REACTION PHASES OF THE WOOD CONSTITUENTS' DEGRADATION DURING KRAFT COOKING OF SPRUCE CHIPS

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ABSTRACT

In this study, the changes of the individual constituents of wood, mainly lignin fraction, and carbohydrate fraction of partially delignified wood chips were investigated. The concentration of alkali during kraft cooking of spruce chips were characterized with respect to the time of kraft cooking, consumed alkali and also to the time-temperature variable (H-factor). The observation brought a new fact, that the extraction of lignin and degradation of the carbohydrate fraction as well as the wood residue itself, were realized in two different reaction phases: initial and residual. The power form dependences between the studied constituents of the wood during kraft cooking were interpreted in a logarithmic coordinate system by the straight line relationship.

KEYWORDS: Kraft cooking, spruce wood, wood constituents, lignin fraction, carbohydrate fraction, active alkali.

INTRODUCTION

Wood biomass during a chemical processing within the pulp and paper industry is undergoing strong degradation. Apart from pulp and cellulose as main products, as well as other by-products with utilization can be obtained by several processes (Mikulášik et al. 2008). Pulp yield can be improved by a more homogeneous delignification of the chips by impregnation prior to cooking by means of impregnation liquor with a high initial effective alkali concentration (Brännvall 2018). Mass losses, that also need to be noticed, occur in the paper production process in retention systems. It's also significant, mainly from the environmental point of view (Kuňa et al. 2016).

Wood contains of two main fractions, the lignin fraction and carbohydrate fraction, which play the main role during kraft pulping. The removal of wood constituents during pulping, or bleaching as well, creates macro pores in cell walls. The wall becomes more fragile and damaged. The cell wall fragility enables the fibres to suffer more and to deform when mechanical forces are applied to them. Deformations and lumen collapses become more frequent (Fišerová et al. 2010). A partial replacement of the coniferous wood pulp for fibrous products by sources with a weaker cell wall can be valuable for environment (Ihnát et al. 2015). Degradation losses are caused by chemicals used in process. Balance between alkali concentration and hemicellulose degradation was discussed by Montana (Montana et al. 2015). The cellulose degradation kinetic was described by different models (Jafari et al. 2015). Better yields than at kraft pulping can be achieved at the production of semi-chemical pulp (yield of about 80%) by the neutral sulphite cooking process (NSSC). The mildly alkaline sulphur-free technology as a replacement of the NSSC is much more gentle to wood mass (Balberčák et al. 2017, Balberčák et al. 2018). Compared with the production of chemical pulp, the thermo-mechanical production brings considerable savings resulting from significantly better utilization of basic raw materials (95% yield) (Ihnát et al. 2018).

The changes in the composition of the wood residue during the kraft pulping were studied by many researchers. Earlier authors concerned their study to the extraction of the lignin fraction of wood, to improve the selectivity of the extraction of lignin fraction of wood by addition of the sodium sulfide to cooking liquor (Aurell and Hartler 1965, Hatton and Hejjas 1972, Cho and Sarkanen 1985, Fleming et al. 1980, Olm and Tistad 1979, Tasman 1980, Hartler 1978). The improving the selectivity of delignification by addition of sodium borohydride has been studied by Aurell and Hartler (1965). The improving the technology of delignification was studied by introducing so-called extended delignification by Hartler (1978). Mathematical models that describe the course of delignification and carbohydrate degradation during cooking processes as a function of cooking temperature and cooking chemicals concentrations were developed in the past (Nieminen 2015).

A relationships between the dependent and independent variables of the pulping reaction are based and described by the power function or by the logarithmic function. The method to demonstrate the relationship between the dependent and independent variables is to express it in a logarithmic coordinate system as the logarithmic function or as its power form equivalent function. In our earlier work we have confirmed that the reaction rate of the kraft delignification of spruce wood was realized with respect to the time variable during four different reaction phases: initial, transitional, bulk and residual.

