Effect of Temperature on the Soda and Kraft Cooking of Corn Stalks

ZEINAT A. NAGIEB, *Cellulose and Paper Laboratory, National Research Centre, Dokki, Cairo, Egypt*

Synopsis

This study included soda and kraft process of corn stalks at constant active alkali, the kraft liquor having 25% sulfidity. Five cookings were made at different temperatures, 80, 120, 140, 160, and 180°C, each for 1 h. Under the condition of the study the following temperature effects were noted: (1) Delignification could be approximated by a first-order reaction. (2) The kraft process exhibited twice the rate of lignin removal as the soda of the same digestion temperature. (3) The rate of removal of carbohydrates in the kraft process is faster than soda process due to presence of sulfide ion. (4) The carbon content of thiolignin increased hydrogen and oxygen content decreased while in soda lignin the opposite occurs. (5) The amount of phenolic OH increased with increasing the cooking temperature and was more noticeable in thiolignins than in soda lignins. (6) Demethoxylation occurs in kraft cooking at elevated temperature rather than soda cooking.

INTRODUCTION

Pulping processes are carried out under widely varying conditions with respect to structure and concentration of the lignin, pH, and temperature as well as type and concentration of the delignifing reagent. In spite of this great variety of conditions, the reaction responsible for dilignification can be rationalized in terms of conmmon mechanistic features and a general concept, covering the main lignin modifying reactions of the pulping currently used can apply. It is a well-established fact that kraft cooking removes lignin from wood more easily than does alkai cooking. This difference may be due to many factors and a number of theories have been advanced to interpret it.[1-4]

During the kraft cooking process the lignin is fragmented predominantly by ether cleavage reactions in phenyl propane–α- and β-aryl ether stractures.[4] These reactions simultaneously to the new phenolic hydroxyl groups in the lignin macromolecules, thus increasing their solubility at high temperature 180°C in aqueous alkaline media. These reactions promoting delignification are assumed to be counter balanced to some extent by a number of different condensation reactions.[5]

In order to gain further knowledge about the structural changes during soda and kraft cooking and their importance for delignification. Soda and kraft lignin samples withdrawn after various cooking times have been analyzed for phenolic hydroxyl groups and methoxyl groups. Furthermore, the average elemental compositions of the various lignin samples were calculated.

The main objectives of this study in a preliminary manner are (a) delignification rates, (b) carbohydrate retention relative to lignin removal, and

(c) elemental composition and functional group analysis of two types of lignin isolated at different cooking temperatures.

The general plan used to implement the investigation was the preparation of five kraft and soda cookings at different temperatures, 80, 120, 140, 160, and 180°C, covering a yield range 45–65%.

EXPERIMENTAL

Preparation of the Sample

Corn stalks were reduced to small chips, and then extracted in a soxhlet apparatus for 6 h by methanol–benzene mixture (1:1) to remove waxes and resins. The residual material was left to dry in air, and then conditioned for experimenting.

Pulping

Thiolignin was prepared from kraft pulps which were prepared by cooking the chips under the following conditions: total alkali = 20%; sulfidity = 25%; liquor:wood, 5:1; cooking temperature 80, 120, 140, 160, and 180°C, each for 1 h. Soda lignin was prepared from soda pulps under the same conditions without addition of Na_2S.

Chemical Analysis. Chemical properties were determined on dry air, pulp samples, pulp Evaluation. Yield: pulp yields were determined by dewatering the screened pulp in a Büchner funnel using course filter paper. The pulp was then crumbled by hand, placed in a sealed plastic bag, and stored at 4°C. Moisture samples were run in triplicate to determine solids content and yield.

Analysis of Lignin

The percentage of C, H, and S was determined by using the normal combustion method. The percent of O was obtained by difference. The analysis have been carried out in the Microanalytical Laboratory, National Research Centre.

