

## THERMAL DECOMPOSITION OF CELLULOSE

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Cellulose has been pyrolysed in nitrogen at two heating rates, and the rates of formation of total gases, and the oxides of carbon, have been measured. The quantities of products formed, and their first order kinetic parameters, are strongly dependent on the heating rate.

There has been a growing interest in the thermal degradation of cellulose during the past twenty years [1, 2], mainly because of its importance in the ignition of wood. Kinetic analyses of the overall reaction have been carried out by many techniques, including dynamic thermogravimetry and differential thermal analysis [e.g. 1, 3–9], measurement of evolved gases [10–12], density-change measurements [13], isothermal weight loss [7, 14, 15] and viscosity measurements on the pyrolysis residue [16]. Many kinetics studies have been recently reviewed by Okamoto [17], who shows that there is a large variation in reported kinetics parameters. Furthermore, the dynamic heating rates employed in the determinations were often two or three orders of magnitude lower than those occurring in burning processes, and so the resultant parameters may not be relevant to combustion conditions [10].

There are at least fifty nine volatile products from the decomposition of cellulose [14, 18–20]. As far as is known, there is no kinetic data available on the formation of products of the decomposition at the heating rates obtained in burning. This data is provided in the present study for the products carbon monoxide and carbon dioxide, as well as for the overall reaction.

### Experimental

1 g of  $\alpha$ -cellulose (Kipawa 97, 1 mm thick sheet cut into strips 2 mm  $\times$  10 mm) was heated under flow conditions in a silica tube 8 mm i.d. (Fig. 1). The inlet flow of nitrogen into the furnace was kept constant at 3.33 cm<sup>3</sup> s<sup>-1</sup>. The gases flowing out of the furnace were passed through a Cambridge filter to remove tarry material, and were analysed for CO<sub>2</sub> and CO using an A. E. I. MS2 mass spectrometer and a Bosch infra-red analyser type Efaw 215 respectively, as described previously [21].

The rates of formation of the products are quoted in moles<sup>-1</sup>, calculated assuming ideal gas behaviour of the flowing gases. In calculating the results, account has been taken of the transit time of the pyrolysis products from their formation region inside the furnace to their point of analysis (3.0 seconds). Further details of the technique, and calculations, are given in reference [22].

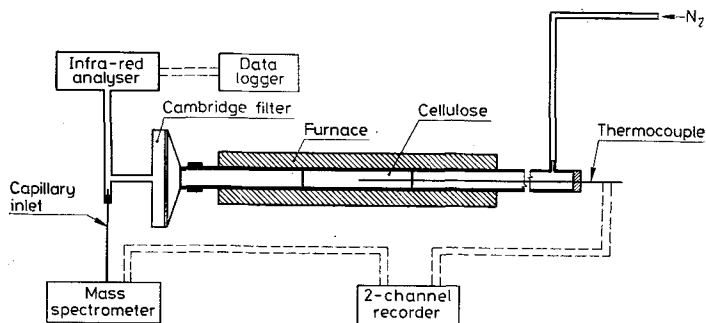


Fig. 1. Pyrolysis apparatus

With the thermocouple in a given position in the cellulose, each experiment was performed at least twice, and the results averaged. Experiments were always performed under three conditions:

(a) with the thermocouple at the linear and axial centres of the cellulose (note: the axial temperatures along the furnace lay within  $\pm 4^\circ$  of the mean for the temperature range and gas flow conditions used),

(b) with the thermocouple at the linear centre of the cellulose and 1 mm from the furnace wall,

(c) with the thermocouple at the linear and axial centres of the furnace, but with no cellulose present.

The cellulose was pyrolysed at two heating rates, referred to as the "slow" and "fast" heating rates.