In this work the relationship of the extracted lignin fraction, degradation of the carbohydrate fraction as well as the degradation of the wood residue fraction as a main component of wood with respect to the time of pulping, or with respect to the alkali concentration, or with respect to the time-temperature variable was studied.

MATERIALS AND METHODS

The pulping of spruce wood chips (*Picea excelsa*) was studied by applying the active alkali charge of 16% of Na_2O per wood weight, liquor-to-wood ratio was 4:1 and sulfidity of the cooking liquor was 25%. At this charge of alkali, the initial concentration of the active alkali in cooking liquor was 40 $g \cdot L^{-1}$ of Na_2O. The 6 pieces of stainless steel digesters heated in an oil bath with the temperature increasing from 100°C up to 170°C during 2 hours and dwelling at this temperature for different time intervals were used for cooking. After cooking for particular

time interval, the digesters were cooled to the room temperature by cold running water. The partially cooked wood chips were washed to the neutral reaction and dried at a room temperature. After determining the yield of the wood residue part of the dried chips, the wood residue part was converted into sawdust in a Wiley mill. The sawdust was screened according to the Tappi Standards T12 os-75 and T11 os-74. The lignin content in screened sawdust and the content of extracts were determined according to the Tappi Standards T222 os-74 and T204 os-76, respectively. The analysis of the alkali concentration in the white and black cooking liquor was made according the methods described in Tappi Standards T624 cm-00 and in T625 cm-85.

The obtained experimental data were converted to their logarithmus naturalis data and drawn in the appropriate figures. The straight line relationship for the individual pulping phases was obtained. The straight line relationship of the individual pulping phases was expressed in some cases by the straight line equations calculated by the least squares method. The applied method of evaluation of the results was described in details in the earlier papers (Mašura 1997, 1999, 2002).

RESULTS AND DISCUSSION

Extraction of the lignin fraction and degradation of carbohydrate fraction of spruce wood during kraft cooking

The study of the wood constituents' behaviour during kraft cooking was based on the results presented in Fig. 1. The decrease of the wood residue fraction and lignin fraction in the wood residue, as well as the decrease of the total active alkali concentration in cooking liquor during the kraft pulping of spruce wood is shown.
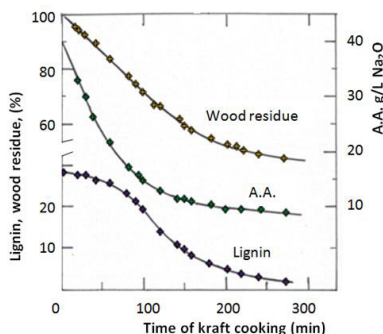

Fig. 1: Variation of the lignin fraction, wood residue fraction and residual alkali concentration in cooking liquor during kraft cooking of spruce chips.

The degradation of the carbohydrate fraction of wood in dependence on the extraction of lignin fraction of wood during kraft pulping is presented in Fig. 2. The mutual dependence is expressed as a three phases: initial, bulk and residual. The dependence of carbohydrate fraction of wood on the lignin fraction, from a point of view of practical application, is not important. The content of the carbohydrate fraction of wood residue and the lignin fraction of wood residue during kraft pulping is important from the practical point of view only as the dependence on the time variable or time-temperature variable (H-factor) or even as the dependence on the residual alkali concentration in cooking liquor. These dependences are the subject of study in the

following paragraphs. The relationship between the content of the carbohydrate fraction of wood and the lignin fraction of spruce wood during kraft pulping was published earlier (Mašura 1997).
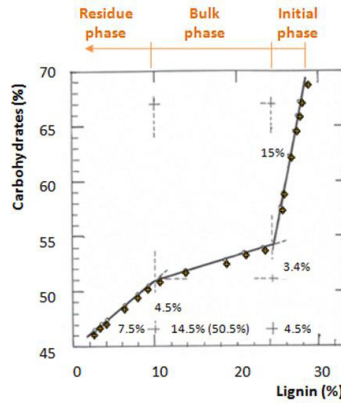

Fig. 2: The Relationship of the carbohydrate fraction on the lignin fraction of wood during kraft pulping of spruce chips. (The figure represents the quantity of the extracted lignin fraction or degraded carbohydrate fraction of wood during the individual delignification phases expressed in percentage of wood).