Methoxyl Content

This was determined by a modified Zeisel viebock method.[6]

Phenolic OH by Electronic Spectra

This method is based on the characteristic ultraviolet absorption of phenols in alkaline solution.[7,8] The absorption of an alkaline solution of the sample is measured directly against that of a neutralized portion of the same solution. The phenolic OH content of the sample is measured directly against that of a neutralized portion of the same solution. The phenolic OH content of the sample is calculated from the resulting difference curve, and the molar absorption maximum of model phenols is determined in the same manner. In this work the phenolic OH has been estimated using the absorption at 250 μm as described by Wexler[7] rather than the absorbance at

300 μm as described by Goldschmidt[8] because the latter method is limited for the determination of phenolic OH groups which are not conjugated with C=O groups: On the other hand, the 250 μm maximum is common for both conjugated and nonconjugated phenolic compounds. According to Wexler,[7] the percentage of phenolic hydroxyl groups is

$$\Delta a_{max} \times 0.192$$

where Δa is the difference absorbance between the alkaline and acidic references.

Molecular Weight

Molecular weight was determined by vapor pressure Osmometry in D.M.F. solution on a Knauer instrument.

Estimation of Sugar

Sugar was measured according to the Dubois method.[9]

RESULTS AND DISCUSSION

Under alkaline pulping conditions, phenolic structure (A) are converted partially into alkali-soluble (C) via the formation of methylene quinone intermediate (B) and subsequent elimination of CH_2O:
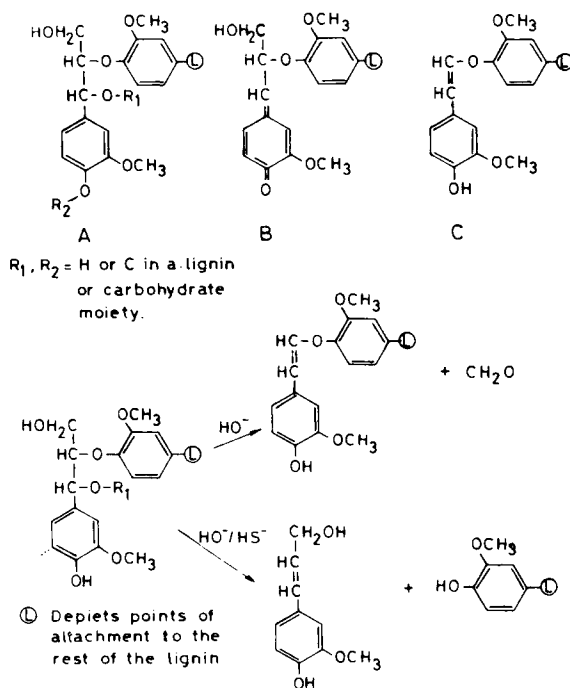
Scheme 1: Reaction pathways for phenolic phenyl-propane-β-aryl ether structures in alkaline and sulfate pulping.

In kraft cooking, however, the formation of styryl arylether structures seems to occur to only a small extent and a sulfidolytic cleavage of the β-arylether bond Figure 1 constitutes the major reaction.[10]

Figure 2 presents the lignin–time and carbohydrate–time relationships obtained at 160°C. These curves are typical of the behavior observed at all temperatures studied. It is apparent that, although the sulfide ion speeds up lignin removal, it also accelerates the removal of carbohydrate material. The difference cannot be accounted for merely by hydroxide ions produced from the hydrolysis of sulfide ions. Rydholm[2] shows that the sulfide ion is not consumed as rapidly as the hydroxide, and the need to replenish the chemical by the diffusion is therefore not as critical in the case of the kraft digestions. Another interesting observation can be made from these curves. It appears that with the kraft liquors the delignification rate is higher than the carbohydrate removal rate. Vroom[11] and Ljunggern[12] have shown that delignification is approximately first order with respect to lignin weight content in the wood (pulp) and that the temperature is adequately accounted for by use of Arrhenius equation.

