RAPID PYROLYSIS OF CELLULOSE

by

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Submitted to the Department of Chemical Engineering in October, 1980 in partial fulfillment of the requirements for the degree of Doctor of Philosophy from the Massachusetts Institute of Technology

ABSTRACT

Systematic studies of the independent effects of temperature (250-1100°C), solid residence time (0-30 s), heating rate ($\leq$ 100 - 15,000°C/sec), and sample thickness (0.01 - 0.04 cm) on the yields, compositions, and rates of formation of key products from the rapid pyrolysis of cellulose under 0.1 mm Hg, 5 psig and 1000 psig pressure of helium have been performed.

Thin layers of cellulose in the form of single rectangular strips (6x2x0.01 cm^3) and composition of (C:43.96 wt.%, H: 6.23 wt.%, O:49.82 wt.% and Ash: 0.007 wt.%) were pyrolyzed in strips of stainless steel wire mesh in a captive sample apparatus for the above conditions. Gaseous and light liquid products were analyzed by gas-chromatography, tars (heavy liquids) and char were characterized by elemental analysis.

Temperature and sample holding time are the most important reaction conditions in determining the pyrolysis behavior, while heating rate effects are explicable in terms of their influence on these two parameters. Pressure is important in the secondary reactions of products. Sample thickness up to 200 μm is not important, but for thicknesses above this value it does affect the secondary reactions of products.

A heavy liquid product (tar) of complex molecular composition accounted for 40 to 83 wt.% of the volatiles above 400°C. Secondary cracking of this material increased with increasing holding time, temperature, and pressure and was the major pathway for production of light gases and low molecular weight oxygenates. For 1000°C/sec heating rate, 5 psig He pressure, and short sample holding times these gases included modest quantities of H_2 ($\sim$ 1.0 wt.%), CH_4, C_2H_4, C_2H_6, C_3H_6 ($\sim$ 0.2 - 2.5 wt.% each) and light oxygenated liquids such as acetaldehyde, methanol, and acetone/furan mixture ($\sim$ 0.8 - 1.5 wt.% each) most of which were formed over the temperature range 600 - 800°C. At all holding times, pressures, and heating rates, for temperature above 750°C, CO dominated the product gases, and attained a yield above 23 wt.% at 1000°C. Char yields decreased monotonically with increasing temperature to a minimum of $\sim$ 3 wt.% at temperatures of 700 and 800°C at sample holding times of 2 and 0 sec respectively. It then increases slightly with further increase in temperature, undoubtedly due to secondary reactions of tar and other volatiles. However, at above 1300°C complete conversion of cellulose can be achieved.

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October, 1980

Professor George C. Newton
Secretary to the Faculty
Massachusetts Institute of Technology

Dear Professor Newton:

In accordance with the regulations of the faculty, I submit herewith a thesis entitled "Rapid Pyrolysis of Cellulose", in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Mohammad R. Hajaligol

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TO

MY PARENTS

I owe an immeasurable debt of gratitude

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Summary

1. Introduction

Previous studies of biomass pyrolysis show that biomass offers a great potential as a source of high quality gaseous and liquid fuels. Of many types of biomass, cellulosic materials are of special interest because of their widespread utilization in fiber, textile, and construction materials.

Knowledge of the pyrolysis behavior of cellulosic materials can also shed light on ignition, flame propagation, and other flame related phenomena of importance in fire research.

2. Previous Work

2.1 Effect of Reaction Conditions

Previous work on the thermal degradation of cellulosic materials is extensive and several reviews have appeared in the past few years[1-5]. Most of this work, which focussed on the effect of reaction conditions on product quality has left a number of important questions unanswered. For example, only a few studies presented adequate material balances and frequently the interaction between heating rate, temperature, pressure, volatiles and solid residence time, and sample size have been taken into account. Most studies of cellulosic material pyrolysis are characterized by long heat up times, with periods at final temperature extending to several hours or days. In some studies large efforts were expended to increase the yield of certain products[8-9]. Solid residue was found in all studies and ranged from a few percent to over 50 wt.% of the original sample.

Among the studies which have given quantitative data is one done by Tsuchiya and Sumi[10]. The results from this study show that the yield of water and heavy products such as levoglucosan increased with temperature to a maximum at about 450°C and then started to decrease with a further increase in temperature. On the other hand, yield of fixed gases and volatiles increased continuously as temperature increased (Figure 1).

Some of the most important contributions to understand the thermal degradation of biomass related materials, especially cellulose, have been made by Shafizadeh and his associates [1,11-12]. Some results from this group on the pyrolysis of pure cellulose at 600°C under one atomsphere of nitrogen and long residence time are shown in Table 1. A comparison of results for cellulose pyrolysis at 300°C for 2.5 hours under vacuum and at one atmosphere of nitrogen is shown in Table 2. It can be seen that decreasing the pressure lead to significant increase in tar yield.

In recent years, some work under rapid heating condition has been performed by Howard and his colleagues at M.I.T.[6]. A significant finding of this research was that virtually total conversion of cellulose to volatiles with no char formation, could be achieved by pyrolysis under one atmosphere of helium, at solid residence times ranging from 0.2 sec above 800°C to 30 sec below 400°C.

These studies demonstrated the importance of separate understanding of the effect of reaction conditions as well as primary and secondary reactions involved in cellulose pyrolysis.

2.2 Kinetics

The overall rate and kinetics of the thermal degradation of cellulosic materials has been investigated under a variety of conditions. Recent reviews[2-4] discuss some of these results. Most of the authors attempted to correlate overall pyrolysis rates using a single-step first-order expression with an Arrhenius rate constant:

$$\frac{dv}{dt} = k(V^* - V)$$

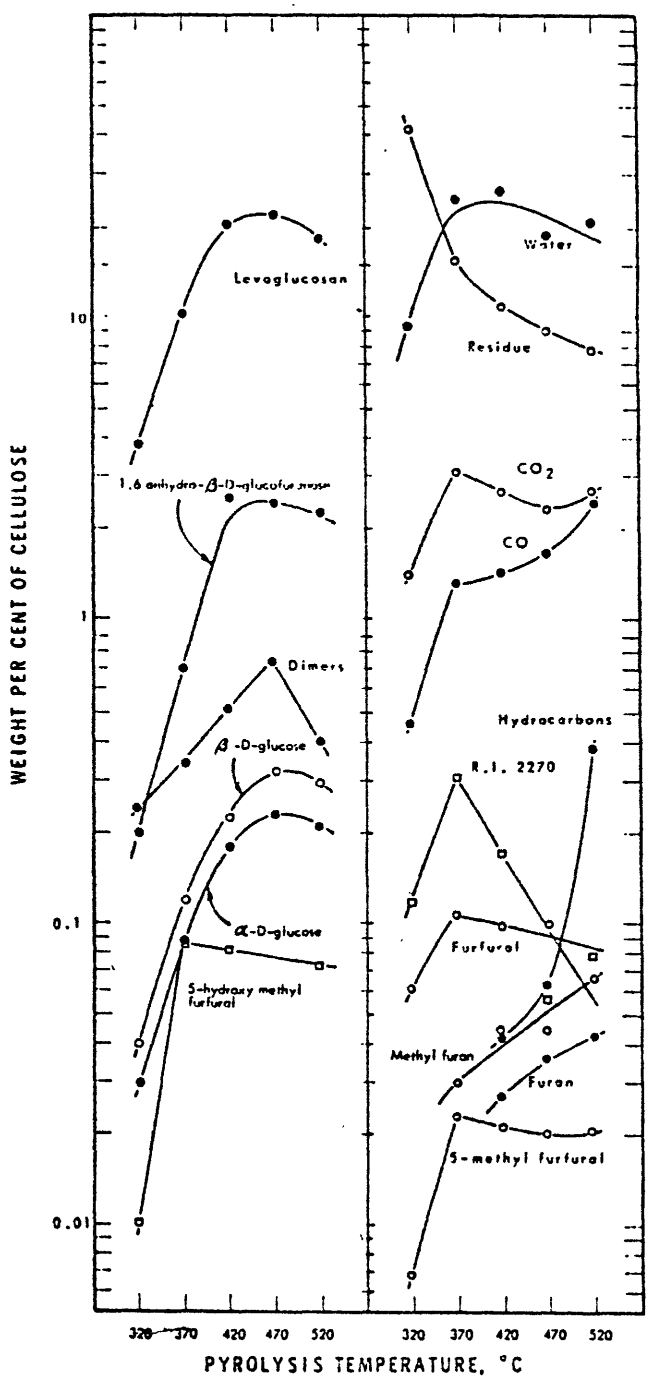

Figure 1. Decomposition Products of Cellulose at Various Temperature(10).

