

# Kinetics of acid-catalysed delignification of *Eucalyptus globulus* wood by acetic acid

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**Summary** The kinetics of HCl-catalysed delignification of *Eucalyptus globulus* wood by 70% (w/w) acetic acid solution were satisfactorily explained by a model in which 5% of the lignin fraction could not be eliminated and the remaining 95% was eliminated by a single process which, in view of the activation energy calculated from the data was attributed to the hydrolysis of  $\alpha$ -aryl ether bonds. The selectivity of the process was effectively independent of HCl concentration and operating temperature for pulp yields > 50%. At high temperature (160 °C) and catalyst concentration (0.027 M HCl), lignin condensation and precipitation became significant and the data were better fitted by a model comprising two consecutive processes: lignin solubilization followed by lignin condensation.

## Introduction

The kinetics of the delignification of lignocellulosic materials have been most extensively studied for the soda and kraft processes (Gierer 1980; Dolk et al. 1989; Chiang et al. 1990; Labidi, Pla 1992). These processes are satisfactorily modelled by equations corresponding to the simultaneous occurrence of three parallel reactions which are all of order one with respect to lignin concentration but have different rate constants. Comparison of the activation energies of these three processes with those of reactions in which model compounds are subjected to the same “delignification” conditions suggests that the fastest of the three, which predominates in the initial stage of delignification, consists in the cleavage of  $\alpha$ -aryl ether bonds (Gierer 1980; Ljunggren 1980), although the diffusion of macromolecules of relatively low molecular weight may also play a role; that the second fastest (the dominant reaction accounting for dissolution of about 75% of the lignin) consists in the cleavage of  $\beta$ -aryl ether bonds (Gierer 1980); and that the slowest may consist in the cleavage of covalent lignin-carbohydrate bonds (Dolk et al. 1989) or others (Labidi, Pla 1992).

Research on the kinetics of delignification by organic solvents has been limited to systems using aqueous solutions of methanol or ethanol under acid, basic or buffered conditions (Tirtowidjojo et al. 1988; Park, Phillips 1988; Faass et al. 1989). In all cases,

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the kinetics have fitted equations for two simultaneous first-order processes rather than three, the majority of the lignin being solubilized by the faster of the two. In the case of acid or buffered conditions, comparison of the activation energy of the fast process with that of model reactions (80–118 kJ/mol; Meshgini, Sarkanen 1989) again suggests that the fast process consists in the cleavage of  $\alpha$ -aryl ether bonds. The cleavage of  $\beta$ -aryl ether bonds in model compounds is about 100 times slower (Johansson, Miksche 1972), in keeping with its higher activation energy of 148–151 kJ/mol (Sarkanen, Hoo 1981; Hoo et al. 1983), although experiments on the hydrolysis of model compounds by concentrated organic acids (Shimada et al. 1991) and on the HCl-catalysed delignification of spruce by acetic acid (Nimz, Robert 1985) show that the extent of  $\beta$ -aryl ether cleavage increases with the acidity of the medium.

Of course, delignification kinetics also depend on the nature of the substrate. It is well known that the delignification of hardwoods is faster and more selective than that of softwoods. This may be due not only to the higher lignin content of softwoods, but also because softwood lignin has a smaller proportion of easily hydrolysed  $\alpha$ -aryl ether bonds, and is more prone to intermolecular condensation (Sarkanen 1980). Adequate kinetic modelling of the delignification of *Pinus pinaster* bark by acetic acid, for example, requires the inclusion of terms for both solubilization and condensation processes (Vázquez et al. 1994).

In this work we studied the influence of temperature, time and catalyst concentration on the rate and selectivity of HCl-catalysed delignification of *Eucalyptus globulus* wood by acetic acid; modelled the observed kinetics with equations including terms for solubilization and, when necessary, condensation processes; and used the kinetic data to calculate activation energies whose comparison with published results for model compounds allowed deduction of the nature of the bonds most susceptible to hydrolysis.

## Experimental

*Eucalyptus globulus* wood from a local sawmill was air-dried and ground in a crusher mill, and the fraction of particle size less than 1 mm was selected.