A first-order reaction is defined by the equation

$$ln\frac{L_0}{L} = K_0 t$$

where L = unremoved lignin (g lignin/100 g wood), L_0 = the apparent initial lignin content as obtained from the first-order rate approximation (g lignin/100 g wood) = digestion time (min), and K_0 = rate "constant," function of liquor composition, liquor concentration, and digestion temperature (min^{-1}). From the equation we see that a plot of the (lignin) vs. pulping time are shown in Figures 3 and 4 for the kraft and soda cookings, respectively. It is readily apparent from these graphs that the results are well approximated by a first-order reaction rate equation. The intercept L_0, was constant at 27.1 g/100 g wood for both the kraft and soda pulps, regardless of temperature. Giere[13] has shown that the formation of (β) methylene quinone intermediate was the rate determining step of the overall degra-
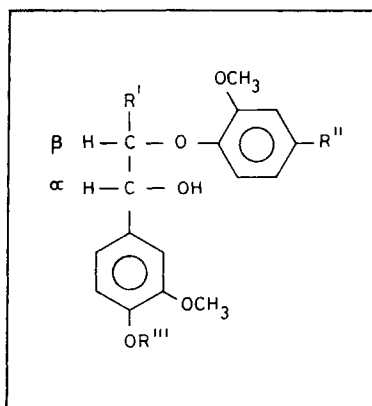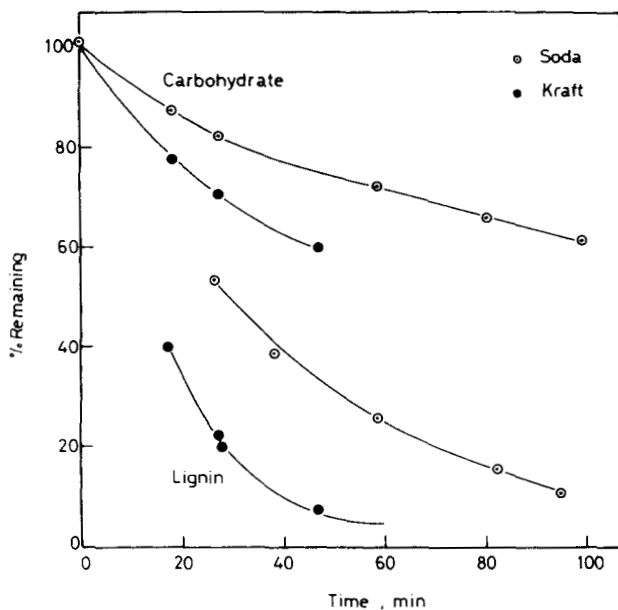

Fig. 1. β-aryl ether.

Fig. 2. Carbohydrate and lignin–time relationships with cooking temperature at 160°C: (○) soda; (●) kraft.

dation and condensation of reactions of these compounds; both types of reaction followed the first-order kientics with respect to the starting compound and the rate of cleavage of β-aryl ether linkage depend on the concentration of NaOH and Na_2S used. The relation between degradation and condensation of lignin structure of β-aryl ether type was interpreted as a competition of SH^- ions with carbon ions for methylene quinone.
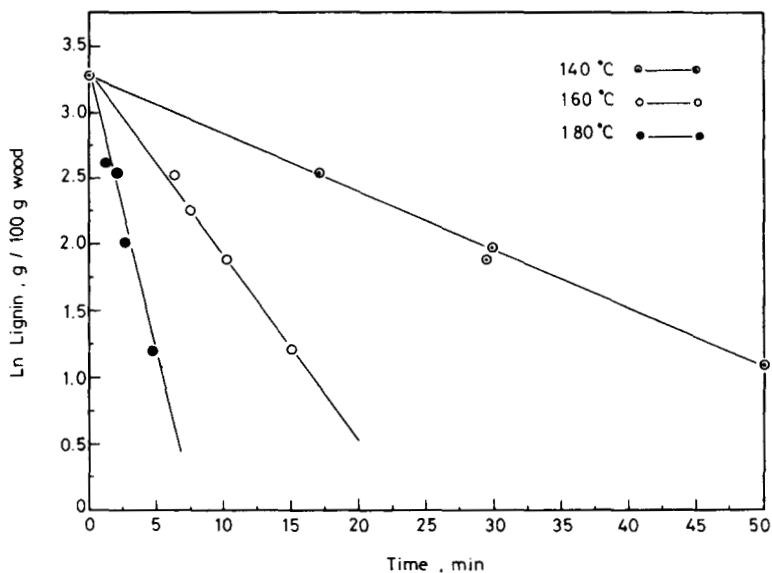