Table 1. Pyrolysis Products of Cellulose and Treated Cellulose at 600°C[1]

Product	Neat	+5% H_3PO_4	+5% $(NH_4)_2HPO_4$	+5% $ZnCl_2$
Acetaldehyde	1.5[a]	0.9	0.4	1.0
Furan	0.7	0.7	0.5	3.2
Propenal	0.8	0.4	0.2	T
Methanol	1.1	0.7	0.9	0.5
2-Methylfuran	T	0.5	0.5	2.1
2,3-Butanedione	2.0	2.0	1.6	1.2
1-Hydroxy-2-propanone Glyoxal	2.8	0.2	T	0.4
Acetic acid	1.0	1.0	0.9	0.8
2-Furaldehyde	1.3	1.3	1.3	2.1
5-Methyl-2-furaldehyde	0.5	1.1	1.0	0.3
Carbon dioxide	6	5	6	3
Water	11	21	26	23
Char	5	24	35	31
Balance (tar)	66	41	26	31

[a] Percentage, yield based on the weight of the sample; T = trace amounts.

[1] Data of Shafizadeh and Chin(12).

Table 2. Pyrolysis Products of Cellulose at 300°C Under Nitrogen[1,2]

	Yield, Wt % of Original Cellulose			
	Pressure, mm Hg			
	760		1.5	
Char	34.2		17.8	
Tar	19.1		55.8	
Levoglucosan		3.6		28.1
1,6-Anhydro-β-D-glucofuranose		0.4		5.6
Other materials hydrolyzable to glucose		6.1		20.9
Total materials hydrolyzable to glucose		10.1		54.6

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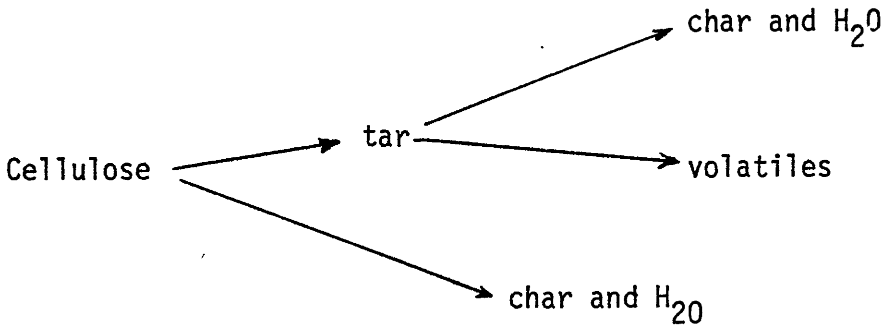
[1] Data of Shafizadeh and Fu(11).

[2] Thermal Analysis experiment with decomposition occurring mainly from 300-400°C; heating rate believed to be 6°C/min.

where V is mass of volatiles, per mass of original material, evolved at time t; V* is the value of V at t = ∞. The rate constant k is equal to k_0 exp(-E/RT); where k_0 and E are the apparent frequency factor and activation energy, R is the ideal gas constant, and T is the absolute temperature.

Some other studies[13-15] have yielded data in which the reaction in one region of temperature is first-order and zero-order in another. Some, such as Tang and Neil[16] suggested that initial phase of pyrolysis of cellulose is controlled by pseudo-zero-order kinetics, and the final phase is of pseudo first-order. Some investigators such as Broido and Weinstein[17] and Aldrich[2] suggest that the decomposition process goes through a multi-step reaction with a first-order reaction in each step:



A more sophisticated pyrolysis model (multiple-reaction) is based on the concept that the thermal decomposition of a complex compound consists of a large number of independent parallel first-order reactions, and assumes identical pre-exponential factors, k_0, and a continuous Gaussian distribution of activation energies with a mean value of E_0 and a standard deviation σ[18]. However, these models address overall kinetics of cellulose pyrolysis. Few results have been reported on the rate of formation of individual products.

It is shown in Figure 2 that the value of rate constant may differ

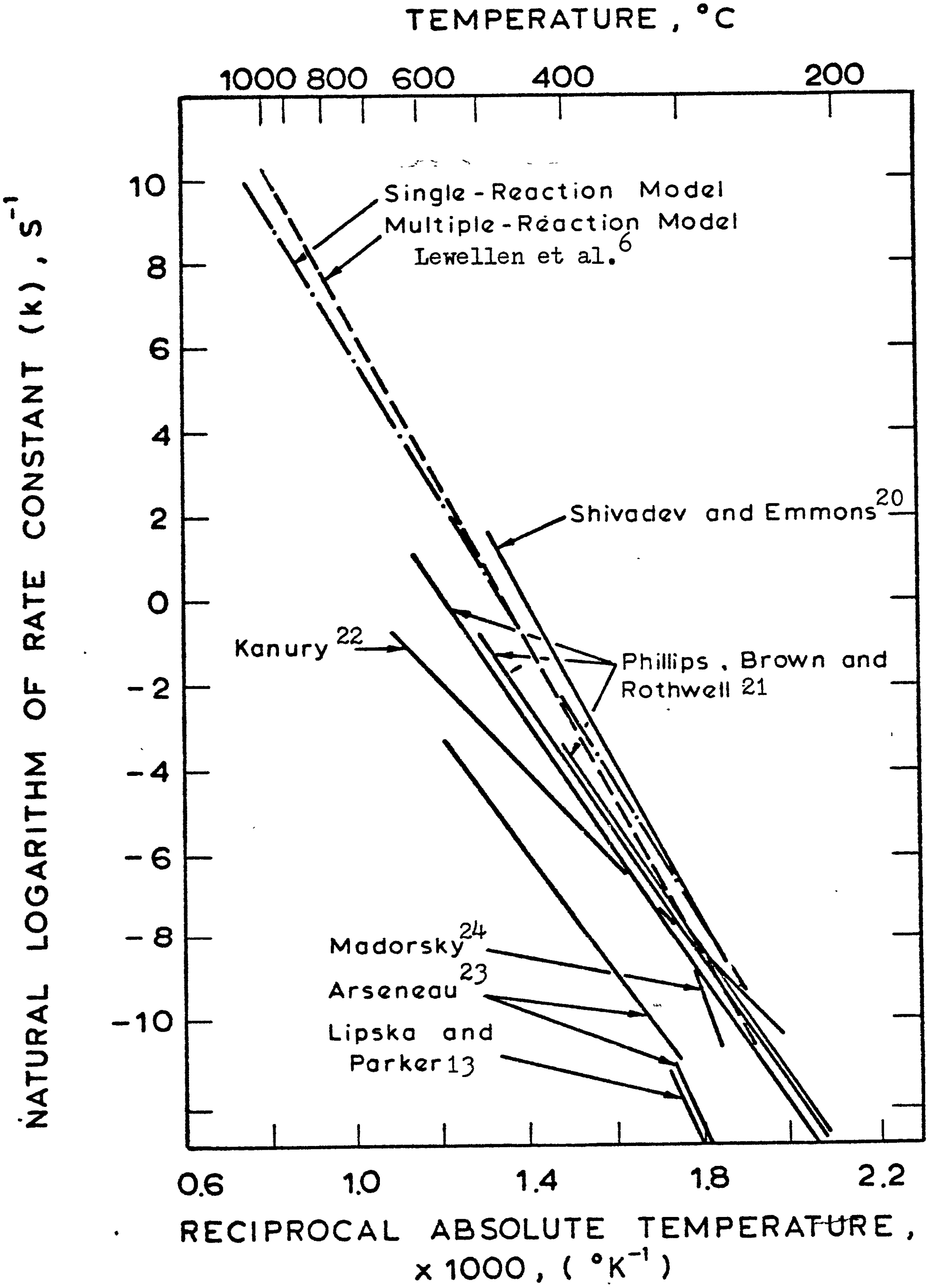


Figure 2. Rate Constant of Cellulose Pyrolysis Measured by Various Investigators(6).

from various authors by several order of magnitude over the temperature range of 200 to 600°C, while activation energies ranges from 19 kcal/mole to above 50 kcal/mole. The lack of agreement among the many investigations shows that pyrolysis is an extremely complex combination of chemical and physical processes, especially at elevated temperature, where enough energy is available to allow many reaction pathways to contribute to the observed decomposition behavior.

2.3 Mechanism of Pyrolysis

Much of the evidence in the literature[1-2,5,7,14] strongly suggests that when cellulose is heated the following sequence of reactions occurs:

1) Dehydration and char formation reactions at low temperatures. These reactions begin at temperatures as low as 180-210 °C and result in water, carbon dioxide, and char. This water is not absorbed water, but apparently results from the dehydration of random glucosan units along the cellulose molecule.

