

Char Yield on Pyrolysis of Cellulose

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Whether the pyrolysis of cellulose is conducted in an inert medium or in air, partial pyrolysis at a lower temperature increases the char yield subsequently obtained after 1 h at 370°C. The results are consistent with a pyrolysis scheme in which two competing sequences of cellulose pyrolysis reactions are initiated by (1) an intermolecular dehydration leading to char formation and, in air, to glowing combustion; and (2) a char-free depolymerization leading, in air, to flaming combustion.

1. Introduction

In a recent publication [1], Shivadev and Emmons approximate the thermal degradation of cellulose by two reactions and, "for want of any compelling information", assume "that both pyrolysis reactions result in the same fraction, $\beta (= 0.2)$, of char". Such an assumption requires not only that low temperature char yields not deviate significantly from 20%, but that a "high-temperature pyrolysis", if conducted in an inert medium, also yield 20% char. Such a result would directly contradict the pyrolysis scheme [2,3] in which two competing sequences of cellulose pyrolysis reactions are initiated by (1) an intermolecular dehydration (i.e., a cross-linking) predominating at low temperatures and leading ultimately to char formation, and, in air, to glowing combustion; and (2) a char-free depolymerization predominating at higher temperatures and leading to combustible volatile products and, in air, to flaming combustion.

Our own investigations, among others, have established that the char yield from vacuum pyrolysis of cellulose samples depends on such factors as the ash content of the material [4], its crystallinity [5] and the quality of the vacuum [6]. Not surprisingly, the presence of oxygen greatly increases the weight loss on heating at relatively low temperatures [7]. Also, as pointed out by Shivadev and Emmons, sufficiently rapid heating to a high enough temperature leads to flaming combustion "which consumes everything" [1].

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At intermediate temperatures and atmospheric pressure, however, gas evolution as a result of pyrolysis of pure cellulose is sufficiently rapid to prevent significant air-solid contact, but yet not rapid enough to produce ignition [4]. Under such circumstances the char yield in air and in an inert medium, e.g., nitrogen, should not differ significantly. Further, such a result would imply that at even higher temperatures in air the pyrolysis reactions (uncomplicated by the high rate combustion process) would follow closely the results obtained in nitrogen. Consequently, measurements of the char yields from pyrolysis in nitrogen could be meaningfully applied to the high temperature behavior of cellulose in air.

The major difference between the two conflicting pyrolysis schemes is that the first attributes no "memory" to the sample, and the second requires that char yield at "high temperature" depends on the previous heating history of the sample—with yields increasing significantly if the sample is held at a lower temperature at which significant dehydration occurs. To distinguish between the two schemes, we conducted a few simple experiments.

2. Experimental

All pyrolyses were carried out in the central uniform-temperature region of a horizontal Heviduty 70-T tube furnace, 30 cm long and 3.2 cm i.d. The temperature of the furnace was controlled by a Hallikainen "Thermotrol" and was measured

continuously by a 0.08 cm in diam iron-constantan thermocouple. For pyrolysis in air, the glass reaction tube was simply left open to the atmosphere. Two inert atmospheres were used: vacuum with continuous pumping (10^{-4} mm Hg, rising by an order of magnitude during active pyrolysis) and flowing nitrogen (Liquid Carbonic, purity > 99.997%, at a flow rate ~ 10 ml/min vented to the atmosphere). The cellulose samples were cut from Whatman # 41H "ashless" filter paper (ash content < 0.01%) and weighed after drying in a vacuum oven for 2 h at 60°C . The experiments in air were repeated on similar samples that had been decrystallized by swelling in ammonia [5].

One series of experiments in nitrogen was performed by shredding about 100 mg of paper into a porcelain boat. The boat was inserted into a cold portion of the reaction tube. The tube was evacuated and flushed with nitrogen while the furnace was heated to the prescribed temperature. Then the boat was moved into position in the furnace magnetically.

