

Radiant Flash Pyrolysis of Biomass Using a Xenon Flashtube

MARK WILLARD HOPKINS and MICHAEL JERRY ANTAL, JR.,*
Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, and JACK G. KAY, Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Synopsis

Biomass materials, including lignin, redwood, corn cob, Calotropis Procera, Leucaena wood, Kraft paper, newsprint, cow manure, D-glucose, and D-cellobiose, were pyrolyzed in vacuum by the visible radiant flux emitted from a Xenon flashtube. The flux density exceeded 8 kW/cm^2 during the 1 ms flash. Sirup yields were low (avg 25%), while the gas yield was high (avg 32%). The gaseous products were composed primarily of CO and CO₂. The high relative yields of CO establish the existence of a high temperature fragmentation pathway active during the flash pyrolysis of all biomass materials.

INTRODUCTION

The flash pyrolysis of biomass has recently attracted attention as a way of producing fuels and chemicals from renewable resources.¹⁻⁴ Previous work in cellulose flash pyrolysis began shortly after World War II, arising from interest in the effects of nuclear weapon detonations on exposed cellulosic materials⁵⁻⁷ and fire research.⁸ Today, attention comes mainly from those concerned with either fire prevention or fuel production. Both groups of researchers share the similar goals of learning how to predict and control the production of flammable products which evolve from cellulosic and lignocellulosic materials undergoing pyrolysis.

Previously, the radiant pyrolysis of biomass has not been studied extensively at the high flux levels used in this research. Only Lincoln⁹ and Antal et al.¹⁰ have used a flux of more than 1000 W/cm^2 to pyrolyze biomass. The purpose of using such a high flux level is to test the validity of posited cellulose pyrolysis mechanisms, which predict higher sirup yields at the rapid heating rates effected by high flux levels.

The Xenon flashlamp was chosen for use in these experiments because no other radiant sources can provide such an intense flux. In addition, much experience had been accumulated with its operation.¹¹ Another feature of the Xenon lamp was the similarity of its spectral distribution with that of arc image and solar furnaces used in earlier work.^{10,12,13} Although no evidence has been reported which indicates an effect of photon energy on the pyrolysis product distribution, we have made an effort to use similar radiant energy sources in all the experiments conducted in our laboratory. The Xenon lamp used in this experiment

* To whom correspondence should be addressed: Coral Industries Professor—Hawaii Natural Energy Institute, University of Hawaii, 2540 Dole Street, Honolulu, HI 96822.

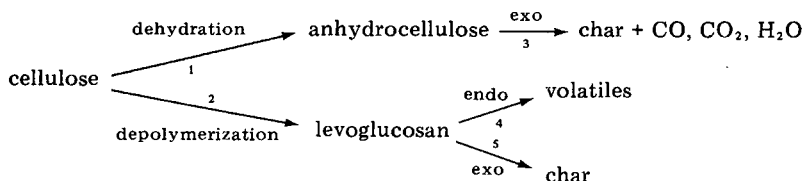
produces a spectrum similar to solar radiation.¹⁴ In the visible region, the lamp's output is approximated by a blackbody radiating at 6000–7000 K, although somewhat deficient in the IR and UV.¹⁵

The use of visible radiant energy has several advantages for those conducting basic research. No metal is present in the reactor [steel is known to catalyze pyrolysis reactions¹⁶]. In addition, very small particles can be used, reducing the time that any volatile product spends in the solid matrix, thereby minimizing secondary reactions. Finally, because the reactor wall remains cold, wall-catalyzed reactions do not affect the pyrolysis chemistry.

From a more practical point of view, with visible radiant heating it is possible to effect two temperatures within a functioning chemical reactor. In a two-temperature reactor, the opaque biomass is rapidly heated to a high temperature by the visible radiant energy while the transparent gaseous products in the reactor and the reactor itself remain "cool." Since the gaseous environment is "cool," volatile products leaving the hot particle surface are rapidly quenched. This quenching effect prevents the primary volatile products from further decomposing, thereby providing high yields of sirups from the biomass feedstock.^{12,17} Another advantage is that if the radiant flash pyrolysis process is to be scaled up to pilot or commercial size, it will readily accept solar radiation as a heat source.

PYROLYSIS MECHANISM

The mechanism of cellulose pyrolysis has been under study for many years. However, this mechanism has been developed at lower temperatures and heating rates than those used in this research. The mechanism that has become generally accepted in the literature is shown below^{18–21}:



This mechanism predicts higher sirup yields as the heating rate increases, since the sirup-forming depolymerization reactions are favored by higher temperatures (due to their higher activation energy) over the condensation reactions. Thus, at our very rapid heating rates it was expected that the cellulose portion of the biomass would depolymerize to levoglucosan and then, depending on the conditions, either vaporize or further decompose to form gases and char. The sirup, levoglucosan, is more valuable than the other pyrolysis products, and has many potential uses.¹³ At the onset of these experiments, it was hoped that high sirup yields could be obtained by pyrolyzing biomass at very high flux levels.