2) Depolymerization reactions at higher temperatures. These reactions which become significant at about 300°C, yield anhydrosugars, such as levoglucosan, and tars, which are volatile at the reaction temperature, but condense when the temperature drops.

3) Decomposition reaction. Cellulose and the tar which is produced in the previous steps undergo decomposition to produce low molecular weight compounds.

At higher temperatures, dehydration, depolymerization, and decomposition occur simultaneously. With different reaction conditions, different reactions dominate the process.

As an example, an overall mechanism for rapid decomposition of cellulose is shown in Figure 3.

3. Objectives

Systematic studies of the effect of sample size, heating rate, temperature, solid residence time, and total pressure on rates and extents of primary conversion of cellulose have not been reported, and no previous studies have systematically determined if improved product selectivity could be achieved through optimization of the above reaction conditions. Therefore, specific objectives of this study were; 1) to study the effect of reaction conditions on the yield, composition, and type of products of cellulose pyrolysis in apparatus designed to minimize secondary reactions. 2) to obtain kinetic data on the rate of formation of individual compounds and of the total weight loss, and 3) to obtain a better understanding of the pyrolysis process by extending the range of experimental conditions and measurements previously studied and to develop a model of the thermal decomposition of cellulose.

4. Apparatus and Procedure

4.1 Apparatus

A schematic of the apparatus is shown in Figure 4. The reactor is designed for atmospheric pressure and vacuum pyrolysis work. It is a Corning pyrex, cylindrical pipe, nine inches in diameter and nine inches long. It is closed at each end with stainless steel plate flanges, with electrical feed throughs and gas inlet and outlet ports. The sample is heated within a folded strip of 325 mesh stainless steel screen held between two massive brass electrodes. The heating circuit consists of 100 and 50 amp variable transformers (variacs) connected to two 100 amp

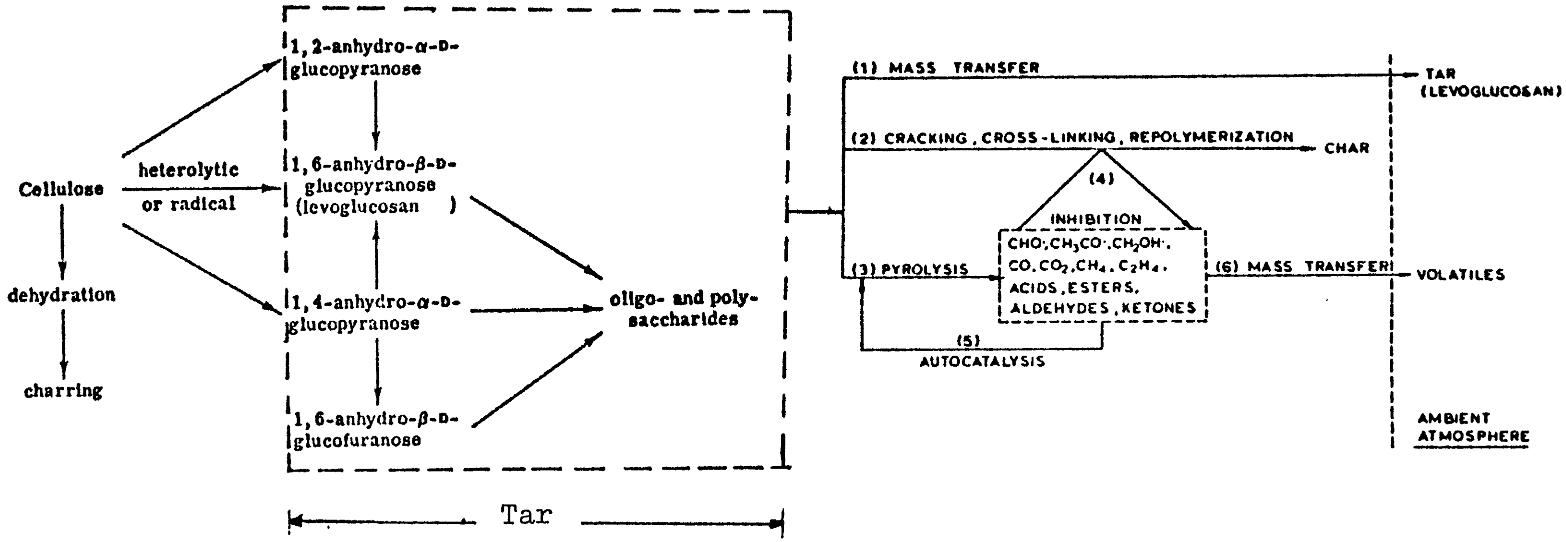


Figure 3. Possible Reaction Pathways for Thermal Degradation of Cellulose.

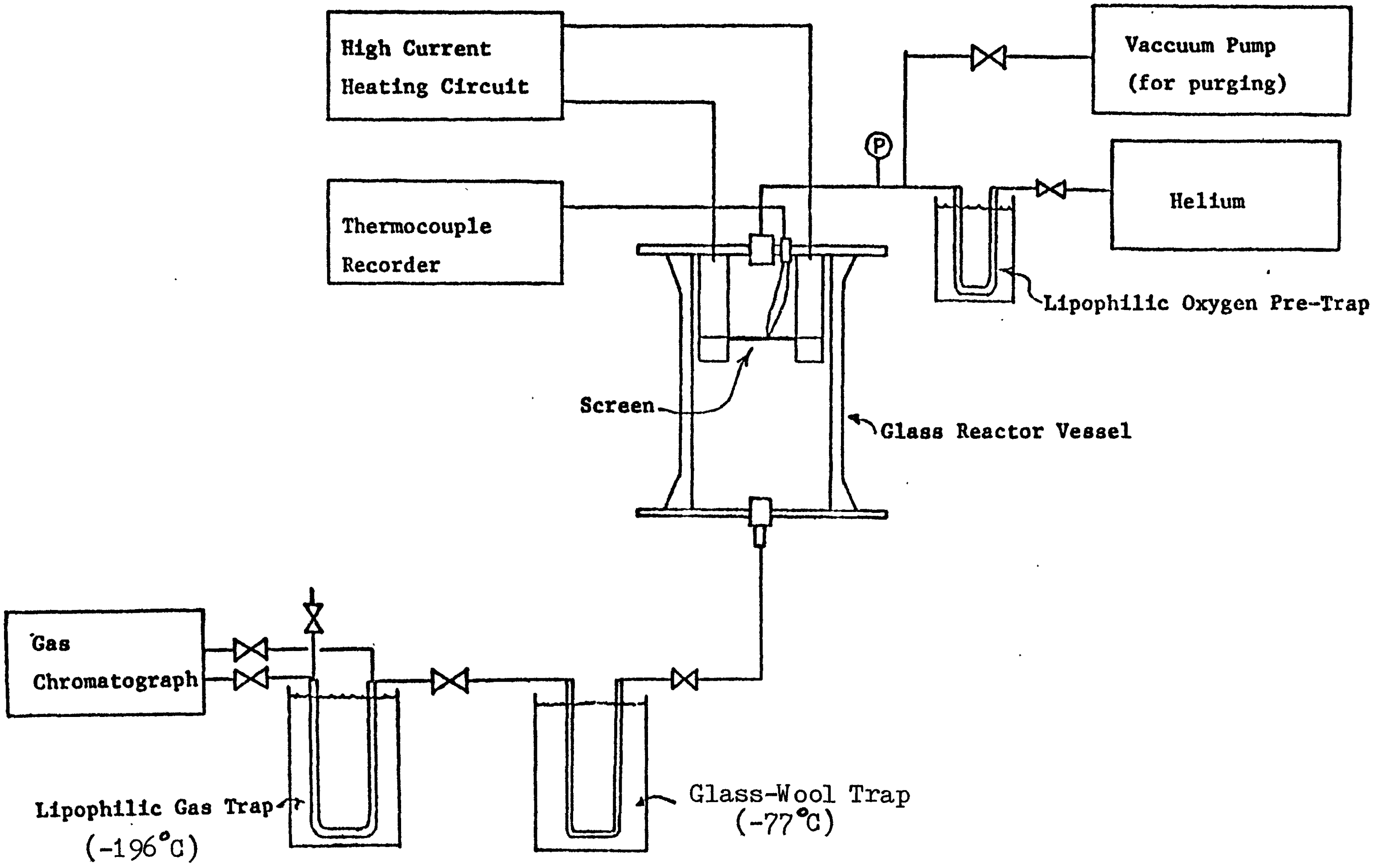


Figure 4. Captive Sample Apparatus Flow Diagram

relays which are in turn respectively activated by 0-1 sec and 0-60 sec industrial timers. This system allows independent variation of the following reaction conditions over the indicated ranges: heating rates (100 - 100,000°C/sec), final temperature (200 - 1100°C), sample residence time at final temperature (0 - ∞ sec).

