

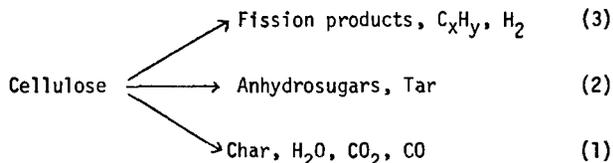
ALTERNATIVE PATHWAYS FOR PYROLYSIS OF CELLULOSE

Fred Shafizadeh

Department of Chemistry, University of Montana
Missoula, Montana 59812

INTRODUCTION

Pyrolysis of biomass involves heterogeneous substrates and complex reactions. The substrate may contain various amounts of cellulose, hemicelluloses, lignin, extractives and inorganics with different thermal properties. The reactions involve alternative pathways and consecutive series, which are affected by pyrolytic conditions including the time and temperature profile, ambient atmosphere and catalysis by inorganic materials. Consequently, composition, yield and rate of formation of the products are highly dependent on the employed substrate and pyrolytic condition. This situation accounts for variation of the results, particularly on kinetic studies, which may range from kinetics of specific chemical reactions to global kinetics or modeling of an entire process. The latter may be based on a rate determining chemical step or even a physical process such as heat or material transfer. Pyrolysis of cellulose illustrates these points. The alternative pathways proposed for pyrolysis of this material is shown below (1,2).



Pyrolysis at temperatures below 300°C involves depolymerization, dehydration, rearrangement and formation of carboxyl and carbonyl groups, evolution of CO and CO₂, development of free radicals and condensation to char. At temperatures above 300°C, these reactions are accompanied by the conversion of the glycosyl units to levoglucosan by transglycosylation. This reaction is preceded by the activation of the molecule, presumably through glass transition, which gives the required conformational flexibility. At still higher temperatures (above 500°C), the glycosyl structure of the levoglucosan or cellulose rapidly breaks down to provide a variety of low molecular weight fission products, including hydrocarbons and hydrogen as well as CO, CO₂ and H₂O obtained at lower temperatures. The pyrolysis products could further react to alter the composition of the pyrolysate. The secondary reaction may proceed in the gas phase as further decomposition of levoglucosan, in the solid phase as the condensation and crosslinking of intermediate chars to highly condensed polycyclic aromatic structures, or by interaction of both phases as gasification of char by reaction with H₂O and CO₂ at high temperatures to produce CO and H₂. In view of all these possibilities the kinetic data are valid only for specific chemical reactions or well defined systems. Generalization could be misleading and controversial, because of major differences in the results obtained under different conditions. These differences are shown in the following examples of pyrolysis of cellulose under different conditions.

KINETICS OF CELLULOSE PYROLYSIS

Global Kinetics

The global kinetics for isothermal evolution of volatile pyrolysis products from purified cotton linter cellulose, within the temperature range of 275-310°C, has been studied in air and nitrogen (3). The Arrhenius plot of the results on first order kinetics is shown in Figure 1. These data gave activation energies of 37 and 17 Kcal/mole in air and nitrogen. Figure 1 indicates a transition at ca. 300°C which reflects the existence of two different pathways. As seen in Figure 2, the rate of pyrolysis measured by weight loss under isothermal conditions, shows an initial period of acceleration and proceeds much faster in air than in inert atmosphere. As the pyrolysis temperature is increased, the initiation period and the differences between pyrolysis under nitrogen and air gradually diminish and disappear at 310°C when pyrolysis by the second pathway takes over.

Kinetics of the lower temperature pathway

The reactions in the first pathway, which dominates at lower temperatures, involve reduction in molecular weight or DP by bond scission, appearance of free radicals, elimination of water, formation of carbonyl, carboxyl and hydroperoxide groups (in air), evolution of carbon monoxide and carbon dioxide, and finally production of a charred residue. These reactions, which contribute to the overall rates of pyrolysis of cellulosic materials, have been individually investigated. Reduction in the degree of polymerization of cellulose on isothermal heating in air or nitrogen at a temperature within the range of 150-190°C has been measured by the viscosity method. The resulting data have been correlated with rates of bond scission and used for calculating the kinetic parameters. These calculations give an activation energy of 21 Kcal/mole for bond scission in air and 27 Kcal/mole in nitrogen, and indicate that at low temperatures a larger number of bonds are broken in air than in nitrogen.