Klason lignin and acid-soluble lignin were respectively determined by the T 13-m standard method and as per Maekawa et al. (1989), and summed to give the total lignin content of the wood ( $L_0$ , % of oven-dried wood).

Delignification experiments were carried out in 200 ml Teflon-lined stainless steel reactors. In all cases, 70% w/w aqueous acetic acid was used with a solid/liquid ratio of 1:10 (w/w); HCl was added to give a concentration of 0, 0.0069, 0.014 or 0.027 M. Operating temperature was 120, 140, 160 or 180 °C, and was controlled by means of a thermostatted oil bath. In the light of the results of preliminary experiments, the bath temperature was initially set some 10–20 °C higher than the required reaction temperature; this allowed the heating stage of the experiments to be limited to 30 min and thus reduced the period of non-isothermal operation. Operating time varied according to HCl concentration and operating temperature, but in no case exceeded 7.5 h. When the selected time had elapsed, the reaction was quenched by rapidly cooling the reactor, then the suspension was suction filtered and the solid was successively washed with acetic acid solution and copious water, and air-dried. The pulp yield ( $Y$ , as % of oven-dried wood), and the pulp moisture content and total pulp lignin content ( $L_T$ , as % of oven-dried pulp) were then determined; the latter was calculated as the sum of the Klason lignin (T 222m-54 standard method) and acid soluble lignin (as per Maekawa et al. 1989), and also from the Kappa number (determined by the modified method for small samples in accordance with the SCAN-C 1:77 standard method).

During non-isothermal delignification (i.e. the heating stage) the proportion of lignin solubilized varied according to the operating conditions. For kinetic modelling (which was performed using a non-linear regression program based on the simplex algorithm), only data for the isothermal period were used.

## Results and discussion

### Kappa number and total lignin content

In commercial pulping processes, the lignin content of the pulp is simply and rapidly estimated by the Kappa number, whose correlation with Klason or total lignin varies with the lignocellulosic material and the pulping process employed (Oreopoulou 1988; Dence 1992). In our experiments, total lignin content increased linearly with the Kappa number; this increase was practically independent of HCl concentration, but was slightly sharper for pulps obtained at higher temperatures (Fig. 1).

### Selectivity

In order to assess the effects of delignification conditions on selectivity, pulp yield (Y) was plotted against residual lignin content ( $L_r$ , as % of oven-dried wood). The data for all pulps obtained with  $>50\%$  yield and  $L_r > 1.4\%$  lay on an essentially straight line but for yields  $<50\%$ , Y fell abruptly with  $L_r$  (especially for pulps obtained at high operating temperatures and HCl concentrations) and it was not possible to reduce lignin content to below  $L_r = 1.4\%$  even at the expense of yield. Linear regression of Y on  $L_r$  for  $Y > 50\%$  gave the line shown in Fig. 2. The selectivity of the delignification process, as measured by the slope of this plot was better than those reported by Pascoal, Robert (1992) for the autocatalytic or  $O_2$ -catalysed delignification of *Eucalyptus globulus* wood with 80% acetic acid (although the  $O_2$ -catalysed process afforded better

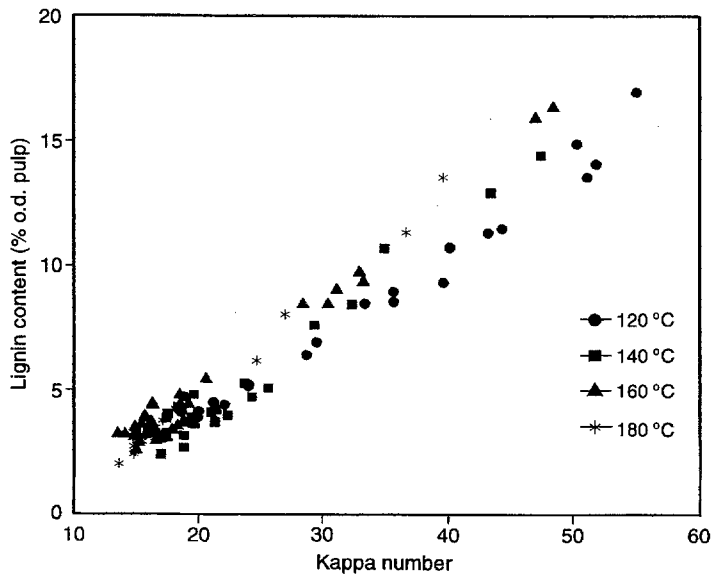


Fig. 1. Variation of total lignin content with the Kappa number for *E. globulus* wood delignified by acetic acid

