

KINETICS OF ALKALINE DELIGNIFICATION OF FLAX FIBRE

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It is shown that alkaline delignification of flax fibre is polychronic and is characterized by an uneven increase in the maximum effective rate constant when the temperature is increased from 328 to 358 K. It is hypothesized that the jump in k_{max} is due to a sharp increase in the number of fibre microvolumes accessible to the reagent while their distribution with respect to the kinetic nonequivalence parameter remains unchanged. The reaction of hydrolysis of cellulose with formation of soluble oligosaccharides accompanying alkaline delignification of flax makes it inexpedient to totally remove the lignin by significantly increasing the treatment temperature.

Interest has recently increased in chemical processing of annually renewable plant raw material that can in many cases replace wood and cotton for obtaining cellulose-containing materials [1]. Flax cellulose is of relatively high quality and can be used in production of different industrial products. Alkaline delignification of intermediate flax fibre, a low-quality type of flax basically used for production of oil-bearing seeds, is examined here. The fibre itself still has no practical application, although it could be a technically convenient source of cellulose.

Samples of chaff-free fibre weighing 10 g were placed in 500-cm³ steel beakers, filled with a six-fold (by weight) amount of 4% aqueous NaOH solution, sealed, and immersed in a water thermostat which maintained the temperature with an accuracy of ± 0.5 K.

The process was conducted in the 298-371 K temperature and 5-120 min time range whose reference point was the time the reaction mass attained the experimental temperature. The duration of the nonisothermal period increased from 11 min at 328 K to 25 min at 371 K. After the given time elapsed, the vessel with the reaction mass was rapidly cooled, the intermediate fibre product was washed to a neutral reaction for phenolphthalein, and dried to a 6% moisture content. The lignin content in the fibre was determined by the sulfuric acid method [2] and the degree of elimination of carbohydrates was calculated with the difference between the total weight loss of the sample and amount of lignin removed. The character of the products passing from the fibre into the alkaline solution at different temperatures was judged by the UV spectra of these solutions obtained on a Specord M-40 spectrophotometer.

The results of the kinetic experiments are shown in Fig. 1 in the form of the time curves of the relative content of lignin in the treated fibre and alkali-insoluble polysaccharides.

Lignin partially dissolves during heating of the reaction mixture, and the kinetic curves at all temperatures investigated rapidly go beyond the limits. The degree of delignification of the fibre attained in 2 h of treatment increases almost proportionally to the increase in the process temperature (Fig. 2). It is important to note here that judging by the UV spectroscopic data (Fig. 3), the character of the products of degradation of lignin and hydrocarbons passing into solution is not a function of the temperature and consequently the rapid cutoff of the kinetic curves is due to the polychronicity of the process and not to a change in its chemistry as the temperature rises, as in delignification of wood cellulose [3].

A different situation was observed in removal of soluble oligosaccharides from the fibre. At 298 K and treatment time in isothermal conditions greater than 5 min, the amount of extracted carbohydrates was not a function of the treatment time and was 10.9 ± 0.5 wt. %, while it increased uniformly and significantly at the higher temperature, and the kinetic curves became similar to the delignification curves.

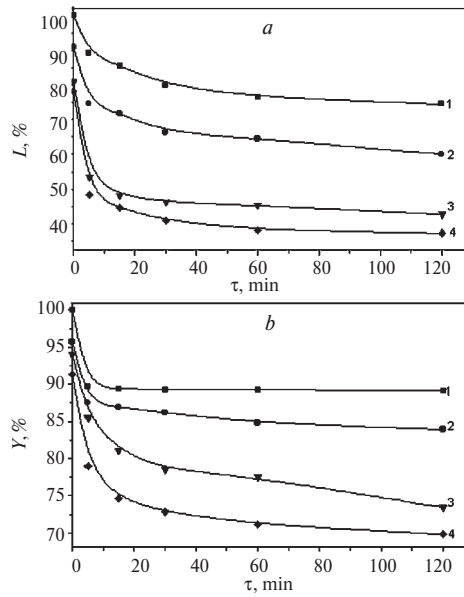


Fig. 1. Kinetic curves of the change in the relative content of lignin L (a) and polysaccharides insoluble in an aqueous solution of alkali (b) at 298 (1), 328 (2), 358 (3), and 371 K (4).