## Results

### *The rate of increase in temperature*

The rates of increase in temperature of 1 g of  $\alpha$ -cellulose when heated in nitrogen at the slow and fast rates are shown in Fig. 2. At the fast heating rate ( $5-10 \text{ deg s}^{-1}$ ), where thermal equilibria is further from being attained, time-dependent effects are more apparent. The temperature in the centre of the cellulose initially rises very slowly up to about  $100^\circ$ , when the heat input is used mainly in evaporating the absorbed water from the cellulose. At about  $350^\circ-400^\circ$ , there is a second endothermic plateau region, where the rate of temperature increase in

the centre of the cellulose is reduced. This behaviour is also noticeable in the peripheral region of the cellulose at the fast heating rate, and in the centre of the cellulose at the slow heating rate ( $1.1 \text{ deg}^{-1}$ ). The same endothermic region has also been observed in the centre of pyrolysing  $\alpha$ -cellulose in other studies [3, 6, 8, 10, 13]. The reason for the heat absorption at  $350^\circ\text{--}400^\circ$  is not clear, but suggested possibilities are given below.

1. Relaxation of hydrogen-bonding in the supramolecular structure of the cellulose prior to the depolymerization of the cellulose polymer chains [10].

2. Physical interactions, such as a coupling between thermal and mass diffusion, which can decelerate the local heating rate in the centre of a solid [13, 23].

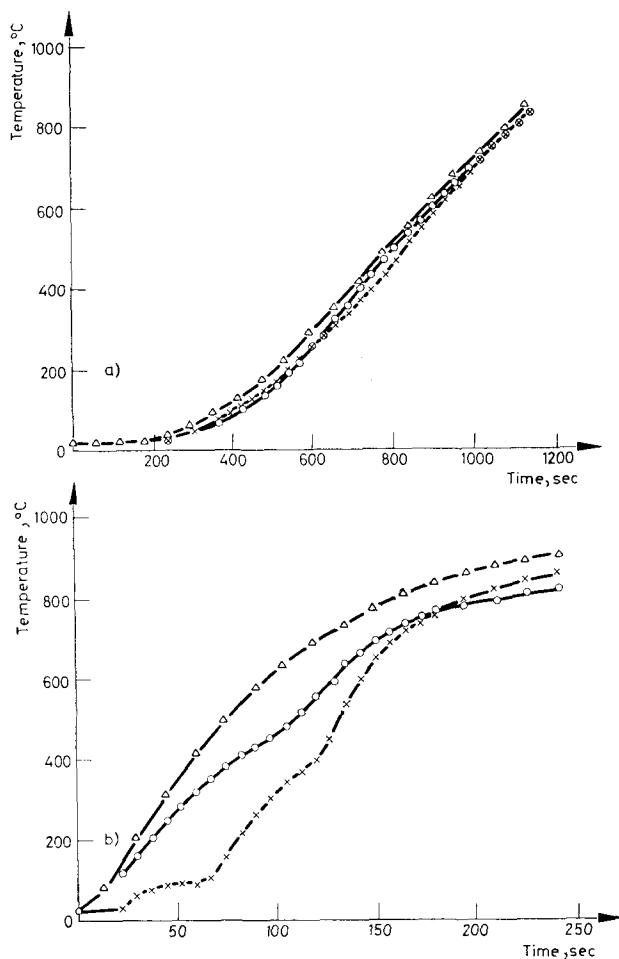


Fig. 2. Temperature rise of 1 g of cellulose heated in nitrogen: a. Slow heating rate; b. fast heating rate;  $\Delta$  temperature at wall of furnace;  $\circ$  temperature in cellulose 1 mm from furnace wall;  $\times$  temperature in centre of cellulose

At temperatures above 765° (fast heating rate), the temperature at the centre of the cellulose rises above that at the side of the sample, due to a local exothermic reaction. This exothermicity could be caused by carbon polymerization reactions forming carbon chains in the carbonaceous residue [24].

Because of the radial temperature distribution in the cellulose sample, quoted results refer to the mean cellulose temperature.