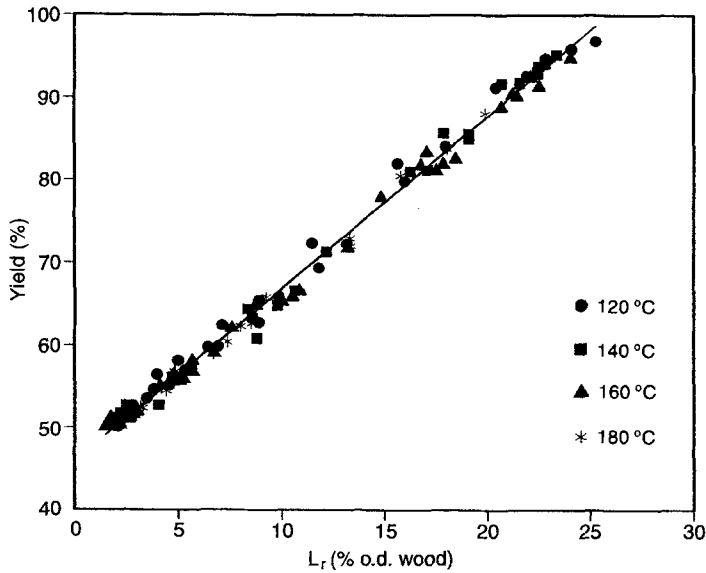


Fig. 2. Variation of pulp yield with residual lignin content ( $L_r$ ), showing the selectivity of HCl-catalysed delignification of *E. globulus* wood by acetic acid

yields than ours at high lignin content, the yields for pulps with lower lignin contents were no better than those obtained in our work).

Since for reasonable yields ( $Y > 50\%$ ) the selectivity of our delignification process was effectively independent of operating conditions (in the range studied), selection of the most favourable operating conditions can be based on kinetic criteria.

#### Delignification kinetics

As summarized in the Introduction, previous studies have successfully modelled delignification kinetics in terms of two or three simultaneous first order processes. We accordingly fitted the experimental data for the isothermal regime with equations of the form

$$\frac{L_r}{L_0} = \sum_{i=1}^n \frac{L_{0i}}{L_0} \exp(-k_i t)$$

where  $L_r/L_0 = (L_r \cdot Y)/(100 \cdot L_0)$  is the fraction of wood lignin remaining in the pulp,  $L_{0i}/L_0$  is the fraction of native lignin susceptible to solubilization by process  $i$ , and  $k_i$  is the corresponding rate constant.

Unlike the previous studies mentioned above, which employed different materials and conditions from this work, we found that the data for HCl-catalysed delignification of *E. globulus* wood by 70% acetic acid were best fitted by an equation with a single exponential term and a constant term representing a lignin fraction which could not be removed under any of our working conditions:

$$\frac{L_r}{L_0} = C_1 \exp(-kt) + C_2 \quad (1)$$

where  $C_1$  is the proportion of potentially soluble native lignin,  $C_2 = 0.05$ , and time  $t$  is measured from the start of the isothermal stage of the process (for the lowest operating

temperature the value  $C_2 = 0.05$  was assumed to hold even though these reactions were so slow that  $L_r/L_0$  did not reach 0.05 within the maximum time studied). Table 1 lists the values of  $k$  and  $C_1$  obtained at the various temperatures and HCl concentrations used. The proportion of lignin solubilized in the non-isothermal (heating) stage of the process is given by  $1 - (C_1 + C_2)$ ; at the highest temperature (180 °C) and HCl concentration (0.027 M) most lignin dissolved during this stage, and Table 1 accordingly shows no data for delignification under these conditions.

