*Russian Journal of Applied Chemistry, Vol. 78, No. 8, 2005, pp. 1333–1336. Translated from Zhurnal Prikladnoi Khimii, Vol. 78, No. 8, 2005, pp. 1357–1360.*
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MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

# Degradation of Hardwood Sulfate Pulp in Aqueous Dioxane

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Received March 2, 2005

**Abstract**—Degradation of unbleached hardwood sulfate pulp in aqueous dioxane in the presence of catalytic amounts of HCl was studied. The kinetic constants and the apparent activation energy of pulp degradation in the range 343–363 K were calculated.

Treatment of cellulose with organic solvents containing a mineral acid in the presence or in the absence of water results in cleavage of glycoside bonds between its monomeric units, which leads to a decrease in the degree of polymerization, i.e., to degradation [1]. In production of fibrous semifinished products for paper, the pulp degradation is undesirable. By contrast, preparation of powdered cellulose products, including microcrystalline cellulose, is based on the pulp degradation.

The objectives of this study are determined by the growing researchers' interest in the development of nonaqueous processes for pulp production, based on organic liquids, with complete regeneration and recycling of the solvents [2, 3]. These processes show much promise, as they decrease the consumption of natural water and energy for the process. Although delignification of wood with organic solvents has been the subject of numerous studies, the effect of organic solvents on sulfate pulp and the possibilities of using these processes for pulp bleaching are insufficiently understood. In this study, we examined the degradation of unbleached sulfate pulp in aqueous dioxane. This treatment was used in [4] for recovering residual lignin with the aim to study its properties. In [5], we showed that, depending on treatment conditions, 29–80% of residual lignin dissolves on treatment of sulfate pulp with aqueous dioxane in the course of its bleaching.

## EXPERIMENTAL

Experiments were performed with unbleached hardwood sulfate pulp with a Bjorkman hardness of 77 permanganate units and a degree of polymerization of 1031. The pulp was treated in a 9 : 1 dioxane–water mixture in the presence of an acid catalyst (0.0–0.2 M HCl) at a slurry concentration of 5 wt % absolutely dry pulp. Treatments were performed at 343–363 K for 1–5 h. The treated pulp was washed with warm distilled water and dried. The pulp degradation was evaluated by a decrease in its degree of polymerization, determined viscometrically in Cadoxen [6]. The resulting pulp samples were also analyzed photometrically for lignin [7].

We examined how the degradation of sulfate pulp is influenced by the acid catalyst (HCl) concentration (first series of experiments) and temperature (second series). The first series was performed in the course of 1 h at 343 K, and the acid catalyst concentration was varied from 0.00 to 0.20 M. Preliminary studies of sulfate pulp delignification in this medium showed that, at lower temperatures, the degree of removal of residual lignin is unsatisfactory. Data on the intrinsic viscosity in Cadoxen and degree of polymerization of the pulp are listed in Table 1.

**Table 1.** Intrinsic viscosities in Cadoxen $[\eta]$ and degrees of polymerization $[\mathrm{DP}]_\eta$ of hardwood sulfate pulp after its treatment in aqueous dioxane at various HCl concentrations

| Run no. | HCl concentration, M | $[\eta]$ | $\mathrm{DP}^*_\eta$ | Relative lignin content |
|---|---|---|---|---|
| 1 | Initial pulp | 4.95 | 1031 | 1.00 |
| 2 | 0.000 | 4.30 | 910 | 0.90 |
| 3 | 0.005 | 4.23 | 890 | 0.74 |
| 4 | 0.010 | 3.68 | 770 | 0.69 |
| 5 | 0.020 | 3.12 | 650 | 0.63 |
| 6 | 0.050 | 2.92 | 600 | 0.60 |
| 7 | 0.200 | 2.01 | 400 | 0.45 |

[*] The degree of polymerization was estimated from the equation $[\eta] = \mathrm{DP}^{0.04} \times 7.1 \times 10^{-3}$ [5].