### *Gases produced by pyrolysis in nitrogen*

The volumetric outlet flow from the furnace during the pyrolysis of 1 g of cellulose is shown in Fig. 3. The curves consist of one main peak, with the maxima occurring at 415° and 425°, at the slow and fast heating rates respectively. The fast

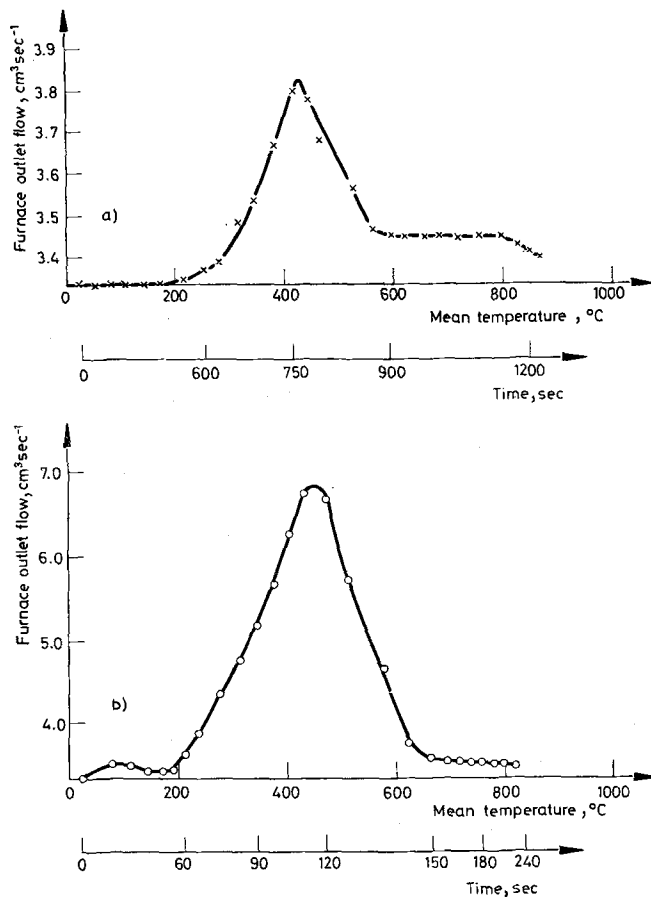


Fig. 3. Furnace outlet flow from pyrolysis of 1 g of cellulose in nitrogen (inlet nitrogen flow  $3.33 \text{ cm}^3\text{sec}^{-1}$ ): a. slow heating rate; b. fast heating rate

heating rate curve also has a small peak with a maximum at 100°, equivalent to a total of 5.6 cm<sup>3</sup> of evolved vapour. This is undoubtedly due to a small portion of the desorbed water from the cellulose penetrating the Cambridge filter, which was positioned between the pyrolysis furnace and the rotameter.\* Both curves also

Table 1

Total quantities of CO and CO<sub>2</sub> produced per gram of cellulose pyrolysed in nitrogen

Heating Rate	CO (μmol)			CO <sub>2</sub> (μmol)			Total (CO + CO <sub>2</sub> ) (μmol)
	Total	Low-temp. region (100-600°)	High-temp. region (600-900°)	Total	Low-temp. region (100-600°)	High-temp. region (600-900°)	
Slow	1,388	1,182	206*	738	714	24*	2,126
Fast	4,173	4,153	20*	1,113	1,109	4*	5,286

\* Poorly resolved formation regions.

Table 2

Percentage of CO and CO<sub>2</sub> in the gases evolved from the pyrolysis of cellulose in nitrogen

Heating Rate	Volume of CO + CO <sub>2</sub> evolved Total gas volume evolved × 100%		
	Over whole temperature range	Low-temp. region (100-600°)	High-temp. region (600-900°)
Slow	65	62	100*
Fast	81	83	33*

\* Approximate figure, based on a poorly resolved formation region.

have shoulders on the main peak, occurring at temperatures of 600–900°, which are probably due to the final degradation of the cellulose-pyrolysis residue, left after the main pyrolysis reactions have occurred [7, 10].