The experimental data and fitted curves for 0 and 0.027 M HCl are plotted in Fig. 3a and b, respectively. The lignin content of the pulp decreases as reaction time is prolonged until the limiting value of  $L_r/L_0 = 0.05$  is reached. Increasing operating time further leads to reductions in pulp yield due to hydrolysis of carbohydrates (as discussed above under Selectivity) or to condensation and deposition of lignin (points not shown in Fig. 3b; vide infra).

Table 2 lists the experimental activation energies ( $E_a$ ) and frequency factors ( $k_0$ ) obtained from the corresponding rate constants ( $k$ ) by means of an Arrhenius plot.

In Fig. 4 the variation of the rate constant with HCl concentration is shown for each operating temperature. These data are fitted by Eq. 2,

$$k = k_a + k_c [H^+] \quad (2)$$

where  $k_a$  and  $k_c$  are the rate constants for the autocatalysed and HCl catalysed processes, respectively. Similar linear relationships also hold for the acid-catalysed hydrolysis of  $\alpha$ -aryl ethers modelling lignin at catalyst concentration  $< 0.3$  M (Meshgini, Sarkanen 1989); for HCl-catalysed delignification of spruce by ethanol at HCl concentrations  $< 0.1$  M (Lai, Guo 1992); and for  $H_2SO_4$ -catalysed delignification of pretreated black cottonwood by methanol (pretreatment by acetic acid was intended to eliminate compounds which might otherwise have neutralized the catalyst).

An Arrhenius plot of  $k_c$  against temperature gave the activation energy and frequency factor for the HCl-catalysed process as 81.9 kJ/mol and  $1.77 \cdot 10^{12}$  l/mol·h respectively.

**Table 1.** Observed first-order rate constant ( $k$ ) and proportion of native lignin potentially soluble during the isothermal stage ( $C_1$ ) (Eq. 1)

T (°C)	[HCl] (mol/l)	k (h <sup>-1</sup> )	C <sub>1</sub>
120	0	0.294	0.904
140	0	1.225	0.813
160	0	2.921	0.776
180	0	7.439	0.684
120	0.007	0.436	0.865
140	0.007	1.606	0.787
160	0.007	3.707	0.753
180	0.007	11.449	0.440
120	0.014	0.722	0.802
140	0.014	2.076	0.715
160	0.014	5.259	0.638
180	0.014	15.840	0.270
120	0.027	1.017	0.789
140	0.027	2.937	0.785
160	0.027	6.756	0.691