The rates of production of carbon monoxide and carbon dioxide at 170°C are much faster in air than in nitrogen, and furthermore, accelerate on continued heating. It is instructive to compare the initial linear rates for the evolution of these gases with the rates of bond scission obtained for depolymerization at 170°C. As can be seen in Table I the rate of bond scission in air approximately equals the rate of production of carbon dioxide plus carbon monoxide in moles per glucose unit. In nitrogen, however, the rate of bond scission is greater than the rates of carbon monoxide and carbon dioxide evolution combined.

Table I. Initial rates of glycosidic bond scission and carbon monoxide and carbon dioxide formation at 170°C.

Reaction	Rate X 10 ⁵ in N ₂ mole/162 gm hr	Rate X 10 ⁵ in air mole/162 gm hr
Bond Scission	2.7	9.0
CO Evolution	0.6	6.4
CO ₂ Evolution	0.4	2.1

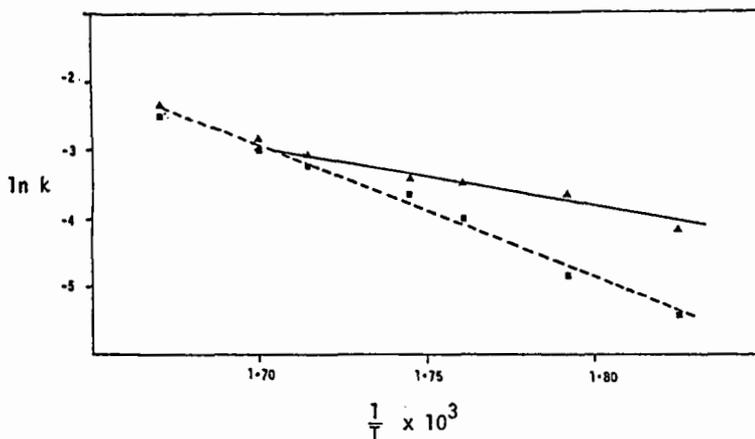


Figure 1. Arrhenius plots for first order reactions in the isothermal degradation of cellulose in air (--- \square ---) and nitrogen (--- \triangle ---).

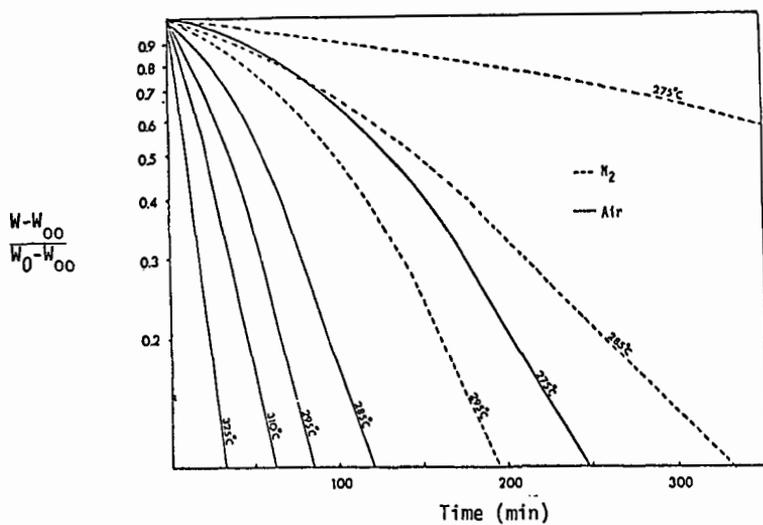


Figure 2. First order plot for the residual cellulose weight (normalized) versus time. Plots at 310°C and 325°C for air and nitrogen are similar.

On heating cellulose in air, hydroperoxide functions are simultaneously formed and decomposed, and their concentration climbs until a steady state is reached. At 170°C the steady state is reached in about 100 min. The decomposition of the hydroperoxide function appeared to follow first-order kinetics with a rate constant of $2.5 \cdot 10^{-2} \text{ min}^{-1}$ at 170°C. From the steady-state concentration of $3.0 \cdot 10^{-5} \text{ mole/162 g min}$, the rate of hydroperoxide decomposition is therefore $7.5 \times 10^{-7} \text{ mole/162 g min}$. When compared with the initial rate of bond scission in air at 170°C (Table I), it is apparent that hydroperoxide formation could make a significant contribution to bond scission.

