Kinetics of the Pyrolysis of Cellulose in the Temperature Range 250–300°C.

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Synopsis

Samples of α-cellulose, containing 0.11–0.14% ash, were isothermally pyrolyzed in a fluidized bath in a nitrogen environment at 250–298°C. Results were reported in terms of volatilization (based on weight-loss measurements) and decomposition (in term of glucosan loss). The findings show three distinct stages of pyrolysis: (*1*) an initial period of rapid decomposition and weight loss; (*2*) a range in which both the volatilization and decomposition are of zero order; (*3*) a region in which the volatilization follows a first-order rate, leaving a char deposit which does not undergo further pyrolysis. The degree of decomposition and volatilization occurring during the zero-order phase increases with increasing temperature. A single activation energy of 42 kcal./mole describes both the decomposition and volatilization rates in the zero-order phase over the entire 250–298°C. range.

INTRODUCTION

Considerable effort has been expended in the study of thermal decomposition of cellulosic materials because of the central importance of the data in relation to fire phenomenology.[1–8] Despite extensive experimentation on the pyrolytic degradation of cellulose, the exact kinetics and mechanisms of the process have remained highly controversial. Some investigators proposed that thermal degradation of cellulose follows a first-order expression,[9,10] while others suggested that cellulosic decomposition is controlled by zero-order kinetics.[11] In 1964 Tang and Neil[12] on the basis of their thermogravimetric analyses suggested that the initial stage of pyrolysis is controlled by pseudo zero-order kinetics and that the final stage is pseudo first-order.

In the past, decomposition rates and activation energies have generally been inferred from weight-loss measurements. In our investigation the rate of decomposition was observed directly by measuring the remaining glucosan units as a function of time during isothermal pyrolysis. The activation energy was obtained by conducting these measurements over the temperature range between 250 and 300°C. For correlation purposes the weight-loss rates were measured at the same time.

The specimens were heated rapidly to the pyrolysis temperature in a nitrogen atmosphere by a fluidized bath, thereby sharply reducing the

rather long nonisothermal heating periods encountered in previous pyrolysis investigations.

EXPERIMENTAL APPARATUS AND PROCEDURE

Description of Equipment

The apparatus for thermal degradation of cellulose was designed to meet the following requirements: (*1*) rapid and uniform heating of the samples to the controlled temperatures; (*2*) uniformity of temperature throughout the pyrolysis chamber; (*3*) constancy of temperature to within 0.2°C. over prolonged time intervals; (*4*) continuous removal of volatile products and rapid recovery of solid residue.

The cellulose samples were raised to the pyrolysis temperature in 1 min. and were kept isothermal within ± 0.12°C. throughout the length of all the runs. The temperature variation throughout the pyrolysis chamber at any one time was no greater than 0.1°C. Accumulation of the degradation products in the chamber was prevented by continuous removal of the volatiles through a vent and by changing the fluidizing medium with each cellulose sample. The pyrolyzed sample was recovered from the reaction chamber in 5 sec. or less at the conclusion of each heating period.

The arrangement of the pyrolysis chamber and the outer fluidized bath is shown in Figure 1. The heavily insulated external bath was fluidized by preheated air at a pressure of 3–4 psig. Removal of the preheater oven (110°C.) from the system resulted in temperature variation of 1.0°C. in the region in which the sample was located. In addition to the 750-w. heating element, precise temperature control in the main bath was attained by a 40-mil platinum wire wound on a ceramic rod and immersed in the fluidized medium. Voltage supplied to the heater was regulated by a mercury thermoregulator.

The pyrolysis unit (comprised of the sample-loading chamber and the reaction chamber) was constructed of glass. The loading chamber consisted of a sample-bottle holder and stainless-steel, spring-operated forceps. The reaction chamber was constructed from a 50-mm. sintered-glass funnel. It contained 60–85 mesh thoroughly cleaned Monterey sand, and a 30-mil nichrome-wire basket, a chromel–alumel thermocouple, retractable gas vent, and a nitrogen-purging inlet. The reaction chamber was fluidized by preheated 99.997% pure nitrogen with an approximate flow rate range of 15–25 l./min., depending upon the temperature.

