

CELLULOSE PYROLYSIS KINETICS AND CHAR FORMATION MECHANISM

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The pyrolysis of cellulose was studied by electrically heating in helium single strips (0.75 cm \times 2.5 cm) of low ash (<0.07%) predried filter paper (\sim 0.01 cm thick) supported inside a folded wire mesh heating element mounted in a sealed vessel. The samples were rapidly brought to a desired temperature, held there for a desired time and then rapidly cooled. Extents of conversion to volatiles, measured by weighing samples before and after experiments of known duration, were determined as a function of residence time (0.2–75,600 s), final temperature (250–1,000°C), heating rate (400–10,000°C/s), and ambient pressure (0.0005–1 atm). Pyrolysis kinetics was determined by nonisothermal techniques to account for substantial reaction occurring during sample heat-up and cool-down. All of the cellulose was converted to volatiles without char formation, except when an extended heating period at a low temperature (e.g., an hour or longer at 250°C) preceded the pyrolysis at higher temperatures. The latter procedure resulted in char yields of about 2% by weight of the original cellulose. The kinetics data are well described by a single-reaction first-order decomposition model with an activation energy of 33.4 kcal/mole and a frequency factor of $6.79 \times 10^9 \text{ s}^{-1}$. The correlation is slightly improved by use of a multiple-reaction model based on a set of independent parallel first-order reactions represented by a Gaussian distribution of activation energies with a mean of 37.0 kcal/mole and a standard deviation of 1.1 kcal/mole. Selected experiments at reduced pressures (0.0005 atm), elevated heating rates (10,000°C/s), or both resulted in rate constants smaller than those obtained at 400°C/s and 1 atm. The results indicate that the residence time of volatile products within the pyrolyzing cellulose matrix is extremely important in determining conversion. Suggested pathways for cellulose pyrolysis that are consistent with these findings and with much of the pertinent literature involve primary decomposition to an oxygen-rich intermediate (probably levoglucosan) which then participates in three processes to extents depending on experimental conditions: (a) direct escape from the decomposing material into the ambient gas; (b) polymerization, cross-linking and cracking to form char and (c) pyrolysis to smaller volatiles some of which inhibit the char formation in (b) or autocatalyze (c). Accordingly, char is not a primary product, and the yield of char is zero for extremely short residence times of the primary products within the matrix of the decomposing material or for conditions that permit complete inhibition of char formation by secondary pyrolysis products.

Introduction

Pyrolytic decomposition supplies the volatiles that sustain flaming combustion of most polymeric materials, and interest in the

pyrolysis of cellulose and related materials has prevailed for some time particularly in the areas of fire research, fabric flammability, and solid detonation and explosion phenomena. Cellulosic materials are of special interest because of their wide-spread utilization in fibers, textiles, and construction materials, in the fabrication of temperature resistant materials, and as binders for solid propellants. Cellulose is also an important constituent of

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wood, paper, and cardboard, and hence an important component of urban refuse. The design of optimum incineration or pyrolysis processes for urban waste disposal requires improved fundamental understanding of the mechanism of cellulose degradation under severe thermal treatment.

The literature on the thermal degradation of cellulosic materials pertinent to these areas is extensive and several reviews have appeared in the past few years.¹⁻⁴ Previous investigations have included studies of the pyrolysis of pure cellulose,^{1,5-15,27} cottons,¹⁶⁻²² cellulosic derivatives,^{16,21,22} and wood^{2,23,24} in atmospheres ranging from vacuum and inert gases to air. Most studies were characterized by long heatup times, with periods at final temperature extending to several hours^{14,31} or days.⁵ In some work volatile products were separated into fractions condensable between selected temperatures such as liquid nitrogen, dry ice, ambient, etc., and then subjected to further chemical characterization.^{16,17} Solid residue was found in all studies and ranged from a few percent^{5,17} to over 50 percent¹⁶ by weight of the original sample. Rapid heating of cellulosic materials has been employed in a few studies. Radiative heating of thin samples was used to obtain heating rates estimated to approach 60°C/s with cellulose in air,⁶ and 300-1,500°C/s for treated and untreated cottons in helium.¹⁷ One investigation achieved very rapid rates estimated to exceed 20,000°C/s by flash heating optically black materials embedded in a matrix of untreated cellulose.^{25,26} The resulting degradation however probably reflected predominantly heterogeneous decomposition at the absorbing sites rather than true pyrolysis of the cellulose.