Kinetics of the intermediate pathway

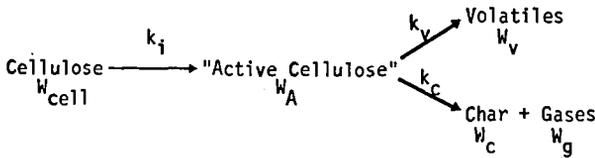
The primary reaction in this pathway involves depolymerization by transglycolation forming a tar containing anhydrosugars (levoglucosan and its isomer), randomly linked oligosaccharides and various dehydration and fission products. As the reaction proceeds, the residue contains some glycosyl units that have been detected by CP/MAS ^{13}C -NMR and FTIR, and some char (4). The char is formed partly from direct decomposition of cellulose as discussed earlier and partly by decomposition of the tar. On raising the temperature the tar forming reactions accelerate rapidly and overshadow the production of char. At this time, it should be pointed out that evaporation of levoglucosan and the volatile pyrolysis products is highly endothermic. Thus, the increased oven temperature could raise the rate of heat transfer but not necessarily the temperature of the ablating substrate which is cooled by the heat of evaporation, especially under vacuum. In other words, at the higher temperatures, the pyrolysis process may be controlled by the rate of heat transfer rather than the kinetics of the chemical reaction. Material transport presents another major obstacle to the investigation of chemical kinetics, because if the products of primary reactions are not removed, they can undergo further decomposition reactions. Table II shows the difference between the yield of different pyrolysis products in vacuum, which removes the primary volatile products, and in nitrogen at atmospheric pressure which allows more decomposition of the anhydrosugars. It also shows the effect of inorganic catalysts in changing the nature of the reactions and products.

Table II. Analysis of the pyrolysis products of cellulose at 300°C under nitrogen and vacuum.

Condition	Atm. pressure	1.5 Mm Hg	1.5 Mm Hg, 5% SbCl_3
Char	34.2% ^a	17.8% ^a	25.8% ^a
Tar	19.1	55.8	32.5
levoglucosan	3.57	28.1	6.68
1,6-anhydro-β-D-glucofuranose	0.38	5.7	0.91
D-glucose	trace	trace	2.68
hydrolyzable materials	6.08	20.9	11.8

^aThe percentages are based on the original amount of cellulose.

In view of these considerations, the chemical kinetics of cellulose pyrolysis have been investigated within the limited temperature range of 260-340°C and under vacuum in order to obtain chemically meaningful data (5). Under these conditions, the chemical kinetics of cellulose pyrolysis could be represented by the three reaction model shown below.



where

$$\frac{-d(W_{\text{cell}})}{dt} = k_i [W_{\text{cell}}]$$

$$\frac{d(W_A)}{dt} = k_i [W_{\text{cell}}] - (k_v + k_c) [W_A]$$

$$\frac{d(W_c)}{dt} = 0.35 k_c [W_A]$$

$$k_i = 1.7 \times 10^{21} e^{-(58,000/RT)} \text{ min}^{-1}$$

$$k_v = 1.9 \times 10^{16} e^{-(47,300/RT)} \text{ min}^{-1}$$

$$k_c = 7.9 \times 10^{11} e^{-(36,000/RT)} \text{ min}^{-1}$$

In this model it is assumed that the initiation reactions discussed earlier lead to the formation of an active cellulose, which subsequently decomposes by two competitive first order reactions, one yielding anhydrosugars (transglycosylation products) and the other char and a gaseous fraction.

Partially pyrolyzed cellulose, in addition to the original sugar (glycosyl) units, contains new functionalities formed by dehydration, rearrangement, decarbonylation, decarboxylation and condensation. In the intermediate chars these functionalities include carbonyl, carboxyl, aromatic and aliphatic carbons as analyzed by CP/MAS ¹³C-NMR (5). After complete pyrolysis of the glycosyl units (5 min at 400°C) a relatively "stable" char is left that contains about 70% aromatic and 27% aliphatic carbons. On heating at 500°C char is converted to a highly condensed and crosslinked material, containing about 90% polycyclic aromatic carbons.

CONCLUSION

Pyrolysis of cellulose proceeds by alternative pathways involving a variety of reactions which provide different products. The kinetics of these reactions are highly dependent on the experimental conditions.

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