It is known that even trace amounts of metallic impurities present in most biomass materials can act to catalyze the gas- and char-forming decomposition reactions over the depolymerization reactions. The effects of the ash content on the pyrolysis reactions may vary from one biomass material to another. For example, Shafizadeh et al.² conducted a series of experiments to evaluate how

acid prewashing affects the pyrolysis of cellulose and lignocellulosic materials. He found that acid treatments enhanced the sirup yields from all the materials studied, and suggested that this effect may result from the removal of metallic impurities which catalyze the decomposition reactions. Even the sirup yields from materials classified as "low ash" were improved by the acid pretreatment.

Berkowitz-Mattuck and Noguchi⁷ conducted experiments for the U.S. military to determine the effects of APO-THPC, a flame retardant, on the pyrolysis of cotton cellulose. The cellulose was exposed to flux levels of 20–100 W/cm² for 1 s. They noted decreasing char and increasing gas yields as the flux level increased. They concluded that the product distribution depends on the heating rate, but they did not develop a quantitative relationship for this dependence because of instrumental limitations.

Martin⁵ exposed cellulose to flux levels of 18 and 49 W/cm² for times of 0.4–8.0 s. His cellulose was initially darkened with 2% carbon black to facilitate the absorption of radiant energy. He found that the yields of the primary volatile products (acetaldehyde, acrolein, ethylene, and hydrogen) increased with increasing flux levels and decreasing residence times. The proportion of tars, including levoglucosan, also increased with increasing flux while the char fraction decreased. He reported tar yields as high as 64%, and char yields of less than 4%. He suggested that at flux levels of 400–4000 W/cm² cellulose may volatilize without charring.

Lincoln⁹ has performed experiments with a flashtube similar to the one used in this work. Cellulose (darkened with 2% carbon black) was pyrolyzed in a radiant flux of 12,000 W/cm² under 1 atm of helium. He reported that no tar and only 1% char were produced. The major volatile pyrolysis products were H₂O, CO, CO₂, and a set of products which he referred to as "volatile organics." He attributed the lack of tar to experimental difficulties with his apparatus, which allowed the tars to condense before they reached the mass spectrometer. He also used lasers operating at flux levels of 6700 W/cm² and 250,000 W/cm² to pyrolyze cellulose. In an exposure time of only 0.4 ms, all the cellulose was vaporized by the laser, leaving no char or tar residue. In agreement with Kothari,²² he proposed that the pyrolysis was controlled by an ablation process which limited the temperature of the solid to approximately 600°C. Lincoln suggested that the absence of tars in the laser experiments may have been due to the thermal cracking of the tars and not to a change in the pyrolysis mechanism.

The work of Lewellen et al.⁸ explored the rapid pyrolysis of low ash filter paper in helium using an electrically heated screen reactor. They proposed that, to maximize volatile formation, there may be an optimum residence time for the volatiles within the pyrolyzing cellulose matrix. In addition, they concluded that char formation need not be a primary step in the pyrolysis process.

Hajaligol et al.²³ studied the effects of temperature, solids residence time, and heating rate on the pyrolysis of cellulose heated between stainless steel screens. Their results show decreasing tar yields with increasing heating rates. Tar production peaked at 700°C but decreased as the temperature continued to rise. One explanation for their results is the possibility that primary tars were cracked to low molecular weight gases on the stainless steel screen used to heat the cellulose. Steel has been shown to act as a catalyst for the secondary pyrolysis reactions of cellulosic volatile matter at high temperatures.¹⁶

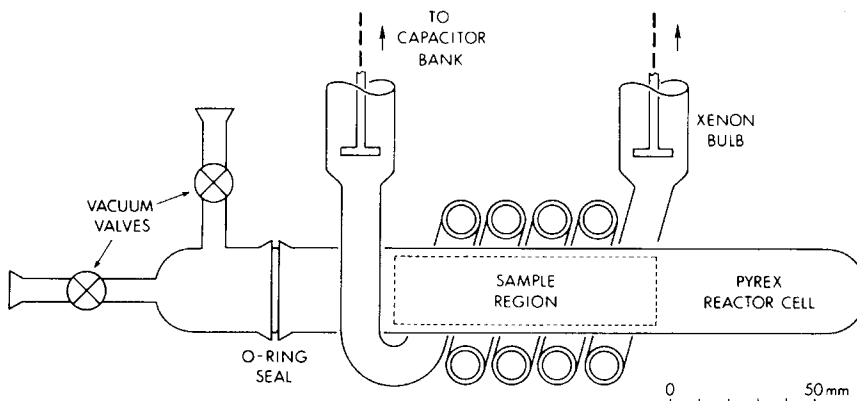


Fig. 1. Schematic diagram of reactor cell within the Xenon flashtube.

