

The Kinetic Behavior of Intermediate Compounds During the Pyrolysis of Cellulose

The interesting paper by Lipska and Parker¹ provides further insight into the kinetics of the pyrolysis of cellulose in two ways. Firstly, the use of a fluidized bed technique brings the sample of cellulose rapidly to the required constant temperature, so that the pyrolysis can be studied from its inception. Secondly, the information on the loss of weight of a sample heated for a known time at a constant temperature is supplemented by analysis of the pyrolyzed sample for its residual cellulose content.

The general progress of the pyrolysis at a particular temperature is shown to be as follows:

(1) The residual weight of the pyrolyzed sample decreases steadily from 100% to about 16% of the original weight of the sample.

(2) The weight of residual cellulose decreases steadily from 100% to 0% of the original weight of the sample.

(3) The weight of residual matter other than cellulose, i.e., the difference between (1) and (2), increases from 0% to a maximum value of 25%–30% and then decreases to about 16% of the original sample weight.

The pyrolysis of cellulose to a residual char can therefore be considered in two stages:

1st Stage: cellulose → nonvolatile intermediates + volatiles

2nd Stage: nonvolatile intermediates → nonreacting solid residue + volatiles

A first look at the data suggests that in the first stage of the process, approximately 30% of the cellulose reacted is converted to volatile matter and 70% to nonvolatile intermediates. The second stage is therefore an important one as it controls the rate of evolution of the majority of the evolved volatile matter and the rate of formation of the residual char. If the first stage proceeds much more rapidly than the second stage, then the overall rate of loss of weight will be controlled by the kinetics of the second stage reactions and vice versa.

Lipska and Parker¹ provided kinetic analyses for the conversion of cellulose and for the overall weight loss. In the present note the author uses the data of Lipska and Parker to examine the kinetics of the second stage in the pyrolysis of cellulose.

The variation in the weight of nonvolatile intermediates present at any time is obviously controlled by the relationship between the rate of their formation from cellulose and the rate of their conversion in the second stage of the pyrolysis. Estimates of the kinetics of these two reactions can be obtained from the available data.

KINETICS OF THE 1ST STAGE IN THE PYROLYSIS OF CELLULOSE

In their analysis of the data for the rate of disappearance of cellulose from the samples, Lipska and Parker¹ observed that the initial stages of the reaction appeared to be governed by zero-order kinetics, but the later stages were not. In the present exercise the data were reexamined to seek a mathematical relationship valid for the entire reaction. It was found that assuming the order of reaction to be $1/2$ throughout the reaction gave a reasonable representation of the data. This is illustrated in Figure 1 where $(\% \text{ residual cellulose})^{1/2}$ is plotted against time.

Thus it will be assumed that the conversion of cellulose can be represented by

$$-\frac{dc}{dt} = K_1 c^{1/2} \quad (1)$$

where c = % of cellulose remaining after a heating time of t . Values of K_1 obtained from Figure 1 are given in Table I. These values give an apparent activation energy of 48 kcal/mole.

TABLE I

	Temperature, °C				
	250	262	276	288	298
$K_1, (\%)^{1/2}/\text{hr}$	0.14	0.28	1.06	2.70	6.10
$K_2, /\text{hr}$	0.027	0.066	0.166	0.455	0.700
$F, \%$			16.8	14.0	16.8

KINETICS OF THE FORMATION OF THE RESIDUAL CHAR

When the percentage of residual cellulose in the sample has dropped to zero (i.e., when the first stage of the pyrolysis is complete), the kinetics of the conversion of intermediate compounds to residual char may be studied independently. Data for this region are available for three of the operating temperatures studied by Lipska and Parker. The data can be represented by the first-order equation

$$-\frac{dw}{dt} = K_2(w - F) \quad (2)$$

where $w = \%$ of initial sample weight remaining after a heating time t , and $F =$ final residual weight (as $\%$ of initial sample weight).

Values of K_2 and F are given in Table I. The values of K_2 for temperatures of 276°C and greater were obtained as stated above. Those for 250°C and 262°C were obtained by extrapolation from the three experimental values, using an apparent activation energy of 42 kcal/mole.

In general, $w - c = i + r$, so that in the region where $c = 0$, $w = i + r$, where $i =$ weight of intermediates at time t (as $\%$ of initial sample weight), and $r =$ weight of nonreacting residue at time t (as $\%$ of initial sample weight).

