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KINETICS OF WHEAT STRAW DELIGNIFICATION IN SODA AND KRAFT PULPING

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ABSTRACT.

Kraft and soda delignification kinetics of wheat straw, *Triticum aestivum*, have been studied as a function of OH⁻ concentration, HS⁻ concentration, and temperature. It was found that about 90% of the lignin is dissolved in the rapid initial phase. The rates of delignification in the bulk and residual phases were found to be similar to those of birch wood, *Betula pubescens*. The amount of residual phase lignin was found to be considerably less than in birch or spruce, *Picea abies*, and it was affected by the same factors. A model that accurately describes the delignification of wheat straw was derived.

INTRODUCTION.

Straw is an important raw material in many countries, particularly in Asia, Africa, Eastern Europe, and Latin America. It has been reported that the world straw production is approximately 545 million tons per year.¹ Half this amount is used mainly in farming, while the other half is destroyed as waste, either burned or ploughed into the ground. The quantity of waste straw would be sufficient for the production of 100 million tons of papermaking fibers a year, but only 4.5 million

tons of straw pulp are manufactured each year (less than 2% of the paper industry's total consumption²).

The main argument in support of using straw as a raw material is its ready availability as a residue from wheat crops, together with the fact that protective measures being adopted to prevent the indiscriminate cutting of wood mean that the paper industry is facing a shortage of wood material.

However: as a papermaking material, straw has some drawbacks compared with wood. Since it is an annual crop, there are problems of storage, delivery, and quality (annual fibers deteriorate on storage). There are also difficulties in designing an environmentally acceptable chemical recovery system, owing to the high silica content of straw.

Kraft pulping of wood can be divided into three phases; initial, bulk and residual phases,^{3,4,5} but a review of the literature shows that few investigations have been carried out focusing on the kinetics of the delignification of wheat straw. This paper presents the results of delignification studies in the soda and kraft pulping of wheat straw under laboratory conditions using bombs. The object of the investigation was to study the influences of temperature, chemical charge (OH^- concentration and HS^- concentration) and time on the pulping of wheat straw, to seek to optimize pulp yield at a given lignin content.

The other main objective was to verify the application of the kinetics model used by Lindgren and Lindström^{6,7} for the rate of delignification in the kraft pulping of spruce wood and birch wood. Wheat straw lignin contains more p-hydroxyphenyl units and fewer β -aryl-ether linkages than softwood and hardwood lignins. In addition there is a large amount of ester linkages.^{8,9} Differences in delignification can thus be expected.

EXPERIMENTAL.

Wheat straw (*Triticum aestivum*) harvested on a Swedish farm was used as raw material. It was dried immediately after harvest. For pulping, leaves (blade

and sheaths) and nodes were removed, because the lignin content changes according to the component considered: The internodes are the most lignified parts of the straw, whereas the leaves are less lignified,¹⁰ and both contain large amounts of silica. The straw was then hand-cut to lengths of 8.5 cm prior to pulping. Cooks were performed in stainless steel cylinders with a gauze lid and base, filled with the air-dried wheat straw samples of 5.5010 ± 0.0010 g.

Conventional soda pulps were prepared from wheat straw to provide a basis for comparison with kraft pulps. To determine the optimum soda/kraft pulping conditions for wheat straw, the concentration of OH^- (0.25, 0.5, 1.0 mol/L), the concentration of HS^- (0, 0.10, 0.30 mol/L), and maximum the temperature (120, 140, 150, 160°C) were varied, while the concentration of Na^+ was held constant at 1.3 mol/L. Chemicals were mixed to reach the calculated charge, and were added to the straw in an aqueous solution. The liquor-to-straw ratio was 100:1 in all the experiments. The cooking was conducted in 1 L bombs. Each bomb was charged with one sample of wheat straw. The bombs were continuously rotated in a polyglycol bath that was heated electrically. The temperature was increased at a rate of 1°C per min from 100°C to the preset temperature and then kept constant until the desired H-factor was reached. The cooks were stopped by rapidly cooling the bombs with tap water. After 30 min, the pressure was released, the bombs were opened, and the black liquor was collected for analysis. The pulps obtained were then washed thoroughly with deionized water, defibrated in a disintegrator, and washed and again filtered before drying.