Kinetic data on cellulose pyrolysis were obtained in several studies,^{1,6,8,10,11,14,16} usually as Arrhenius constants for an assumed single step first-order decomposition. Variations of several factors of 10 are observed in the rate constants over the temperature range 200-600°C, while activation energies range from 19 kcal/mole to above 50 kcal/mole. Systematic studies of the effect of sample size, heating rate and total pressure on rates and extents of conversion have not been reported. Although some workers^{1,13} have recognized the importance of thermochemical, heat and mass transfer effects in determining the yields of pyrolysis products, the detailed molecular mechanism of cellulose pyrolysis, including char formation, remains uncertain and heavy reliance on assumptions and empiricism is too often a necessity in the prediction of cellulose pyrolysis behavior in practical situations.²⁸

The objective of the present study was to measure the rate and extent of conversion of cellulose to volatile products under well defined conditions and to determine from the results a descriptive model of the conversion process. To that end systematic variations of pyrolysis conditions over ranges of practical interest were performed to eliminate or minimize the effects of heat transfer, mass transfer, and secondary chemical reactions that often obscure the true pyrolysis behavior itself.^{1,13} Apparatus previously developed²⁹ for coal studies was employed to measure weight loss from small captive samples of filter paper pyrolyzed in inert gas or vacuum under various conditions of heating rate, final temperature, residence time and total pressure. A multiple-reaction model previously developed to describe the complex decomposition of coal was successfully applied in the present work and a simpler single-reaction description was also found adequate.

Apparatus and Procedure

Details of the apparatus and procedure are given elsewhere.²⁹ Pyrolysis samples were single strips, 0.75 cm × 2.5 cm (× ~0.01 cm thick) of low ash (<0.07%) S and S No. 589 Black Label filter paper, weighing approximately 10 mg. The strips were predried over CaSO₄ desiccant at ambient conditions for at least one week. The pyrolysis sample was placed in a 1.5 × 5.1 cm sandwich of folded 325 mesh stainless steel screen which was then suspended horizontally between relatively massive brass electrodes. The sample was heated electrically to a desired temperature, held there for a desired time, and then allowed to cool rapidly by radiation and convection when the electrical circuit was broken. The hot stage was enclosed in a vessel capable of operating under vacuum or at pressures up to 200 atm. The heating circuit consisted of two branches, the first for rapid heating (65 to 12,000°C/s), the second for maintenance of final temperature (250-1,100°C). Switching was accomplished with a timer-actuated relay, and large electrical currents were obtained using lead acid storage batteries and variable resistors. The time-temperature history for each run was measured with a chromel-alumel thermocouple (25μm wire diameter, 75μm bead diameter) inserted between the folds of the screen and connected to a fast-response Sanborn 380 recorder.

The reaction vessel was evacuated and repressurized with helium several times before

each run to remove trace quantities of oxygen, after which the desired pressure of helium, or vacuum was established. The fractional weight loss of the cellulose sample was determined by weighing the screen and sample before and after heating using a balance accurate to ± 0.01 mg giving an experimental precision of 0.1–0.2% of the sample weight. Precautions were taken to minimize moisture absorption during sample handling and weighing.

Results

Decomposition of the cellulose began during heat-up and, in the shorter runs, continued into the first part of the quenching period. Therefore a nonisothermal kinetic analysis using the time-temperature history for each run was required to obtain apparent rate parameters from the measurements of weight loss occurring during heatup, time at final temperature, and quenching. Initially, a simple decomposition model was used based on a single reaction assumed to be first-order in the mass of material yet to be converted to volatiles. Accordingly, the rate of cellulose decomposition is given by

$$dM/dt = -kM \quad (1)$$

and

$$k = k_o \exp(-E/RT) \quad (2)$$

The quantity measured in an experiment of total duration t' is the fractional weight loss $W_{t'}$, given by the single-reaction model as

$$W_{t'} = 1 - \exp \left[- \int_0^{t'} k_o \exp(-E/RT(t)dt) \right] \quad (3)$$

Systematic measurements of the rate and extent of pyrolysis of cellulose were performed at one atm of helium for a nominal heating rate of 400°C/s as a function of residence time (0.2 to 30 s) and final temperature (250–1,000°C). Essentially all of the cellulose was converted to volatiles without char formation in relatively short residence times ranging from 0.2 s above 800°C to about 30 s below 400°C . Analysis of the data with Eq. (3) using a nonlinear least squares regression method gave $E = 33.4$ kcal/mole and $k_o = 6.79 \times 10^9 \text{ s}^{-1}$. Figure 1 shows fractional weight losses mea-