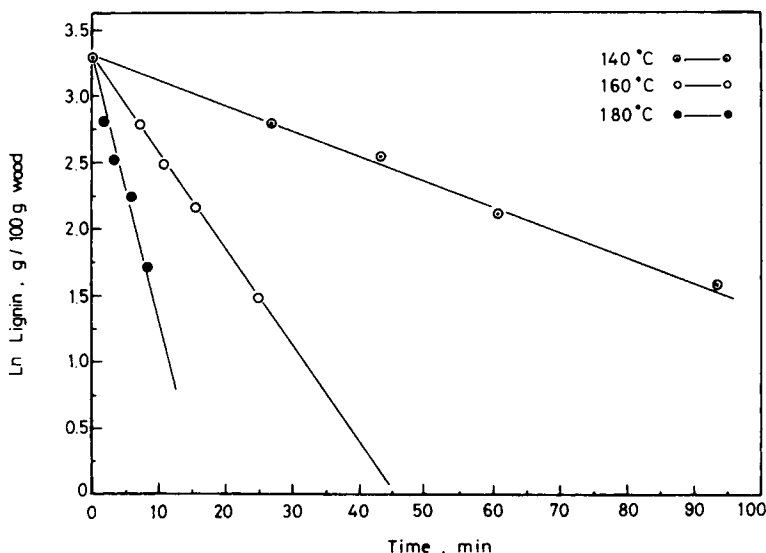Fig. 3. Kraft lignin–time relationship.

Fig. 4. Soda lignin–time relationship.

From the results of elemental and function group analysis are shown in Table I. The carbon contents of lignons isolated at different temperatures from the black liquor of sulfate cooking is somewhat lower than the carbon content of soda lignins obtained from soda cooking of the corn stalks. In soda cooking the carbon content of alkali lignins decreased. Hydrogen and oxygen content increased with increasing the cooking temperature, but in sulfate cooking the carbon content of thiolignins increased while hydrogen and oxygen content decreased. Soda lignin underwent intensive changes during soda cooking. The amount of phenolic OH increased with increasing the cooking temperature and was more noticeable in thiolignins than in soda lignins; the amount of methoxyl groups decreased only in kraft cooking. Therefore, thiolignins isolated from kraft process at high cooking temperature become more condensed than soda lignins.[14]

The sulfur content/C_9 is almost the same at various cooking temperatures. The ratio of phenolic OH/OCH$_3$ in lignin for kraft cooks or corn stalks are higher than those from soda cooks. This ratio increased with increasing temperature. This ratio appears to be dependent on the method of cooking (Table II). Molecular weights determined by vapor pressure Osmometry in D.M.F. solution on a Knauer instrument are listed in Table II; the molecular weight of thiolignins is higher than that of akali lignins and increased with increasing the cooking temperature.

The molecular formulae calculations for both types of lignin of corn stalks at different cooking temperatures are as follows:

Soda Lignins

(1)	80°C:	C_{42}	H_{36}	O_{11}	$(OH)_{1.1}$	$(OCH_3)_4$;
(2)	120°C:	C_{42}	N_{37}	O_{11}	$(OH)_{1.2}$	$(OCH_3)_4$;
(3)	140°C:	C_{40}	H_{37}	O_{12}	$(OH)_{1.3}$	$(OCH_3)_5$;
(4)	160°C:	C_{40}	H_{39}	O_{12}	$(OH)_{1.4}$	$(OCH_3)_5$;
(5)	180°C:	C_{40}	H_{41}	O_{13}	$(OH)_{1.5}$	$(OCH_3)_5$.

TABLE I

Elementary Analysis and Functional Groups of Soda and Thiolignin of Corn Stalks Isolated at Different Cooking Temperature