Klason and acid-soluble lignin (STFI-method) were determined to give the total amount of native lignin in the straw. The Kappa number was determined for pulps pulped with low liquor-to-wood ratios according to SCAN C1:77. The lignin content of the pulp was measured by the chlorine number (SCAN C29:72), calculated according to the relationship:¹¹ $\text{Lignin content}(\%) = 0.9 \times \text{chlorine number}$. The pulp yield in each experiment was calculated from the dry weight of the whole pulps and the weight of initial sample. The moisture content was established by drying the pulp samples to constant weight at 105°C.

Potentiometric titration with HCl was employed on the black liquor to determine the residual alkali, and the sulfide ion concentration was determined by titration with AgNO_3 .¹²

RESULTS AND DISCUSSIONS.

Modeling and Calculation.

The pulping of wheat straw can be accurately described by three expressions, describing the initial, bulk and residual phases. Each expression is of first order with respect to lignin. The amount of lignin, L , remaining after time, t , in a constant composition cook at constant temperature can be described by the expression:

$$L = e^{\ln L_i^0 - k_i t} + e^{\ln L_b^0 - k_b t} + e^{\ln L_r^0 - k_r t} \quad [1]$$

where the subscripts i , b , and r refer, respectively, to the initial, bulk and residual phases. L_i^0 is the amount of lignin originally present that reacts according to the initial delignification kinetics, and k_i is the rate constant of this reaction, t is the time in min, etc. The three reactions are considered to take place simultaneously.

The experimental data show that there is a rapid initial phase and a slow residual delignification phase. However, it is not possible to describe the system with only two first order phases, so that the model includes a small bulk phase involving the removal of about 1.5% lignin on straw. The rate of delignification in this bulk phase is comparable to that in the bulk phase of birch.⁷ With a total amount of Klason and acid soluble lignin amounting to 23.7%, this leaves 22.2% for the sum of the initial and residual phase lignins.

The initial phase is so rapid that it was not possible to build a reliable model. The bulk delignification was well described by an equation of the form:

$$k_b = (a \cdot [\text{OH}^-] + b \cdot [\text{OH}^-] \cdot [\text{HS}^-] + c) \cdot \exp^{\frac{E_{a_b}}{R} \left(\frac{1}{T} - \frac{1}{443} \right)} \quad [2]$$

But, since the bulk delignification phase for straw is short, other models are probably also possible. The residual delignification was unaffected by hydroxide ion or hydrosulfide ion concentration and the influence of temperature was described by an Arrhenius equation:

$$k_r = d \cdot \exp^{\frac{E_{a_r}}{R} \left(\frac{1}{T} - \frac{1}{443} \right)} \quad [3]$$

Based on the results of the black liquor analysis, a model describing the delignification was developed. The standard error of estimate between the model and the experimental results was 6% for the 24 kraft cooks, 24 soda pulping experiments and one Klason and acid soluble analysis of the virgin straw. The model is displayed as solid lines in Figures 1 to 4 and 6.

The Delignification in the Initial Phase.

The delignification of wheat straw, just like that of softwood and hardwood, can be described by three phases, Figure 1, although, there are some significant differences. As illustrated in Figure 1, it has been found that about 90% of the lignin reacts according to a rapid initial delignification phase. In softwood and hardwood, in contrast to wheat straw, only 15-25 % of the lignin is removed during this rapid initial phase.

It has been reported⁸ that wheat straw lignin contains more p-hydroxyphenyl units and fewer β -aryl-ether linkages than softwood or hardwood lignins. The free phenolic content is 20-30 % of the lignin units¹³ and there are a large number of ester linkages.⁹ The initial phase in wood was attributed by Gierer¹⁴ to the cleavage of α - and β -aryl ether bonds in phenolic phenylpropane structures. The lignin removal in the initial phase can thus be explained as being due largely to