The time-temperature history of the sample is measured for each run using a type K rapid response (time constant = 0.003 sec) chromel/alumel thermocouple fabricated from .001 inch bare wire joined to give an approximately .003 inch diameter bead. The thermocouple is placed within the folded screen and the millivolt signal is monitored by a fast response strip chart recorder.

4.2 Run Procedure

Approximately 100 mg of cellulose in the form of a single rectangular strip, 2 cm x 6 cm x 0.01 cm of low ash (0.007 wt%) content, #507, S & S filter paper of the composition (C: 43.96 wt%, H: 6.23 wt%, O: 49.82 wt%,) are placed in a preweighed screen which is reweighed and inserted between the brass electrodes. The reactor is evacuated to a pressure of 0.1 mm Hg and flushed 3 to 5 times with helium and then set at the desired pressure. The sample temperature is raised at a desired rate to a desired holding value which is then maintained until the circuit is broken. The screen and remaining solid material then cool primarily by radiation and natural convection at an initial rate of about 200°C/sec.

The yield of char, which remains on the screen is determined gravimetrically. Tar is operationally defined as material condensed: (a) within the reactor vessel at room temperature on the walls and flanges, and (b) in the glass wool trap and not evolved by heating to 100°C. It is recovered by washing the above locations with a 2:1 (v/v) mixture of methanol and acetone. Its yield is determined gravimetrically after evaporating the solvent.

Products in the vapor phase (gases and light liquids) are collected by purging the reactor vessel with 3 to 5 volume of helium and transporting them to two traps. The first trap consists of a 14 inch long x 3/8 inch O.D. U-shaped tube packed with glass-wool and is immersed in a bath of dry ice/alcohol (-77°C). The second (downstream) trap has the same geometry and is packed with 50/80 mesh Porapak QS and immersed in a bath of liquid nitrogen (-196°C).

Products are recovered from the traps for gas chromatographic analysis by warming them to 100°C. All volatile products except hydrogen are analyzed on a 12' x 1/4", 50/80 mesh Porapak QS column, temperature programmed from -70°C to 240°C at a rate of 16°C/min using helium carrier gas at a 60 ml/min flow rate.

Hydrogen, which is recovered by direct sampling of the reactor atmosphere with a precision gas syringe, is analyzed on a 3.05 m x 0.32 cm O.D. 80/100 mesh, spherocarb column, operated isothermally at 0°C using nitrogen carrier gas at a flow rate of 30 ml/min. A thermal conductivity detector is used in both analyses.

Elemental analysis of the cellulose, selected tar and char samples, were performed by Huffmann Laboratories, Wheatridge, Colorado.

5. Results and Discussion

All the data reported in this section are for cellulose samples which were described in Section 4.2. All yields are presented as a percent by weight of initial cellulose, except when otherwise specified.

5.1 Evaluation of Apparatus

In evaluating the apparatus, in addition to the independent variation of reaction conditions which could be achieved by this apparatus, the extention of secondary reactions as well as reproducibility of material should be considered.

5.1.1. Material Balance

The apparatus described in Section 4 gave very good total material balance and reproducibility in the product yields and composition data. In most experiments the total material balance closure was 100 ± 5% although in some runs only 90 to 95% of the original mass of cellulose was accounted for. Elemental balances for carbon, hydrogen and oxygen were calculated for selected experiments where the yield and composition of volatile products and where elemental analysis of the produced tar and char were available. Typical results for four runs are presented in Table 3 along with the total mass balances. The four balances are seen to be excellent for each of the cases. In this calculation the total amount of nitrogen, sulfur and ash were assumed to be virtually zero.

One of the important contributions from this study is the excellent material balance which have been consistently good for wide ranges of experimental conditions. This level of performance is believed not to have achieved in previous studies.

5.1.2. Extent of Secondary Reactions on the Screen

The wire mesh screen used to support and heat the cellulose sample could cause catalytic or other secondary reactions during the cellulose decomposition. As part of the routine run procedure the screens are prefired in helium which contains a small amount of oxygen impurity. During this operation the latter is believed to react with chromium in

Table 3. Carbon, Hydrogen, Oxygen and Total Mass Balance for Cellulose Pyrolysis

Products	Peak Temperature 500°C				Holding Temperature[1] 400°C				Peak Temperature 750°C				Peak Temperature 1000°C			
	Total	C	H	O	Total	C	H	O	Total	C	H	O	Total	C	H	O
CO	.99	.42	-	.57	.25	.11	-	.14	15.82	6.78	-	9.04	22.57	9.67	-	12.9
CO_2	.3	.08	-	.22	1.45	.40	-	1.05	2.38	.65	-	1.73	3.36	.92	-	2.44
H_2O	3.55	-	.39	3.16	6.49	0.	.72	5.77	8.72	-	.97	7.75	9.22	-	1.03	8.19
CH_4	0.	0.	0.	-	0.	0.	0.	-	1.11	.83	.28	-	2.62	1.96	.66	-
C_2H_4	0.	0.	0.	-	0.	0.	0.	-	1.05	0.9	.15	-	2.18	1.87	.31	-
C_2H_6	0.0	0.	0.	-	0.	0.	0.	-	.17	.14	.03	-	.28	.22	.06	-
C_3H_6	0.	0.	0.	-	0.	-	0.	-	.70	.6	.1	-	.80	.69	.11	-
H_2	0.	-	0.	-	0.	0.	0.	-	.36	-	.86	-	1.18	-	1.18	-
CH_3OH	.25	.09	.02	.14	.21	.08	.03	.1	1.03	.39	.13	.51	.98	.37	.12	.49
CH_3CHO	.01	.01	.0	0.	.05	.03	0.	.02	1.58	.86	.14	.58	1.7	.93	.15	.62
C_4+ Ethanol	.00	0.	0.0	0.	0.	0.	0.	0.	.29	.15	.04	.10	.38	.2	.05	.13
AC + FU	0.07	.04	.01	.02	.16	.1	.02	.04	1.00	.62	.10	.28	.82	.51	.08	.23
CHO(CH_3COOH)	.12	.05	.01	.06	.0	0.	0.	0.	.85	.34	.06	.45	.58	.23	.04	.31
Tar	16.37	7.5	.97	7.9	83.35	38.28	4.95	40.32	59.92	27.77	3.63	28.63	49.12	22.89	2.98	23.23
Char	83.63	38.13	5.34	40.16	6.17	4.94	.24	.99	3.32	2.65	.1	.57	3.91	3.46	.13	.32
Total	105.25	46.32	6.74	52.23	98.36	43.96	5.96	48.43	98.8	42.68	6.59	49.53	99.86	43.92	6.9	48.88
Closure	105%	105%	108%	105%	98%	100%	96%	97%	99%	97%	106%	99%	100%	100%	111%	98%

[1] Holding Time = 30s

the stainless steel to produce a layer of chromia which probably reduces the catalytic activity of the screen[19]. Nevertheless, to more quantitatively assess the role of surface effects experiments were performed to either passivate the screen to cracking or to augment its opportunity to cause cracking. To the former end a pyrolysis run was performed with a screen on which a layer of gold had been vacuum deposited while to the latter, runs were carried out using up to five layers of hot screen above the cellulose sample. Operating conditions in all cases were 5 psig of helium pressure, 1000°C/s heating rate, about 1000°C final temperature, and no holding time. The results in all cases showed almost no difference in the product yields and compositions, except for the small amount of the tar that was collected downstream of the reactor. While the total tar make was essentially unchanged, the yield of the latter constituent increased, from 2.8 wt.% with 2 layers of screen to 3 and $\sim$ 5.5 wt.% respectively with 3 to 5 layers. It was thus concluded that, except possibly for a very minor amount of cracking of heavier tar components to lighter ones, the surface of the screen heater exerted little influence on the data obtained in this reactor.

5.1.3. Extent of Secondary Reactions by Recirculated Gases

As soon as the screen is heated,because of the density difference of hot gases around the screen and cold gas of reactor a free convection flow starts in the reactor. This flow could circulate some of the tar, and gases through the screen especially in holding time runs. This flow also transports away the volatiles from outer layer of screen into the main volume of reactor. The question is how important is this flow in further decomposition of gases which circulate through the screen.