Experimental Procedure

Disks (2.0 cm. in diameter) of α-cellulose containing from 0.11 to 0.14% ash were cut from cellulose sheets 0.030 in. thick. To remove any adsorbed oxygen and water, each sample was evacuated for 30 min., then dried to a constant weight in nitrogen in the presence of phosphorus pentoxide and transferred in a covered, tared weighing bottle to the loading chamber. It was then placed in the reaction chamber (Fig. 1). Five
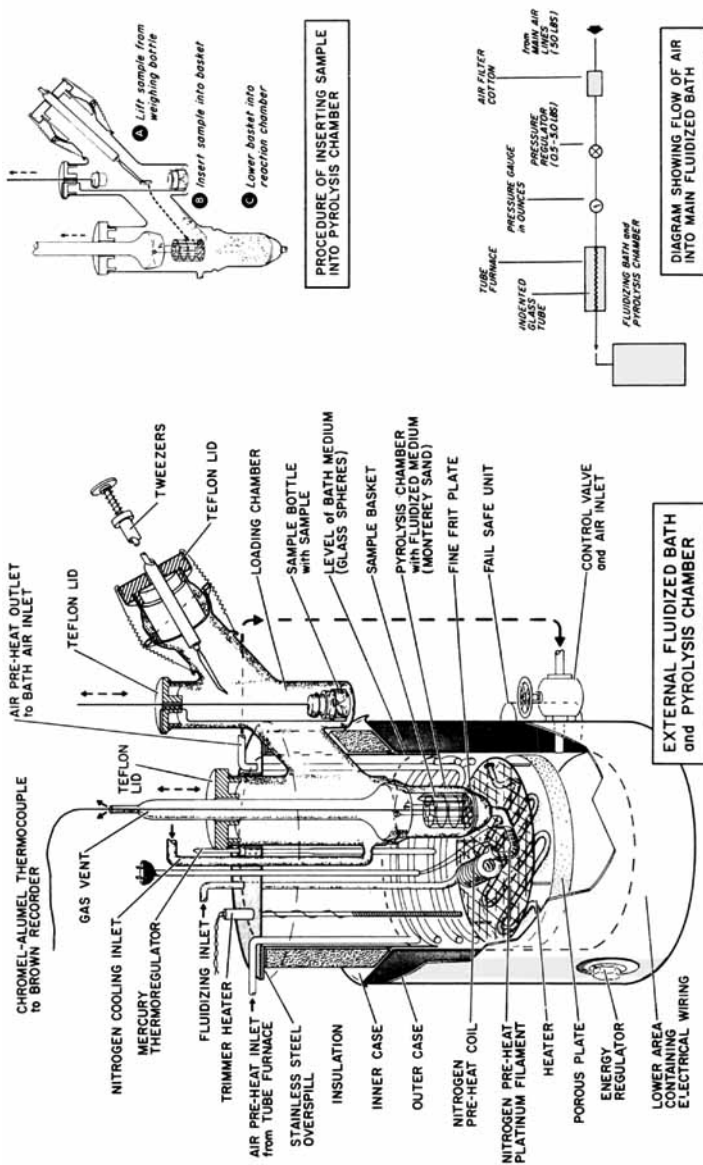
Fig. 1. Apparatus for the study of isothermal degradation of cellulosic materials.

temperatures within the range of 250–298°C. were chosen. In addition, some samples were preheated at 250°C. for 90 min. before the subsequent pyrolysis at 298°C. This step was chosen for studying the effect of preheating on char formation. Most of the runs were made in duplicate and varied from 10 minutes to 50 hours in duration. At the end of each run the sample residue was removed from the reaction chamber returned to its weighing bottle, desiccated, and reweighed to obtain the amount of sample converted into volatiles. The pyrolyzed sample was then divided into three fractions: (1) the water-soluble fraction, (2) the hydrolyzable fraction separated by Sacman's hydrolysis procedure,[13] and (3) the unhydrolyzable material.

The hydrolyzable material was subjected to Mendel's glucose analysis.[14] The amount of glucose observed was compared to that obtained from an unpyrolyzed cellulose sample in order to determine the percentage of residual or undecomposed cellulose remaining in the pyrolyzed specimen.

RESULTS AND DISCUSSION

The conditions and results of the pyrolysis experiments are shown in Table I. All percentages of the residual components are based on the weight of the original dry cellulose sample. The tabulated percentage of the unhydrolyzable material in the last column is obtained by taking the difference between column 4 and the sum of columns 5 and 6.

To prove that the rate of weight loss was not influenced by either oxidation or erosion, two preliminary experiments were performed. The results of the first (Fig. 2) indicate that no significant increase in the rate of decomposition occurs until oxygen contamination of the nitrogen exceeds 0.5%. Since the nitrogen used in this investigation was 99.997% pure, the possibility that oxidative decomposition accompanied pyrolysis was ruled out. The results of the second experiment showed that when samples (pyrolyzed at 298°C. for 3 hr.) were held in the reaction chamber at room temperature for 6 hr., the resulting weight change was only 0.008%. Therefore, the influence of erosion upon the rate of weight loss was assumed to be negligible.

Figure 3 is a plot of both the weight and glucosan-loss data at 288°C. After an abrupt drop in both the weight and the glucosan units at the beginning of the pyrolysis, both curves have a linear region in which the rate of decay is constant, indicating a zero-order reaction. After 70% of the cellulose has decomposed, the rate of decomposition decreases until the cellulose is completely depleted, while the residual weight begins to decay exponentially toward a constant value of about 15%.