APPARATUS AND EXPERIMENTAL PROCEDURES

Equipment. The pyrolysis substrate was placed inside a sealed, tubular Pyrex reactor, which was then evacuated and inserted into the core of the helical Xenon flashtube (Fig. 1). The lamp was surrounded by a polished cylindrical aluminum reflector, which served to increase the intensity of light in the reactor. The lamp was oriented so that its helical axis was horizontal, and was powered by the release of energy from a 200- μ F capacitor bank. The capacitors could be charged to a maximum of 100 kV; thus the maximum total energy available for a flash was 10 kJ.

Before the apparatus was used to pyrolyze biomass, the flash tube was calibrated to determine the flux available within the reactor. The procedure developed by Kuebler and Nelson²⁴ and used later by Nelson²⁵ was adopted for this work. Lincoln¹⁵ reported a similar procedure. A small graphite cylinder with a thermocouple at its center was placed inside a reactor cell and exposed to a flash of the bulb. The core temperature of the graphite cylinder was continuously recorded on a strip chart recorder. Knowing the temperature history of the graphite cylinder, as well as its surface area, mass, and specific heat, the energy transferred to a unity area of the cylinder could be determined. The intensity-time history of the flash was monitored by a photcell connected to an oscilloscope. A photograph was taken of the oscilloscope output to obtain a permanent record of the flash intensity profile. Since the energy transferred and the duration of the flash were both known, the flux density could be calculated. This was accomplished for several different voltage charges to provide a curve of intensity versus voltage.

Kuebler and Nelson²⁴ discuss possible errors in this calibration procedure. They conclude that the radiant energy discharge can be measured to $\pm 4\%$ and that the irradiance can be measured just a few percent less accurately due to errors in the oscilloscope and in the interpretation of the photograph.

Results displayed in Table I indicate that the measured output appears to "tail off" at the higher intensity. Lincoln²⁶ noted this phenomenon in his work, and attributed it to a shift in the spectral output of the bulb towards the ultraviolet at high voltages. Ultraviolet light is more readily absorbed by the Pyrex tube surrounding the calorimeter than longer wavelength radiation. This shift

TABLE I
Intensity Calibration

Voltage (kV)	Measured intensity (J/cm ²)	Total energy (J/flash)
5.0	4.146	2500
7.0	6.793	4900
8.0	7.591	6400
9.5	7.463	9025

towards the ultraviolet may also cause a larger fraction of the light to be reflected, since the reflectivity of the graphite is wavelength-dependent.

Materials. The biomass materials pyrolyzed in this experiment were lignin, redwood sawdust, cow manure, dextrose, D-cellobiose, kraft paper, leucaena leucociphala, wood sawdust, corn cob, calotropis procera, and newsprint. Pure Avicel PH-102 microcrystalline cellulose was flashed in a preliminary experiment, but no pyrolysis occurred because of its high reflectivity. Therefore no results for the Avicel cellulose are reported here.

The redwood sawdust was obtained locally and sieved: only that portion passing through the 212- μ m sieve was used. The lignin was Indulin ATR-CK1 RLX 4417-24 obtained from Westvaco. It was used in its dark brown, fine powder form. The kraft paper was from a lightweight brown paper bag. It was cut into a rectangle 2.5 cm \times 9.0 cm weighing 136.0 mg and used in that form. The leucaena leucaciphala wood was obtained in a dry sawdust form. It was sieved, and only that portion passing through the 212- μ m sieve was used. The cow manure was obtained in a dry, powdered state and used without sieving. The corn cob was obtained in a dry granular form. It was sieved, and only particles ranging from 212 to 425 μ m in diameter were used. The newsprint was from *The New York Times*. It was cut into a rectangle weighing 84.4 mg and measuring 2.0 cm \times 9.0 cm, and used in that form. The Calotropis Procera was obtained from Bio-Energy PTY., Ltd., (Australia). It was sieved, and that portion caught between the 212- μ m and the 425- μ m sieves was used. The anhydrous granular D-glucose was obtained commercially from Mallinckrodt, Lot #KJDZ. The D-Cellobiose was obtained commercially from Aldrich, Lot #030557.

The two sugars, dextrose and D-cellobiose, were dissolved in water to make sugar solutions. A Pyrex rod bent into a rectangular shape was wrapped with black graphite fibers, dipped in the sugar solution, removed, and dried under vacuum. The dry, sugar-coated fibers were placed inside the reactor cell and flashed. In this way the graphite fibers absorbed the radiant energy and quickly heated the sugars, which could not otherwise be pyrolyzed because of their high reflectivity. A single blank experiment was run using uncoated carbon fibers. The results of this experiment showed that only trace amounts of gases were produced and that the fibers lost approximately 8% of their weight, forming predominantly condensible products.

Procedures. Each sample was weighed and placed in a properly cleaned reactor cell. The cells were evacuated using a standard vacuum pump and an oil diffusion pump. After the initial evacuation, each cell was filled with argon, evacuated, refilled with argon, and evacuated one last time to a final pressure of 0.001 mm of mercury.