Wood constituents during kraft pulping

The behaviour of the individual wood constituents during cooking is expressed in Fig. 3 as the ratio of the carbohydrate fraction/cooking time (CT), lignin fraction/cooking time and the wood residue fraction/cooking time with respect to the time of kraft cooking. Such expression of the dependent variable on the independent variable of kraft pulping is consequence of their power form relationship. Such way can be power form dependence of the individual wood constituents on the time of pulping expressed in a logarithmic coordinate system by a straight line relationship. Wishing to express the power function relationship to the straight line relationship, it has to be changed to the rectangular hyperbolic function and expressed in a logarithmic coordinate system.

The degradation of the carbohydrate fraction of wood during kraft cooking is shown in Fig. 3 as the two phase process, initial and residual. During the initial phase the degradation of the carbohydrate fraction is increasing and maximum of degradation was reached after 60 min of cooking when the temperature of the cook reached 135°C. The time of increasing degradation of the carbohydrate fraction coincide with the time when the initial phase of the extraction of the lignin fraction changed to the bulk phase of the extraction of lignin fraction during kraft pulping. This finding confirmed the fact that the easily degraded part of the carbohydrate fraction is combined with the easily extracted part of the lignin fraction of wood during the initial phase of kraft pulping. When the carbohydrate fraction of wood reached the maximum degradation, during which mostly the hemicellulosic fraction of wood was degraded, the degradation of the carbohydrate fraction of wood constantly decreased with the time of pulping. The both phases of degradation of the carbohydrate fraction of wood are expressed in Fig. 3 in a logarithmic coordinate system by the straight line relationship.
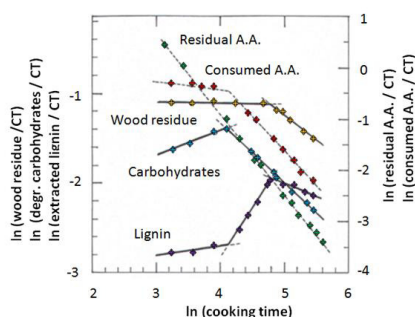
Fig. 3: Logarithmic relationship of the extracted lignin fraction, degraded carbohydrate fraction, wood residue fraction, consumed active alkali and unconsumed residual active alkali in cooking liquor with respect to the cooking time during kraft pulping of spruce chips. (Concentration of the active alkali is expressed in $g \cdot L^{-1} Na_2O$).

The extraction of the lignin fraction of wood during kraft cooking is expressed in Fig. 3 as the three phase process: initial, bulk and residual. During the initial phase the extraction of the lignin fraction of wood is moderately increasing. During the bulk phase the extraction of the lignin fraction of wood sharply increased and reached the maximum of extraction after two hours of pulping when the temperature of cook reached its maximum 170°C. During the residual phase of pulping the extraction of the lignin fraction of wood moderately decreased up to the end of batch. According to our unpublished results also the reaction rate of delignification reached the maximum rate after two hours of pulping when the temperature of cook reached it maximum of 170°C.

The extraction and degradation of the wood residue fraction during the initial and bulk phases of pulping with respect to the time variable of pulping remained constant. The extraction and degradation of the wood residue fraction during residual phase of pulping started to decrease after two hours of pulping when the temperature of pulping was kept at 170°C. The decrease of this fraction of wood continued up to the end of batch. The Fig. 3 enables a sight into a digester and allows seeing the changes of the individual main constituents of spruce wood during the kraft cooking.