The initial drop in weight increases with temperature from 2% at 250°C. to 6.5% at 298°C. Similar weight losses, observed during measurements in an inert atmosphere,[10] have been attributed to the loss of adsorbed moisture or reactions with trapped oxygen in the material. In order to minimize these sources of errors, the samples were first vacuum-desiccated and

TABLE I
Pyrolysis of α-Cellulose in Nitrogen

Temperature, °C.	Duration, hr.	Dry weight original sample, g.	Residual weight of pyrolyzed sample, %	Water-soluble material, %	Residual cellulose, %	Unhydrolyzable material, %
250	1	0.1838	97.12	0.81	92.76	3.55
	2	0.1845	96.37	2.87	89.26	4.24
	4	0.1859	93.62	1.49	85.29	6.84
	8	0.1796	90.76	1.56	80.07	9.13
	13	0.1847	87.06	1.41	74.98	10.67
	39	0.1850	72.49	0.97	46.10	25.42
	50	0.1914	66.25	2.62	40.02	23.61
262	1	0.1878	95.16	4.42	87.91	2.83
	4	0.1814	88.21	2.06	79.60	6.55
	25	0.1837	61.35	—	39.19	22.16
	46	0.1837	38.76	—	9.47	29.29
276	0.166	0.1812	96.42	0.86	89.95	5.61
	0.333	0.1799	95.72	0.44	88.82	6.46
	0.664	0.1844	92.30	0.71	83.73	7.86
	1	0.1825	90.14	—	80.00	10.14
	2	0.1732	85.86	0.54	68.12	17.20
	4	0.1827	74.17	0.44	55.33	18.40
	8	0.1865	54.16	—	27.23	26.93
	13	0.1809	37.48	—	7.90	29.58
	17	0.1764	27.16	—	—	27.16
	22	0.1859	20.82	—	—	20.82
	26	0.1795	18.90	—	—	18.90
	32	0.1792	17.58	—	—	17.58
288	0.333	0.1817	90.48	—	84.70	5.78
	1	0.1842	82.08	—	74.53	7.55
	1.664	0.1797	73.73	—	57.04	16.69
	2	0.1877	66.87	—	50.98	15.89
	2.498	0.1832	63.21	—	43.78	19.43
	3	0.1790	55.64	—	33.80	21.84
	4	0.1843	41.35	—	19.47	21.88
	5.250	0.1829	34.88	—	9.63	25.25
	6	0.1778	26.60	—	0.0523	26.55
	7	0.1850	22.10	—	—	22.10
	10	0.1819	15.89	—	—	15.89
	12	0.1881	15.79	—	—	15.79
298	1	0.1814	65.93	—	46.30	19.63
	2	0.1834	40.52	—	13.74	26.78
	3	0.1849	27.59	—	—	27.59
	6	0.1880	18.09	—	—	18.09
	0.084	0.1868	93.23	1.21	90.68	1.34
	0.252	0.1805	90.36	—	80.00	10.36
	0.504	0.1892	82.35	—	71.51	10.84
Preheated at 250° for 90 min.	0.504	0.1780	81.86	1.37	72.47	8.02
	1	0.1856	72.25	1.93	54.14	16.18
	3	0.1829	32.48	0.50	0.05	31.93
	6	0.1859	21.95	—	—	21.95

then dried in nitrogen to a constant weight prior to the pyrolysis. Even if moisture were still present, neither the dependence of the weight loss on temperature nor the rapid decomposition of the cellulose could be explained simply by the loss of water.

Figures 4 and 5 show the residual weight, and Figure 6 shows the glucosan units remaining as a function of time for all temperatures over a limited
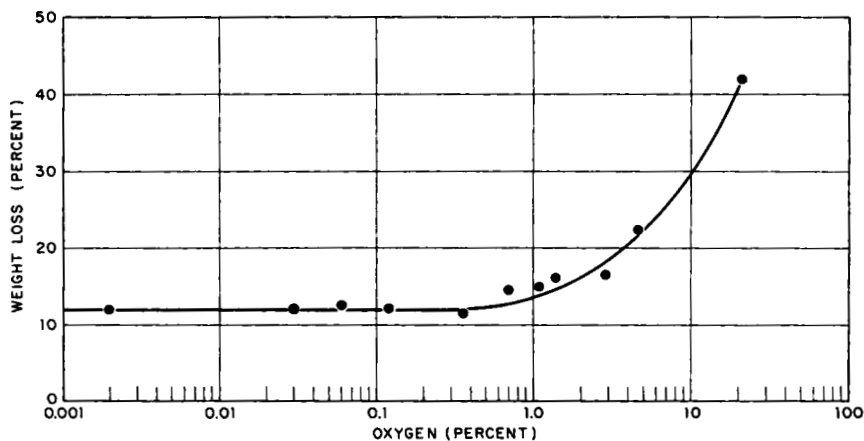