TABLE II
Products of the Flash Pyrolysis of Various Biomass Materials (Mass % Yields of Original Sample)

Sample	CO ₂	CO	H ₂	C ₂ H ₂	CH ₄	C ₂ H ₄	HC	Gas	Liq	Sol ^a	Total
Lignin	2.1	31.6	4.0	3.9	0.2	0.2	0.0	42.0	13.2	20.0 S	75.2
Lignin	1.1	26.9	3.3	3.9	0.3	0.2	0.0	35.7	18.2	26.1 S	80.0
Redwood	4.2	42.3	3.3	5.9	0.6	0.5	0.0	56.8	15.1	6.7 SP	78.6
Redwood	2.3	26.2	1.8	4.7	0.7	0.5	0.0	36.2	16.3	31.7 SP	84.2
Dextrose	3.6	24.8	1.9	4.1	0.7	0.0	0.0	35.1	54.2	10.1 U	99.4
Dextrose	2.5	14.6	0.9	2.2	0.9	0.4	0.0	21.5	62.7	16.5 U	100.7
D-cellobiose	4.5	23.9	1.5	3.2	1.0	1.6	0.0	35.7	49.4	8.9 U	94.0
D-cellobiose	4.3	22.1	1.5	3.3	1.1	1.6	0.1	34.0	52.0	38.7 U	124.7
Kraft paper	2.4	22.8	1.3	1.8	0.7	0.5	0.1	29.6	10.0	43.1 PA	82.7
Kraft paper	2.1	14.9	0.7	1.3	0.6	0.4	0.1	20.1	12.3	52.0 PA	84.4
Leucaena	3.2	49.3	3.3	5.5	0.7	0.5	0.1	62.6	10.1	8.2 P	80.9
Corn cob	4.0	4.3	0.3	0.7	0.2	0.0	0.0	9.5	11.2	73.4 U	94.1
Corn cob	1.5	4.3	0.4	0.7	0.2	0.3	0.3	7.7	7.6	83.0 U	98.3
Calotropis	3.1	20.8	1.6	2.1	0.5	0.2	0.1	28.4	26.0	34.4 P	88.8
Newsprint	1.9	20.3	1.1	2.5	0.7	0.5	0.5	27.5	17.1	42.3 PA	86.9
Cow manure	3.0	37.9	2.8	3.0	0.5	0.0	0.0	47.2	8.9	21.4 P	77.5

^a The form of the solid remaining in the reactor after the flash varied with the substrate. The letters to the right of the solid mass fraction yield indicate the type of solid found in the reactor cell after the experiment: P = primary char, S = secondary char, A = ash, U = unpyrolyzed substrate.

TABLE III
Low Temperature Pyrolysis Product Ratios

Material	Pyrolysis conditions	Mass ratio (CO/CO ₂)
Cellulose ⁵	46 W/cm ² , 4 s	1.17
Cellulose ²⁷	156–337°C	0.20
Starch ²⁷	156–337°C	0.15
Dextrose ²⁸	200°C, 8.5 h	0.14
Cellobiose ²⁸	230°C, 7.25 h	0.12
Cellulose ²¹	170°C	1.05

Following the final evacuation, the cell was placed in the flashtube and secured. The capacitors were charged to 9 kV and the flashtube was triggered. The flash was accompanied by a loud "pop." Immediately after flashing, the test cell could easily be held in bare hands since its temperature rose only slightly above the room temperature. The cells were removed from the flashtube and attached to the vacuum line which had been evacuated and then filled with argon. Argon was then bled into the test cell, which remained below atmospheric pressure, even though it contained all the gaseous pyrolysis products. Argon was introduced into the cell to raise its pressure and prevent air from leaking into it before the gaseous products could be analyzed.

Gas samples taken from each cell were injected into an HP5840 Gas Chromatograph. A 4.9 m × 3.2 mm stainless-steel column was used, the first 3.0 m filled with 50–80-mesh Porapak QS, and the remaining 1.9 filled with 80–100-mesh Porasil A. The column temperature was held at –50°C for 2 min and then programmed to 240°C at 30°C/min.

Following the gas analysis, each cell was opened, and any solid remaining in the cell was emptied into filter paper placed in a funnel. Each cell was washed first with water and then with acetone. These washes were filtered and collected in plastic vials. The mass of the solid product was calculated by measuring the weight gain of the filter paper after it had dried. A portion of each wash was placed in an aluminum pan and weighed. The wash was allowed to evaporate in air at room temperature. The pan was reweighed and the mass of the sirup remaining in the pan was determined and used to calculate the total mass of sirup collected.

In the cases of lignin and redwood, a black film on the interior of each cell could not be washed into the filter paper with solvent. It was removed by wiping with a towel, but its mass could not be determined and was not included in the mass balance.