The rate of formation curves for the production of carbon oxides are shown in Fig. 4. The area under the rate of formation/time curves gives the total amount of product formed during the pyrolysis (Tables 1 and 2). The major gaseous decomposition product from cellulose not accounted for is probably hydrogen [25].

The final pyrolysis residue is an amorphous carbon containing some hydrogen

\* The cellulose sample contained 6.2% w/w water, and so the total amount of desorbed water from the 1 g of cellulose used is equivalent to 85 cm<sup>3</sup> (measured at room temperature and pressure). Consequently, the Cambridge filter traps 93% and 100% of the evolved water at the fast and slow heating rates respectively.

and oxygen [26], and the results in Table 3 indicate that the exact composition, and surface area, of the residue depend on the heating rate. Tang and Bacon [24] have suggested that the pyrolysis mechanism includes a dehydration process and results in the formation of 4-carbon residues which undergo carbon polymerization reactions to form carbon chains that are replicas of the original cellulose chain. Dollimore and Holt [7] point out that cellulose chains can orientate themselves into cylindrical fibrils about 10 nm in diameter, and that the dehydration and polymerization reactions may establish inter-fibril bonds. Such cross-linking is exothermic [27, 28] and, together with the carbon polymerization, could be responsible for the slight exothermicity observed above 765° in Fig. 2 (b). The results in Table 3 shows that such polymerization and cross-linking processes, and the resultant microporous structure of the pyrolysis residue, are dependent on the heating rate.

From Table 3 it is seen that 0.35 g of carbon is lost from the cellulose during pyrolysis. The total amounts of carbon oxides evolved during the slow and fast pyrolyses are equivalent to 0.0255 and 0.0634 g of carbon respectively (Table 1), indicating that the formation of carbon oxides only accounts for a minor proportion (7 and 18% at the slow and fast heating rates respectively) of the carbon lost from cellulose. Since the carbon oxides account for 65 and 81% of the gases measured from the slow and fast pyrolyses respectively (Table 2), the major proportion of carbon lost during cellulose pyrolysis must be in the form of relatively involatile material, which condenses on the cooler parts of the furnace walls and is trapped