As the results for 1000°C/sec heating rate and 5 psig He runs show it has no significant effect on secondary reactions. It can be seen from

Figure 13 that increasing holding time at higher temperatures which increase the quantity of circulated gases doesn't have any effect of tar yield. This effect at vacuum is even less important. Rough calculation of Grashof number (Gr) for vacuum and atmospheric cases shows that free convection at a pressure of 0.1 mm Hg is very small:

$$Gr = \frac{\bar{\rho} b g^3 \Delta\rho}{\mu^2}$$

where $\bar{\rho} = \frac{MP}{R\bar{T}}$ = density; $\Delta\rho = \frac{MP}{R} \left(\frac{1}{T_c} - \frac{1}{T_c}\right)$ = density difference; b = some characteristic length of reactor which is this calculation is taken as half way from the reactor wall to the screen (4.75 cm); μ = viscosity; g = 980 cm/sec^2. For vacuum, gases are assumed to be mainly a mixture of CO_2, H_2O, and CO with an average molecular weight of 28 which is close to CO. For atmospheric case it is assumed to be helium. The viscosity of helium is close to that of CO. Therefore at 5 psig He, 1000K temperature, $Gr \cong 10^4$. Which it corresponds to lower boundary of laminar regim in free convection around a horizontal flat plate. For the same conditions except different pressure (5 psig and 0.1 mm Hg):

$$\frac{(Gr)_{p\,=\,5\text{ psig}}}{(Gr)_{p\,=\,0.1\text{ mm Hg}}} = \frac{\dfrac{\bar{\rho}_p g b^3 \Delta\rho_p}{\mu_p^2}}{\dfrac{\rho_v g b^3 \Delta\rho_v}{\mu_v^2}} \propto \left(\frac{M_p P_p}{M_v P_v}\right)^2 \sim 10^6$$

The results from holding time runs at vacuum however do show a decrease in tar and oxygenated products yield and an increase in char and fixed gases yield with increasing holding time at high temperature (> 850°C). However as will be discussed in section 5.2.2., this behavior is consistent with a lack of strong free convection flows under vacuum conditions.

5.1.4. Extent of Secondary Reactions within the Sample

It is obvious that in any pyrolysis apparatus there is a maximum sample dimension above which heat and mass transfer limitation will exert a significant influence on the observed thermal decomposition behavior. Experiments were performed with the present equipment to determine if 0.01 cm thick samples were thin enough so that these effects would be unimportant. The results showed that doubling the thickness of the sample (.019 cm) has no significant effect on the total decomposition or total yields of tar and volatiles. However increasing the sample thickness to 0.04 cm decreased tar production and a proportional increase in total gas yield. The latter result is believed to come from enhanced secondary cracking due to increased tar and oxygenated volatiles residence time within the thicker sample and from temperature variations due to thermal lags between the centerline and the surface of the sample. Heat transfer calculations showed that during heating at rates of up to 1000°C/sec the centerline temperature of a 0.01 cm thick sample lags its surface temperature by no more than 11-30°C.

Based on the above measurements and calculations it was thus concluded that the 0.0101 cm thick cellulose sheets are sufficiently small that contribution to their pyrolysis behavior from intra-sample heat and mass transfer effects can be neglected.

The space between screen and sample matrix which is created as a result of screen expansion during screen heating is very important in tar secondary reactions, especially at higher temperatures and pressures. This will be discussed later in Sections 5.2.2 and 5.3.

5.2. Effect of Reaction Conditions

5.2.1. Temperature

Figure 5 presents the effects of peak temperature on yields of tar, char, and gases (including water) from cellulose pyrolysis. In these experiments, the cellulose was heated to a peak temperature at a rate of 1000°C/sec, at a pressure of 5 psig He, and then immediately allowed to begin cooling by convection and radiation, at an initial rate of 200°C/sec. As the results in this figure show, the decomposition of cellulose begins between 300 and 400°C and increases with temperature until most of the sample is converted to volatiles and a few percent to char. It is clear from the result that most of the weight loss takes place between 500 - 700°C. Above 750°C the change in the yield of char is not significant, although it decreases to about 3% between 800 and 900°C. Because of cracking of volatiles which occurs at very high temperatures, it then increases very slowly, reaching about 4% at 1000°C.

Tar yield increases with temperature to a maximum at around 700°C, for the stated conditions , where maximum production of volatiles from the cellulose is achieved. It then decreases with further temperature increase undoubtedly because cracking reactions become more favored at higher temperature.

For significant yields of volatiles by cellulose pyrolysis under these conditions, the sample must remain above its decomposition temperature for a time which depends on the heating and cooling rate, final temperature, the sample size, and operating pressure. For zero holding time conditions, complete decomposition can be achieved at or above 750°C for a 1000°C/sec heating rate. Most of the decomposition occurs during the heat-up period. Thus when peak temperature is reached, tar

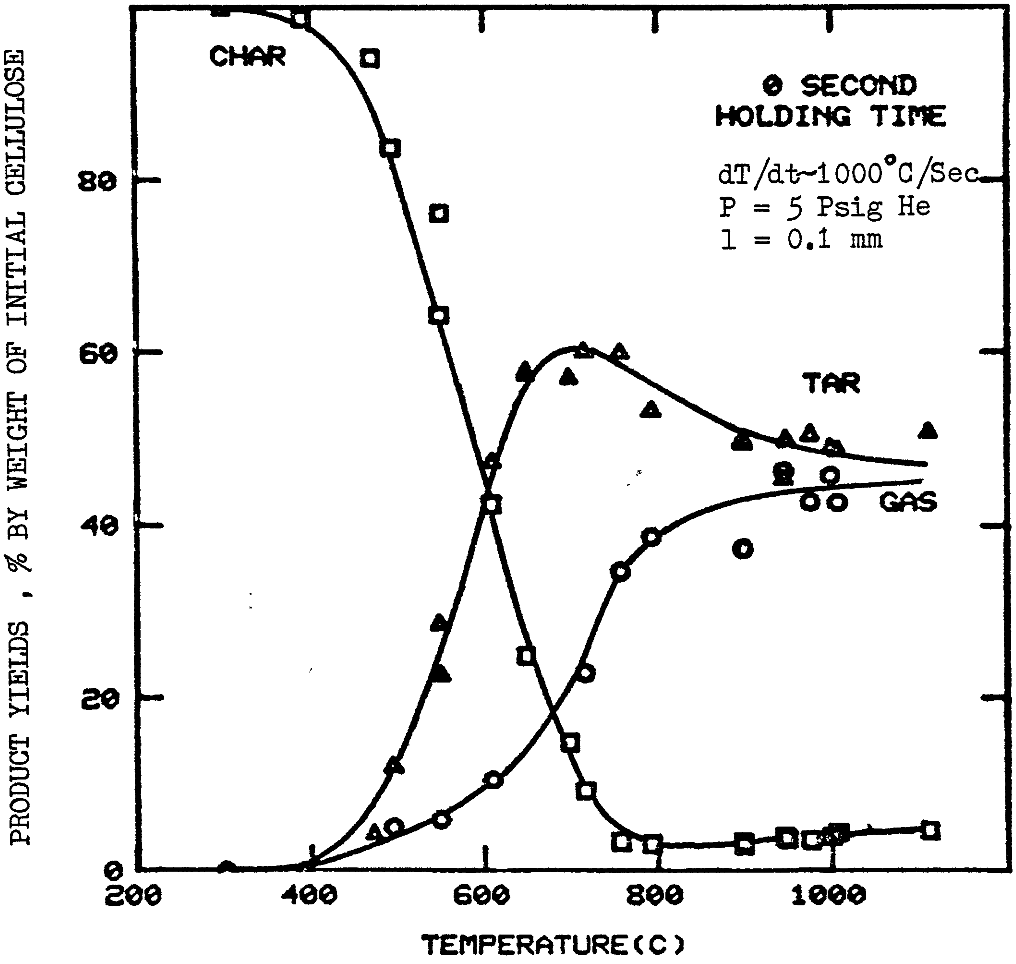


Figure 5. Effect of Peak Temperature on Yields of Char, Tar, and Total Gases at 5 Psig He Pressure.

which could not escape the hot reaction zone during the heatup period, could participate in secondary cracking to yield lighter volatiles.

The total gas yield, which includes water, also increases as peak temperature increases, but at the temperature where tar yield goes through a maximum, the slope of the gas yield vs temperature curve increases. This is probably because the tar is cracked primarily to gases with little if any coke being formed.

The effect of peak temperature on the gases including CH_4, C_2H_4, C_2H_6, C_3H_6, H_2, H_2O, CO, CO_2, methanol, acetaldehyde, ethanol, acetone and furan, etc., are presented in Figures 6-9.

As the results show, all the products are in small yield at low temperatures except water, which has a quite high yield right after decomposition starts. Oxygenated compounds, such as methanol, acetaldehyde, etc., have a relatively higher yield at lower temperatures than hydrocarbons. CO_2 appears in a higher quantity, at a lower temperature, than CO, but above 750°C CO is by far the most abundant gaseous product. When temperature increases further and maximum tar yield is achieved, however, the yields of the volatiles, except for water, suddently increase. This is an indication that most of the gases are products of secondary reactions and tar decomposition rather than the result of the direct decomposition of cellulose.

