Kinetics of delignification in kraft pulping of wheat straw and hemp

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ABSTRACT: The kinetics of kraft pulping of Hungarian wheat straw and hemp were studied in model pulping experiments carried out under constant and well-defined conditions. The delignification was found to be first order with respect to residual lignin and was chemically controlled. The observed specific reaction rate of delignification was constant at a given pulping time but changed with pulping temperatures. The activation energy of the delignification reaction was 31,395 cal/mole and 26,228 cal/mole for wheat straw and hemp, respectively.

KEYWORDS: Alkaline pulping, bast fibers, delignification, hemp, kinetics, kraft pulping, kraft pulps, reaction kinetics, temperature, wheat straw.

In the kraft pulping process, delignification occurs in three stages that can best be described in graphs with three intersecting lines. The initial delignification stage is the first, the bulk delignification is the second, and the residual delignification is the third stage *(1–7)*. In the initial stage, 15–25% of the lignin is removed, depending on the species of wood and on the cooking conditions. Simultaneously, a great part of the carbohydrates becomes dissolved in this stage *(8)*.

According to a study with softwood *(8)*, about 50% of the effective alkali charge is consumed in the initial stage for neutralizing acidic reaction products during the decomposition of extractives and carbohydrates.

In the initial stage, diffusion is the controlling factor for the chemical reactions. The initial stage is also very dependent on the quality and the species of wood. The bulk stage begins at 140–150°C and is the most effective in the delignifying process. The carbohydrate yield and the alkali concentration of the cooking liquor decrease only slightly in this stage. In the residual delignification stage, however, the dissolution of lignin is retarded again, while the carbohydrate yield and alkali concentration start to decrease rapidly after the second transition point.

Knowledge of the kinetics is an important tool in controlling kraft cooking. The kinetics of cooking have proved to be quite complicated, because there are many variables that affect the yield and quality of the produced pulp. Industrial research has been done to quantify the effect of reaction variables on pulp quality expressed as total yield and as remaining lignin content. Summarized here are the most important results, with an emphasis on the details of the behavior of the process variables that must be accounted for in any kinetic model attempting to explain kraft delignification.

Because of its simplicity of concept and analysis, a first-order representation of the pulping reactions has been commonly used *(9–11)*. Interpretation of kinetic data in terms of a first-order representation has provided a measure of quantitative information, particularly in the area of temperature sensitivity of the pulping reaction and less so in the area of reaction rate dependence on concentrations of wood components and pulping liquor.

Temperature sensitivity as expressed by activation energy in the Arrhenius form of the rate coefficient has been reported on the order