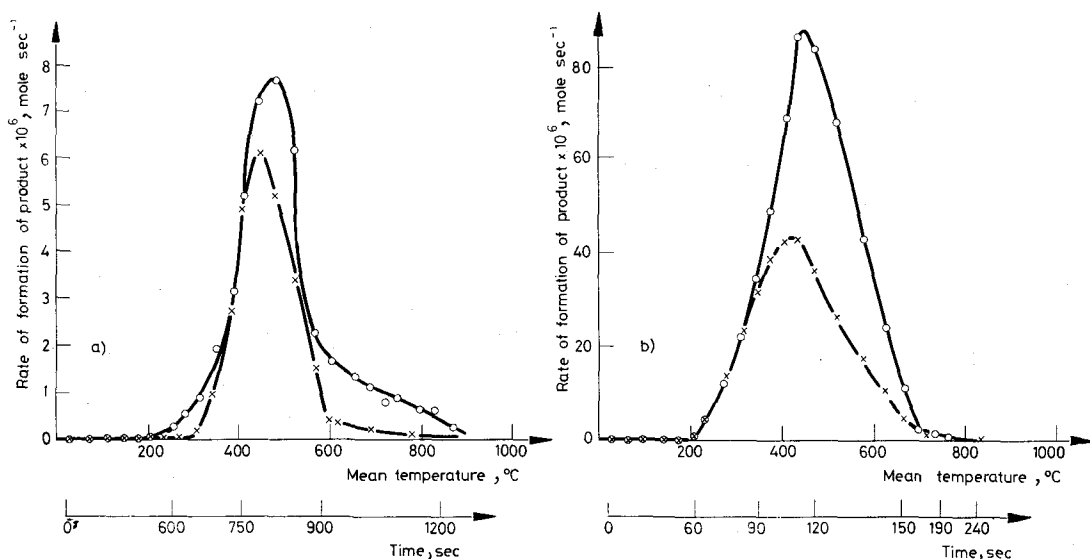


Fig. 4. Production of the oxides of carbon by pyrolysis of 1g of cellulose: a. slow heating rate;  $\times$  CO<sub>2</sub>;  $\circ$  CO; b. fast heating rate;  $\times$  CO<sub>2</sub> $\times$ 2;  $\circ$  CO

Table 3  
Analysis of the cellulose and its pyrolysis residue

Substance	% w/w of component				Surface area <sup>++</sup> (m <sup>2</sup> g <sup>-1</sup> )
	Water*	Non-combustible Residue	C <sup>+</sup>	H <sup>+</sup>	
Cellulose (sample)	6.2	0.0	43.53	6.53	**
Cellulose (theoretical)	—	0.0	44.45	6.22	—
Cellulose after slow pyrolysis	0.0	0.0	92.93	1.13	445.3 ± 3.7
Cellulose after fast pyrolysis	0.0	0.0	91.65	0.66	226.0 ± 1.6

1 g of cellulose initially; 0.065 g of residue left after pyrolysis in nitrogen.

\* Spectroscopic analysis in the infra-red.

\*\* Not measured.

<sup>+</sup> Quoted as the percentage of the element present in the organic part of the material.

<sup>++</sup> Nitrogen B.E.T. adsorption.

on the Cambridge pad. A principal component of this tarry material is levoglucosan [2, 18, 19], which is a primary product of cellulose degradation, formed by scission of the 1,4 glucosidic linkage in the cellulose molecule, followed by intramolecular rearrangement of the monomer units [2, 15, 24, 29, 30]. Furthermore, the results in Table 1 indicate that the total amounts of carbon dioxide, and carbon monoxide in particular, depend very critically on the heating rate: three times as much carbon monoxide, and 50% more carbon dioxide, are produced at the fast heating rate. The carbon oxides can either be formed by further degradation of levoglucosan [19, 29], or directly from cellulose itself by rupture of bonds in the D-glucose rings [2, 24]. Thus the relative proportions of these two general processes depends on the heating rate, although the fraction of carbon oxides in the total gases is relatively insensitive to the heating rate (Table 2).

Heating Rate	Number of molecules of product from one repeat unit	
	CO	CO <sub>2</sub>
Slow	0.23	0.12
Fast	0.68	0.18

Cellulose is a giant molecule built up of D-glucose units, and so the molecular formula of the repeat unit is C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> (molecular weight = 162). Since 1 g of cellulose was pyrolysed in the present experiments, the number of product molecules formed from one repeat unit are as follows, using the data in Table 1.

### The rate of formation of products

From the profiles of overall rate of pyrolysis (Fig. 3) and rates of formation of the oxides of carbon (Fig. 4), first-order Arrhenius parameters for cellulose pyrolysis can be calculated, as described by McCarter [10]. For these calculations, it must be assumed that:

either (a) the evolved gases being measured are primary products from the cellulose,

or (b) if the gases are formed via intermediate products, these intermediate products are present under stationary state conditions.