The yield of these products become constant after a certain temperature, from 700°C for H_2O, to $\sim$ 800°C for CO_2, C_3H_6, acetaldehyde, methanol, and acetone and furan, to 900-950°C for H_2, CH_4 and C_2H_4. The data on CO yields (Fig. 6) exhibit some scatter that arises from interferences from air impurity during the gas chromatographic analysis. It is nevertheless believed that a true asymptote for these conditions is attained at around 1000 - 1100°C. The yields of the light oxygenated

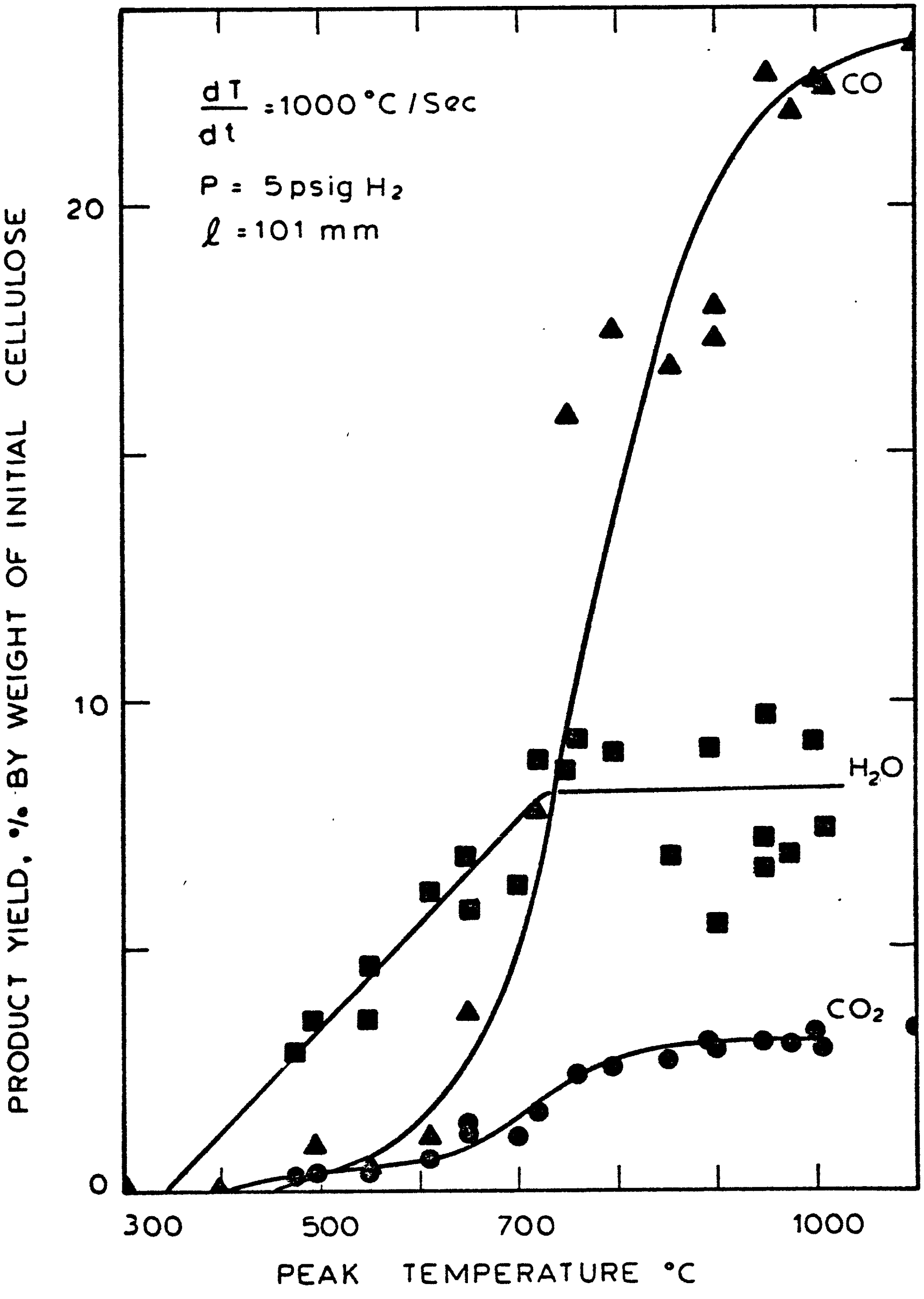


Figure 6. Effect of Peak Temperature on Yields of CO, CO2, and H20 at 5 psig He Pressure.

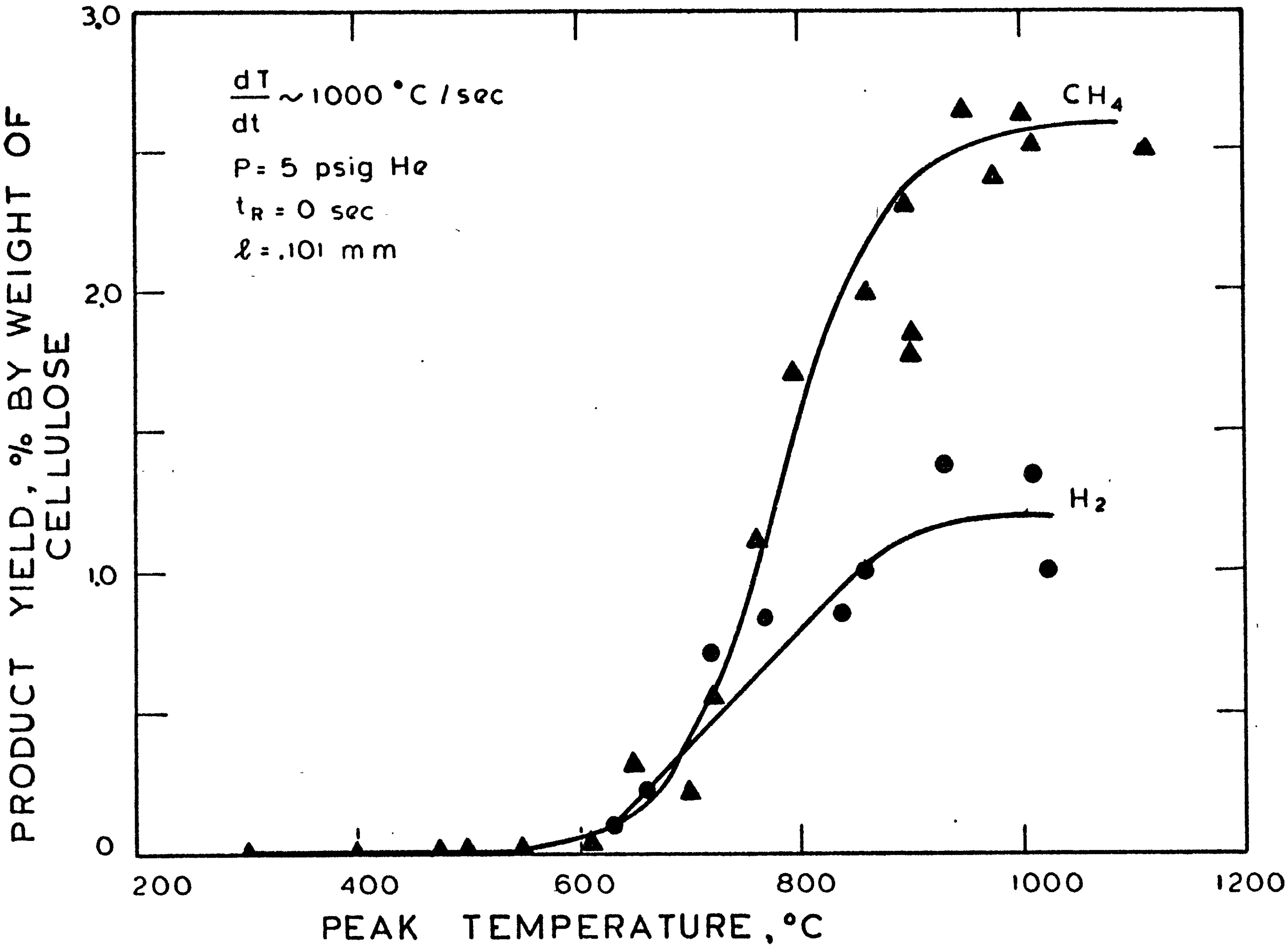


Figure 7. Effect of Peak Temperature on Yields of CH4, and H2 at 5 psig He Pressure.