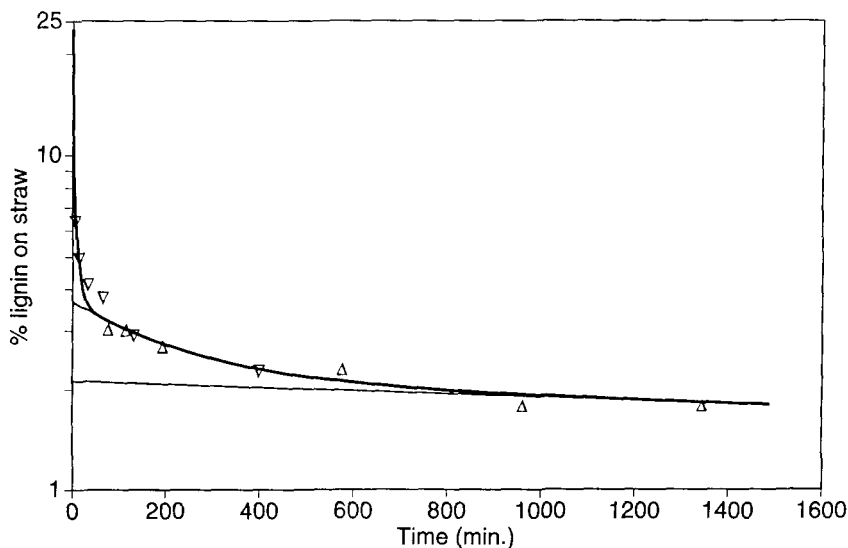


FIGURE 1. Kinetics for the delignification of wheat straw. The thick line is the sum of the initial, bulk and residual lignin according to the model. The amounts of residual and bulk + residual lignin are extrapolated to the beginning of the cook with thin lines. ∇ denote experiments carried out at 120°C, Δ denote experiments carried out at 140°C and recalculated to 120°C. The lignin content is plotted on a logarithmic scale.

saponification of ester linkages, cleavage of phenolic α -arylethers and, in kraft pulping cleavage of the β -arylether bonds.

Since data for the initial phase are available only at 120°C, the activation energy could not be calculated but it is safe to assume that the reaction is diffusion-controlled. The reaction rate of the initial phase in Eq. 1 at 120°C is 0.12 min^{-1} .

The Rate of Delignification in the Bulk Phase.

It is not possible to model soda pulping according to the equations derived by Lindgren and Lindström⁶ for the rate of delignification in the bulk phase.. These

equations are based on a proportional product of the concentration of the hydrosulfide ions and the hydroxide ions. A modified rate equation of LéMon and Teder¹⁵ has therefore been chosen to describe the bulk phase:

$$k_b = a [\text{OH}^-] + b [\text{OH}^-][\text{HS}^-] + c \quad [4]$$

where $a = 0.06$, $b = 0.1$, and $c = 0.1$ for soda and kraft pulping at 170°C.

Using the Arrhenius equation, the activation energy for the bulk delignification of straw was found to be 93 kJ/mol, which is much lower than the values 127 kJ/mol and the 117 kJ/mol reported from studies of spruce and birch respectively.^{6,7}

The Rate of Delignification in the Residual Phase.

A fundamental principle of kinetics is that the rate of an elementary reaction is approximately proportional to the product of the concentrations of the reactants. In accordance with this and earlier considerations, and as shown in Figure 2, the hydrosulfide ion concentration has hardly any influence on the rate of delignification in the residual phase.

It has been found that the concentration of hydroxide ion had a slight influence on the rate of delignification of hardwood and softwood. This was however, not found for wheat straw, as is shown in Figure 3. The rate of delignification in the residual phase is not affected by the concentration of hydroxide ion within the 0.25-1.0 mol/L range studied, but only by the temperature. The constant d in Eq. 3 was found to be 0.003 at 170°C.

The influence of the temperature on the rate of residual phase can be described by an activation energy of 97 kJ/mol. It is worth mentioning that wheat straw like spruce and birch shows an apparent activation energy during the residual phase higher than that during the bulk phase.