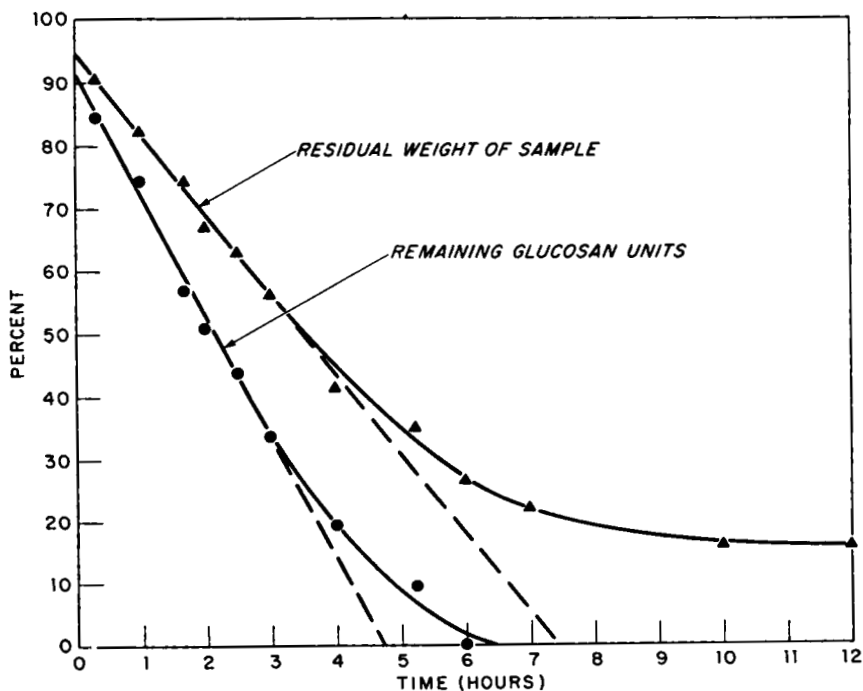Fig. 2. Effect of oxygen on the rate of pyrolysis of cellulose at 270°C. for 40 min.

Fig. 3. Pyrolysis of α-cellulose in nitrogen at 288°C.

time interval. Although the general shape of the curves is the same as for 288°C., the extent of the linear region of decomposition increases with temperature. At 250 and 262°C. it seems to be so short that the present measurements cannot establish whether a linear region definitely exists.
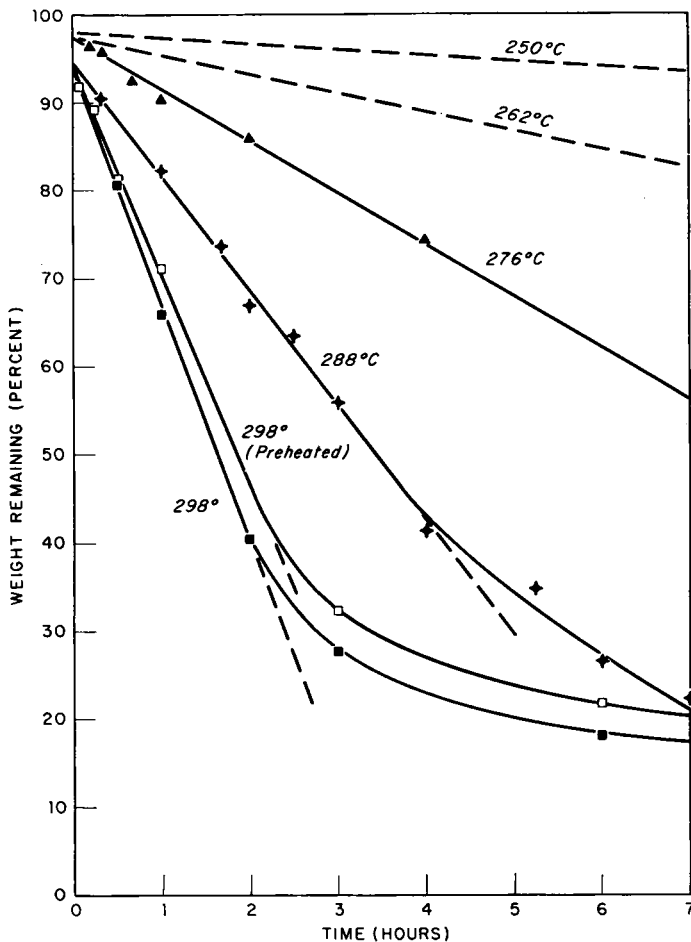
Fig. 4. Residual weight of samples as a function of time for all temperatures over a limited time interval.