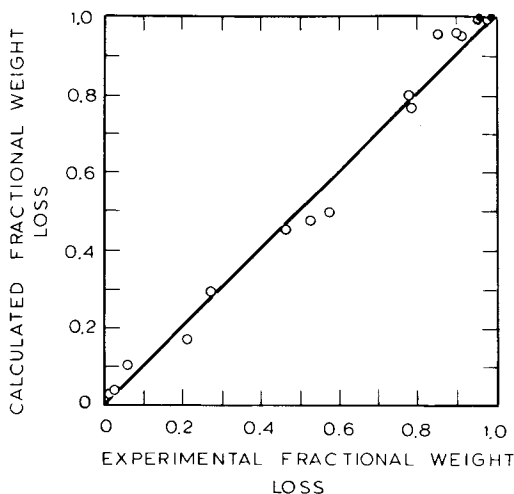


FIG. 1. Comparison of calculated and measured cellulose fractional weight losses for experiments purposely terminated before complete conversion [calculated values from Eq. (3), parameters from single-reaction model, and experimental time-temperature histories; experimental values 400°C/s , 1 atm helium; residence times 0.2–30 s; perfect fit (45° line)].

sured in experiments purposely terminated before complete conversion in order to obtain kinetic data, and compares them with corresponding values calculated with the above parameters using Eq. (3). The simple single-reaction model is seen to correlate the data quite successfully under these conditions.

Although the use of thin samples and high heating rates was expected to minimize the complicating effects of heat transfer, mass transfer, and secondary chemical reactions, the success of the simple analytical treatment was somewhat surprising, given the complex decomposition patterns previously reported.^{1,4,5,17} In order to assess further the validity of the single-reaction model the same data were also analyzed with a more sophisticated pyrolysis model based on the concept that thermal decomposition of a complex compound or mixture of compounds consists of a large number of independent, parallel first-order decomposition reactions the rate constant of each of which may be represented by the usual Arrhenius formula.³⁰ These reactions are further assumed to have identical pre-exponential factors k_o and a continuous distribution of activation energies represented by a distribution function $f(E)$ such that $f(E)dE$ is the fraction of reactions having activation energies between E and $E + dE$.

The fractional weight loss $W_{t',i}$ contributed by any one of the reactions in a time interval t' is then

$$W_{t',i} = 1 - \exp \left(- \int_0^{t'} k_i dt \right) \quad (4)$$

For mathematical tractability the distribution function $f(E)$ is assumed to be Gaussian with a mean activation energy E_o and a standard deviation σ which indicates the range of activation energies of reactions contributing significantly to the decomposition, ($E_o \pm 2\sigma$ includes 95.5% of the total reaction set):

$$f(E)dE = [1/\sigma(2\pi)^{1/2}] \exp[-(E - E_o)^2/2\sigma^2] dE \quad (5)$$

The total fractional weight loss in an experiment of duration t' is

$$W_{t'} = 1 - [1/\sigma(2\pi)^{1/2}] \int_{-\infty}^{\infty} \exp \left[- \int_0^{t'} k(E) dt \exp[-(E - E_o)^2/2\sigma^2] \right] dE \quad (6)$$

with recognition of the negligible numerical effect of altering the lower limit of integration from 0 to $-\infty$. Introduction of just one adjustable parameter σ , gives a mathematically manageable yet physically more flexible description of a complex decomposition process.

Reanalysis of the data using Eq. (6) and a non-linear least squares regression method gave $E_o = 37.0$ kcal/mole, $\sigma = 1.10$ kcal/mole, and $k_o = 7.67 \times 10^{10} \text{ s}^{-1}$. The effective first-order rate constant at different temperatures calculated from these parameters is compared in Fig. 2 with the first-order rate constant computed using the above parameters for the single-reaction model. The excellent agreement over the entire temperature range 250–1,000°C together with the small value of σ indicates that the single-reaction model is adequate under these conditions.