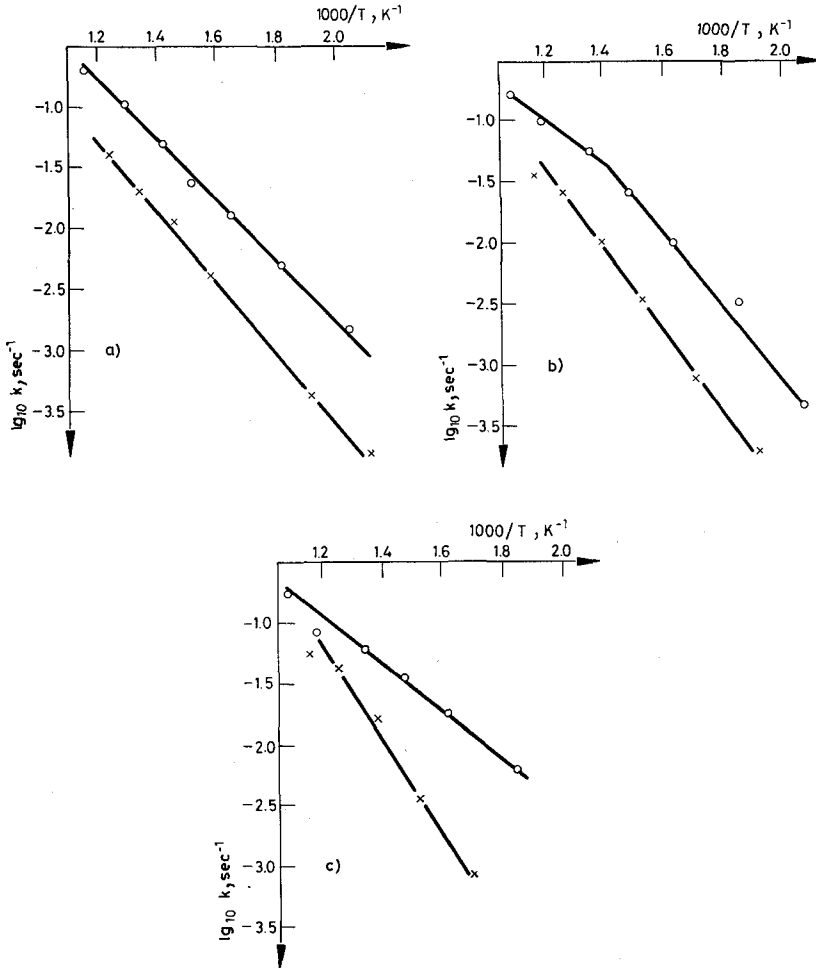


Fig. 5. Arrhenius plots for the pyrolysis of 1 g of cellulose in nitrogen: a. overall pyrolysis;  $\times$  slow heating rate;  $\circ$  fast heating rate; b. formation of CO;  $\times$  slow heating rate;  $\circ$  fast heating rate; c. formation of CO<sub>2</sub>;  $\times$  slow heating rate;  $\circ$  fast heating rate



Arrhenius plots for the overall pyrolysis reaction, and the formation of the oxides of carbon, are shown in Fig. 5, and the kinetic parameters obtained from these plots are summarised in Table 4. In view of the variation with heating rate of the quantities of the carbon oxides produced, it is not surprising that the Arrhenius parameters also vary with heating rate. It is generally accepted that the decomposition products from cellulose depends on whether the pyrolysis is rapid or slow [1], and the present results indicate that the kinetic parameters for pyrolysis to specific products also depends on the heating rate.

Table 4

First order Arrhenius parameters for the pyrolysis of  $\alpha$ -cellulose in nitrogen

Reaction	Heating Rate	Arrhenius Parameters		Temperature of transition of parameters (if any)
		E kcal mole <sup>-1</sup>	A s <sup>-1</sup>	
Overall pyrolysis	Slow	13.3	186	
Overall pyrolysis	Fast	11.5	178	
CO Formation	Slow	15.3	473	
CO Formation	Fast	{ 13.7	{ 832	below 440° above 440°
		{ 8.1	{ 14.3	
CO <sub>2</sub> Formation	Slow	17.8	3,590	
CO <sub>2</sub> Formation	Fast	9.0	27.5	