Wood constituents during kraft cooking with respect to the consumed alkali charge

The course of the extraction of lignin fraction, degradation of carbohydrate fraction and the degradation of wood fraction with respect to the consumed active alkali during entire kraft pulping process is shown in Fig. 4. From the results present in this figure it follows that with respect to the consumed active alkali the pulping reaction is divided on two different phases. During the initial phase of pulping the concentration of the consumed total active alkali decreased from 40 $g \cdot L^{-1}$ of Na_2O to 20 $g \cdot L^{-1}$ of Na_2O; i.e. to the half of the quantity charged to a digester. The extraction of the lignin fraction during the initial phase of pulping was low and the degradation of the carbohydrate fraction increased to a maximum. The residual phase of cooking began when the concentration of active alkali in cooking liquor decreased to the half of the charge put into a digester. Due to the degradation of the main part of the hemicellulosic fraction of wood during the initial phase of cooking the extraction of the lignin fraction during the residual phase of pulping sharply increased until to the end of cooking. The degradation of the carbohydrate fraction of wood during the initial phase of cooking moderately increased and then during the

residual phase of cooking moderately decreased. The course of the carbohydrate fraction of wood at the end of cooking blended with the course of the extraction of lignin fraction of wood. The change of the initial phase of cooking to the residual phase happened for all constituents of wood at the same concentration of the consumed active alkali, i.e. at Na_2O 20 $g \cdot L^{-1}$.
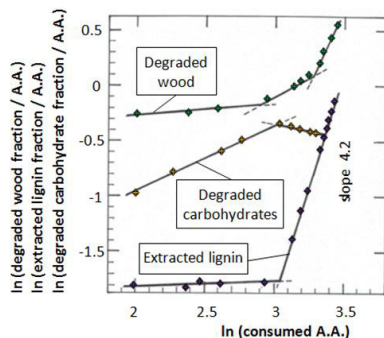
Fig. 4: Logarithmic relationship of the extracted lignin fraction, degraded wood residue fraction and degraded carbohydrate fraction with respect to the consumed active alkali during kraft cooking of spruce chips. (The individual fractions are expressed as the logarithmic ratio with consumed alkali in $g \cdot L^{-1}$ Na_2O).

The change of the extracted and degraded wood residue fraction during the initial phase of kraft pulping was moderate. During the residual phase of cooking the extraction and degradation of the wood residue fraction increased mainly due to the extraction of the lignin fraction and the degradation of the carbohydrate fraction of wood.

Resistant wood constituents with respect to the residual alkali concentration in cooking liquor

The resistant, i.e. not extracted lignin fraction and the resistant, i.e. not degraded carbohydrate fraction of wood which has resistant the cooking condition and remained inside of the wood residue during kraft cooking of spruce wood are shown in Fig. 5.

The presented resistant fraction of the lignin and carbohydrates inside of the wood residue were evaluated with respect to the residual alkali concentration in cooking liquor determined by the titration. The concentration of the active alkali in the cooking liquor at the beginning of pulping was 40 $g \cdot L^{-1}$ Na_2O (charge was 16% Na_2O on wood), which has changed to 9-10 $g \cdot L^{-1}$ Na_2O at the end of pulping. Results shown in Fig. 5 confirmed that the carbohydrate fraction of wood constantly increased inside of the partially delignified wood chips during the entire kraft cooking. The content of the lignin fraction inside of the partially delignified wood chips has changed and was expressed by the four phase process. The content of the lignin fraction in the wood residue during cooking reached a maximum after the 75 min cooking when the residual concentration of alkali in cooking liquor decreased from 40 $g \cdot L^{-1}$ of Na_2O to 18 $g \cdot L^{-1}$ of Na_2O, i.e. to less than half of the alkali charged into a digester.
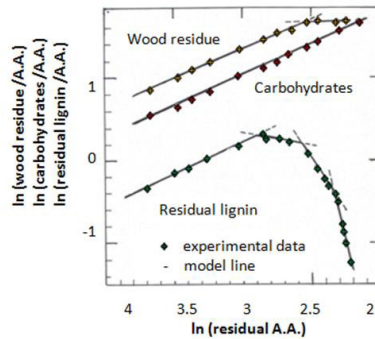
Fig. 5: Logarithmic relationship of the residual lignin fraction, the residual carbohydrate fraction and the wood residue fraction with respect to the residual active alkali in cooking liquor during kraft cooking of spruce wood. (The individual fractions are expressed as the logarithmic ratio with unconsumed active alkali present in cooking liquor in $g \cdot L^{-1}$ Na_2O).