If one assumes that 1 g of intermediates $\rightarrow B$ g of residue, it follows that $-B(di/dt) = dr/dt$ and $r = F - iB$. When $c = 0$, eq. (2) can be rewritten

$$-\frac{d}{dt}(i + r) = K_2(i + r - F)$$

so that

$$-\frac{di}{dt}(1 - B) = K_2i(1 - B)$$

and

$$-\frac{di}{dt} = K_2i. \quad (3)$$

Thus, with a constant fraction of the intermediate compounds converted to nonreacting residue, the conversion of the intermediate compounds is also first order with a rate constant of K_2 .

THE VARIATION IN THE PERCENTAGE OF INTERMEDIATE COMPOUNDS PRESENT

If one assumes that 1 g of cellulose $\rightarrow A$ g of intermediate compounds, then it follows from eq. (1) that the rate of formation of intermediate compounds is equal to $AK_1c^{1/2}$.

The simplest assumption to make concerning the conversion of intermediate compounds into nonreactive residue and volatiles is that eq. (3), determined for the final

stages of the process, is valid throughout the pyrolysis process. One then has, for $c > 0, t < t_1$,

$$\frac{di}{dt} = AK_1c^{1/2} - K_2i$$

and for $c = 0, t > t_1$,

$$\frac{di}{dt} = -K_2i.$$

The solutions of these differential equations, with $c = c_0$ and $i = 0$ at $t = 0$, and $i = i_1$ at $t = t_1$, the time when c becomes zero, are as follows:

$$t < t_1 \quad i = \left[\frac{AK_1}{K_2} \left(c_0^{1/2} + \frac{K_1}{2K_2} \right) (1 - \exp \{-K_2t\}) \right] - \frac{AK_1^2t}{2K_2} \quad (4)$$

$$t > t_1 \quad \frac{i}{i_1} = \exp \{-K_2(t - t_1)\} \quad (5)$$

The variation of r with time can also be calculated, assuming the fractional conversion of i to r to be B throughout the process:

$$r = B[A(c_0 - c) - i]. \quad (6)$$

Hence, the variation of $(w - c)$ with time is

$$(w - c) = i(1 - B) + BA(c_0 - c). \quad (7)$$

For each of the operating temperatures used by Lipska and Parker, $(w - c)$ was calculated as a function of t using eqs. (1) to (7) and the values of K_1 and K_2 given in Table I. The values of A and B were adjusted to give the best agreement between the calculated curve and the experimental points. There is the additional relationship $AB = F$ to be satisfied during this phase. The values selected for A and B are given in Table II, while the calculated and experimental variations of $(w - c)$ with time are shown in Figure 2. In the majority of cases the calculated function provides a good representation of the experimental data.

TABLE II

	Temperature, °C				
	250	262	276	288	298
A, %	70	70	65	56	54
B, %	33	33	26	25	31
F, %	23.1	23.1	16.8	14.0	16.8

DISCUSSION

The pyrolysis of cellulose to volatile products can be considered in two stages. The cellulose is initially converted to a certain proportion of volatile compounds which are evolved from the solid and to nonvolatile intermediate compounds. Simultaneously, the intermediate compounds undergo conversion to a nonreacting solid residue and more volatile compounds. Different kinetics relationships are applicable to these two stages. The conversion of cellulose appears to follow a $1/2$ -order relationship with an activation energy of 48 kcal/mole, while the conversion of intermediate compounds appears to follow a first-order relationship with an activation energy of 42 kcal/mole.

Combining the relationships for the formation and for the conversion of intermediate compounds gives expressions for the variation with time of nonvolatile compounds other than residual cellulose in the pyrolyzed samples. The calculated variation of this quantity agrees satisfactorily with the experimental data of Lipska and Parker¹ obtained at five different operating temperatures.

The calculations suggest that, at heating temperatures of 250–276°C, the initial conversion of cellulose yields 65%–70% of nonvolatile compounds and 30%–35% of volatile compounds. At temperatures of 288°–298°C, these figures are 54%–56% and 44%–46%, respectively. The greater yield of volatile products in this initial stage at higher temperatures may result from the increased volatility of any liquid products formed, or from the pyrolysis of cellulose being affected by the competition between alternative reactions, as discussed by Kilzer and Broido.² This trend, if it continued to higher temperatures, would mean that the overall weight loss of the samples was increasingly dominated by the kinetics of the initial conversion of cellulose.

In general, a partially pyrolyzed sample of cellulose will contain residual cellulose, nonvolatile intermediate compounds, and nonreacting residue. Any kinetics analysis based on the changes in the total weight of a sample necessarily averages the effects of large numbers of simultaneous and consecutive reactions. Even the description of cellulose pyrolysis in terms of two consecutive reactions, as considered in this note, shows that experimental variations such as the use of nonisothermal conditions will change the apparent kinetics based on overall weight loss, although the kinetics of the individual stages may be unaltered.

References

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