RESULTS

The gaseous product compositions and mass balances are given in Table II. The solid product was not analyzed, but its mass yield is listed. Analysis of the sirup products was attempted, but no constituents could be identified because the absolute yield of the sirups was too low.

In each case, the most abundant gaseous product was carbon monoxide. This product was present in unusually large proportions, ranging in most cases from 20% to 30% mass yield. The next most plentiful products were CO₂, C₂H₂, and H₂. The yield of CH₄, C₂H₄, and other hydrocarbons was minimal, totaling less



Fig. 2. Pyrolytic char residue within reactor cell following an experiment with Indulin AT Kraft pine lignin polymer.

than 3% of each material pyrolyzed. In these experiments the CO/CO_2 mass ratio was quite large, ranging between 8 and 20. This contrasts with low temperature pyrolysis studies, where the ratio was generally less than 1.^{5,21,27,28} Selected low temperature pyrolysis product ratios are presented in Table III.

An unusual occurrence was noted in the cells containing lignin and to a lesser extent in those containing redwood. After the flash the cells were filled with a filamentary black, cobweblike material (see Fig. 2). This material was very light and fragile. It felt slightly greasy or powdery (slippery) and looked very much like the soot from an acetylene flame. The filaments were not solely on the cell walls, but had a 3-dimensional nature and filled the interior of the cell. They were attached everywhere in the reactor, even to those places which were not in a "line of sight" with the location of the feedstock prior to the flash. We conclude that these fibers resulted from the rapid condensation of a vapor phase product immediately after the flash. An extensive literature search produced only one other report of this sooting phenomenon, although one of us had observed it in experiments with lead and fluorine in the cell.²⁹ In 1949, Norrish and Porter³⁰ described an experiment involving acetone and ketene contained in a long quartz tube next to a gas-filled flash lamp. When the lamp was discharged the same filamentous carbon was observed. They attributed this unusual result to a photochemical phenomenon. We believe that it is more likely a result of the sudden condensation of a supersaturated vapor.

DISCUSSION

These experiments demonstrate that almost any biomass material can be pyrolyzed with visible radiant energy. The only limiting factor appears to be

the absorptivity of the material. While corn cob and Avicel cellulose were pyrolyzed with little success in this reactor, they have been pyrolyzed by visible radiant energy under somewhat different conditions.³¹

Careful attention must be given to the type of solid remaining in each cell after the experiment. In the case of lignin, the solid was all secondary char: a char which did not have the same physical structure as the substrate. The redwood cell contained both the secondary char, and what appeared to be a small fraction of primary char. It is possible that this primary char was actually a thin char coating on an otherwise unpyrolyzed particle. The solid residue of the D-glucose and D-cellobiose experiments was not visible to the eye, and may have been simply unpyrolyzed raw substrate. Both kraft paper and newsprint were pyrolyzed in the form of a thin rectangular sheet. This shape was maintained to a large extent in the material removed from the reactor, which appeared to be primary char or ash, and had little structural integrity. The *Leucaena*, the *Calatropis*, and the cow manure all appeared to leave a primary char in the reactor.

It is apparent from the results that the specific product gases did not vary greatly between types of feedstocks. It would be difficult to examine a set of gaseous product yields and deduce from the data alone which substrate had produced them.

The most surprising finding of this series of experiments relate to the distribution of products between the solid, liquid, and gas phases. According to the accepted mechanism for cellulose pyrolysis, vacuum conditions and rapid heating should favor the formation of sirup at the expense of char and gas yields. Vacuum conditions increase the rate at which volatile products leave the hot char substrates, thereby preserving the integrity of the initial degradation products. The collision probability of gaseous products is reduced at lower pressures, thereby minimizing the effects of secondary gas phase reactions. Finally, rapid heating increases the depolymerization (sirup-forming) reaction rate over the dehydration reaction rate. Nevertheless, the sirup yields reported here are smaller than those obtained at lower heating rates,¹² where yields as high as 30% (kraft paper) and 63% (Avicel cellulose) were obtained.

The sugars, D-glucose and D-cellobiose, were heated indirectly by the radiant energy and produced much higher sirup yields (avg. 55%) than the other materials tested (avg. 14%). This difference may reflect the large thermal mass of the sugar-coated carbon fibers, which reduced the heating rate of the carbohydrate. Another reason for the high sirup yield from the sugars may have been the absence of metallic impurities in the pyrolysis substrate.

Insight into the mechanism of flash pyrolysis can be gained through a consideration of the ratios of gaseous product yields obtained from various experiments. Data summarized in Table IV have been listed in two separate groups: (1) those experiments where the feedstock was heated in a tube furnace (unless noted otherwise) and (2) experiments heated by visible radiant energy. While most authors do not indicate the heating rate used in their experiments, relative comparisons of heating rate can be made by examining the temperature or radiant flux level used in the experiment. Of course, these parameters offer only an indication of the heating rate, since it depends on several other parameters as well.