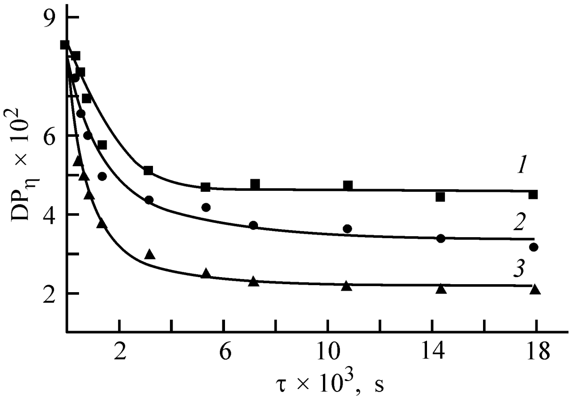

**Fig. 1.** Degree of polymerization $DP_\eta$ of pulp vs. the treatment time $\tau$ at various temperatures. Temperature, K: (*1*) 343, (*2*) 353, and (*3*) 363; the same for Figs. 2 and 4.

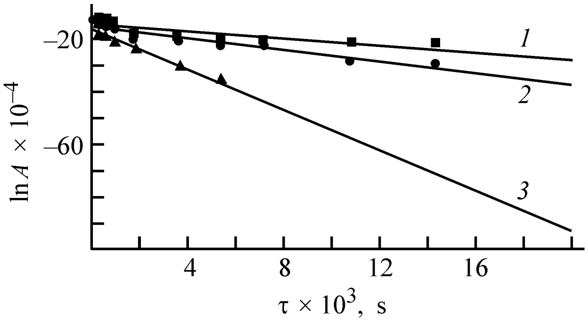

**Fig. 2.** Semilog kinetic plots of pulp degradation at 343–363 K. $A = (DP^n - 1)/DP^n$; ($\tau$) treatment time.

In the absence of an acid and at its small amounts in the system (run nos. 2, 3), the degree of polymerization of the pulp after an 1-h treatment decreased, on the average, by 12% relative to the initial values, and at HCl concentrations of 0.01–0.05 M, by 25–42% (to 770–600, respectively). At the HCl concentration increased to 0.20 M, the degree of polymerization decreased drastically, to 400, i.e., by almost a factor of 3, compared to the initial sample.

**Table 2.** Calculated kinetic parameters of delignification of hardwood sulfate pulp in aqueous dioxane

| Treatment temperature, K | Calculated kinetic parameters | | |
|---|---|---|---|
| | $k_{app} \times 10^8$, $s^{-1}$ | $-\ln k_{app}$ | $E_{app}$, kJ mol$^{-1}$ |
| 343 | 6.9 | 16.5 | 88.6 ± 11.8 |
| 353 | 11.4 | 16.0 | |
| 363 | 38.4 | 14.8 | |

Data on the relative content of lignin in the pulp treated with aqueous dioxane solutions are also listed in Table 1. As the acid catalyst concentration is increased from 0.00 to 0.05 M, the residual lignin content decreases from 0.90 to 0.60 relative to the initial level. At the highest tested concentration of HCl, the residual lignin is removed by half. Taking into account published data [8], we can suggest that, in the solvent system examined, residual lignin of sulfate pulp undergoes degradation with partial dissolution.

The dependence of the DP of pulp on the treatment temperature was examined in the range 343–363 K at an acid catalyst concentration of 0.02 M. At this acid content (which is ten times lower than that in classical acidolysis of wood), lignin undergoes relatively deep degradation (Table 1, run no. 5), but the DP of pulp remains sufficient for the use in paper production. The upper limit of the temperature range examined corresponds to the boiling point of the solvent mixture.

The kinetic curves of pulp degradation are shown in Fig. 1.