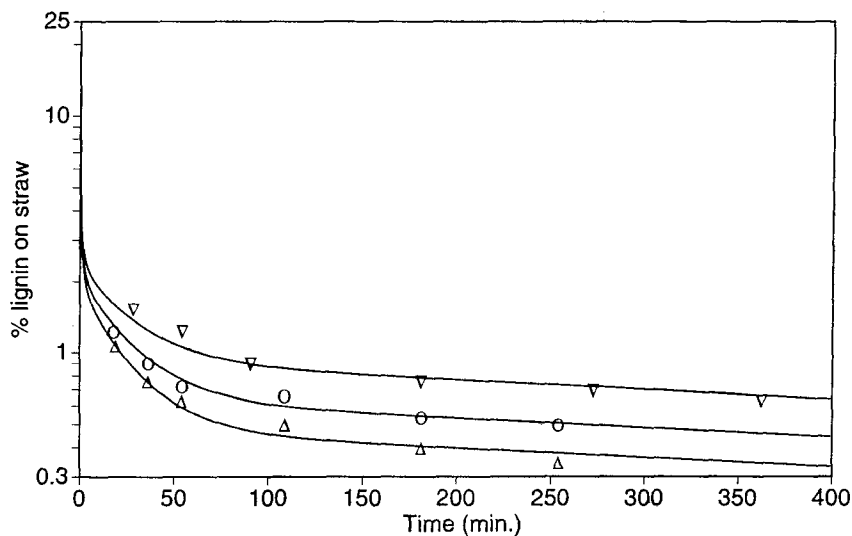


FIGURE 2. The effect of HS^- concentration ($\nabla=0.0$, $\circ=0.1$, $\Delta=0.3$ mol/L) in the initial, bulk and residual phases on the delignification rate. $[\text{OH}^-]=0.5$ mol/L. Temperature 150°C .

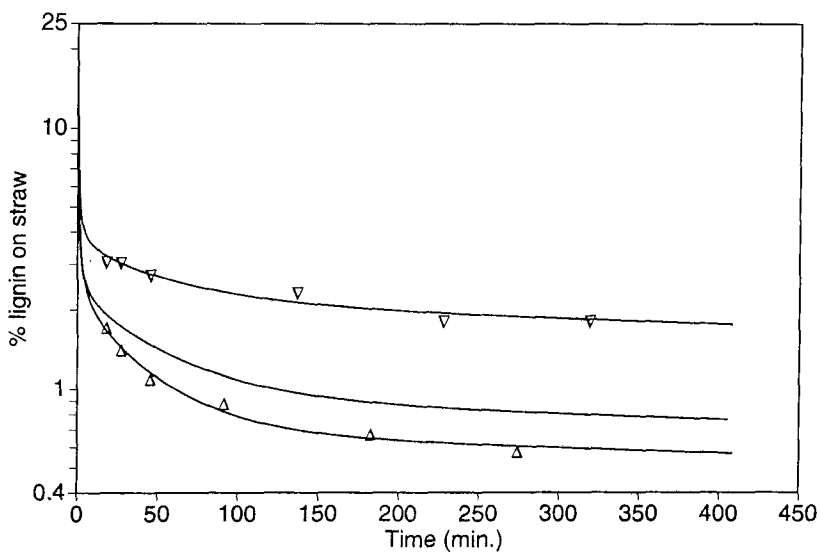


FIGURE 3. The influence of the OH^- concentration ($\Delta=1.0$, $-=0.5$, $\nabla=0.25$ mol/L) on the rate of delignification. $[\text{HS}^-]=0.0$ mol/L and temperature 140°C .

The Amount of Residual Phase Lignin.

The amount of residual phase lignin was determined by extrapolation of the delignification rate in the residual phase to the beginning of the cook. This is the same definition as was used in the previous work on spruce and birch.^{6,7} The influence of hydroxide and hydrosulfide ion concentrations and of temperature on the pulping of wheat straw has been studied. The fraction of lignin that is dissolved according to the slow residual phase kinetics is greatly influenced by the hydroxide ion concentration during the cook, as is shown in Figure 3. Comparing these results with those obtained with spruce and birch, it is obvious that the hydroxide ion concentration has an remarkable influence on the amount of residual phase lignin in straw. Whereas in spruce and birch a four-fold decrease in hydroxide ion concentration gave a two-fold increase in residual phase lignin content, this decrease gives a three-fold increase in wheat straw. Furthermore, as shown in Figure 2, the influence of hydrosulfide ion concentration is lower than the influence of hydroxide ion concentration on the amount of residual phase lignin. A three-fold decrease in hydrosulfide ion concentration gives an approximately two-fold increase in the amount of residual phase lignin. The effect of $[\text{HS}^-]$ on the amount of residual phase lignin can be explained by cleavage of phenolic β -0-4 linkages resulting in dissolution instead of the formation of stable enol ethers. The decrease in the amount of residual phase lignin caused by increasing $[\text{OH}^-]$ may be explained through increased reactivity of the lignin⁶ or possibly to be a consequence of the increased loss of hemicelluloses which accompany an increased $[\text{OH}^-]$.

