

A Kinetic Model for Pyrolysis of Cellulose

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Synopsis

It has been shown that the pyrolysis of cellulose at low pressure (1.5 Torr) can be described by a three reaction model. In this model, it is assumed that an "initiation reaction" leads to formation of an "active cellulose" which subsequently decomposes by two competitive first-order reactions, one yielding volatiles and the other char and a gaseous fraction. Over the temperature range of 259–341°C, the rate constants of these reactions, k_i (for cellulose → "active cellulose"), k_v (for "active cellulose" → "volatiles"), and k_c (for "active cellulose" → char + the gaseous fraction) are given by $k_i = 1.7 \times 10^{21} e^{-58,000/RT} \text{ min}^{-1}$, $k_v = 1.9 \times 10^{16} e^{-47,300/RT} \text{ min}^{-1}$, and $k_c = 7.9 \times 10^{11} e^{-36,600/RT} \text{ min}^{-1}$, respectively.

INTRODUCTION

In this laboratory,¹⁻³ we have studied the pyrolysis of cellulosic materials which is of considerable significance in the conversion of biomass to sugar, chemical feedstock, and fuel, as well as controlling hazardous cellulosic fires.

In these studies we have observed that the rate of pyrolysis, as followed by weight loss under isothermal conditions, shows an initial period of acceleration before the maximum rate is reached. Thereafter, the rate decreases asymptotically until a final charred residue is obtained. This type of weight loss has been previously reported in other investigations of the kinetics and mechanism of cellulose pyrolysis.⁴⁻⁸ Some of these kinetic treatments assume an initial zero-order weight loss reaction followed by a reaction that is first order in the mass of unreacted cellulose.^{4,5} It has also been claimed that cellulose decomposes by means of two competitive endothermic processes.^{1,9} Broido⁸ developed a kinetic model in which the residual weight-time curves for a number of isothermal experiments between 226 and 259°C were simulated by computing the rate equation of six different reaction steps.

Our studies described in this article show that a simple three reaction, kinetic model could describe the pyrolysis data obtained at low pressure (1.5 Torr) in the temperature range 259–341°C. This range incorporates the temperatures used in the preparation of levoglucosan and related products obtained by the pyrolysis of cellulose.^{1,2,10}

EXPERIMENTAL

The pyrolysis apparatus consisted of a horizontal, cylindrical, electrically heated furnace (25 cm long) containing a Pyrex tube (diameter 2.5 cm) in which another Pyrex tube (diameter 2.0 cm) was placed. One end of the former tube was connected to a vacuum pump (capable of reaching a vacuum of 0.2 Torr) and the other end was connected via a valve, to a nitrogen cylinder, from which a small

nitrogen flow (raising the pressure to 1.5 Torr) was bled into the system. Aluminum boats containing weighed samples of cellulose powder (250 mg, Whatman CF 11) were magnetically moved into the pyrolysis area. The system was calibrated at the pyrolysis temperatures, using chromel-alumel thermocouples placed in four different positions in the cellulose sample. Temperatures were monitored using a Leeds and Northrup 620 recorder. A maximum temperature gradient of 2°C could be detected in the samples (volume $2 \times 1 \times 0.5 \text{ cm}^3$) during reaction in the temperature range studied. The reaction temperature used in the kinetic analysis was taken at the center of the sample 2 mm above the floor of the boat.

In order to ensure that no catalytic effects due to aluminum were operative, some pyrolyses were carried out using thermogravimetric analysis on small cellulose samples in aluminum and gold boats. No difference in pyrolysis rates were observed. This result is not unexpected, because the observed catalytic effect of metals on pyrolysis of cellulose is due to ionic species.

Samples were pyrolyzed at a series of oven temperatures in the range 259–341°C. Condensable volatiles were collected in a water-cooled condenser situated between the pyrolysis oven and the vacuum pump. At desired reaction times, samples were moved into a cooler part of the tube and then after release of vacuum, removed, allowed to cool in a desiccator for two minutes and then reweighed. Moisture content determinations indicated that adsorbed water was rapidly removed in the initial stages of reaction. Consequently, cellulose was used as received and sample weights corrected for adsorbed water content.