All other experiments were performed with single sheets of paper, about 7 cm $\times$ 3 cm, mounted so as to provide minimum contact with a glass rod sample holder (Fig. 1). For most of these experiments the furnace was heated to the prescribed temperature, then the reaction tube was inserted with the sample in place. To speed up the heating of the sample, several additional experiments in air were done with the reaction tube in the furnace and heated to temperature before the sample and holder were inserted.

Cellulose decomposes rapidly at temperatures above 350°C , while flaming combustion is associated with appreciably higher temperatures. Therefore, the pyrolysis conditions that we chose were 1 h at 370°C . The dry samples were weighed, heated for 1 to 21 h at a pretreatment temperature of 230 to 370°C , cooled and reweighed, and then reheated for 1 h at 370°C . Residual weights after pretreatment and char weights after the standard pyrolysis treatment were computed as percent of the original cellulose.

3. Results

The first two experiments in Table 1 both show that pyrolysis at 370°C was essentially complete

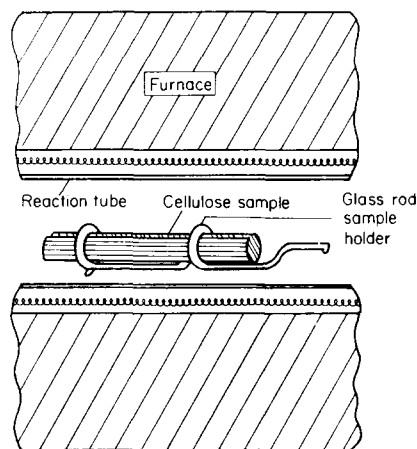


Fig. 1. Apparatus for cellulose pyrolysis.

after 1 h, with only a small additional weight loss occurring during a second hour of heating. Char weights for the two experiments are somewhat different, suggesting that the weight loss in the two methods of heating are not identical. The results in air with both the ordinary and the decrystallized samples support the contention that these differences are due to differences in the rate of heating up to the pyrolysis temperatures.

If the cellulose is preheated under nitrogen for 21 h at 230°C with a resultant 5% weight loss and the residue is then heated for 1 h at 370°C , the char yield is somewhat higher than it would have been without preheating. A one hour pretreatment at 250°C , with a similar 5% weight loss, provided a similar ultimate char yield. As the duration of pretreatment at 250°C increased, with consequent increasing weight loss during pretreatment, so did the ultimate char yield. At 275°C , pretreatment for 21 h resulted in the expected increase in weight loss during pretreatment—and an even greater char yield at 370°C .

Heating in vacuum directly to 370°C provided a significantly lower char yield than that obtained in nitrogen. However, pretreatment at 250°C in vacuum resulted in a weight loss comparable to that in nitrogen, with a comparable ultimate char yield. When the samples were heated directly to 370°C in air, the char yield was essentially identical to that in nitrogen even though, as expected, heating in air for 21 h at 250°C resulted in a much

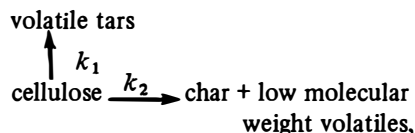
greater weight loss than in the inert media. Finally, and again as expected, the lowest char yields were obtained by heating the decrystallized cellulose directly to 370°C.

4. Discussion

Under the conditions of these experiments, the char yield on heating cellulose for 1 h at 370°C varied by a factor of five. The lowest yield, 5.6%, was obtained for the ammonia-swelled material heated in air in the preheated reaction tube. However, the results obtained with the slower methods of heating samples directly to 370°C imply that essentially the same char yield would have been obtained in an inert medium had we been able to preheat the reaction tube without heating the sample under those conditions. Since the ammonia-swelled cellulose rapidly regains crystallinity on heating [8], pretreatment of this material at the lower temperatures would be expected to give the same high char yields as obtained for the unswelled samples.

Even for a single method of heating unswelled cellulose under nitrogen, the char yield was increased by a factor of $2\frac{1}{2}$ with pretreatment at the lower temperatures. This result contradicts the assumption [1] of two pyrolysis reactions yielding the same fraction of char. Instead, the results of these experiments are quite consistent with the alternative pyrolysis scheme, with zero residue in the depolymerization process and approximately 36% char yield in the reaction sequence initiated by dehydration [3].