The kinetic curves indicate that a major decrease in the degree of polymerization of pulp occurs in the initial period of the treatment. Within 5 h, the DP of the pulp decreases to 541 at 343 K, to 328 at 353 K, and to 219 at 363 K; in the last case, the pulp loses the fibrous structure.

To determine the kinetic parameters of degradation of sulfate pulp, we used a first-order equation characterizing the concentration of bonds in the cellulose macromolecule, which has the following form in the logarithmic coordinates [9]:

$$-\ln[(DP^n - 1)/(DP^n)] = -\ln[(DP_0^n - 1)/(DP_0^n)] + k\tau,$$

where $DP^n$ is the number-average degree of polymerization, determined using the formula for the mean polydispersity coefficient: $n = DP_\eta/DP^n$.

According to [10], $n = 1.25$.

The rate constants of pulp degradation were calculated from the equations for the kinetic curves linearized in the semilog coordinates (Fig. 2). When plotting these straight lines, we used the initial DP of the pulp.

The apparent rate constants $k_{app}$ of pulp degradation in aqueous dioxane increase from $6.9 \times 10^{-8}$ to $38.4 \times 10^{-8}$ $s^{-1}$ in going from 343 to 363 K (Table 2).

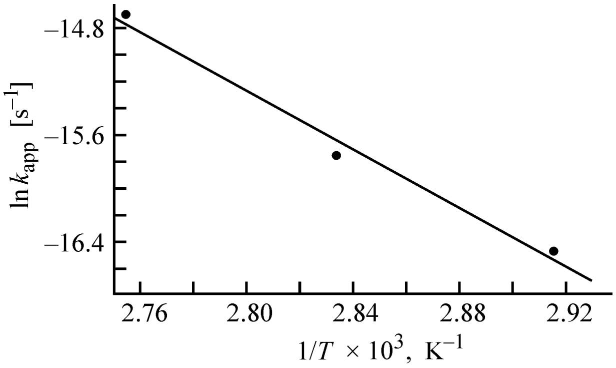

**Fig. 3.** Arrhenius plot for degradation of sulfate pulp in the range 343–363 K. Fitting equation: $\ln k_{app} = (14.50 \pm 4.04) - (10.66 \pm 1.42) \times 10^3/T$, $R = 0.99$; ($T$) temperature.

The temperature coefficient $\alpha(T^{10})$, i.e., the factor by which $k_{app}$ increases as the temperature is elevated by 10 K, is 1.7–3.4.

From the slope $B$ of the Arrhenius dependence $\ln k_{app}$–$1/T$ (Fig. 3),

$$B = \ln(k_1/k_2)/(1/T_2 - 1/T_1)$$

we calculated the apparent activation energy $E_{app}$ by the equation

$$E = BR,$$

where $R$ is the universal gas constant. We obtained $E_{app} = 88.6 \pm 11.8$ kJ mol$^{-1}$, which is comparable with $E_{app}$ of oxidative hydrolysis and acid hydrolysis reactions [11], ~95–100 kJ mol$^{-1}$.

We assessed the feasibility of aqueous-dioxane treatment of sulfate pulp in the course of bleaching, in particular, in the first steps of delignification. The major parameter of the bleaching process is the delignification selectivity. It can be characterized by the dependence of $DP_\eta$ on $\theta$, where $\theta$ is the degree of pulp delignification (Fig. 4).

The curves obtained show that both lignin and cellulose undergo simultaneous and substantial degradation even under mild treatment conditions (343 K). Raising the temperature to 353–363 K favors degradation of cellulose to a greater extent, compared with residual lignin.

Thus, treatment of sulfate pulp in aqueous dioxane occurs with a low selectivity and may be of limited use in pulp treatment for paper production. However, treatment under mild conditions can be used for delignification in production of fibrous cellulose, and treatment under more severe conditions, in production of powdered cellulose materials for chemical processing, e.g., of microcrystalline cellulose.