Figure 2 also compares the present rate constants with literature values representing a variety of temperatures, heating rates, and sample sizes.^{6,8,10,11,14,16} The present results are generally higher than previous values at temperatures above 250°C which may in part be a consequence of the enhanced escape of volatiles experimentally promoted in the present study. At temperatures below 250°C some

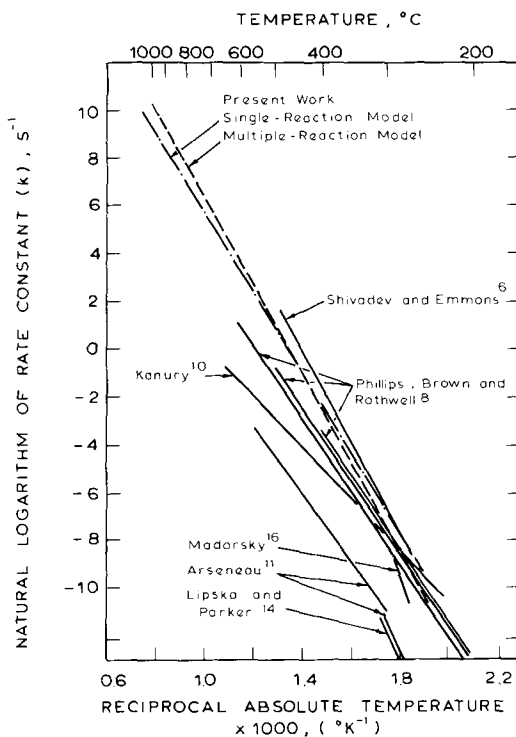


FIG. 2. Arrhenius plot of effective first order rate constants from different investigations.

of the literature values^{8,10} converged with the present work, and one recent study⁶ correlates extremely well with the present results over the temperature range 280–430°C.

Selected experiments were also performed at reduced pressure (0.0005 atm) or higher nominal heating rate (10,000°C/s), or both. The objective was to assess the suitability of the single-reaction first-order model under reaction conditions expected to enhance even further rapid transfer of volatiles from the pyrolyzing cellulose matrix. The results are summarized in Fig. 3 where as in Fig. 1, fractional weight losses from experiments purposely terminated before complete conversion are compared with the corresponding values calculated using the single-reaction model and its associated rate parameters given above. Char formation was again not observed but the experimental volatile yields are lower than the predicted values in every case, indicating that the overall pyrolysis process is slower under these conditions.

A third series of experiments focussed on the intentional promotion of char formation by preheating samples at 250°C and 1 atm of helium for times ranging from 1 to 21 hrs

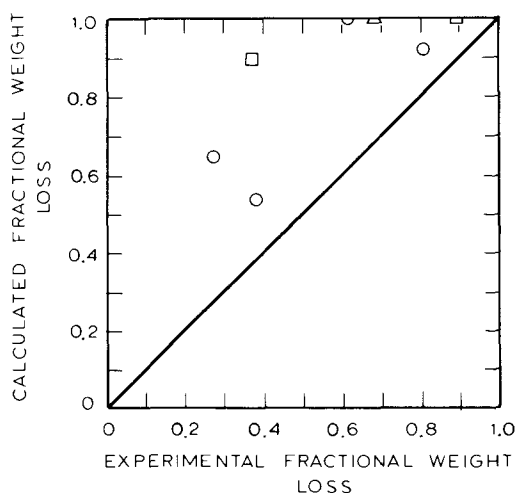


FIG. 3. Comparison of calculated and measured cellulose fractional weight losses for experiments purposely terminated before complete conversion [calculated values from Eq. (3), parameters from single-reaction model, and experimental time-temperature histories; experimental values 400°C/s, 0.0005 atm (o); 10,000°C/s, 1 atm helium (□); 10,000°C/s, 0.0005 atm (Δ); perfect fit (45° line)].

prior to heating to 1,000°C at 400°C/s. Very small char yields were observed, with preheating at 250°C for 1 hour followed by pyrolysis at the stated conditions giving only 2% of the original sample as char. Since preheating was performed under essentially isothermal conditions, apparent rate constants were calculated from these data using the isothermal version of Eq. (3), namely

$$W_t = 1 - \exp(-kt') \quad (7)$$

The results are summarized in Fig. 4 where the rate constants derived from Eq. (7) are compared with the corresponding values calculated using Eq. (3) and the single-reaction rate parameters given above. The preheating results are smaller than the predicted values in all cases.