Figures 4 and 6 also show the effect of preheating the samples at 250°C. for 90 min. on char formation and rate of glucosan loss during subsequent pyrolysis at 298°C. A greater decrease in both the weight loss and glucosan loss is observed in the preheated samples during the initial first hour of heating at 298°C. than during the subsequent hours of pyrolysis. Thus, heating for 1 hr. at 298°C. results in a decrease in weight loss of 6% and glucosan loss of 8%, whereas pyrolysis for 6 hr. at 298°C. produces a 4% decrease in weight loss accompanied by an increase in char of about 4%. The observed overall increase in the char formation tends to support the
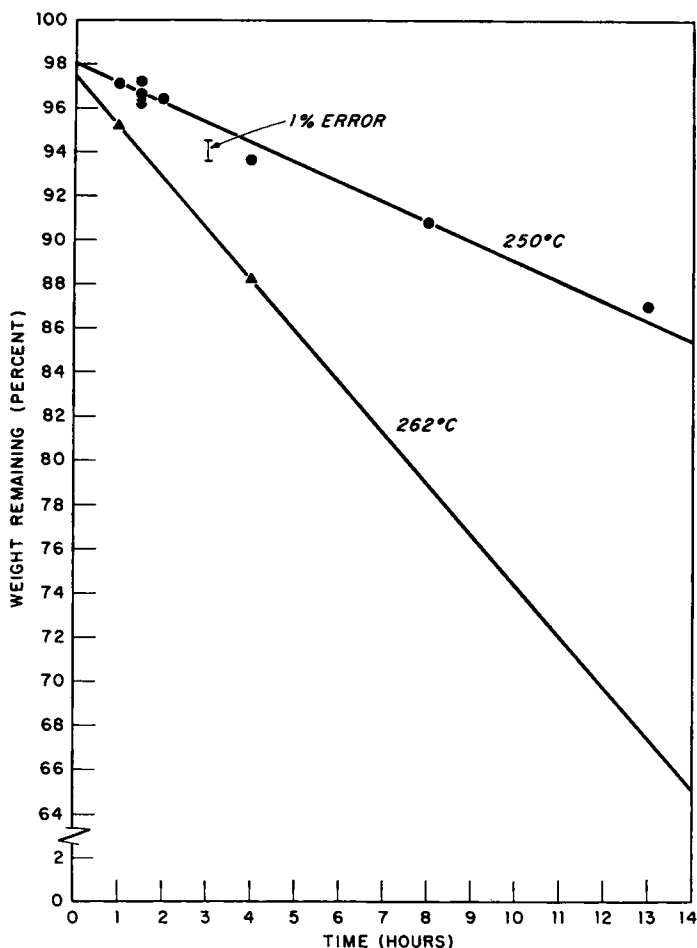
Fig. 5. Residual weight of samples as a function of time at 250 and 262°C. over a limited time interval.

findings of Kilzer and Broido,[15] who stated that a cellulose sample first heated for a day at 250°C. forms about three times as much char when subsequently heated at 400°C. as does a sample heated directly to 400°C.

Figure 7 shows both the rates of volatilization and glucosan loss. The rates of volatilization were determined from the zero-order region shown by Figures 4 and 5. The initial rates of decomposition for 276°C. and above were found from the linear regions of Figure 6 and those at 250° were taken from the semilogarithmic plot of remaining glucosan units in Figure 8. A single activation energy of 42 kcal./mole was determined for both the volatilization and decomposition for the 250–298°C. range.

It was found that the difference between the remaining weight of cellulose heated at any of the three highest temperatures and the weight of the final residual char fell off exponentially with time as shown in Figure 9.
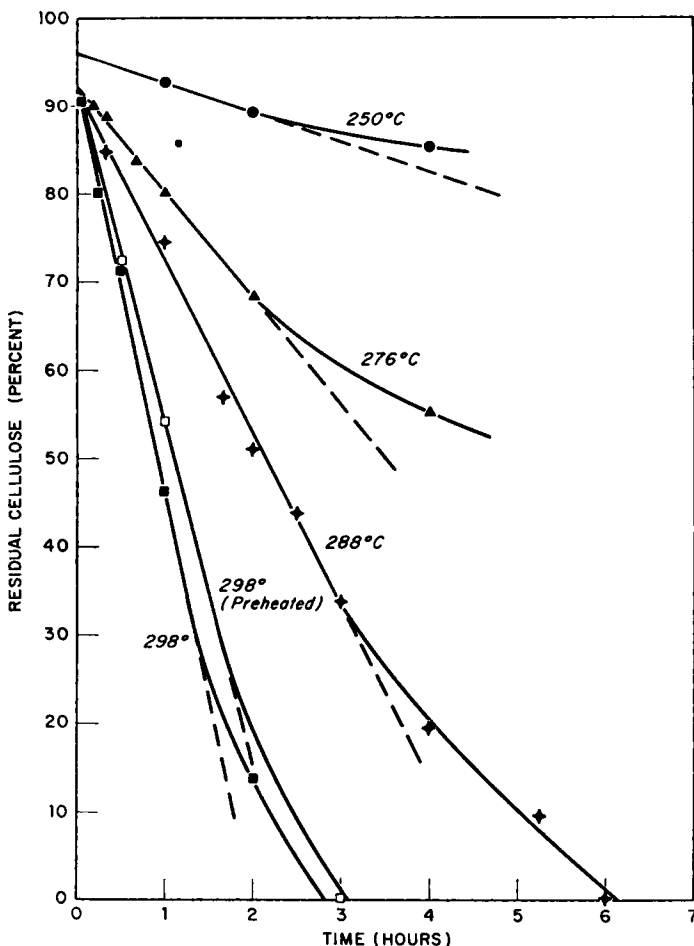
Fig. 6. Residual glucosan units in samples as a function of time for all temperatures over a limited time interval.

The points obtained early in the pyrolysis show a definite departure from the straight line.

While Figure 4 demonstrates a zero-order reaction during the first part of the pyrolysis, Figure 9 shows that this changes to first-order in the later part of the pyrolysis, and leads to a constant char of about 16% for temperatures of 276, 288, and 298°C. A nearly constant weight of 23% was attained after 172 hr. of pyrolysis at 250°C. as shown in Figure 10. Upon subtracting 23% from the data at 250°C., all of the points fit a straight line on semilog paper, suggesting that the weight loss is first-order throughout the pyrolysis at this temperature.