Shivadev and Emmons [1] were interested only in an approximation to the conceded "chemically complex degradation reactions". Under many circumstances, reaction yields of $18 \pm 6\%$ justifiably may be considered essentially constant. For cellulose decomposing by a scheme such as we propose, however, such a spread is far from trivial. This can be seen by considering the scheme in its simplest form, i.e., by lumping the consecutive steps in each of the two competing processes into a single, overall, first-order reaction. Thus, at any temperature T



where k_1 and k_2 are the rate constants for the competing processes.

If a sample of initial weight 100% is heated isothermally for time, t , to give a residual weight $W_{T,t}$, $W_{T,\infty} = 36\%$ when $k_1 \ll k_2$. In general,

$$W_{T,\infty} = 36k_2/(k_1 + k_2). \quad (1)$$

Thus, the range from 12% to 24% char yield corresponds to the range from $k_1 = 2k_2$ to $k_2 = 2k_1$ and, thus, in air can cover a change from 2/1 in favor of flaming combustion to 2/1 in favor of glowing. Our results show that changes even beyond this range can be obtained by varying the temperature history of the sample before ignition.

Within the accuracy of the data, the above pyrolysis scheme provides a straightforward means of calculating char yield over the temperature range of these experiments and permitting reasonable extrapolation to a broader range of temperature histories. For this purpose the actual values of k_1 and k_2 are not needed; it is sufficient to have their ratio at any temperature of interest,

$$F_T = (k_1)_T/(k_2)_T. \quad (2)$$

Taking $W_{370,\infty}$ as 12%, then, Eqs. (1) and (2) give $F_{370} = 2$. If a sample is partially pyrolyzed at some lower temperature, and the residue, $W_{T,t}$, assumed to consist only of unpyrolyzed cellulose and char, is then heated at 370°C, the ultimate char yield can be shown to be given by

$$\begin{aligned} Y &= .12W_{T,t} \\ &+ (1 - .12) \left[\left(\frac{k_1 + k_2}{k_1 + (1 - .36)k_2} - 1 \right) (100 - W_{T,t}) \right] \\ &= \frac{31.7}{F_T + .64} - \left[\frac{.317}{F_T + .64} - .12 \right] W_{T,t}; \\ Y &\leq W_{T,t} \leq 100. \end{aligned} \quad (3)$$

Empirically, the results in Table 1 for experiments in nitrogen at atmospheric pressure in the temperature range 230-275°C agree fairly well (Fig. 2) with a constant value $F_T = .08$, corresponding to

$$Y = 44 - .32W_{T,t}; \quad 33.3 \leq W_t \leq 100. \quad (4)$$

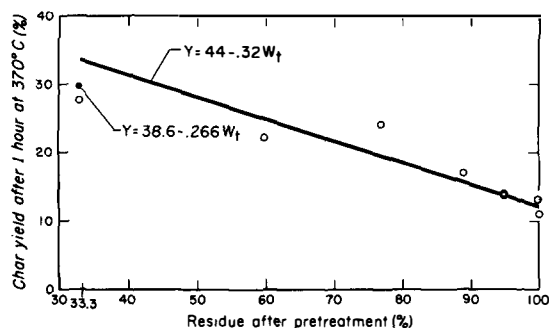


Fig. 2. Comparison of experimental char yields with the empirical equation $Y = 44 - .32W_t$ (line) and, for 275°C, with $Y = 38.6 - .266W_t$ (point).