Discussion

The ability to achieve essentially complete volatilization of cellulose in an inert atmosphere in relatively short residence times by appropriate choice of final temperature and heating rate is consistent with trends reported by Berkowitz-Mattuck and Noguchi¹⁷ and Martin,²⁷ but differs from the results of several

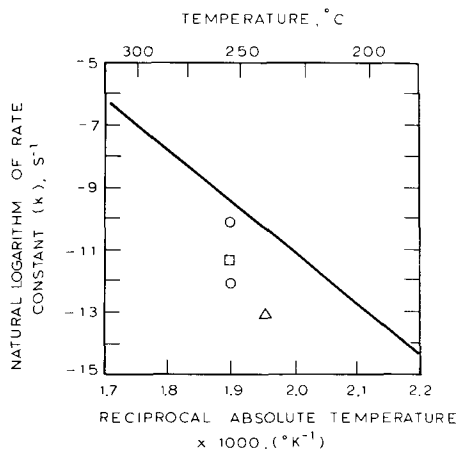


FIG. 4. Comparison of predicted and measured long residence time low temperature first-order rate constants [solid line calculated values from Eq. (3), parameters from single-reaction model, (400°C/s, 0.2–30 s residence time data); experimental values 3600 s, 250°C (o); 43,200 s, 235°C (□); 75,600 s, 250°C (Δ)].

investigators who found significant char yields^{1,5,16,24} and in some cases incorporated a fixed ultimate char yield as a feature of their predictive models.^{5,6} Char formation has in fact been postulated as a primary step in cellulose pyrolysis.⁵ The success of the single-reaction model in correlating the data obtained at 400°C/s and 1 atm helium and the similarity of the resulting rate parameters with those obtained from the more complex multiple-reaction model was unexpected. Cellulose is a high molecular weight polysaccharide consisting of cellobiose units bound by glycosidic linkages at the 1,4 positions as shown in Fig. 5. The thermal decomposition behavior of such a structurally complex molecule might well be expected to defy simple description. A large variety of end products including significant fractions of CO₂, CO, CH₄, C₂H₄, H₂, H₂O, several low molecular weight organic acids, and levoglucosan (1,6-anhydro-β-D-glucopyranose) are reported for the low-temperature pyrolysis of cellulose.^{21,22} Similarly, cotton heated at estimated rates of 300–1500°C/s for about 1 s reportedly produces CO₂, CO, CH₄, C₂H₄, H₂O, several aldehydes, ketones, esters, organic acids, and levoglucosan, but no H₂.¹⁷ Char yields associated with the later data were found to decrease markedly with heating rate going from around 20 wt% at ~300°C/s to approximately 2 wt% at ~1500°C/s.

The small char yields, rapid conversion rates

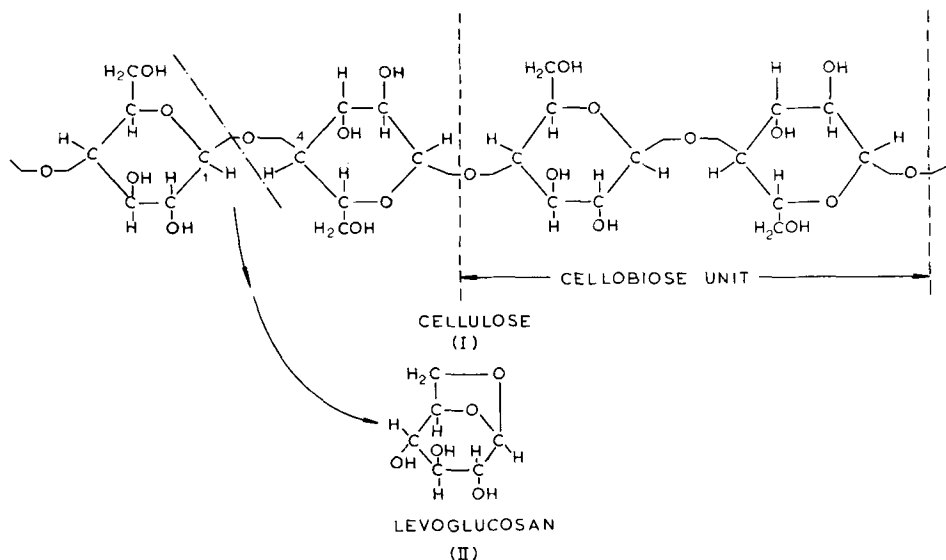


FIG. 5. Structural formula of cellulose (I), showing scission of 1-4 glycosidic linkage to yield (after rearrangement) levoglucosan (II).

and relatively simple apparent kinetics observed in the present work are probably a consequence of the enhanced transfer of volatiles out of the pyrolyzing cellulose matrix achieved with the thin samples and rapid heating rates. This effect would reduce the time available for primary volatile products to undergo secondary reactions such as repolymerization and cracking that lead to char formation. Madorsky¹⁶ used this explanation for reduced yields of tar from cellulose pyrolysis under 1 atm of nitrogen as opposed to vacuum conditions, and a similar interpretation was employed in recent studies of the pressure dependence of volatile yields from the rapid devolatilization of bituminous coal.³⁰