The results of the thermal degradation studies of wood-derived cellulose in nitrogen agree well with data taken by other observers on cotton cellulose in a vacuum. The apparent discrepancy between our activa-

tion energy and the 50 kcal./mole activation energy reported by Mador-sky[16] is not due to a disagreement in data but rather to a different means of calculation.   His value is based on weight-loss rates taken near the middle of the pyrolysis range without taking char formation into account. Indeed, the overall activation energy calculated from rates obtained by
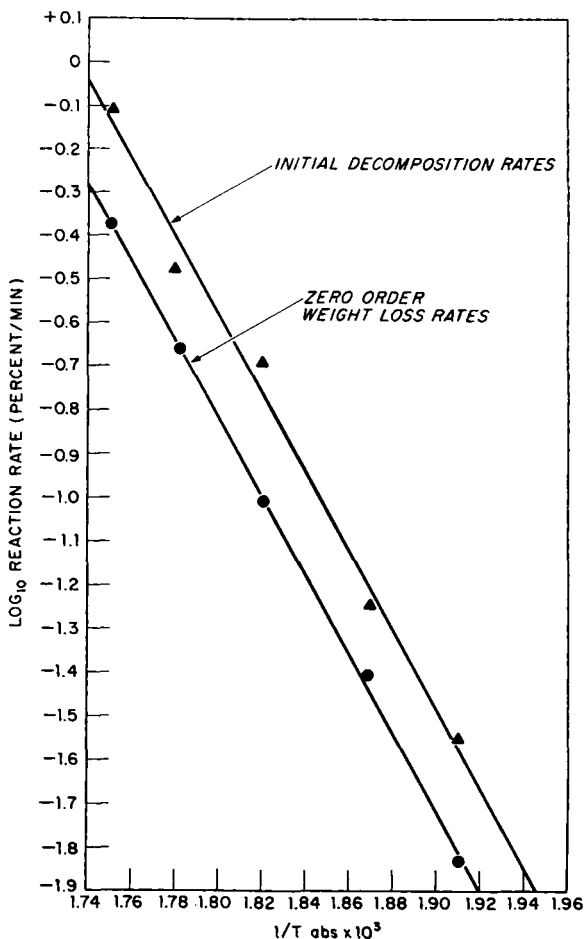

Fig. 7. Activation energy of thermal degradation of cellulose based on zero-order weight-loss rates and initial decomposition rates.

using the best fit of the present weight-loss data on a semilog plot, ignor-ing sizable deviations at the beginning and the end of the pyrolysis, was 50 kcal./mole.   Such a procedure, however, washes out the very details that need to be elucidated in the search for a workable mechanism of pyrolysis.

    After some lapse of time from the beginning of the pyrolysis, Mador-sky's[16] data on cotton also exhibit linear regions whose rates are repro-duced in Figure 11 for comparison with the present data.   The decom-

position rate of cotton cellulose measured at 300°C. by Golova[11] is also displayed on the same graph.

There are, however, distinct and unexplained differences in the behavior of the two types of cellulose at the beginning of the pyrolysis, where initially slow rates were observed for cotton, rather than an abrupt change in
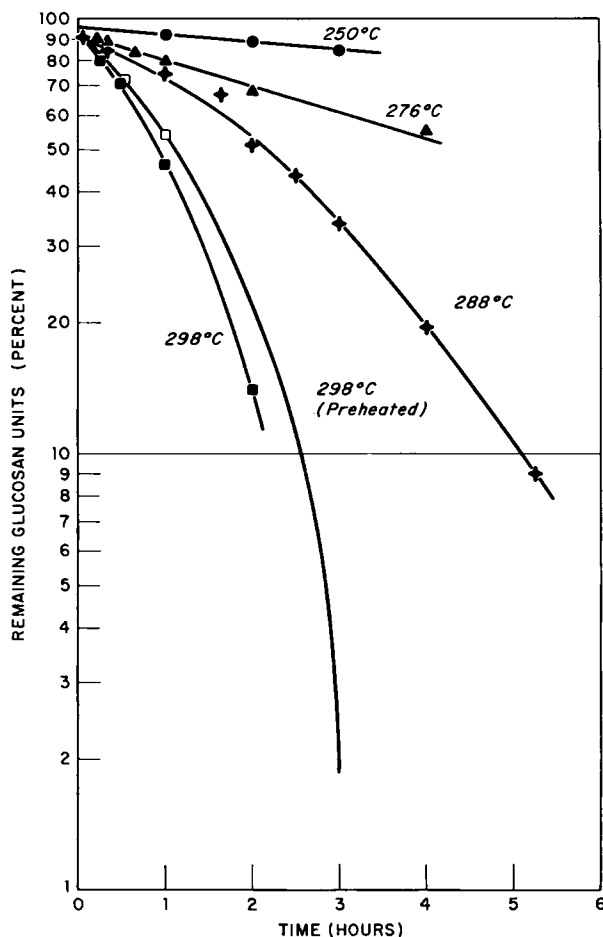

Fig. 8. Residual glucosan units in samples as a function of time for all temperatures over a limited time interval on a semilog scale.

weight and composition, followed by a constant and then monotonically decreasing rate as observed in this research.