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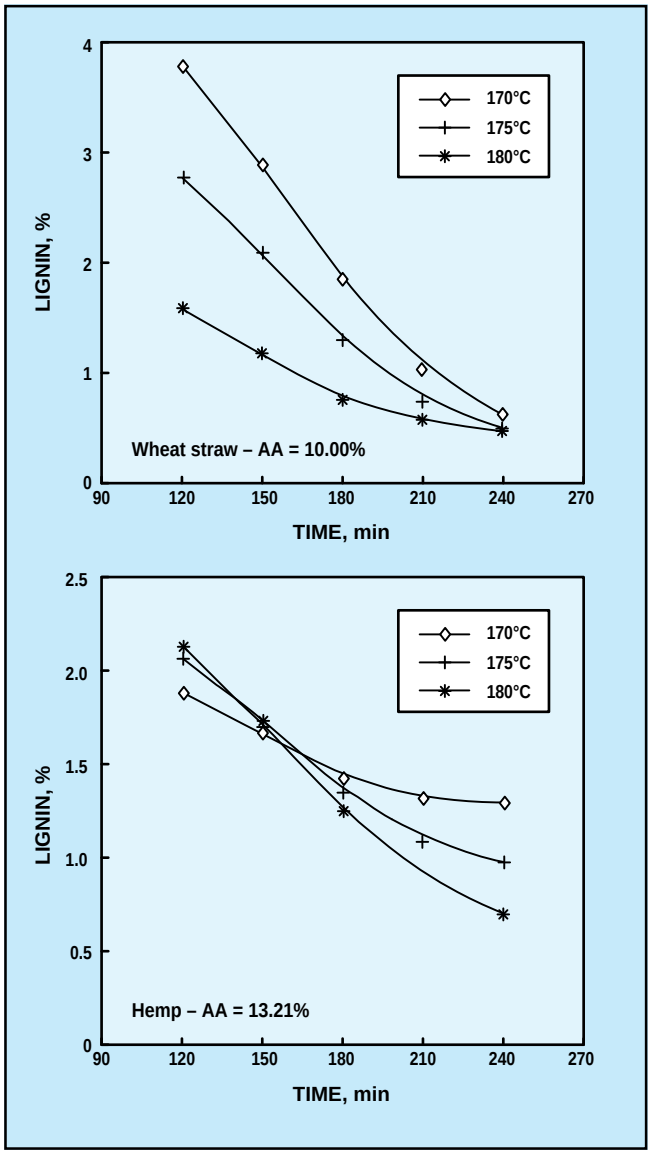
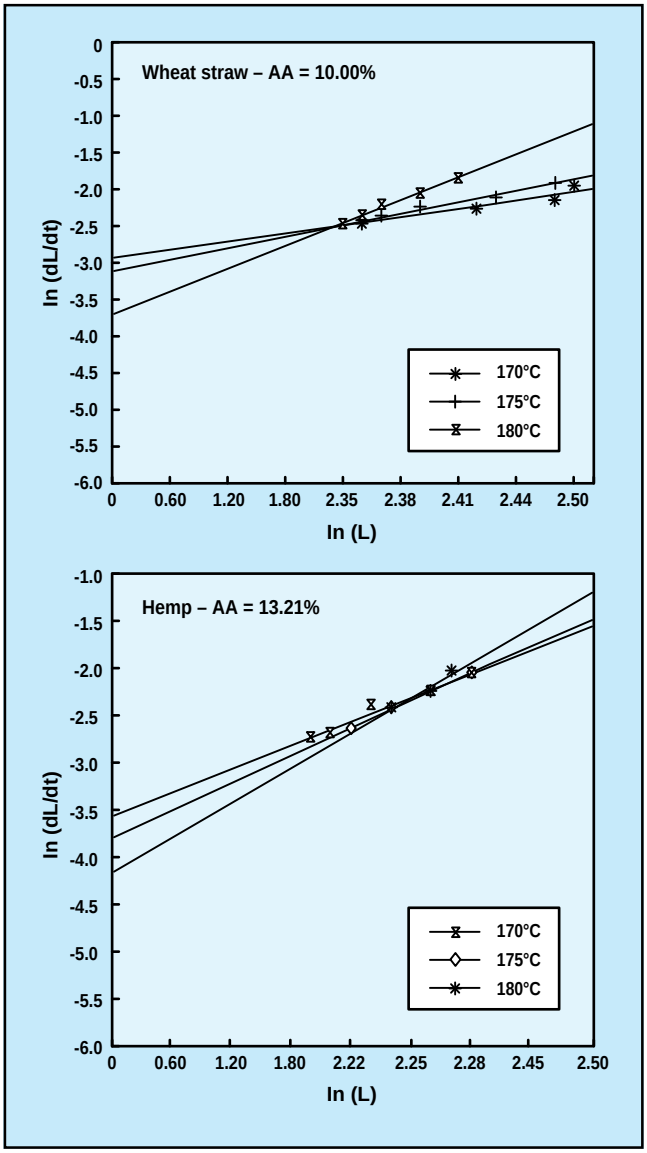
1. Time effect of kraft pulping on the lignin content of the pulp



2. Specific rate (k_o) and order of delignification of kraft pulping



of 30–35 kcal/g·mole for soda pulping *(11–13)* and 25 kcal/g·mole for kraft pulping *(11, 12, 14)*. The effects of chemical concentration have also been related to a first-order representative of the delignification reaction. Linear dependence of reaction rate on liquor concentration has been shown *(11, 13)*.