The small apparent decomposition rates observed in the experiments at reduced pressures, higher heating rates or both (Fig. 3) give insights into the possible complexity of these "secondary reaction" processes. Since these conditions would be expected to promote rapid escape of primary volatiles from the cellulose, the observed lower apparent rates might suggest the importance of some autocatalytic step. For example, some of the primary volatiles might remain within the decomposing matrix long enough to react with the parent cellulose and convert more of it to volatiles, yet not long enough to crack and form char. However, the success of the single-reaction model without the incorporation of any autocatalytic step and the very narrow distribution of activation energies obtained with the multiple-reaction

model suggest that any "catalytic" effects on primary decomposition products are probably more subtle than conventional autocatalysis. Competitive pathways, such as escape from the matrix, inhibition of char formation and autocatalysis of secondary pyrolysis, may exist whose rates and extents depend upon residence times of certain products within the cellulose.

It is not possible using the present data to establish a quantitative mechanism of cellulose pyrolysis based on the foregoing concepts since compositions of volatiles were not determined. However, possible pathways contributing to weight loss and consistent with the present findings and much of the pertinent literature are suggested in Fig. 6 where bracketed numbers label steps discussed below. Cellulose could decompose rapidly to an intermediate, tentatively identified as levoglucosan, by scission of its 1,4 glycosidic linkages¹⁶ followed by rearrangement (Fig. 5), or by other mechanisms discussed by Aldrich¹ and Shafizadeh.⁴ The levoglucosan may then (1) be transported from the cellulose matrix to give a product tar; (2) repolymerize, crack, or be cross-linked, to yield char; (3) be pyrolyzed to lighter volatile products including CO, CO₂, fixed gases, organic acids, ketones, esters, aldehydes, and free radicals, some of which could (4) inhibit char formation or (5) autocatalyze step (3). Lighter stable products could of course also (6) escape the matrix to yield volatiles.

Under the rapid-heating and thin-specimen

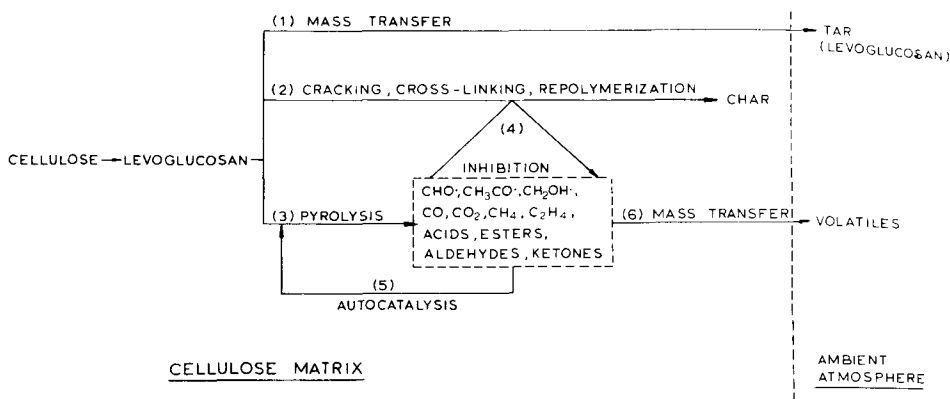


FIG. 6. Possible reaction pathways for thermal degradation of cellulose under rapid heating conditions.

conditions characterizing most of the present results, pathways (1) and (3) plus (4) plus (6) would be expected to dominate giving no char formation. The accelerated rates for complete volatilization observed for the 400°C/s, 1 atm helium conditions compared to those observed for more rapid heating and vacuum conditions may reflect complex interactions of several secondary chemical reactions and transport processes which are conveniently masked in pathways (1) to (6) above. Conditions promoting very rapid transfer of certain species from the cellulose could reduce their effectiveness in accelerating the rates of volatilization by pathways such as (4) and (5). At the other extreme, low-temperature isothermal or low heating rate conditions, particularly involving large samples, would promote longer residence times of all primary products within the pyrolyzing matrix and step (2) could then dominate, accounting for the large char yields reported for such conditions.^{1,5,14,16,19,21,22}