Somewhat greater accuracy may be obtained by estimating F_T for each temperature. This can be done readily if one has experimental values at two temperatures — preferably bracketing the temperature range of interest. The Arrhenius equation for F_T is simply

$$F_T = A \exp(-E/RT), \quad (5)$$

in which $A = A_1/A_2$, the ratio of the pre-exponential factors of the competing reactions, and $E = E_1 - E_2$, the difference in their activation energies. Thus, for example, combining the value of F_T at 370°C with $F_{226} = .0369$ from [3], one obtains

$$F_T = 2.05 \times 10^6 \exp(-8900/T).^\circ \quad (6)$$

Equation (3), then, ranges from

$$Y = 38.6 - .266W_t; \quad 30.5 \leq W_t \leq 100 \quad (7)$$

for pretreatment at 275°C to

$$Y = 46.5 - .345W_t; \quad 34.5 \leq W_t \leq 100 \quad (8)$$

for pretreatment at 230°C. As is evident from Fig. 2, Eq. (7) is better than Eq. (4) for estimating the experimental result at 275°C. At still higher temperatures such improvement over Eq. (4) becomes increasingly important. Thus, for the isothermal experiment at 370°C, Eq. (4) gives a char

yield of 40%, while Eq. (3) with $F_T = 2$ of necessity gives a char yield identical with the experimental value of 12%.

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Appendix

Elemental analysis of the pyrolysis residue would be expected to provide additional information concerning the pyrolysis mechanism. Unfortunately, the accuracy attainable is limited by two major complications. First, the analytical procedures require combustion of the samples; thus the analyses determine carbon and hydrogen—with oxygen obtained only by difference. Second, facilities are not usually available for handling, weighing, and analyzing the sample without exposure to the atmosphere with the resultant absorption of atmospheric gases—primarily water. As a result, measurements of replicate samples at a single commercial analytical laboratory or of different fractions of the same sample at different analytical laboratories differed by more than 5% in the carbon measurement and by as much as 1% in the hydrogen measurement.

The results in Table 2 are consistent in the sense that they were analyzed by the same individual in a single laboratory. Sample preparation involved weighing the dry sample, then letting it equilibrate with the atmosphere, and reweighing before submission for analysis. The corrected values assume that weight increase was due to moisture alone and that no further weight change occurred during subsequent handling of the sample. The results show the expected increase in carbon content with increasing weight loss on pyrolysis. Even under the most severe pyrolysis conditions used, however, a significant residual hydrogen content is found.

TABLE 1
Representative Char Yields after Heating Cellulose for 1 Hour at 370°C

Pretreatment Time(h)	Pretreatment Temp.(°C)	Residue after pretreatment (%)	Char after heating Residue 1 h at 370°C(%)
Ambient atmosphere: Nitrogen			
1 ^a	370	11.5	11.0
1 ^b	370	13.1	12.7
21 ^a	230	95	13.8
1 ^a	250	95	13.7
2 ^a	250	89	17.0
21 ^b	250	60	22.1
21 ^a	245	77	24.2
21 ^a	275	33	27.6
0 ^b	—	100	13.1
Ambient atmosphere: Air			
0 ^b	—	100	13.2
0 ^c	—	100	9.5
21 ^b	250	30	19.1
Ambient atmosphere: Vacuum(10 ⁻⁴ mm Hg)			
0 ^b	—	100	8.5
21 ^b	250	63	20.1
Decrystallized cellulose; Ambient atmosphere: Air			
0 ^b	—	100	8.8
0 ^c	—	100	5.6

^a Furnace and reaction tube preheated; sample in porcelain boat moved into position with magnet.

^b Furnace preheated; tube inserted with sample in place.

^c Furnace and reaction tube preheated; sample and glass rod holder inserted with tube in place. In this mode of heating, an additional 3 mg of char was found spread fairly uniformly along the glass rod sample holder.

TABLE 2
Elemental Analysis of Pyrolysis Residue

Heating regime in Nitrogen	Residual weight(%)	Elemental analysis		Corrected for moisture	
		C(%)	H(%)	C(%)	H(%)
Original sample	100	42.9	6.3	44.4	6.2
35 h at 235°C	88	45.4	5.9	47.2	5.6
46 h at 250°C	46	61	4.5	66	4.0
23 h at 275°C	33				
+ 1 h at 370°C	28	73	3.4	78	2.9
46 h at 220°C	96				
+ 1 h at 370°C	15	76	4.1	83	3.5
2 h at 370°C	11	79	3.0	86	2.4
4 h at 500°C	6	81	3.3	95	2.0

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