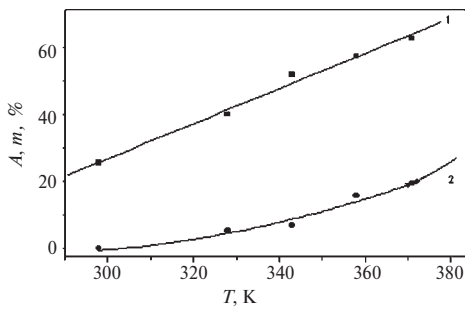


Fig.2

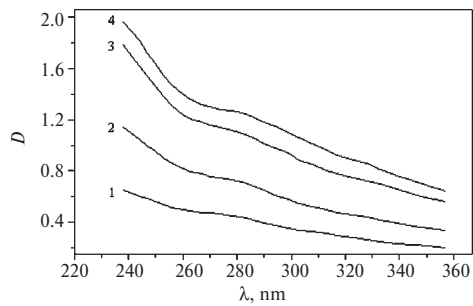


Fig.3

Fig. 2. Effect of temperature on the degree of washout of lignin A (1) and weight loss m of the fibre as a result of hydrolysis of cellulose (2) after 120 min of treatment of the fibre with an aqueous solution of alkali.

Fig. 3. Absorption spectra of alkaline cooking liquors obtained after 60 min at 298 (1), 328 (2), 358 (3), and 370 K (4).

It is somewhat obvious that only the oligosaccharides initially present in the fibre are washed out at 298 K, while those formed as a result of hydrolysis of cellulose macromolecules are also washed out at the higher temperatures. Since the amount of the latter relatively rapidly increases with an increase in the alkaline treatment temperature (see Fig. 2), attempts to attain exhaustive delignification of flax fibre by increasing the process temperature (T) to values above 373 K are not expedient from our point of view.

The delignification kinetic curves are satisfactorily linearized (Fig. 4, Table 1) in coordinates of the equation [4, 5]

$$\frac{C}{C_0} = -\frac{1}{S} [\ln(1.76k_{\max}) - S + \ln \tau], \quad (1)$$

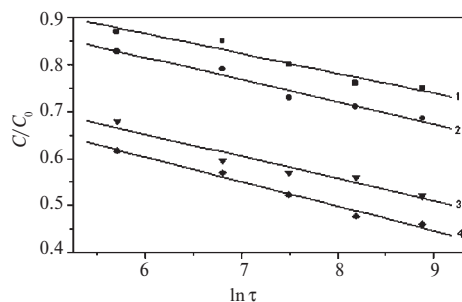


Fig. 4. Results of processing the kinetic curves in Fig. 1a with Eq. (1). 1-4) See Fig. 1.

TABLE 1. Kinetic Parameters of Delignification of Flax Fibre

T, K	S	$\sigma\Delta E, \text{kJ/mole}$	$k_{\text{max}}, \text{sec}^{-1}$	k_0, sec^{-1}	$\Delta E_{\text{min}}, \text{kJ/mole}$
298	24±3	59±8	0.034±0.02	1.2·10 ²	20.1
328	21±2	58±6	0.074±0.04	1.2·10 ²	20.1
358	21±3	63±9	2.3±0.6	39.0·10 ²	22.2
371	19±1	59±4	2.9±0.5	39.0·10 ²	22.2

where C_0 , C are the initial and current concentrations of lignin in the fibre; τ is the time; S is the kinetic nonequivalence parameter for the particles participating in the process, equal to the ratio

$$S = \frac{\delta\Delta E}{RT} = \frac{\Delta E_{\text{max}} - \Delta E_{\text{min}}}{RT}, \quad (2)$$

which includes the difference $\delta\Delta E$ between the maximum ΔE_{max} and minimum ΔE_{min} values of the activation energy of the process; k_{max} is the maximum value of its effective rate constant.

Using Eq. (1), which only holds for processes limited by a stage which is a first or pseudofirst order reaction in the formally kinetic sense, we hypothesized that delignification of flax fibre would be limited by diffusion of either OH⁻ ions, similar to what occurs in alkaline cooking of wood pulp [3], or soluble products of decomposition of lignin.

The results of the calculations with Eq. (1) reported in Table 1 suggest that in the temperature range investigated, $\delta\Delta E$ is constant (60±2 kJ/mole), while the temperature curve of k_{max} is clearly divided into three intervals: 298-328 K (temperature coefficient $\alpha = 7.8 \cdot 10^{-2} \text{ K}^{-1}$), 328-358 K ($\alpha = 1.09 \text{ K}^{-1}$), and 358-371 K ($\alpha = 9.7 \cdot 10^{-2} \text{ K}^{-1}$).

This unusual type of temperature curve of the rate constant of the process is in our opinion due to the fact that the effect of the temperature can be manifested not only as a change in the exponent $e^{-(\Delta E/RT)}$, but also as a change in pre-exponential function k_0 .

Actually, processing of pairs of constants k_{max} comprising the first and third intervals with the Arrhenius equation resulted (see Table 1) in very similar values of ΔE_{min} (21±1 kJ/mole) and values of k_0 that differed by more than 30 times.

From a physical point of view, this means that the amount of microvolumes accessible to the reagent increases sharply in the 328-358 K range in the treated material, while their distribution by parameter S remains unchanged. The low values of the minimum effective activation energy of delignification of flax fibre supports our hypothesis that the limiting stage of the process is diffusion-controlled.

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