These steps are consistent with much of the literature on cellulose decomposition. For example, Madorsky and co-workers^{16,21,22} have postulated the rate controlling step in low temperature cellulose pyrolysis to be the formation of levoglucosan by rearrangement of fragments formed by scission of the cellulose 1,4 glycosidic bonds. The levoglucosan is then postulated to follow two reaction paths, dehydration and polymerization to char, and pyrolysis to more volatile species—permanent gases, acids, ketones, aldehydes, etc. Berkowitz-Mattuck and Noguchi¹⁷ in their very rapid (estimated 1,500°C/s) pyrolysis of cotton identified levoglucosan as an important product and present a detailed molecular mechanism demonstrating how several low molecular weight esters, aldehydes, ketones and acids and free radicals could all be produced by

its further pyrolysis. In flammability studies on cotton in air at 350°C, Schwenker and Pacsu²⁰ postulated levoglucosan to be the common intermediate in the thermal degradation of cellulose and attributed cotton flammability to the volatile products produced by its subsequent decomposition. Homes and Shaw¹⁹ pyrolyzed cottons in dry air at 418°C and in a vacuum and identified levoglucosan as the main component in the resulting tars and Lipska and Wadley¹² obtained this product when pyrolyzing cellulose directly in the inlet of a mass spectrometer. Aldrich¹ has concluded that while temperature, heating rate, and mass transfer are all very important in determining net cellulose pyrolysis yields, an intermediate of a levoglucosan type structure is to be expected.

Literature data also support the existence of an initial thermal decomposition step in the overall thermal degradation of cellulose including formation of free radicals. Authur and Hinojosa³¹ on the basis of ESR data claimed the existence of long lived free radical species thermally generated from cellulose at 250°C. Schwenker and Beck¹⁸ analyzed volatile products from cellulose pyrolysis in oxidizing and reducing atmospheres at heating rates of 0.25°C/s and found the resulting chromatograms to be very similar in shape and number of compounds identified. Similar results were found at different rates of heating, 0.25°C/s vs an estimated 40°C/s. These data and more recent findings⁶ suggest a common thermal degradation mechanism for cellulose that is non-oxidative in character. Aldrich¹ quotes work by Fung who studied the vacuum pyrolysis of filter paper at 280°C and observed the degree of polymerization to decrease rapidly during the first minute of reaction without any weight loss in the sample. A linear relation

was found between reciprocal degree of polymerization and reaction time at constant temperature implying that a random scission of the cellulose polymer was operative. Broido and Weinstein⁷ found a greatly improved correlation of their cellulose pyrolysis data when they incorporated into their model an initial reaction step corresponding to a sharp decrease in the degree of polymerization without attendant weight loss. All of these findings suggest that thermal decomposition processes, possibly somewhat modulated by their attendant mass transport effects, control cellulose degradation at the more rapid heating rates.

With regard to the present observation that some char can be formed from cellulose even under rapid pyrolysis conditions if the sample is preheated for relatively long periods at low temperatures, several previously advanced mechanisms include char formation as a primary step,⁵ by secondary cracking of volatiles¹ and by cross-linking and repolymerization.^{1,4} Aldrich¹ notes that the latter process may proceed via furan-like structures and suggests that both secondary cracking and condensation mechanisms are probably important since char formation is observed under both low and high temperature conditions. As noted, the preheating periods in the present study ranged from 1 to 21 hours at 250°C, which is about 20°C below the decomposition temperature of levoglucosan. Thus if some levoglucosan were formed via the mechanism suggested above it would be expected to undergo relatively little decomposition to more volatile products and to have ample time to repolymerize to char, thus accounting for lower apparent rate constants for overall weight loss under these conditions.

In summary the results of the present study strongly suggest that, irrespective of the detailed molecular mechanism, a critical parameter in cellulose pyrolysis is the residence time of volatiles in the pyrolyzing cellulose matrix. The existence of an optimum residence time for obtaining a maximum rate of volatilization is indicated. It is suggested that cracking, cross-linking and repolymerization reactions occur if this time is substantially exceeded and that volatile yields also decrease if certain volatile species that could enhance the rate of conversion spend too little time in the substrate. It has also been shown that char formation need not be a primary step in cellulose pyrolysis and that proper selection of temperature and heating rate, even at quite small residence times (0.2 to 30 sec) can result in virtual elimination of char formation from thin samples. This result has important practi-

cal implications in the design of processes for pyrolytic conversion of solid refuse to gaseous and liquid fuels as well as in the development of improved incinerators. It may also be important in the development of effective methods to retard ignition and fire spread in cellulosic materials.

Possible reaction pathways for cellulose degradation consistent with the present findings and much of the pertinent literature have been suggested but a quantitative mechanism cannot be derived with confidence from the present results. Additional systematic investigations covering the present conditions and focussing on measurements of volatile product compositions would provide further insight into the detailed mechanistic processes occurring during cellulose pyrolysis.