Tang and Neil[12] observed a zero-order weight loss by TGA up to 310°C., where the total loss was 15% on Whatman grade 1 chromatography paper, which was at least 99.3% pure cellulose. Their observed volatilization rates in vacuum were about three times as great as those of the present experiments with a resulting activation energy of 34 kcal./mole.
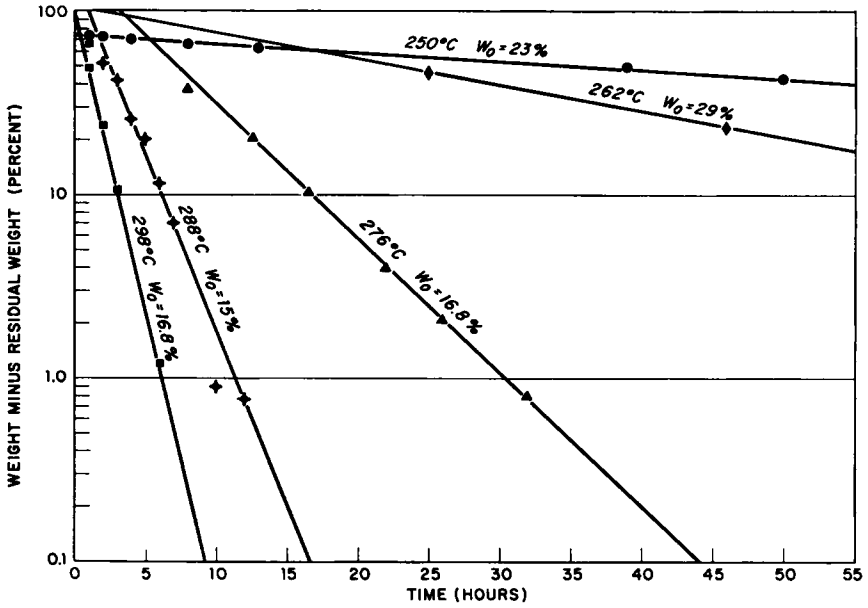
Fig. 9. Difference between the remaining weight of samples and the weight of the final residual char as a function of time on a semilog scale.
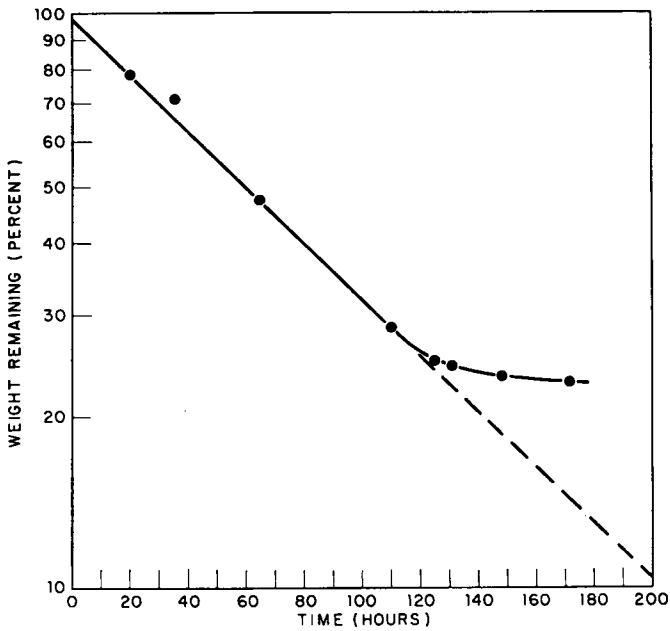

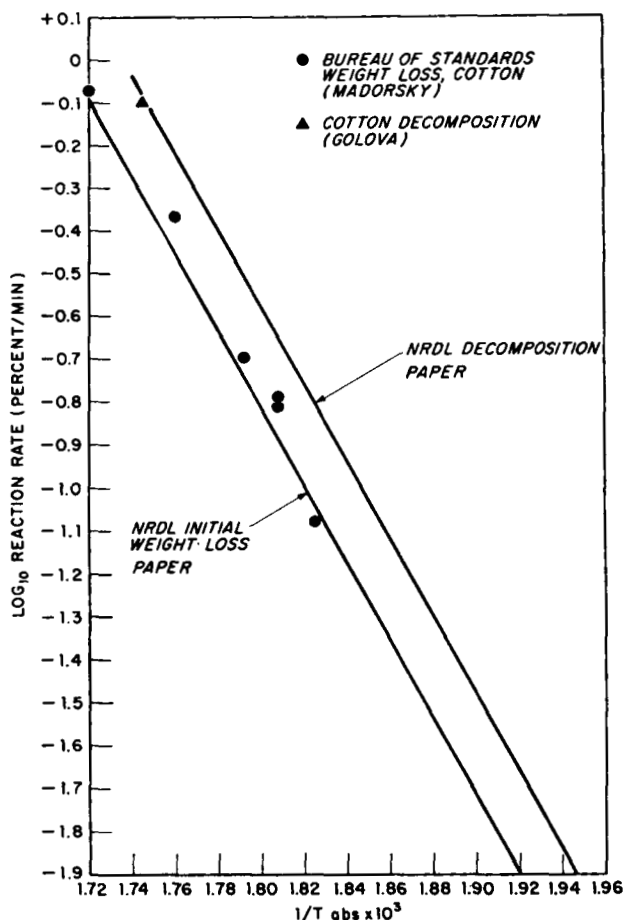Fig. 10. Residual weight of samples as a function of time at 252°C. for 172 hr.