Cooking temp	% of atoms and functional groups						No. of atoms and functional groups						Structural wt	Molecular wt
	C	H	S	O	OH	OCH$_3$	C	H	S	O	OH	OCH$_3$		
80	64.2	5.8	—	30.0	2.1	15.5	9	7.7	—	2.3	0.23	0.93	185.2	860
120	63.4	5.9	—	30.7	2.3	16.0	9	8.0	—	2.4	0.26	0.98	184.2	860
140	62.2	6.0	—	31.9	2.5	16.7	9	8.3	—	2.6	0.28	1.05	195.2	870
160	60.9	6.2	—	32.9	2.8	16.8	9	8.8	—	2.7	0.33	1.07	198.8	890
180	59.9	6.4	—	33.7	2.9	17.8	9	9.3	—	2.9	0.34	1.17	205.8	920
80	59.5	6.2	5.3	29.0	1.5	21.5	9	8.6	0.35	2.2	0.19	1.5	212.7	920
120	60.7	6.1	4.2	29.0	2.0	20.1	9	8.3	0.26	2.1	0.24	1.3	202.6	940
140	61.5	5.8	4.0	28.7	2.4	18.5	9	7.7	0.25	2.1	0.28	1.2	199.3	980
160	62.3	5.7	3.4	28.6	3.2	16.9	9	7.5	0.20	2.0	0.36	1.0	191.0	1020
180	62.8	5.4	3.4	28.4	3.8	14.2	9	7.1	0.20	2.1	0.42	0.86	188.9	1080

Alkali lignin from soda cooking

Thiolignin from kraft cooking

TABLE II

Ratio of Functional Group/Phenolic (OH) to (OCH₃) Group in Soda and Kraft Cookings of Corn Stalks at Different Cooking Temperatures

Sample	Cooking temp (°C)	Ratio OH/OCH$_3$	Sample	Cooking temp (°C)	Ratio OH/OCH$_3$
Alkali lignins from soda cooking	80	0.26	Thiolignins from Kraft cooking	80	0.13
	120	0.30		120	0.18
	140	0.26		140	0.23
	160	0.28		160	0.33
	180	0.30		180	0.49

Thiolignins:

(1) 80°C: $C_{39}H_{37})_9$ $(S)_{1.5}$ $(OH)_{82}$ $(OCH_3)_{6.5}$

(2) 120°C: $C_{42}H_{39}O_{10}$ $(S)_{1.2}$ $(OH)_{1.1}$ $(OCH_3)_{6.0}$;

(3) 140°C: $C_{44}H_{39}O_{10}$ $(S)_{1.2}$ $(OH)_{1.4}$ $(OCH_3)_{6.0}$;

(4) 160°C: $C_{48}H_{40}O_{11}$ $(S)_{1.1}$ $(OH)_{2.0}$ $(OCH_3)_{5.7}$;

(5) 180°C: $C_{51}H_{41}O_{12}$ $(S)_{1.0}$ $(OH)_{2.4}$ $(OCH_3)_{4.9}$.

From these molecular formula it is clear that the number of carbon atoms are higher for thiolignins than soda lignins. The phenolic (OH) in thioligning is much higher than that of soda lignin which increased with increasing the cooking temperature. The methoxyl group showed a trend of higher retention at elevated temperatures in soda lignins while demethoxylation occur in thiolignins at high temperatures.

References

1. T. Enkvist and B. Alfredsson, *Tappi*, **36**, 211 (1953).

2. S. A. Rydholm, *Pulping Processes*, Wiley-Interscience, New York, 1965, p.587–590.

3. P. J. Kleppe, *Tappi*, **53**, 35 (1970).

4. J. Gierer, *Wood Sci. Technol.*, **14**, 241 (1980).

5. J. Gierer, F. Imsgard, and I. Pettersson, *Appl. Polym. Symp.*, **28**, 1195 (1976).

6. V. A. Klimova, K. S. Zaprodina and N. D. Zelinski, *Anal. Khem.*, **18**, 109 (1963).

7. A. S. Wexler, *Anal. Chem.*, **36**, 213 (1964).

8. O. Goldschmidt, *Anal. Chem.*, **26**, 142 (1954).

9. K. A. Michel Dubois, J. K. Gilles, P. Hamilton, A. Rebers, and Fred Smith, *Anal. Chem.*, **28**, 350 (1954).

10. G. Gellerstedt and E. L. Lindfors, *Svensk Papperst.*, **87**, R61 (1984).

11. K. E. Vroom, *Pulp Paper Mag. Con.*, **58**, 228 (1957).

12. S. Ljunggern, *Svensk Papperst.*, **83**, 363 (1980).

13. J. Gierer and S Ljunggern, *Svensk Papperst.*, **82**, 503 (1979).

14. Z. A. Nagieb and Nadia Shrkry, *Angew. Makromol. Chem.*, **127**, 67 (1984).