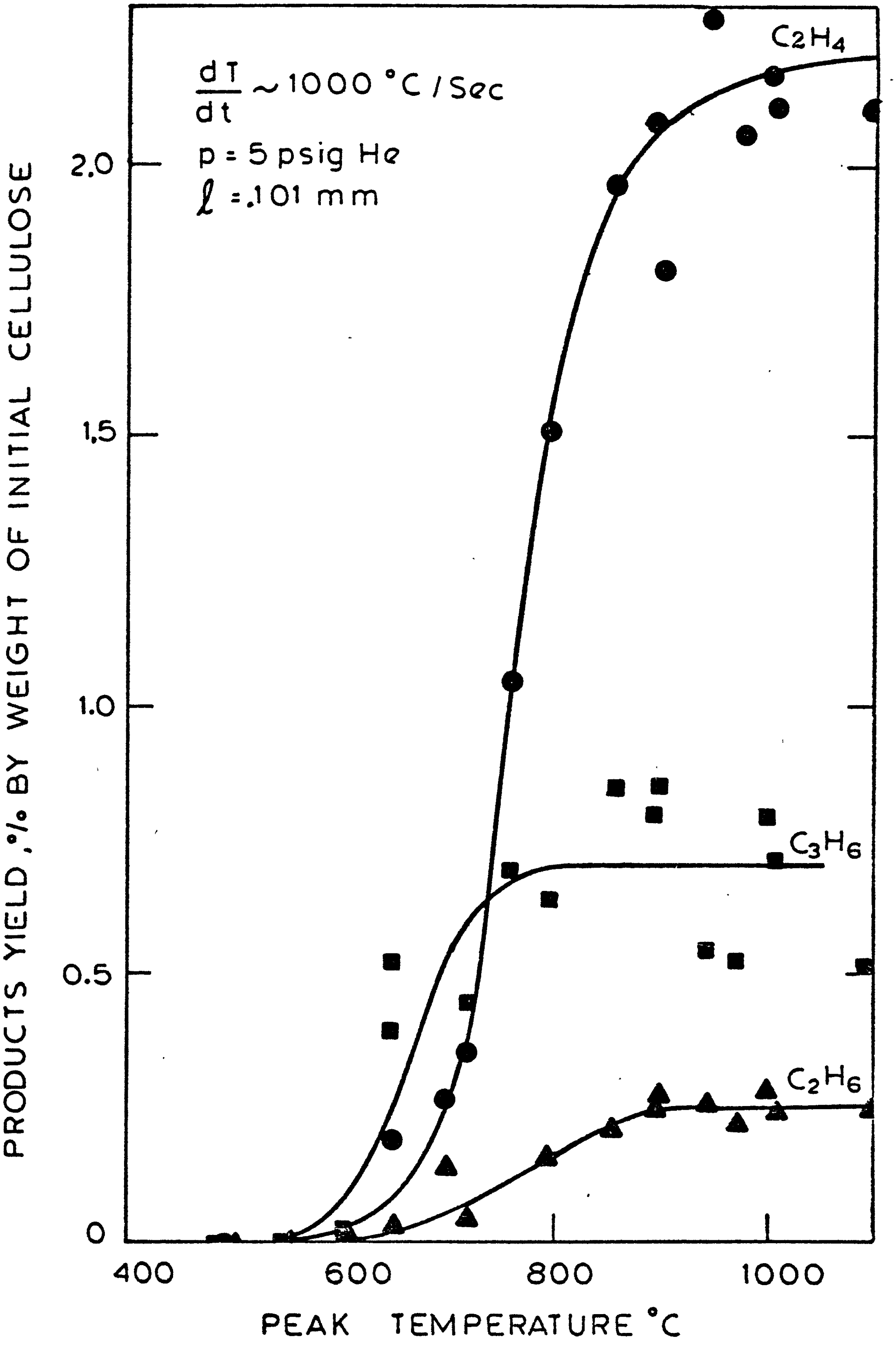


Figure 8. Effect of Peak Temperature on Yields of C2H4, C2H6, and C3H6 at 5 psig He Pressure.

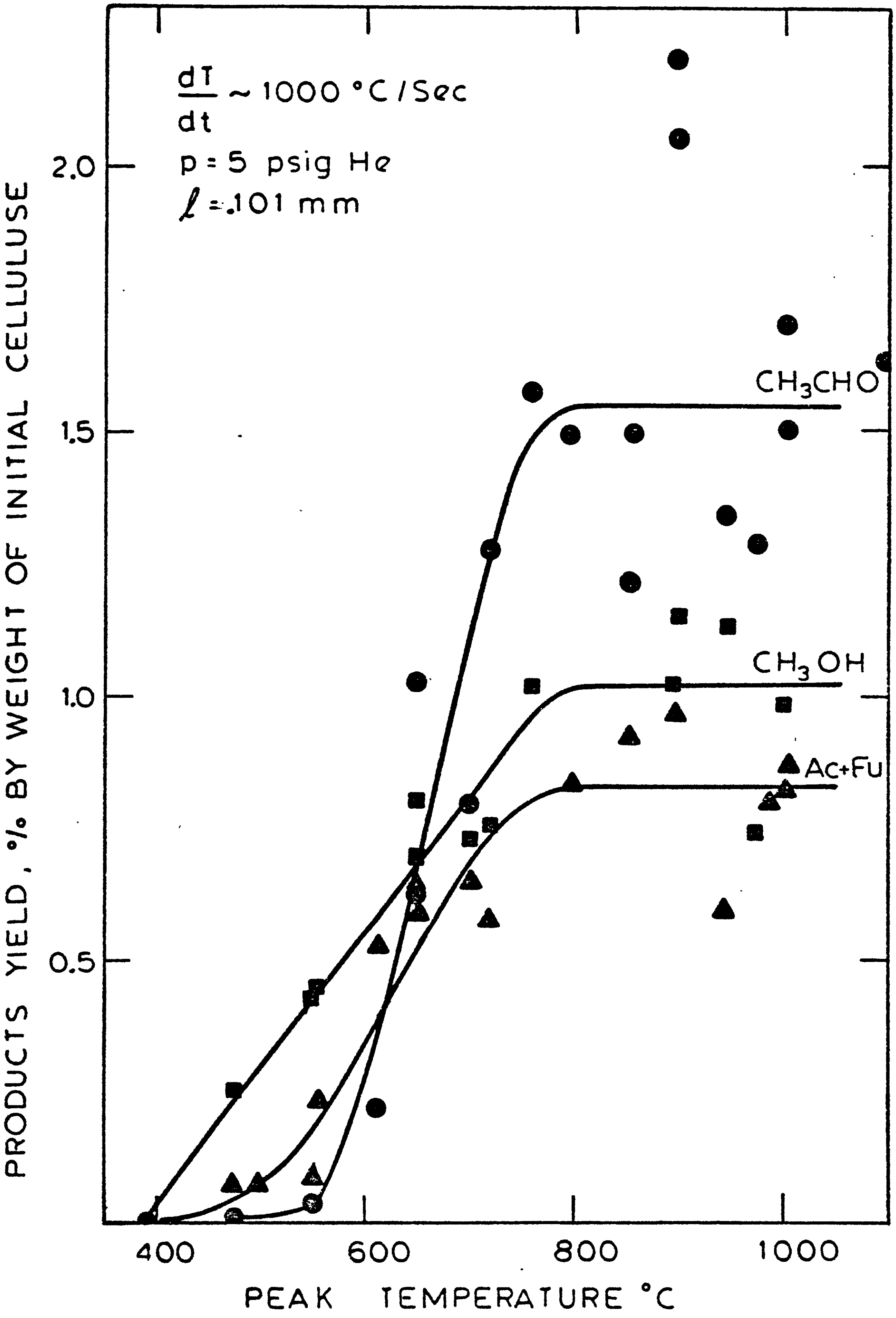


Figure 9. Effect of Peak Temperature on Yields of Acetaldehyde, Methanol, and Acetone+Furan Mixture at 5 psig He Pressure.

liquids methanol, acetaldehyde, acetone and furan may go through a maximum as temperature increases beyond ∿ 800-900°C but the scatter in the data preclude establishing this unequivocally. The existence of such maxima would not be unreasonable since these products can decompose at temperatures as low as 500°C.

The effect of temperature on tar and char elemental analysis are shown in Figures 10-11. Results from tar elemental analysis showed no changes in the composition of carbon, oxygen, and hydrogen, and give an empirical formula of $CH_{1.57}O_{0.78}$ which remains almost constant throughout the temperature range. This indicates that at least some of the tar is some kind of monomer of cellulose initially used. The elemental analysis of char also shows no significant change with temperature except for the temperature interval (400-750°C) where cellulose hasn't been completely converted to char.