Fig. 11. Comparison of published rates on cotton with NRDL data on α-cellulose paper.

This discrepancy might be resolved if the very rapid initial weight loss were taken into account. At 300°C. their accumulated weight loss is no greater than the initial weight loss observed at 298°C. in the present experiment, and hence the rates and activation energies determined from the curves of Figures 4 and 5 could not be expected to apply to their TGA data. In fact, it may be necessary to measure the very rapid rates of pyrolysis and their extent as a function of temperature before we can correlate all isothermal pyrolysis and TGA data.

CONCLUSIONS

(1) The double fluidized bath worked very satisfactorily for the study of the isothermal pyrolysis of cellulose in nitrogen at temperatures ranging from 250–300°C.

(2)   There are three distinct stages of pyrolysis at each temperature. Firstly, there is a rapid decomposition and weight loss occurring in a time interval used in this study.   The extent of this transient pyrolysis increases with an increase in temperature.   Secondly, there is a range in which the decomposition and volatilization are essentially zero-order, and finally there is a region in which the volatilization follows a first-order expression leaving a char deposit which does not undergo further pyrolysis. The transition between the zero- and first-order behavior occurs at a greater degree of pyrolysis as the temperature is increased.   At 288°C., the initial volatilization leaves about 94% of the original weight and the zero-to-first-order transition occurs at about the point where 50% of the original weight remains.   The residual char is around 16% between 276 and 300°C. and is substantially greater at lower temperatures.

(3)   The initial weight loss is due to the decomposition of cellulose rather than simply a loss in adsorbed water.

(4)   The activation energy for the decomposition and volatilization is 42 kcal./mole for the 250–300°C. range in the zero-order stage.

(5)   The reported activation energy for volatilization depends on the region of the weight loss curve over which the determination is made.   An overall best fit of the present weight loss data on a semilog plot yielded a value of 50 kcal./mole which is in agreement with previously reported values in the literature.

(6)   The pyrolysis of cellulose is kinetically similar whether the cellulose is in the form of paper or cotton and whether the experiment is performed in a vacuum or in nitrogen.

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Résumé

Des échantillons d'alpha-cellulose, contenant de 0.11 à 0.14% de cendres, ont été soumis sous atmosphère d'azote à pyrolyse à température constante, dans un bain fluidisé à 250–298°C. Les résultats sont consignés sous forme de la partie volatilisée (basée sur les mesures de perte de poids) et décomposée (basée sur la perte de glucosane). Trois étapes distinctes sont observées au cours de la pyrolyse: (*1*) une période initiale de décomposition rapide et de perte de poids; (*2*) un domaine dans lequel la volatilisation et la décomposition sont d'ordre zéro; (*3*) une région dans laquelle la volatilisation suit une équation de vitesse de premier odre, avec formation de dépôt goudronneux, qui ne subit pas de pyrolyse ultéreure. Le degré de décomposition et de volatilisation au cours de l'étape d'ordre nul croît avec une augmentation de température. Une énergie d'activation unique de 42 Kcal/mole décrit à la fois les vitesses de décomposition et de volatilisation dans l'étape d'ordre nul sur le domaine entier des températures de 250 à 298°C.

Zusammenfassung

Proben von α-Zellulose mit einem Aschegehalt von 0,11 bis 0,14% wurden in einem fluidisierten Bad unter Stickstoff bei 250 bis 298°C isotherm pyrolysiert. Die Ergebnisse werden als Verflüchtigung (auf Grund von Gewichtsverlustmessungen) und Zersetzung (als Glukosanverlust) angegeben. Die Befunde lassen drei Pyrolysestufen erkennen: (*1*) eine Anfangsperiode mit rascher Zersetzung und Gewichtsverlust, (*2*) einen Bereich mit Verflüchtigung und Zersetzung nach nullter Ordnung und (*3*) ein Gebiet, in welchem die Verflüchtigung nach erster Ordnung erfolgt und einen, nicht mehr einer weiteren Pyrolyse fähigen Verkohlungsrückstand hinterlässt. Der in der Phase nullter Ordnung auftretende Zersetzungs- und Verflüchtigungsgrad nimmt mit steigender Temperatur zu. Zur Beschreibung der Zersetzungs- und Verflüchtigungsgeschwindigkeit in der Phase nullter Ordnung reicht im gesamten Temperaturbereich von 250 bis 298°C ein einziger Wert der Aktivierungsenergie von 42 kcal/Mol aus.