This time interval of cooking is initial phase of cooking when the content of the lignin fraction inside of the partially delignified wood chips increased from 28.7% up to 29.8%. Simultaneously the yield of wood residue decreased to 77% of wood and the lignin fraction content calculated on wood was 23%. After this reaction phase follows the transition and bulk phases when the concentration of alkali decreased to 10.5 $g \cdot L^{-1}$ of Na_2O, the yield of wood residue decreased to 55% of wood and the content of the lignin fraction decreased to 6.2% of wood. In the following residual phase of pulping the concentration of the residual alkali in cooking liquor decreased to 9 $g \cdot L^{-1}$ of Na_2O, the content of the lignin fraction decreased to 2% and the yield of wood residue decreased to 49.3% of wood.

The content of the wood residue fraction with respect to the decreasing alkali concentration in a cooking liquor constantly increased and the residual alkali concentration in a cooking liquor decreased to 13 $g \cdot L^{-1}$ of Na_2O. This point of pulping was realized after two hours of kraft pulping when the cooking temperature reached maximum 170°C. Fig. 5 renders a sight into a digester on the remaining wood residue fraction, carbohydrate fraction and the lignin fraction evaluated in dependence on the unconsumed residual active alkali in cooking liquor during kraft pulping of spruce wood.

Wood constituents during kraft pulping with respect to the time-temperature variable (H-factor)

The relationship between the wood constituents and the time-temperature variable during the kraft pulping of spruce chips is shown in Fig. 6.
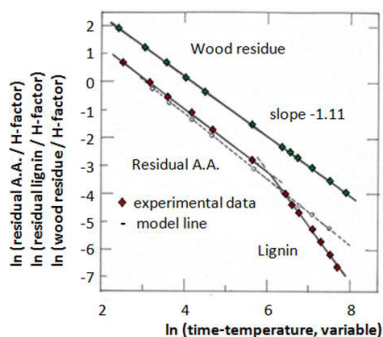
Fig. 6: Logarithmic variation of the wood residue fraction, the lignin fraction and the residual active alkali in cooking liquor with respect to the time–temperature variable (H-factor) during kraft pulping of spruce chips. (The individual fractions are expressed as the logarithmic ratio with the H-factor).

As can be seen from this figure the relationship of the yield of wood residue fraction expressed with respect to the time-temperature variable drawn in a logarithmic coordinate system continually decreased. This relationship expressing the dependence of the decrease of wood residue fraction of wood with the increasing time-temperature variable is expressed as one phase process. The decrease of the wood residue fraction at the increasing time-temperature variable is expressed by a straight line relationship and mathematically can be expressed by the logarithmic straight line equation or its power form equivalent function, as follows:

$$yield/H\text{-factor} = \ln^{-1} (4.7891 - 1.1125 (\ln H\text{-factor}))$$

$$(R^2 = 0.9997) \qquad (1)$$

$$yield = 120.19315 (H)^{-0.1125}$$

where: yield expresses the yield of the wood residue fraction.

The preciseness of the derived equation (1) is very high because its correlation coefficient R^2 is approaching to 1.0.

The relationship of the residual alkali concentration in the cooking liquor with respect to the time-temperature variable is expressed in Fig. 6 also as one phase process. In the modern kraft pulp mills, the digesters are equipped with continual alkali titrator and a view on the change of the carbohydrate fraction or the lignin fraction of wood inside of the partially delignified wood chips at the different concentration of alkali in cooking liquor what can be interesting for the service man.