As in the case of hardwood and softwood, the temperature in the range from 140° to 160°C has no influence on the content of residual phase lignin in wheat straw. It was also found that the transition point between the bulk and the residual phase changed to a lower lignin content for spruce and birch when the temperature was increased. However, in wheat straw, due to the similar activation energies of the bulk and residual phases, this does not occur, Figure 4.

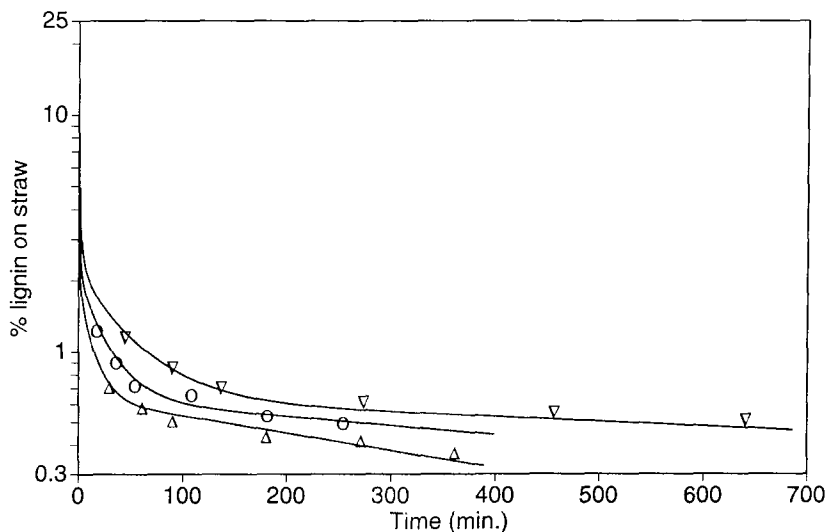


FIGURE 4. The influence of the temperature ($\Delta=160^{\circ}\text{C}$, $\text{O}=150^{\circ}\text{C}$, $\nabla=140^{\circ}\text{C}$) on the delignification rate. $[\text{OH}^-]=0.5 \text{ mol/L}$ and $[\text{HS}^-]=0.1 \text{ mol/L}$.

It has been shown for hardwood and softwood that increasing the ionic strength decreases the bulk delignification rate and increases the amount of residual phase lignin.^{6,7} Although it was beyond the scope of this investigation to study this, it is probable that ionic strength has similar effects on wheat straw pulping.

Yield.

The relationship between yield and chlorine number shown in Figure 5 suggests that alkali pulping at a low hydroxide ion concentration (e.g. 0.5 mol/L rather than 1.0 mol/L) is desirable. In the soda pulping of wheat straw, alkali concentration has a small influence on the delignification rate, but pulping with a higher alkali concentration will result in a lower yield. For optimal yield, it should

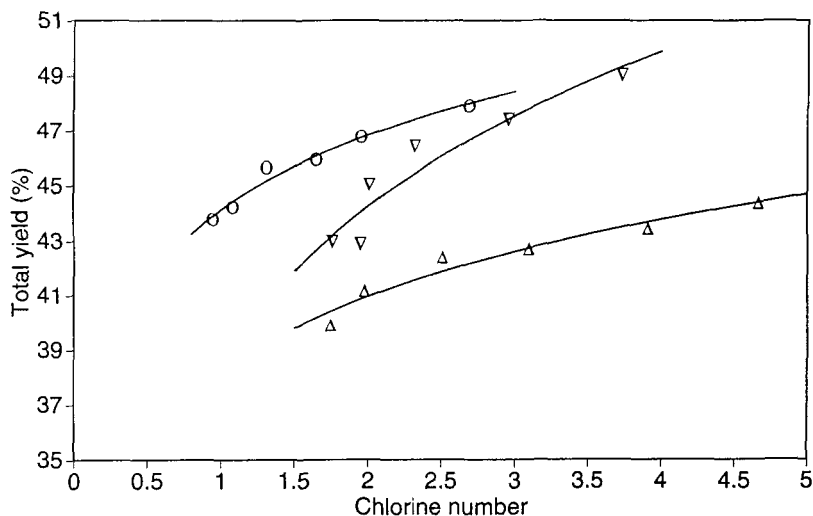


FIGURE 5. Plots of selectivity, expressed as yield versus chlorine number, for different pulping conditions. O=Kraft $[\text{OH}^-]=0.5 \text{ mol/L}$, $[\text{HS}^-]=0.3 \text{ mol/L}$, ∇ =Soda $[\text{OH}^-]=0.5 \text{ mol/L}$, Δ =Soda $[\text{OH}^-]=1.0 \text{ mol/L}$. Temperature is 140°C for O, ∇ and 150°C for Δ .

be advisable to increase other parameters such as the temperature instead of the hydroxide ion concentration.