There are many quoted kinetic parameters in the literature for the pyrolysis of cellulose. Many studies have shown that the overall pyrolysis can be approximately represented by a single first order process [e.g. 1, 4, 6, 13, 16, 17]. On the other hand, Tang and Neill [3] have observed that the first 15% of the weight loss at 240–310° in thermogravimetric experiments is zero order, the remaining 85% of the weight loss being first order. Similar findings have been reported in other studies [5, 14, 17, 31]. However, other studies have been interpreted in terms of two competitive first order processes [32], two consecutive first order processes [10, 33], a half order and first order process [34], and an order variable with temperature, even becoming as high as third order at 270–340° [8]. In view of the obvious uncertainty and variation amongst other studies in the exact order of the overall reaction, and the linearity of the first order plots of the present study (Fig. 5), only first order Arrhenius parameters are presented from the present results.

The overall first order Arrhenius parameters reported in the literature are also extremely variable. The activation energies quoted in the cited references are usually in the range 20 to 60 kcal mole<sup>-1</sup> (1 kcal = 4.184 kJ), although values of 15 kcal mole<sup>-1</sup> [4] and 155 kcal mole<sup>-1</sup> [35] have been reported. Most of the reported parameters are based on dynamic thermogravimetric or differential thermal analysis measurements. The overall heating rates were usually much lower than those of the present study, typically 0.005 to 0.1 deg s<sup>-1</sup>. It is evident that the

kinetics for the overall reaction at these low heating rates are largely irrelevant to those of the present study. More recently, Murty Kanury [13] has obtained the first order Arrhenius parameters  $E = 19 \text{ kcal mole}^{-1}$  and  $A = 1.7 \times 10^4 \text{ s}^{-1}$ , for the pyrolysis of large samples ( $\sim 50 \text{ g}$ ) of  $\alpha$ -cellulose at heating rates of  $0.25\text{--}0.7 \text{ deg} \cdot \text{s}^{-1}$ , by simultaneously measuring density changes (by an X-ray technique) and temperature changes (by embedded thermocouples) in the pyrolysing solid. These parameters give rate constants similar to those of the present study. However, by measuring the rate of total vapour evolution during pyrolysis of cellulose in nitrogen at a heating rate giving temperature rises of  $1.0 \text{ deg} \cdot \text{s}^{-1}$ , McCarter [10] has observed no reaction below  $330^\circ$ , and a sharp transition in kinetics at  $350^\circ$  during pyrolysis. At temperatures below  $350^\circ$  the pyrolysis had an activation energy of  $180 \text{ kcal mole}^{-1}$ , while above  $350^\circ$  the activation energy suddenly decreased to  $25 \text{ kcal mole}^{-1}$ . Clearly, these latter results are in sharp disagreement with those of the present study. The exact kinetics of cellulose pyrolysis must be extremely sensitive to the exact conditions—heating rate, inert gas flow rate, physical condition of the sample etc. The results presented in Table 4 should thus be viewed in this light.

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RÉSUMÉ — On a effectué la pyrolyse de la cellulose en atmosphère d'azote avec deux vitesses de chauffage et l'on a mesuré la vitesse de formation des gaz, dans leur totalité, ainsi que celle des oxydes de carbone. Les quantités de produits formés et leurs paramètres cinétiques du premier ordre dépendent fortement de la vitesse de chauffage.

ZUSAMMENFASSUNG — Cellulose wurde in Stickstoff-Atmosphäre bei zwei Aufheizungsgeschwindigkeiten pyrolysiert und die Bildungsgeschwindigkeiten der Gesamtgase sowie der Kohlenoxide gemessen. Die Mengen der gebildeten Produkte und ihre kinetischen Parameter erster Ordnung hängen stark von der Aufheizungsgeschwindigkeit ab.

Резюме — Был проведен пиролиз целлюлозы в атмосфере азота при двух скоростях нагрева. Скорость образования всех газов и окислов углерода была измерена. Количество образующихся продуктов и их кинетические параметры первого порядка значительно зависели от скорости нагрева.