RESULTS

Figure 1 shows temperature measured at the center of a cellulose sample as a function of time for "final" pyrolysis temperatures, T_f of 259, 335, 375, and 407°C. For the temperature range 259–341°C, the heating rate of the sample was directly related to the difference in the temperatures of the sample and oven. That is,

$$\frac{dT}{dt} = k(T_f - T) \quad (1)$$

where T is the cellulose temperature at time t and k is a rate constant.

Integration of (1) gives

$$\ln[(T_f - T_0)/(T_f - T)] = kt \quad (2)$$

where T_0 is the initial temperature. The value calculated for k was 2.92 min^{-1} for the temperature range used in this investigation.

Thus,

$$T = T_f - (T_f - T_0)e^{-2.92t} \quad (3)$$

At temperatures in excess of 341°C, the endothermic heat of pyrolysis resulted in pyrolysis temperatures lower than those predicted by eq. (3) (see Fig. 1).

Figure 2 gives the measured weight of samples heated at $T_f = 259, 295, 312,$ and 335°C at different times. An initial period of accelerating rate of weight loss is seen to occur at 259, 295, and 335°C . However, at 312°C this initial period

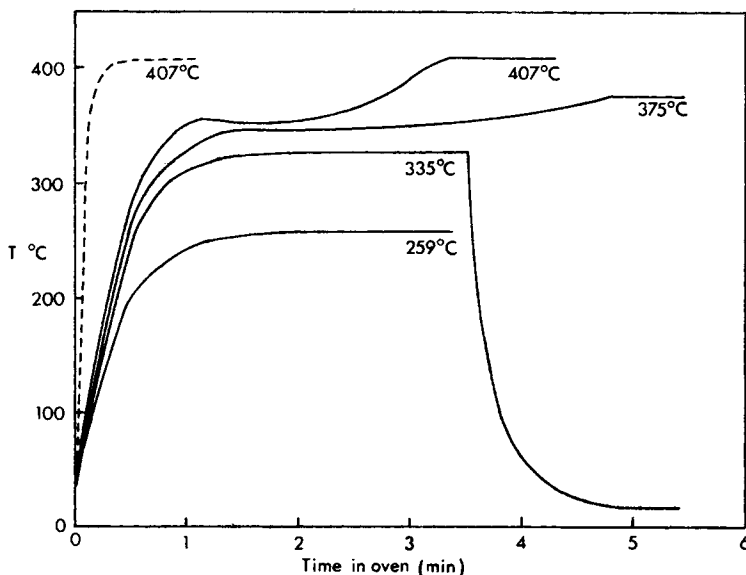


Fig. 1. Temperature of pyrolysis as measured by a thermocouple in cellulose sample. Final temperatures T_f are indicated. (---) temperature measured in empty boat. The cooling curve follows removal of a sample from the oven at 335°C.

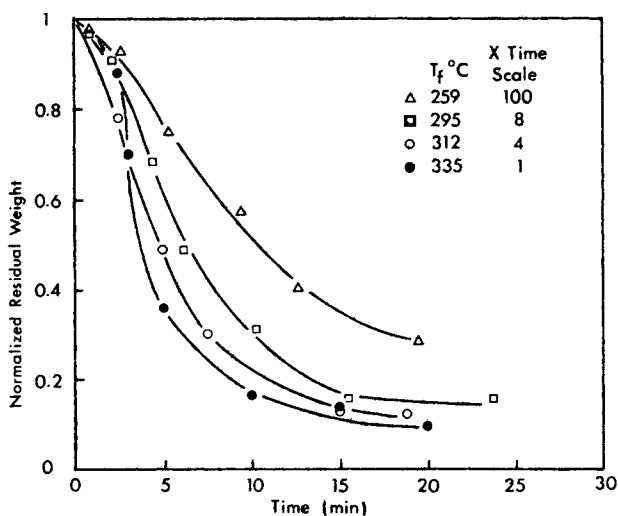
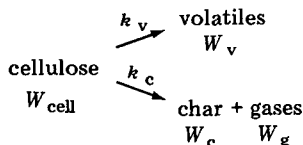