The relationship of the lignin fraction of wood with respect to the time-temperature variable of pulping is in Fig. 6 expressed by the two phase process: initial and residual. The content of the lignin fraction of wood is expressed in both phases in a logarithmic coordinate system by the straight line relationship with the different slope constant. The change of the slope constant of the relationship of lignin fraction vs. the H-factor is realized at the H-factor equal to 450. At the studied conditions of pulping it has happened after two hours of pulping when the temperature of pulping reached 170°C and the concentration of the active alkali in cooking liquor decreased to 12 g·L^{-1} of Na$_2$O. For the commercial application the relationship of the lignin fraction on the H-factor is important at the H-factor higher than 500. The mathematical evaluation of this part

of relationship is expressed in a logarithmic coordinate system by the logarithmic straight line equation or its power form equivalent function, as follows:

$$LiG/H\text{-factor} = \ln^{-1} (9.6316 - 2.1162 \ln H\text{-factor})$$

$$(R^2 = 0.990) \qquad\qquad (2)$$

$$LiG = 15,238.799\ H\text{-factor}^{-1.1162}$$

where: LiG is the content of the lignin fraction in percent of wood.

The preciseness of the derived equation (2) is high enough because the correlation coefficient R^2 is approaching to 1.0.

The quantity of the individual fraction of wood constituents extracted or degraded during kraft pulping with its relation to the time-temperature variable H-factor is shown in Fig. 7.
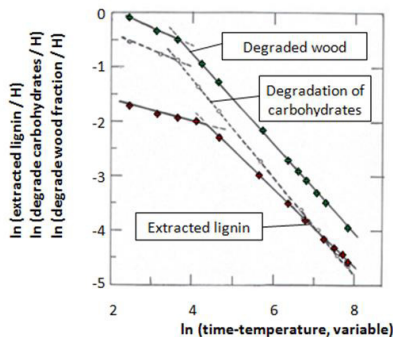

Fig. 7: Logarithmic relationship of the degraded wood residue fraction, the extracted lignin fraction and the degraded carbohydrate fraction (dashed line) with respect to the time–temperature variable (H-factor) during kraft cooking of spruce chips. (The individual fractions are expressed as logarithmic ratio with the H-factor).

From the results shown in this figure is evident that the extraction of the lignin fraction and the degradation of the carbohydrate fraction as well as the wood residue itself was realized in two different reaction phases: initial and residual. The degradation of the carbohydrate fraction and also the fraction of wood residue during initial phase of pulping was realized in a short time interval of 40 min of cooking. After this interval the degradation of both mentioned fraction of wood continued and constantly decreased with respect to the increasing H-factor of cooking. The extraction of the lignin fraction of wood during the initial phase of cooking lasted a little longer time interval of 75 min. After this time interval the extraction of the lignin fraction of wood during the residual phase of pulping constantly decreased with respect to the increasing time-temperature variable of cooking.

CONCLUSION

In this article is described an experimental sight into a digester during entire kraft cooking of spruce chips. The power function relationship between the dependent and independent variables of the kraft cooking reaction of wood is expressed as a relationship in a logarithmic coordinate system by the straight line equation.

The wood constituents such as the lignin fraction, the carbohydrate fraction, the partially delignified wood chips or the alkali concentration in cooking liquor studied with respect to the time variable or to alkali concentration have brought one very important fact that the changes of all wood constituents during kraft pulping are realized in the different reaction phases.

Presented study has confirmed also, that the main constituents of wood, such as the lignin fraction, the carbohydrate fraction, the wood residue fraction and even the applied alkali, behaved with respect to the time-temperature variable (H-factor) of kraft pulping differently during the individual reaction phases.

The fact, that the changes of the wood constituents during a cooking reaction are realized during different reaction phases, is a new phenomenon in the theory of the chemical reactions.

On the base of the obtained results can be postulated that also further chemical reactions are realized thoroughly individual however in different reaction phases.

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27. TAPPI Standard, T625 cm-85: Analysis of Soda and Sulfate Black Liquor.

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