Most of the tube furnace results and the low intensity radiant results display natural logarithms of the product ratios ($\ln \text{CO}/\text{CH}_4$, $\ln \text{CO}/\text{C}_2\text{H}_4$) between two

TABLE IV
A Summary of Reported CO, CH₄, and C₂H₄ Mass Yield Ratios

Author	Material	Temp (°C)	Gas (mass %)	ln of CO/CH ₄	ln of CO/C ₂ H ₄
<i>Electric furnace heating</i>					
Antal et al. ¹³	Cellulose	750	84	1.9	2.2
	Kraft lignin	750	36	0.6	2.1
	D-mannose	750	65	1.9	2.4
Hajaligol et al. ³²	Cellulose	750	36	2.7	2.7
	Cellulose	1000	47	2.2	2.3
Mudge et al. ³³	Wood (with K ₂ CO ₃)	650	— ^a	1.5	3.9
	Wood (no catalyst)	650	—	2.2	3.7
Deglise et al. ³⁴	Dry beech	700	—	1.8	2.1
	Dry beech	1000	—	1.9	2.6
Lede et al. ³⁵	Douglas pine sawdust	700	52	1.8	2.1
	Douglas pine sawdust	1000	62	1.9	2.7
Diebold ³⁶ (cyclone)	Softwood sawdust		34	2.1	2.3
	Birch flour		—	2.1	2.2
Halligan et al. ³⁷ (fluid bed)	Bovine manure	728	—	1.4	1.8
	Bovine manure	796	—	1.1	1.1
Iatridis and Gavalas ³⁸ (screen)	Kraft lignin	400	—	0.8	4.1
	Kraft lignin	650	—	0.6	3.3
<i>Radiant heating</i>					
<i>Flux (W/cm²)</i>					
Antal et al. ¹³	Cellulose	70	—	2.1	2.3
	Corn cob	70	—	2.3	2.3
	Hardwood	70	46	1.9	2.4
Hopkins et al. ¹²	Cellulose	200	26	2.6	2.2
	Kraft paper	200	55	2.3	2.3
Lede et al. ³⁵	Douglas pine sawdust		60	2.9	3.2
	Douglas pine sawdust		—	3.1	3.1
	Douglas pine sawdust		75	2.6	3.7
Martin ⁵	Cellulose (8 s)	17	—	3.1	3.1
	Cellulose (4 s)	46	—	2.6	2.6
	Cellulose (0.965 s)	46	—	4.4	3.8
	Cellulose (0.49 s)	46	—	4.6	4.2
Hopkins (present work)	Lignin	8000	42	5.1	5.1
	Lignin	8000	36	4.5	4.9
	Redwood	8000	57	4.3	4.4
	Redwood	8000	36	3.6	4.0
	Dextrose	8000	35	3.6	—
	Dextrose	8000	21	2.8	3.6
	D-cellobiose	8000	36	3.2	2.7
	D-cellobiose	8000	34	3.0	2.6
	Kraft paper	8000	30	3.5	3.8
	Kraft paper	8000	20	3.2	3.6
	Leucaena	8000	63	4.3	4.6
	Corn cob	8000	10	3.1	—
	Corn cob	8000	8	3.1	2.7
	Calatropis procera	8000	28	3.7	4.6
	Newsprint	8000	28	3.4	3.7
	Cow manure	8000	47	4.3	—

^a The gas yield was not listed or, if found in the third column, no C₂H₄ was observed in the product gases.

and three. Results reported here, which are at a higher heating rate, evidence ratios ranging from 3 to 5. The lowest ratios are associated with the sugars

TABLE V
Thermochemical Equilibria Predictions of Product Yields

Temp (°C)	Pressure ^a (atm)	Mass yields (%)				
		C (solid)	CH ₄	CO	CO ₂	H ₂
500	0.2	68.25	0.10	0.00	25.93	0.08
1000	0.2	41.61	0.01	47.94	4.55	5.53
1500	0.2	36.71	0.00	57.37	0.01	5.91
1000	0.3	43.316	0.02	44.68	6.11	5.37

^a The final pressure in the reactor cell after the experiment was measured to be 0.2 atm.

(D-glucose and D-cellobiose) where the heating was less direct. Thus, fiber-supported materials mimic the furnace-heating behavior.

Unfortunately, the logarithmic ratio cannot be calculated for the results obtained by Lincoln,⁹ who also used high flux levels. However, when comparing his two experiments using neodymium-glass lasers, Lincoln noted that the mass yield of CO increases greatly as the flux level increases and that the volatile organics portion slightly decreases. Thus, his results agree qualitatively with those presented here. Martin's experiments⁵ also show high product ratios, particularly for short exposure times. His high ratios may be a result of lower gasification at the short exposure times. The high ratios may also reflect the fact that, while the flux was not unusually high, the cellulose was darkened with carbon black (providing an overall absorptivity greater than 0.9) and vaporized rapidly.