Fig. 2. Residual weight change at pyrolysis temperatures: $T_f = 259, 295, 312,$ and 335°C .

is not observed. We attribute the appearance of these periods at higher and lower temperatures to two separate phenomena. At lower temperatures the initial period can be explained by a high activation energy process converting the cellulose from an "inactive" to an "active" form. At higher temperatures the initial period results from the time required for the cellulose sample to reach temperature equilibrium according to eq. (3). At intermediate temperatures neither of these processes is important and the cellulose degradation can be treated simply.

As seen in Figure 2, the "leveling-off" weight of the residue becomes smaller

as the reaction temperature is increased. From the experimental results an approximate value of this weight can be estimated for each reaction temperature. This factor serves as the basis of our kinetic treatment. In the temperature range where no initial period of accelerating rate of weight loss is observed, cellulose degradation can be assumed to occur simply via two competitive first-order reactions leading, respectively, to (i) a condensable fraction, termed "volatiles" and (ii) a char and a gaseous fraction, which includes water, carbon dioxide, and carbon monoxide¹ termed "gases," where k_v and k_c are the respective rate constants:



W_{cell} , W_v , W_c , and W_g are the normalized weights of cellulose, volatiles, char and gases, respectively; i.e., $W_{\text{cell}} + W_v + W_c + W_g = 1$. The char fraction, $W_c/(W_c + W_g)$ was estimated to be 0.35 from comparison of the final yields of tar (i.e., condensed volatiles) and char to the overall weight loss at 314°C (see later) and was assumed constant for the range of temperatures investigated. Broido and Nelson¹¹ used a value of 0.36 for their kinetic description of char yields from cellulose pyrolysis.

From the rate equations,

$$\frac{-dW_{\text{cell}}}{dt} = (k_v + k_c)[W_{\text{cell}}] \quad (4)$$

$$\frac{dW_c}{dt} = 0.35k_c[W_{\text{cell}}] \quad (5)$$

it can be shown that the weight of residue at time t , is given by

$$W_{\text{cell}} + W_c = e^{-(k_v+k_c)t} + \frac{0.35k_c}{k_v + k_c} (1 - e^{-(k_v+k_c)t}) \quad (6)$$

The "leveling-off" residue weight observed, at $t = \infty$, is given by

$$(W_{\text{cell}} + W_c)_{\infty} = W_{\infty} = 0.35k_c/(k_v + k_c) \quad (7)$$

Equation (6) can then be rearranged

$$\ln(W_{\text{cell}} + W_c - W_{\infty}) = \ln(1 - W_{\infty}) - (k_v + k_c)t \quad (8)$$

Figure 3 shows plots of $\ln(W_{\text{cell}} + W_c - W_{\infty})$ versus time t for temperatures in the range 295–329°C. From the straight-line region of the plots, the slope $-(k_v + k_c)$ was calculated. It should be noted that at higher t values, $\ln(W_{\text{cell}} + W_c - W_{\infty})$ will decrease in accuracy due to the small difference between the measured residue ($W_{\text{cell}} + W_c$) and that observed for infinite time, W_{∞} . Substitution in eq. (7) gave values of the rate constants, k_v and k_c , which were then expressed in the form of an Arrhenius plot (Fig. 4). A least-squares analysis was used to derive the following Arrhenius relationships:

$$k_v = 1.9 \times 10^{16} e^{-(47,300/RT)} \text{ min}^{-1} \quad (9)$$

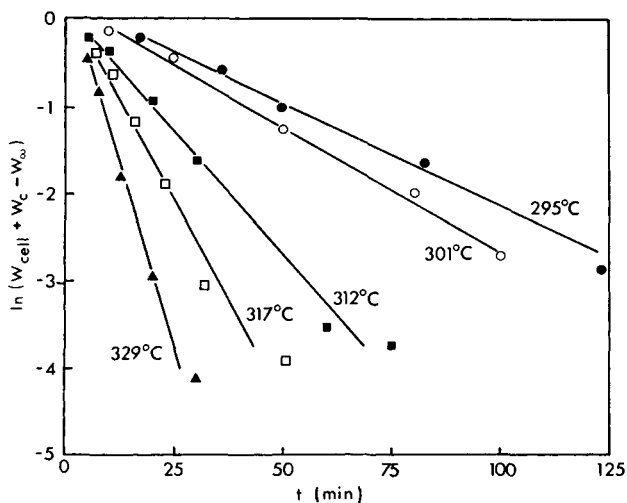


Fig. 3. Plot of $\ln(W_{\text{cell}} + W_c - W_{\infty})$ vs time t at 295–329°C.

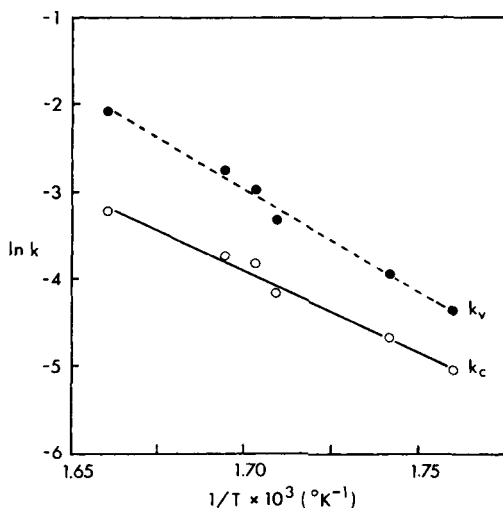


Fig. 4. Arrhenius plot for estimated values of k_v and k_c at 295–329°C.

$$k_c = 7.9 \times 10^{11} e^{-(36,600/RT)} \text{ min}^{-1} \tag{10}$$

As noted before, the lower temperature reactions show an “initiation period” attributed to the activation of cellulose. The activation energy was estimated for this process which was assumed to involve no weight loss. The rate constant of the initiation reaction k_i was assumed to be proportional to the reciprocal of the estimated time t_i required for attainment of maximum rate of weight-loss at temperatures: 259, 267, 285, and 295°C. A plot of $\log 1/t_i$ against reciprocal temperature is shown in Figure 5. From the slope, an activation energy of 58,000 cal was calculated. Thus, the kinetic model for cellulose pyrolysis could be

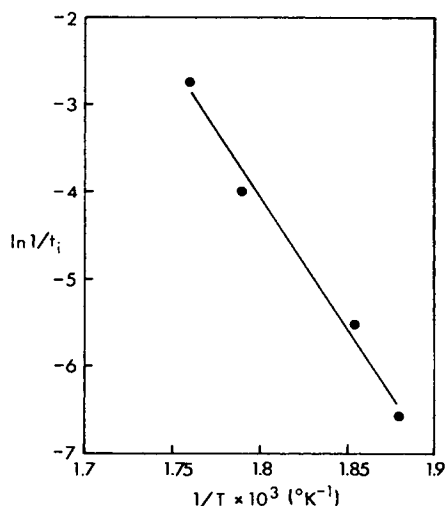
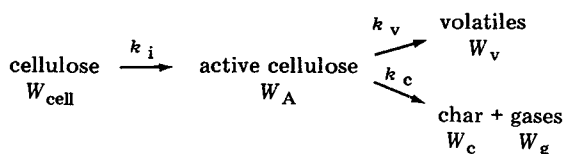


Fig. 5. Plot of $1/t_i$ against reciprocal temperature at 259–295°C.

