivity. The figure shows that the highest reactivity was obtained for the pulp samples that were chlorite delignified, and the negative effect of the lignin content on the pulp reactivity was again verified.

It may seem strange that the hemicellulose content in the pulp samples was constant while the R_{18} value for the same pulps differed. The variation in reactivity of the pulp samples thus correlated negatively with the R_{18} value, but not with the hemicellulose content. The R_{18} value is usually used as a simple measure of the amount of material that cannot be dissolved in strong alkali (18%), and for a dissolving pulp that means mainly the crystalline part of the cellulose, while amorphous cellulose and hemicelluloses, due to their non-crystalline nature, will be dissolved. The explanation for the R_{18} problem outlined above is probably that the carbohydrate analysis measures the total amount of carbohydrate monomers in the pulps, but it does not take into account whether the corresponding carbohydrates are located in an amorphic or in a crystalline area. The R_{18} value on the other hand measures only the non-accessible amount of the sample which usually is considered as being the same as the crystalline part of the cellulose.

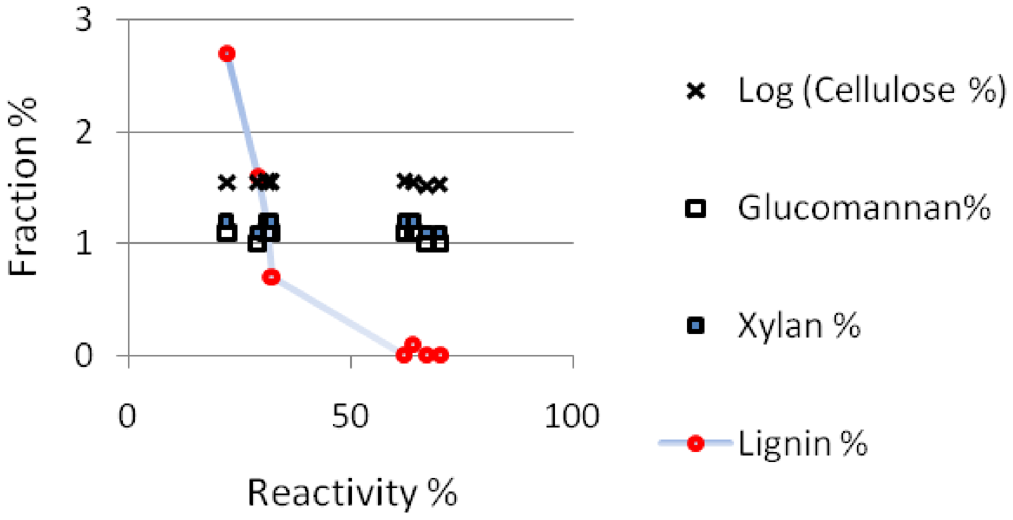

Fig. 8. The relative fractions of different components in the pulps versus the reactivity of the pulps

CONCLUSIONS

1. A dissolving pulp with a certain amount of amorphous cellulose structure, preferentially lignin-free, seems to be the best starting material for viscose preparation.
2. A strong correlation was obtained between the reactivity of prehydrolyzed spruce kraft pulps, measured according to Fock's test, and the lignin content, the LODP, the R_{18} and the intrinsic viscosity.
3. Surprisingly, no correlation was found between the pulp reactivity and the cellulose or hemicellulose contents in the pulp samples.

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