Experimental

Characteristics of raw materials

Before carrying out the pulping experiments, an approximate chemical

I. Characteristics of wheat straw and hemp

Characteristics	*Wheat straw*	*Hemp (whole stem)*
Moisture content, % *(15)*	13.29	12.70
Benzene:ethyl alcohol (2:1) solubility, % *(16)*	2.80	5.76
Lignin content, % *(17)*	20.77	17.50
Alpha-cellulose content, % *(18)*	46.41	54.50
Pentosan content, % *(19)*	21.45	25.10
Holocellulose content, % *(20)*	78.35	79.60
Ash content, % *(21)*	6.50	3.40

II. Observed specific reaction rates (k_o) and order of delignification reaction of kraft pulping of wheat straw and hemp

Pulping temp., °C	Time of pulping, min	Lignin content in pulp, %	Order of reaction, n	Reaction rate (k_o), min^{-1}
		Wheat straw		
170	120	3.78	0.8214	0.0551
	150	2.90	-	-
	180	1.85	-	-
	210	1.04	-	-
	240	0.63	-	-
175	120	2.78	0.9421	0.0451
	150	2.10	-	-
	180	1.30	-	-
	210	0.75	-	-
	240	0.51	-	-
180	120	1.59	1.2141	0.0241
	150	1.17	-	-
	180	0.75	-	-
	210	0.58	-	-
	240	0.48	-	-
		Hemp		
170	120	1.88	1.0102	0.0271
	150	1.67	-	-
	180	1.43	-	-
	210	1.32	-	-
	240	1.30	-	-
175	120	2.06	1.1101	0.0223
	150	1.74	-	-
	180	1.36	-	-
	210	1.09	-	-
	240	0.98	-	-
180	120	2.12	1.2621	0.0142
	150	1.73	-	-
	180	1.25	-	-
	210	0.89	-	-
	240	0.70	-	-

analysis of the wheat straw and hemp was performed in accordance with TAPPI Test Methods *(15–21).* **Table I** lists the characteristics of the wheat straw and hemp used in this study.

Pulping conditions

Chips were hand-cut to lengths of 1–2 cm and pulped in an electrically heated, stainless steel, rotatable digester. The normal charge was 100 g of moisture-free chips (basis of calculation). Active alkali charge was kept constant at 10.00% and 13.21% for wheat straw and hemp, respectively *(22).* Chemicals were mixed to reach the calculated charge of active alkali at 25% sulfidity. All chemicals were added to chips in an aqueous solution. The liquor-to-chips ratio was adjusted to 5:1. This ratio was maintained throughout all experiments.

After the chips and chemicals had been placed in the digester, the lid was closed and the electrical heater and motor were switched on. Thermometer readings were recorded every 5 min until they reached the set value. The heating time was about 1 hour.

At the end of cooking, the digester pressure was reduced to atmospheric level, and the digester was left to cool. The cooled pulp was collected on a muslin cloth and washed with tap water. The pulp was disintegrated in a three-bladed mixer for 3 min at a pulp consistency of 1.5%. The pulp was then screened on a vibrating flat-plate screen with 0.2-mm slots. The screened yield was determined by weighing the air-dried pulp and measuring its moisture content.

Results and discussion

Kinetics of kraft pulping of wheat straw and hemp

Figure 1 shows the change of lignin content during the kraft pulping at different pulping temperatures. In view of the need for quantitative kinetic description of the kraft pulping of wheat straw and hemp, this work pertaining to delignification reaction and pulping was undertaken with respect to (a) order of reaction rate, (b) specific reaction rate, and (c) energy of activation of reaction.

Order of delignification reaction

The order n of the delignification reaction has been determined graphically, using the general differential rate expression:

$$-(dc/dt) = k_o L^n \qquad (1)$$

In its logarithmic form, this becomes:

$$\ln(-dc/dt) = \ln k_o + n \ln L \qquad (2)$$

where L is the average residual lignin in the pulp expressed in grams lignin/100 g of original oven-dry wheat straw and hemp. If L_{t1} and L_{t2} are the amounts of residual lignin at times t_1 and t_2, respectively, then $L = (L_{t1} + L_{t2})/2$, and dL/dt is the average rate of delignification during time interval dt. Therefore, $dL/dt = (L_{t1} - L_{t2})/(t_2 - t_1)$.