modified to



where

$$\frac{-d(W_{\text{cell}})}{dt} = k_i[W_{\text{cell}}] \quad (11)$$

$$\frac{d(W_A)}{dt} = k_i[W_{\text{cell}}] - (k_v + k_c)[W_A] \quad (12)$$

$$\frac{d(W_c)}{dt} = 0.35k_c[W_A] \quad (13)$$

W_A is the weight of active cellulose. The rate constants k_v and k_c were expressed by the Arrhenius relationships in eqs. (9) and (10) and temperature by eq. (3). It was assumed that reaction during cooling of sample was negligible (see Fig. 1). The differential equations were numerically integrated using a Hamming predictor-corrector method.¹²

For the first-order expression [eq. (11)], the following Arrhenius expression for k_i gave the “best-fit” curves to the experimental data:

$$k_i = 1.7 \times 10^{21} e^{-(58,000/RT)} \text{ min}^{-1} \quad (14)$$

Figures 6–9 compare the computed residue weight versus time curves to experimentally measured values for pyrolysis at 259, 285, 312, and 341°C. Predicted variation of W_{cell} , W_A , and W_c is also shown. It must be noted that definition of the initiation reaction is somewhat ambiguous and that by adjustment of the pre-exponential factor in eq. (14), reasonably “good fit” curves could be obtained by using lower orders of reaction than one.

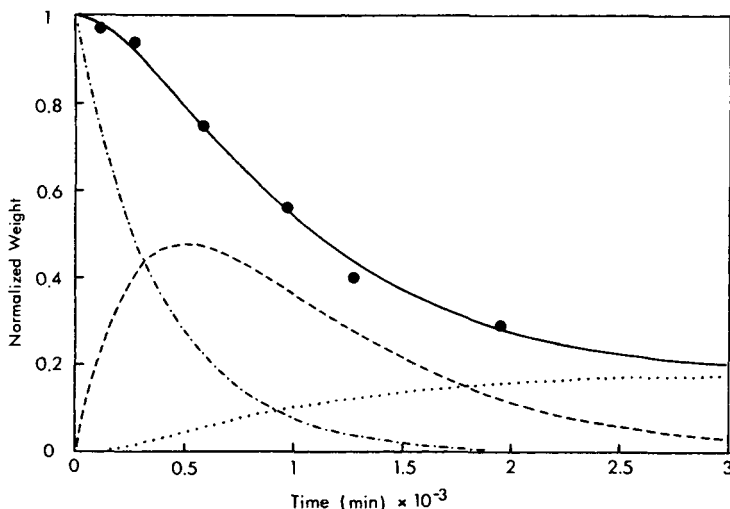


Fig. 6. Comparison of experimental data to residual weight predicted from reaction model for $T_f = 259^\circ\text{C}$. W_{cell} , W_A , and W_C are predicted weights. (●) Experimental residual weight; (—) predicted residual weight; (- - -) W_{cell} ; (- · -) W_A ; (· · ·) W_C .

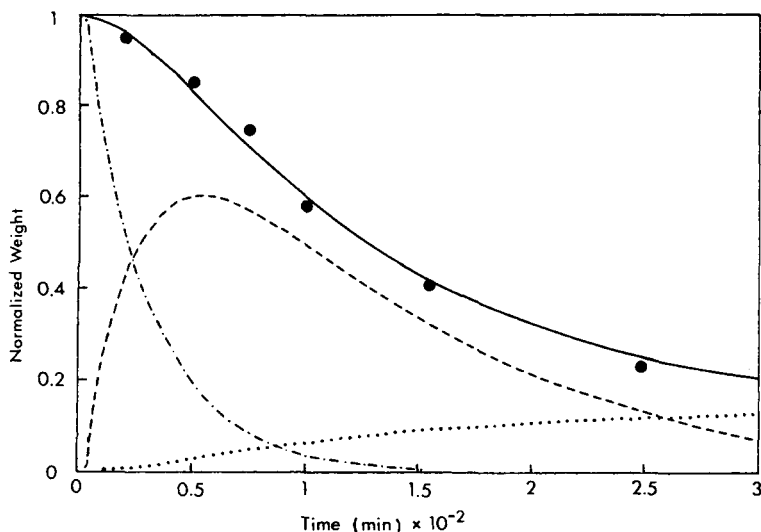


Fig. 7. Comparison of experimental data to residual weight predicted from reaction model for $T_f = 285^\circ\text{C}$. W_{cell} , W_A , and W_C are predicted weights. (●) Experimental residual weight; (—) predicted residual weight; (- - -) W_{cell} ; (- · -) W_A ; (· · ·) W_C .