The results of Antal³⁹ on the gas phase pyrolysis of cellulose and lignin derived volatile matter show that, as the gas phase temperature increases from 550°C to 750°C, the ratios of CO/C₂H₄ and CO/CH₄ decrease. Because the values of ln(CO/CH₄) and ln(CO/C₂H₄) obtained by flash heating are much higher than those obtained by secondary (gas phase) pyrolysis reactions, and because these values decrease with increasing gas phase temperature, it seems unlikely that the anomalously high yields of CO observed in these experiments could be the result of secondary pyrolysis reactions. This conclusion is in keeping with the facts that the experiments were accomplished in vacuum, and the duration of heating was extremely short. These experimental conditions were specifically chosen to minimize the influence of secondary reactions on product formation.

The results of the pyrolysis of one particular substrate (cow manure) were compared with calculated thermochemical equilibrium values using the NASA Chemical Equilibrium Program. The known composition of cow manure (C/H/O = 0.4100/0.0515/0.2500)³⁷ served as a basis for predicting the temperature and pressure dependent equilibrium values of the pyrolysis product yields. Results of the program show that while it is possible to find agreement in a few cases with the experimental yields of individual species, discrepancies still exist. Under no conditions did the calculated values of the acetylene and methane yields approach those found in the experimental results. The high yields of solid carbon and H₂ projected by the program were not achieved in the reactor. This comparison leads to the conclusion that the pyrolysis process experienced by the cow manure is not one that reaches equilibrium. Selected results from the NASA program are given in Table V.

In summary, the high relative yields of CO witnessed in this research cannot

be explained by the low or moderate temperature solid phase pyrolysis pathways discussed earlier. Secondary, vapor phase pyrolysis reactions cannot be responsible for the high relative yields, nor do equilibrium considerations explain them. Consequently, it is necessary to postulate a new solid phase pyrolysis pathway involving the high temperature catastrophic fragmentation of the ring structures of all biomass materials and the formation of CO and H₂.

Shafizadeh²¹ has described the fragmentation pathway for cellulose pyrolysis in many earlier works. However, the data he cites supporting this pathway could also be explained by fragmentation of the anhydrosugar products of the depolymerization pathway 2 discussed earlier. For this reason his data do not provide conclusive proof for the role of a primary fragmentation pathway in cellulose pyrolysis. The experimental results presented in this paper are the first to conclusively establish the role of a catastrophic fragmentation pathway in the pyrolysis of all biomass materials.

CONCLUSIONS

Most biomass materials can be pyrolyzed by radiant energy to form gases, liquids and char. Heating with visible radiant energy allows the use of a reactor having no internal metallic parts which can act to catalyze the pyrolysis reactions and complicate the analysis and interpretation of the results.

While most of these experiments appear to have resulted in similar gaseous product mixtures, the products differ greatly from what would be obtained under conditions of low and moderate temperature pyrolysis. We conclude that, while, in some cases, the pyrolysis may have been incomplete, the product distributions do not resemble those obtained from the low and moderate temperature pyrolysis of common biomass materials. In addition, the products differ from the calculated equilibrium composition within the anticipated temperature and pressure ranges inside the reactor. Thus, we also exclude the possibility that chemical equilibrium was established within the reactor. Finally, the influence of secondary reactions cannot account for the unusually high relative yields of CO obtained in these experiments using pulsed radiant energy with resulting high heating rates.

In light of the foregoing observations, it is necessary to posit the existence of a new high temperature pyrolysis pathway involving the catastrophic fragmentation of the polymer structure composing each of the materials studied. The existence of this pathway for cellulose pyrolysis, as well as for lignin and the other carbohydrates studied, is indicated by the results obtained from complex biomass materials which include cellulose as their major component. Although Shafizadeh²¹ has speculated on the role of this fragmentation pathway in cellulose pyrolysis, we believe the present work to be the first to positively identify this role for all biomass materials, including cellulose.

With the goal of fuel production in mind, it is apparent that these conditions were not ideal for maximizing the yield of sirups from biomass. Lower heating rates should be pursued where the production of high value liquid or gaseous products is the objective.

The authors wish to acknowledge the support of this work by NSF under grant PFR-8008690 and DOE San Francisco under contract DE-AC03-81SF11531. They also thank Dr. O. Zaborsky (NSF), M. Christensen (JPL), and Professor M. Jones, L. Hofmann, W. Edwards, D. Urban, W. Conner, W. Mok, and A. Cutler, all from Princeton University, for their helpful discussions.