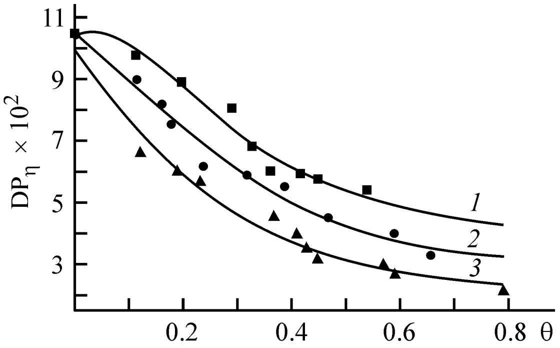

**Fig. 4.** Selectivity of treatment of hardwood sulfate pulp in aqueous dioxane containing 0.02 M HCl at various temperatures. ($DP_\eta$) Degree of polymerization and ($\theta$) degree of delignification of pulp.

## CONCLUSIONS

(1) Treatment of unbleached hardwood sulfate pulp in a dioxane–water–HCl solution results in degradation and partial delignification of the pulp.

(2) With an increase in the temperature by 10 K, the rate of degradation of hardwood sulfate pulp grows by a factor of 2–3. The apparent activation energy of the process is $88.6 \pm 11.8$ kJ mol$^{-1}$.

## REFERENCES

1. Blažej, A. and Košik, M., *Cellulose and Its Derivatives: Chemistry, Biochemistry and Applications,* Kennedy, J.F. *et al.*, Eds., 1985, pp. 97–117.
2. Petrova, S.N., Zakharov, A.G., Matveeva, I.Yu., and Ivanova, O.N., in *5-ya Mezhdunarodnaya nauchnaya konferentsiya “Teoreticheskie i eksperimental’nye osnovy sozdaniya novykh vysokoeffektivnykh khimiko-tekhnologicheskikh protsessov i oborudovaniya”: Sbornik trudov* (Proc. 5th Int. Scientific Conf. “Theoretical and Experimental Principles of Development of New High-Performance Chemical Processes and Equipment”), Ivanovo, 2001, p. 441.
3. Aziz, S. and Sarkanen, K., *TAPPI J.*, 1989, vol. 72, no. 3, pp. 169–175.
4. Bogomolov, V.D., Demin, V.A., Davydov, V.D., and Popova, G.I., *Izv. Vyssh. Uchebn. Zaved., Lesn. Zh.*, 1977, no. 1, pp. 96–99.
5. Udoratina, E.V. and Demin, V.A., in *Khimiya vysokomolekulyarnykh soedinenii, lesokhimiya i organi-*

*cheskii sintez: Sbornik statei Komi nauchnogo tsentra* (Chemistry of Macromolecular Compounds, Forest Chemistry, and Organic Synthesis: Coll. of Papers of Komi Scientific Center), Syktyvkar, 2002, no. 167, p. 19.

6. Bolotnikova, L.S., Danilov, S.N., and Samsonova, T.I., *Zh. Prikl. Khim.*, 1966, vol. 39, no. 1, pp. 176–180.
7. Vlasova, T.E. and Nekhaichuk, A.D., *Tsellyuloza, Bumaga, Karton*, 1974, issue 9, p. 9.
8. Grushnikov, O.P. and Elkin, V.V., *Dostizheniya i problemy khimii lignina* (Advances and Problems of Lignin Chemistry), Moscow: Nauka, 1973.
9. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (A Course of Chemical Kinetics), Moscow: Vysshaya Shkola, 1974.
10. Sokolov, O.M., Demin, V.A., Karmanov, A.P., and Korobova, E.N., *Lesn. Zh.*, 1990, no. 4, pp. 78–83.
11. Khol'kin, Yu.I., *Teoriya gidroliza rastitel'nogo syr'ya* (Theory of Hydrolysis of Plant Raw Materials), Leningrad: Lesotekh. Akad., 1987.