We determined the yield of condensable material (the "tar" trapped in a cold water condenser attached to the pyrolysis outlet tube) with respect to time at 289 and 314°C and subjected it to GC-silylation analysis.¹⁰ Little variation in the nature of the gas chromatogram was apparent throughout the pyrolysis and the yield of levoglucosan, by far the major product identifiable by this method, is shown as a function of time for two different temperatures in Figure 10. These results infer that the nature of the volatile products alters little during progress of the pyrolysis, as would be suggested by our relatively straightforward kinetic model.

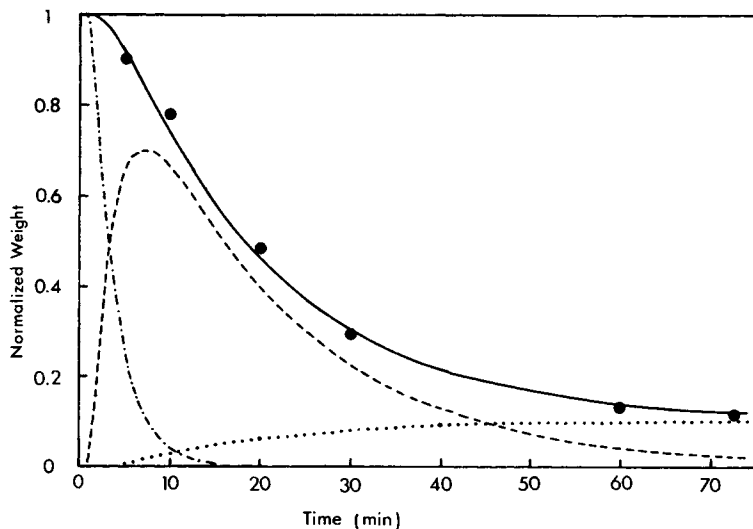


Fig. 8. Comparison of experimentally measured residual weight to that predicted from reaction model at 312°C. W_{cell} , W_A , and W_c are predicted weights. (●) Experimental residual weight; (—) predicted residual weight; (- - -) W_{cell} ; (- · -) W_A ; (· · ·) W_c .

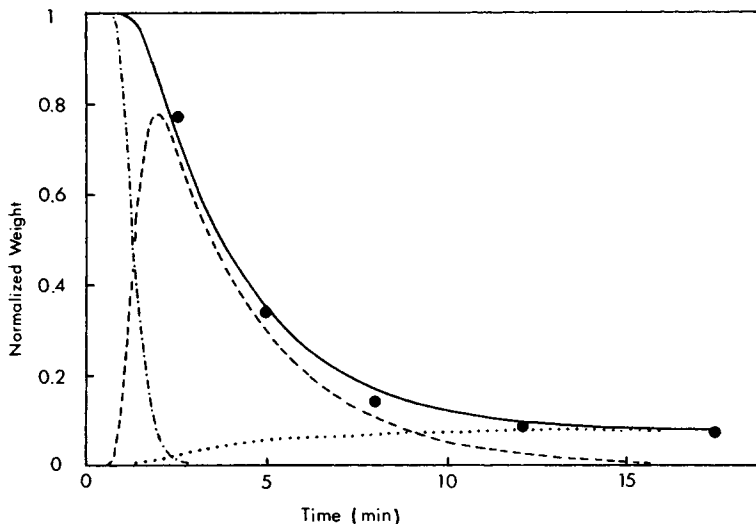


Fig. 9. Comparison of experimentally measured residue weight to that predicted from reaction model at 341°C. W_c and W_{cell} are predicted weights. (●) Experimental residual weight; (—) Predicted residual weight; (- - -) W_{cell} ; (- · -) W_A ; (· · ·) W_c .