References

1. M. J. Antal, Jr., in Proceedings of the World Congress and Exposition Bio-Energy '80, Atlanta, 1980.
2. F. Shafizadeh, R. H. Furneaux, T. C. Cochran, J. P. Scholl, and Y. Sakai, *J. Appl. Polym. Sci.*, **23**, 3525 (1979).
3. E. J. Soltes, *Tappi*, **63**, 75 (1980).
4. Proceedings of the Specialist's Workshop on Flash Pyrolysis, Copper Mt., Col., 1980.
5. S. B. Martin, presented at the Tenth Symposium (International) on Combustion, The Combustion Institute, MIT, Cambridge, Mass., 1965, p. 877.
6. H. C. Hottel and C. C. Williams, III, *Ind. Eng. Chem.*, **47**, 1136 (1955).
7. J. B. Berkowitz-Mattuck and T. Noguchi, *J. Appl. Polym. Sci.*, **7**, 709 (1963).
8. P. C. Lewellen, W. A. Peters, and J. B. Howard, presented at the 16th International Symposium on Combustion, The Combustion Institute, MIT, Cambridge, Mass., 1976.
9. K. A. Lincoln, in Proceedings of the Specialists Workshop on Fast Pyrolysis, Copper Mt., Colorado, 1980.
10. M. J. Antal, Jr., C. Rovere, and A. Vialaron, in *Biomass as a Nonfossil Fuel Source*, D. L. Klass, Ed., ACS Symposium Series 144, American Chemical Society, Washington, D.C. 1981.
11. M. B. Garrett, P. S. T. Lee, and J. G. Kay, *J. Chem. Phys.* **45**, 2698 (1966).
12. M. W. Hopkins, C. I. DeJenga, and M. J. Antal, Jr., *Solar Energy*, to appear.
13. M. J. Antal, Jr., L. Hofmann, J. R. Moriera, C. T. Brown, and R. Steenblik, *Solar Energy* **30**, 299 (1983).
14. H. E. Edgerton, *J. Opt. Soc. Am.*, **36**, 390 (1946).
15. K. A. Lincoln, *Appl. Opt.*, **3**, 405 (1964).
16. E. W. Stern, A. S. Logiudice, and H. Heinemann, *Ind. Eng. Chem. Proc. Res. Dev.*, **4**, 171 (1965).
17. L. Hofmann, MSE thesis, Princeton University, 1981.
18. F. J. Kilzer and A. Broido, *Pyrodynamics*, **2**, 151 (1965).
19. D. F. Arseneau, *Can. J. Chem.*, **49**, 632 (1971).
20. A. G. Bradbury, Y. Sakai, and F. Shafizadeh, *J. Appl. Polym. Sci.*, **23**, 3271 (1979).
21. F. Shafizadeh, in Proceedings of the Specialists Workshop on Fast Pyrolysis, Copper Mt., Colorado, 1980.
22. V. Kothari, MSE thesis, Princeton University, 1978.
23. M. R. Hajaligol, W. A. Peters, J. B. Howard, and J. P. Longwell, *Ind. Eng. Chem. Prod. Res. Dev.*, to appear.
24. N. A. Kuebler and L. S. Nelson, *J. Opt. Soc. Am.*, **51**, 1411 (1961).
25. L. S. Nelson, *Science*, **136**, 296 (1962).
26. K. A. Lincoln, *Pyrodynamics*, **2**, 133 (1965).
27. C. T. Greenwood, *Adv. Carbohydr. Chem.*, **22**, 483 (1967).
28. I. E. Puddington, *Can. J. Res.*, **26**, 415 (1948).
29. J. G. Kay, N. A. Kuebler, and L. S. Nelson, *Nature*, **194**, 671 (1962) and unpublished results.
30. R. G. W. Norrish and G. Porter, *Nature*, **164**, 658 (1949).
31. M. W. Hopkins, MSE thesis, Princeton University (1982).
32. M. R. Hajaligol, W. A. Peters, J. B. Howard, and J. P. Longwell, in Proceedings of the Specialist's Workshop on Fast Pyrolysis, Copper Mt., Colorado, 1980.
33. L. K. Mudge, L. J. Sealock, Jr., and S. L. Weber, *J. Anal. Appl. Pyrolysis*, **1**, 165 (1979).
34. X. Deglise, C. Richard, A. Rolin, and H. Francois, "Fast Pyrolysis/Gasification of Lignocellulosic Materials at Various Moisture Contents," Université de Nancy, Faculté Des Sciences, Case Officielle 140-54037 Nancy, Cedex, France.
35. J. Lede, P. Berthelot, J. Villermaux, A. Rolin, H. Francois, and X. Deglise, *Rev. Phys. Appl.*, **15**, 545 (1980).
36. J. Diebold and J. Seahill, Solar Energy Research Institute/PR-234-1456, 1982.
37. J. E. Halligan, K. L. Herzog, and H. W. Parker, *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 64 (1975).
38. B. Iatridis and G. R. Gavalas, *Ind. Eng. Chem. Prod. Res. Dev.*, **18**, 127 (1979).
39. M. J. Antal, Jr., *Ind. Eng. Chem. Prod. Res. and Dev.*, **22**, 366 (1983).

Received January 1, 1983

Accepted November 16, 1983