Figure 5 shows that Kraft pulping results in a higher yield than soda pulping. In order to verify the results of this investigation with regard to the rapid and selective delignification of wheat straw with low or no hydrosulfide ions present, cooks were conducted on wheat straw without removal of leaves and nodes etc. These cooks were also performed at a liquor-to-straw ratio of 5 which is industrially relevant. The pulping was conducted at 150°C to an H factor of 100 with 20% effective alkali, 10% and 0% sulfidity. The soda cook resulted in a pulp with a kappa number of 13.4 and a yield of 38%. The presence of hydrosulfide ion decreased the amount of lignin by 22% to kappa 10.4 without affecting the yield. The consumption of effective alkali was 14% on straw. The low yield compared to

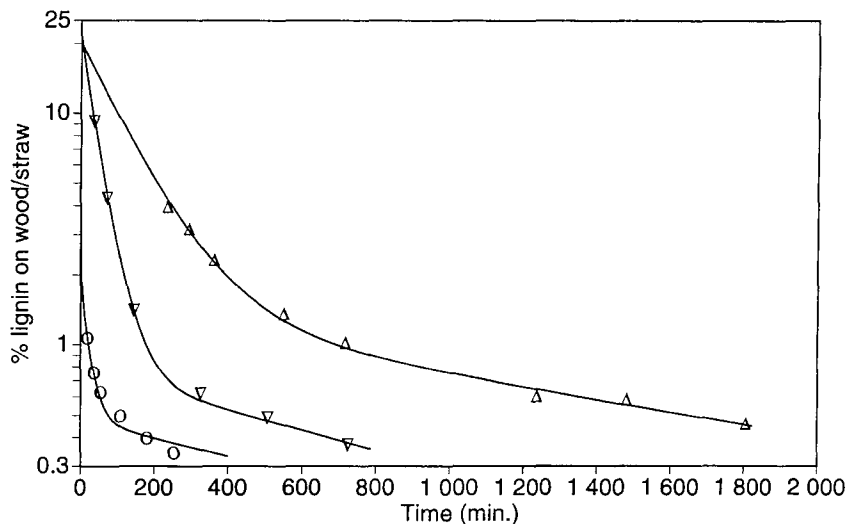


FIGURE 6. The delignification rates for the pulping of birch wood (∇), spruce wood (Δ) and wheat straw (O) under identical conditions; $[\text{OH}^-]=0.5$ mol/L, $[\text{HS}^-]=0.3$ mol/L, and temperature 150°C .

Figure 5 is caused by the inclusion of leaves etc. and it is interesting that this does not hinder the extensive delignification. The addition of hydrosulfide ions gave only a small advantage and there are drawbacks with a more complicated recovery system.

Comparison of Different Lignocellulosic Materials.

Pulping experiments carried out under the same conditions on wheat straw, birch wood and spruce wood, Figure 6, showed that the amount of residual phase lignin in wheat straw is 33% of the amount of residual phase lignin in spruce wood and that the amount of residual phase lignin in birch wood is 53% of the amount of residual phase lignin in spruce wood. The residual delignification kinetics for wheat straw are approximately the same as for birch and spruce at

150°C, but the activation energy for the residual phase is less than that for spruce or birch. The bulk delignification rate is of the same magnitude as that of birch and quicker than for spruce.

CONCLUSIONS.

- Wheat straw pulping can be described by three phases; the initial, bulk and residual phases.
- About 90% of the lignin is dissolved during the initial phase.
- The amount of residual phase lignin in wheat straw is affected by $[OH^-]$, $[HS^-]$ and temperature in a manner similar to the effects on residual phase lignin in spruce and birch.
- The kraft cooking of wheat straw results in a higher yield (2% units) than the soda process. This is due mainly to the lower amount of residual phase lignin.

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