DISCUSSION

Various investigations of cellulose pyrolysis have been carried out and a large number of kinetic models and mechanisms are available in the literature.^{1,4-8,13-15} For example, Broido⁸ used thermogravimetry to study the pyrolysis of filter paper and obtained residual weight-time curves of somewhat different appearance to ours. In the temperature range 226–259°C his reaction rate was very nearly first order in cellulose weight throughout, whereas others^{4-7,13-15} have suggested alternative kinetic schemes involving a variety of activation energies to describe cellulose pyrolysis data. This stresses how variation of reaction conditions has a marked effect on the nature and rates of the pyrolysis reactions.

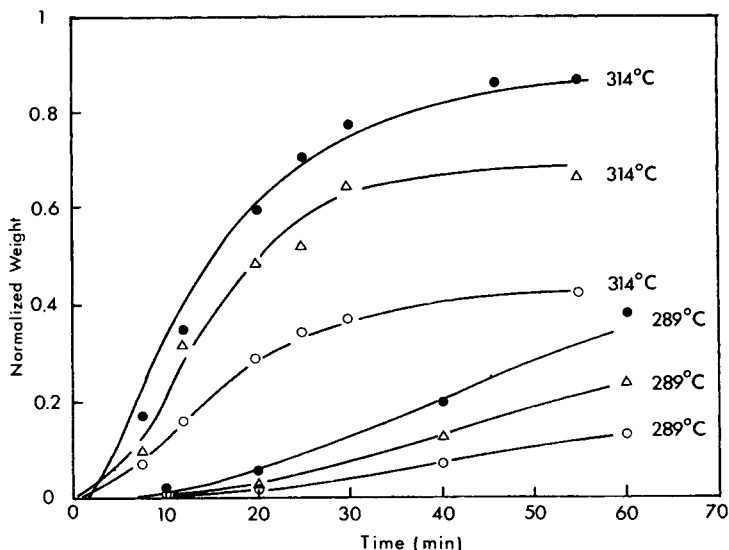


Fig. 10. Comparison of rate of weight loss and formation of condensable tar and levoglucosan at 289 and 314°C (—●—) measured and predicted weight loss; (—△—) measured tar yield; (—○—) measured levoglucosan.

We have found that small sample size (as shown by thermogravimetry on 2-mg samples) leads to smaller char fractions¹⁶ whereas higher pressure (using the procedure in this study with a nitrogen flow at atmospheric pressure) leads to larger char fractions. This indicates that the residence time of the volatiles in the cellulose during the pyrolysis reaction largely influences the extent of char formation. Pyrolysis of levoglucosan is known to give some residual char,¹⁷ and it has even been suggested¹⁵ that char formation is not a primary step but is a result of repolymerization of volatile material. However, any secondary reaction products which do not evaporate could not be discerned by the weight loss measurements and, consequently, are not reflected in the model.

It is generally known that cellulose macromolecules are not directly converted to low molecular weight volatile products, gases and char, but undergo intermediate physical and chemical changes such as a glass transition¹⁸ and depolymerization to DP's of around 200.¹⁶ These changes may be responsible for the activation of the macromolecules before they undergo rapid thermal degradation as discussed before.¹⁹

This investigation provides the kinetic data for pyrolysis of cellulose within the temperature range of 260–340°C where the production of volatiles predominates. The kinetics of pyrolysis at the lower temperatures where production of char and gaseous products dominate was discussed in a recent publication from this laboratory.¹⁶

The authors are pleased to acknowledge the interest and support of the National Science Foundation and the Center for Fire Research, National Bureau of Standards. They also thank Dr. R. J. Field and Dr. R. A. Susott for valuable comments and discussion.

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Received April 10, 1978

Revised July 11, 1978