Accordingly, by plotting ln (dL/dt) vs. ln L, straight lines were obtained (**Fig. 2**). This figure fits the general equation:

$$Y = mx + c \qquad (3)$$

where the slope represents the order of reaction n, and the intercept represents ln k_o. The delignification reaction was first order with respect to residual lignin (Fig. 2) and ranged from 0.82 to 1.21 and from 1.01 to 1.26 for wheat straw and hemp, respectively, at different pulping temperatures, as seen in **Table II.**

Specific reaction rate of delignification reaction

The observed specific reaction rate *(k_o)* of delignification was experimentally constant at a given pulping time but changes with pulping temperature [e.g., the value from 5.5 x 10^{-2} to 2.4 x 10^{-2} and from 2.7 x 10^{-2} to 1.4 x 10^{-2} for wheat straw and hemp, respectively, as the temperature of pulping increased from 170°C to 180°C (Table II)]. The values of specific reaction rate *(k_o)* of delignification at 170°C, 175°C, and 180°C were obtained from the intercepts of the straight lines of Fig. 2 and are disclosed in Table II. Data in **Table III** indicate that the rate of the reaction increased 1.22-and 1.21-folds for a 5°C temperature increase in the range of 170–175°C, and 1.87-and 1.57-fold between 175°C and 180°C for wheat straw and hemp, respectively. Since the diffusion-controlled reactions are characterized by a temperature coefficient of 1.0–1.1, the delignification reaction of wheat straw and hemp in kraft pulping consequently seems to be chemically controlled *(23).*

Activation energy of delignification reaction

The activation energy E was calculated from the Arrhenius equation:

$$\ln k = \ln A - (E/R)\,(1/T) \qquad (4)$$

where

k = specific reaction velocity, min^{-1}

A = frequency factor (experimentally determined)

E = experimental activation energy, cal/mole

III. Temperature coefficient of specific reaction rates

Component	K_{170}/K_{175}	K_{175}/K_{180}
Wheat straw	1.2217	1.8713
Hemp	1.2152	1.5704

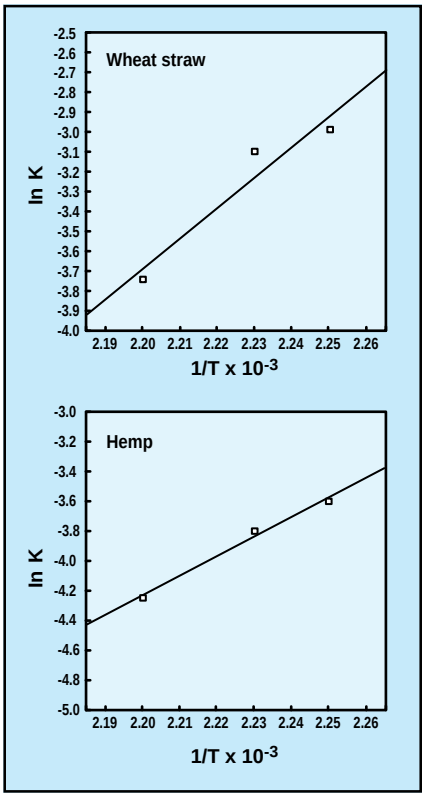
R = gas constant (1.987 cal/mole°K)

T = temperature, °K.

A plot of ln k vs. $(1/T)$, as shown in **Fig. 3,** gave a straight line whose slope is $(-E/R)$ and the intercept is ln A. It is apparent that the Arrhenius equation is applicable, and the value of E is independent of the temperature. The value of the activation energy E of the delignification reaction (derived from Fig. 3) is 31,395 cal/mole and 26,228 cal/mole for wheat straw and hemp, respectively.

The obtained high activation energy indicates that temperature had a great effect on the rate of reaction. This is apparently a chemically controlled reaction since a diffusion-controlled reaction is generally characterized by an activation energy value in the range of 5000 cal/mole *(24)*.

3. Temperature dependence of specific reaction rates



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