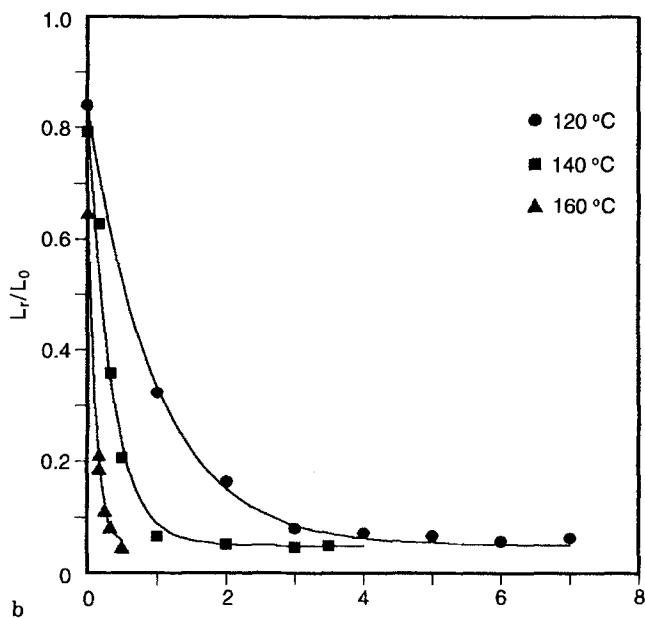
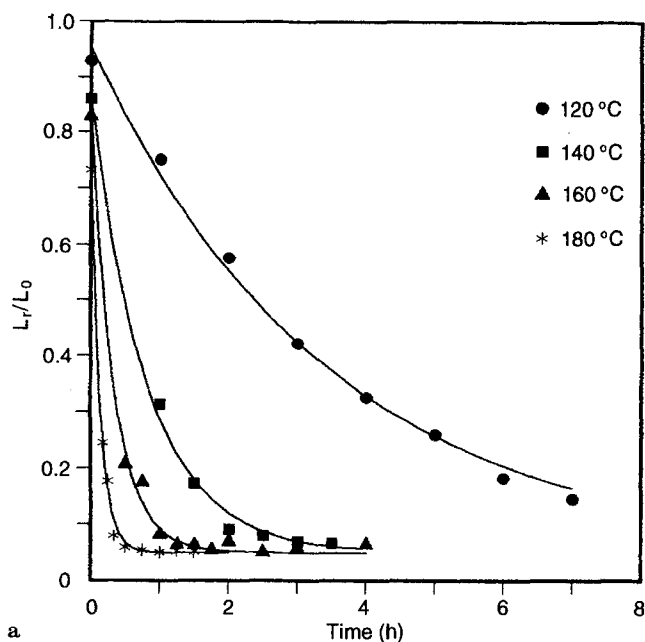
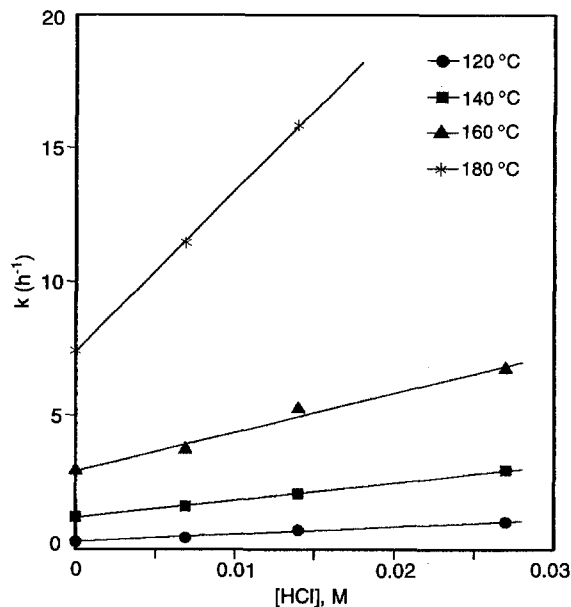


Fig. 3a, b. Variation of the fraction of residual lignin ( $L_t/L_0$ ) with time, describing the kinetics of the isothermal stage of delignification of *E. globulus* wood by acetic acid: a) autocatalysed; b) catalysed by 0.027 M HCl

The activation energies of both the catalysed process and the autocatalysed reaction (78.2 kJ/mol; see Table 2) are at the lower end of the range of values reported by Meshgini, Sarkanen (1989) for the hydrolysis of  $\alpha$ -aryl ethers of modelling lignin, 80 to 118 kJ/mol depending on the substituent. The activation energy reported for  $\beta$ -aryl

**Table 2.** Experimental activation energies ( $E_a$ ) and frequency factors ( $k_0$ ) of the isothermal stage of delignification

[HCl] (mol/l)	$E_a$ (kJ/mol)	$k_0$ ( $\text{h}^{-1}$ )
0	78.2	$8.6 \cdot 10^9$
0.007	78.2	$1.3 \cdot 10^{10}$
0.014	74.8	$7.1 \cdot 10^9$
0.027	66.5	$8.5 \cdot 10^8$



**Fig. 4.** Variation of observed first order rate constant ( $k$ ) with HCl concentration for isothermal delignification of *E. globulus* wood by acetic acid

ether hydrolysis (150 kJ/mol; Sarkanen, Hoo 1981) is considerably higher. Thus the main reaction of our delignification process appears to be the hydrolysis of  $\alpha$ -aryl ether bonds, despite reports that the hydrolysis of  $\beta$ -aryl ether bonds is catalysed by acetic acid (Nimz, Robert 1985; Yasuda et al. 1991).