Nomenclature

E	activation energy, kcal/mole
E_o	mean activation energy, kcal/mole
$f(E)$	distribution function for activation energies
k	first order rate constant, s^{-1}
k_o	frequency factor, s^{-1}
M	sample weight, fraction of original cellulose mass
R	ideal gas constant, kcal/mole °K
t	time, s
t'	total duration of weight loss experiment, s
T	absolute temperature, °K
W_t	total sample weight loss in an experiment of duration t' , fraction of original cellulose mass
σ	standard deviation of activation energy distribution, kcal/mole

Acknowledgments

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COMMENTS

L. Douglas Smoot, Brigham Young University, USA. Since your measured heating rates come from thermocouples attached to the wire mesh, is it possible (or even likely) that your observed lack of correlation of high heating rate data (10^4C/s) with arrhenius coefficients determined from data at lower heating rates (10^3C/S) is due to lack of instantaneous heat transfer between the wire mesh and the cellulose?

Authors' Reply. The thermocouple was not attached to the screen but was placed with the cellulose sample between the layers of the screen. Our calculations of heat transfer rates and thermal lag times indicate that the temperature measurements are accurate at 400°C/s where most of the measurements were performed. At $10,000^\circ\text{C/s}$, the accuracy is not high enough to exclude the possible significance of errors in the measured temperature-time histories.

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Charles A. Garriss, I.V.I.C., Venezuela. In relation to your finding that with sufficiently high heating rates it is possible to nearly eliminate the char-yield, it has been reported that the char-yield of cellulose pyrolysis may be very sensitive to the presence of certain impurities. Would you please comment on your experience in this area?

Authors' Reply. It is true that the presence of impurities could contribute to the pyrolysis of cellulose to volatile products under conditions of rapid heating. For example cellulose pyrolysis experiments in which rapid heating was achieved by radiation to optically black materials embedded in the sample may exhibit significant heterogeneous decomposition at the absorbing sites (see references 25 and 26 in the paper). In the present work, it

seems unlikely that impurities in the predried very low-ash filter paper could have contributed significantly to the observed total conversion of cellulose to volatiles.

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F. A. Williams, University of California, USA.
I am surprised that you propose the low-temperature heating to produce char through repolymerization of levoglucosan, since so many earlier studies have shown that char production and unzipping involve competitive, parallel paths.

Authors' Reply. Since compositions of volatile products were not determined in this work, heavy reliance was placed on literature data on cellulose pyrolysis in order to infer possible reaction pathways that are consistent with the present findings. A detailed discussion of literature supportive to the suggested mechanism including formation of char from levoglucosan by repolymerization, cracking and cross linking is given in the paper. (See References 1, 4, 16, 17, 19-22.) An initial thermal decomposition followed by a sequence of competitive parallel reactions is also consistent with many previous findings. (See References 1, 6, 7, 18 and 31.)

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Richard G. Gann, National Bureau of Standards, USA. In your experimental results, you have reported a significant pressure effect on the smoldering rate which your current model does not explain. On a purely chemical basis, this could be attributed to a change in reaction order. Since your model is built on a sequence of Arrhenius-type rate expressions, can it be made to respond to this? Also, since the chemical processes involved vary widely in nature, why have you selected a single A factor?

Authors' Reply. Rates of unimolecular homogeneous decomposition reactions in the gas phase do

show a marked pressure dependence with the rate constant decreasing linearly with pressure at sufficiently low pressures and becoming independent of pressure at sufficiently high pressures. These pressure effects reflect two limiting cases of gas phase collision phenomena, namely decomposition of an energized intermediate at higher pressures and formation of an energized intermediate at low pressures. The suitability of incorporating these effects in the present model which deals with the (assumed) unimolecular decomposition of a solid is less certain since activation of the decomposing molecule is assumed not to occur by gas phase collisions. Some workers studying coal pyrolysis have utilized decomposition mechanisms that incorporate Arrhenius type rate expressions having different orders for different reaction conditions.^{1,2} However, such higher order rate expressions may actually reflect more complex processes such as coupling of chemical kinetics and transport phenomena rather than pure chemical effects.

It also should be noted that the present model is not built on a "sequence" of Arrhenius type rate expressions but on a set of independent parallel first order decomposition reactions described in Arrhenius formalism by identical preexponential factors and a continuous distribution of activation energies.

A single preexponential (A) factor is preferable for mathematical tractability in cases such as the present where the resulting correlation is good enough without the use of a larger number of adjustable parameters.

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