At low temperatures and catalyst concentrations there was no evidence of lignin condensation, which must have been negligible compared to delignification. However, at high temperatures, the highest HCl concentration and long reaction times, increased condensation and precipitation of solubilized lignin meant that  $L_t/L_0$  rose after passing through the 0.05 minimum. To investigate the condensation process, we fitted the entire data set for  $T = 160\text{ }^\circ\text{C}$  and  $[\text{HCl}] = 0.027\text{ M}$  with an equation for two consecutive first-order processes, one for solubilization and the other for condensation:

$$\frac{L_s}{L_0} = \frac{k_1 A_0}{(k_2 - k_1)} [\exp(-k_1 t) - \exp(-k_2 t)] + B_0 \exp(-k_2 t) \quad (3)$$

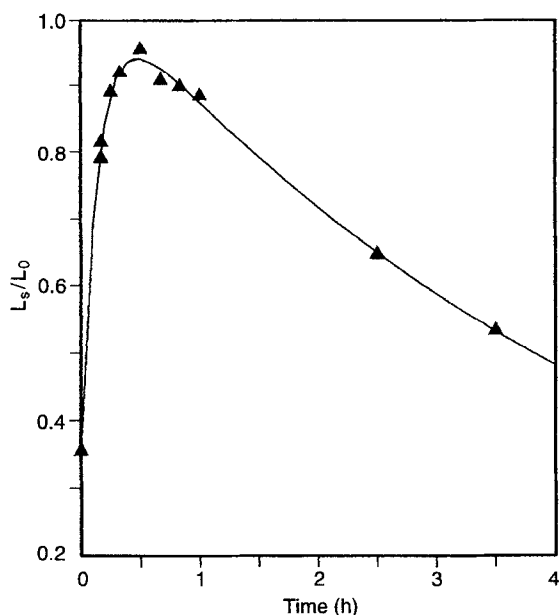


Fig. 5. Variation of the fraction of solubilized lignin ( $L_s/L_0$ ) with time, describing the kinetics of solubilization-condensation/precipitation processes occurring during delignification of *E. globulus* wood by acetic acid at 160 °C, catalysed by 0.027 M HCl

where  $L_s/L_0$  is the proportion of lignin in solution at time  $t$ ,  $A_0$  and  $B_0$  are respectively the proportions of lignin in the substrate and in the solution at  $t=0$ , and  $k_1$  and  $k_2$  are the rate constants for lignin solubilization and lignin condensation, respectively. The optimized values of the constants are:  $A_0=0.069$ ,  $B_0=0.35$ ,  $k_1=6.76 \text{ h}^{-1}$  and  $k_2=0.19 \text{ h}^{-1}$ ; the data and curve are plotted in Fig. 5.

### Conclusion

The total lignin content of pulp obtained by HCl-catalysed delignification of *Eucalyptus globulus* wood with 70% (w/w) acetic acid increases linearly with the Kappa number, the increase being slightly sharper for pulps obtained at higher operating temperatures.

For pulps obtained in >50% yield and with residual lignin content  $L_r > 1.4\%$ , the selectivity of the pulping process is independent of operating conditions. Severer operating conditions led to reduced yields due to polysaccharide hydrolysis without any further reduction in  $L_r$ .

Across the entire range of operating conditions studied, delignification kinetics can be modelled as a single first-order process extracting 95% of the lignin, the remaining 5% being impossible to eliminate under the conditions used in this study. For each temperature studied, the rate of HCl-catalysed delignification can be expressed as the sum of the rates of autocatalysed and catalysed processes, with the latter including a factor corresponding to HCl concentration. The activation energies obtained from the kinetic data for the catalysed and autocatalysed processes are close to those for the hydrolysis of  $\alpha$ -aryl ethers modelling lignin, strongly suggesting that it is the cleavage of  $\alpha$ -aryl ether bonds which controls the rate of the delignification process.

Under the severest operating conditions at which data were obtainable (160 °C and  $[\text{HCl}] = 0.027 \text{ M}$ ), the kinetics were modelled as two consecutive first-order processes



corresponding to lignin solubilization followed by lignin condensation. Lignin condensation and precipitation were only significant under these severe conditions.

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