5.2.2. Holding Time

The effect of holding time on total weight loss, tar yield, and total gas yield, are presented in Figures 12-14 for 1000°C/sec, for 5 psig He conditions. At low temperatures, where the pyrolysis is incomplete at peak temperature, holding time is very effective on increasing sample decomposition and tar yield. However, it has a very small effect on the total gas yield because most of the cellulose goes to tar (84%) at this temperature. This is a further indication that most of the gases are produced through secondary reactions of the tar.

As temperature increases, most of the pyrolysis is complete by the time the cellulose reaches peak temperature, therefore, holding time has no significant effect on the yields of tar, char, and gases. The results from the vacuum runs differ slightly from the 5 psig runs. At

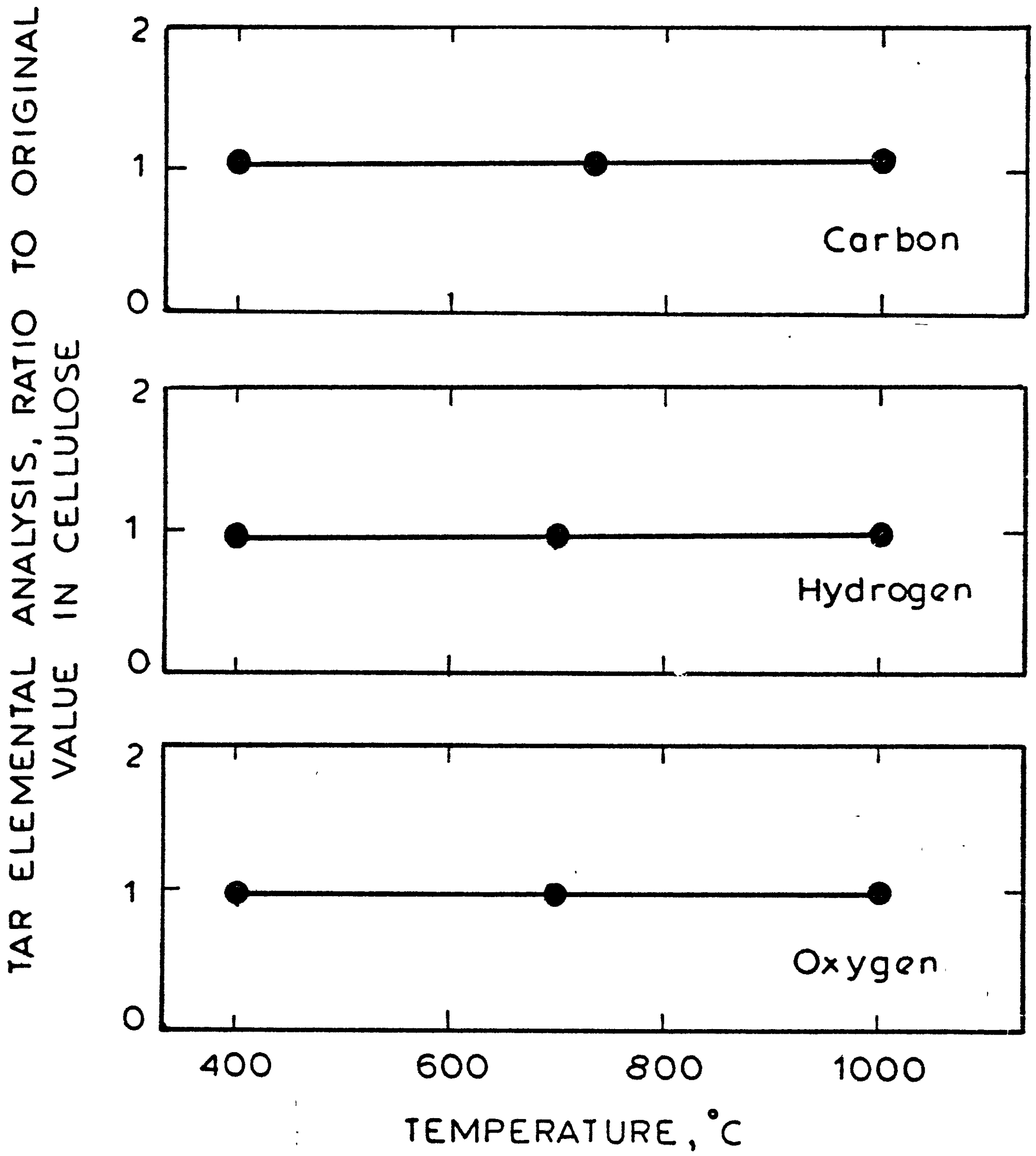


Figure 10. Effect of Temperature on Elemental Composition of Tar at 1000°C/Sec Heating Rate, 5 psig He Pressure, o.1 mm Sample Thickness, and 0-30 Sec Holding Time.

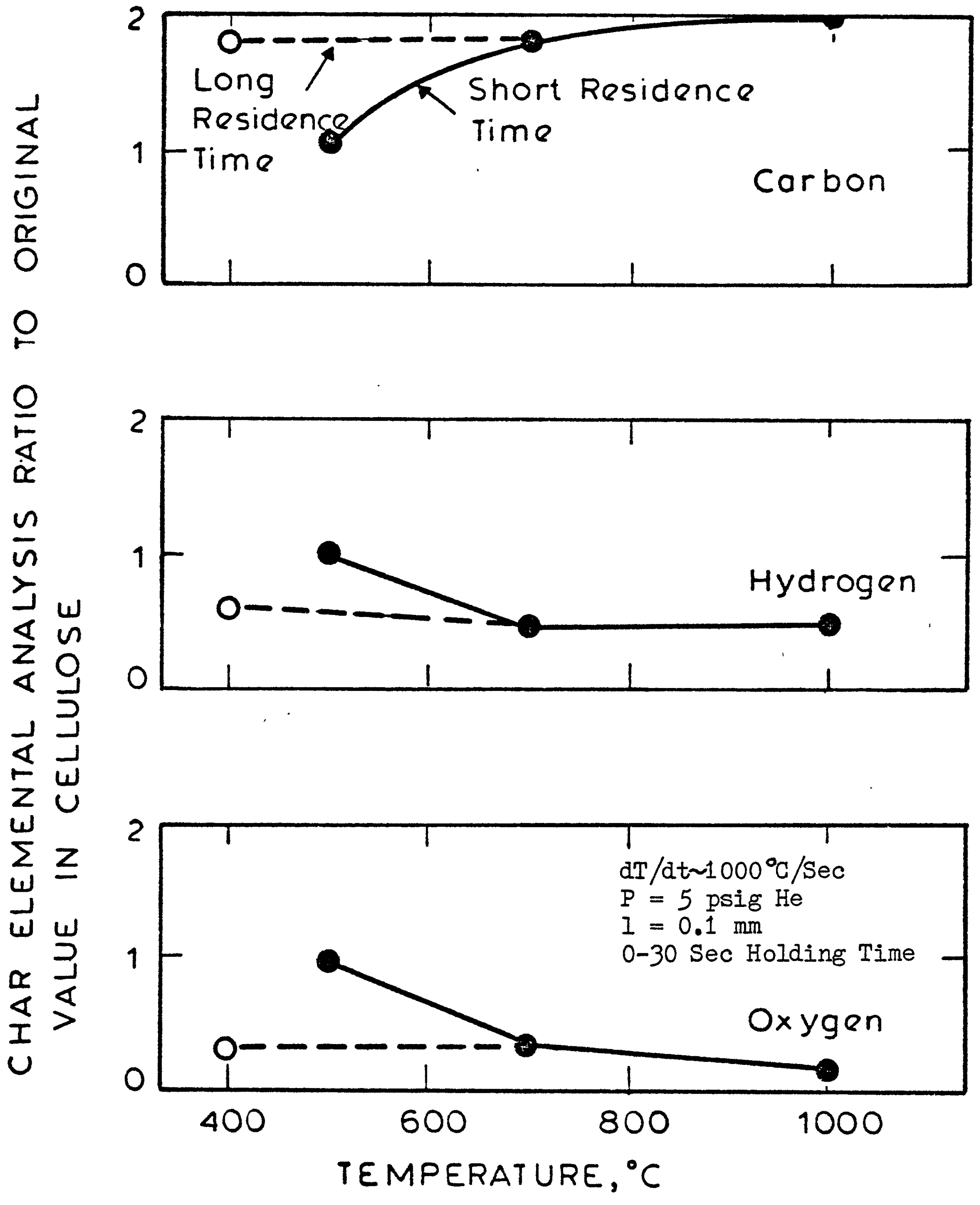


Figure 11. Effect of Temperature and Holding Time on Elemental Composition of Char.

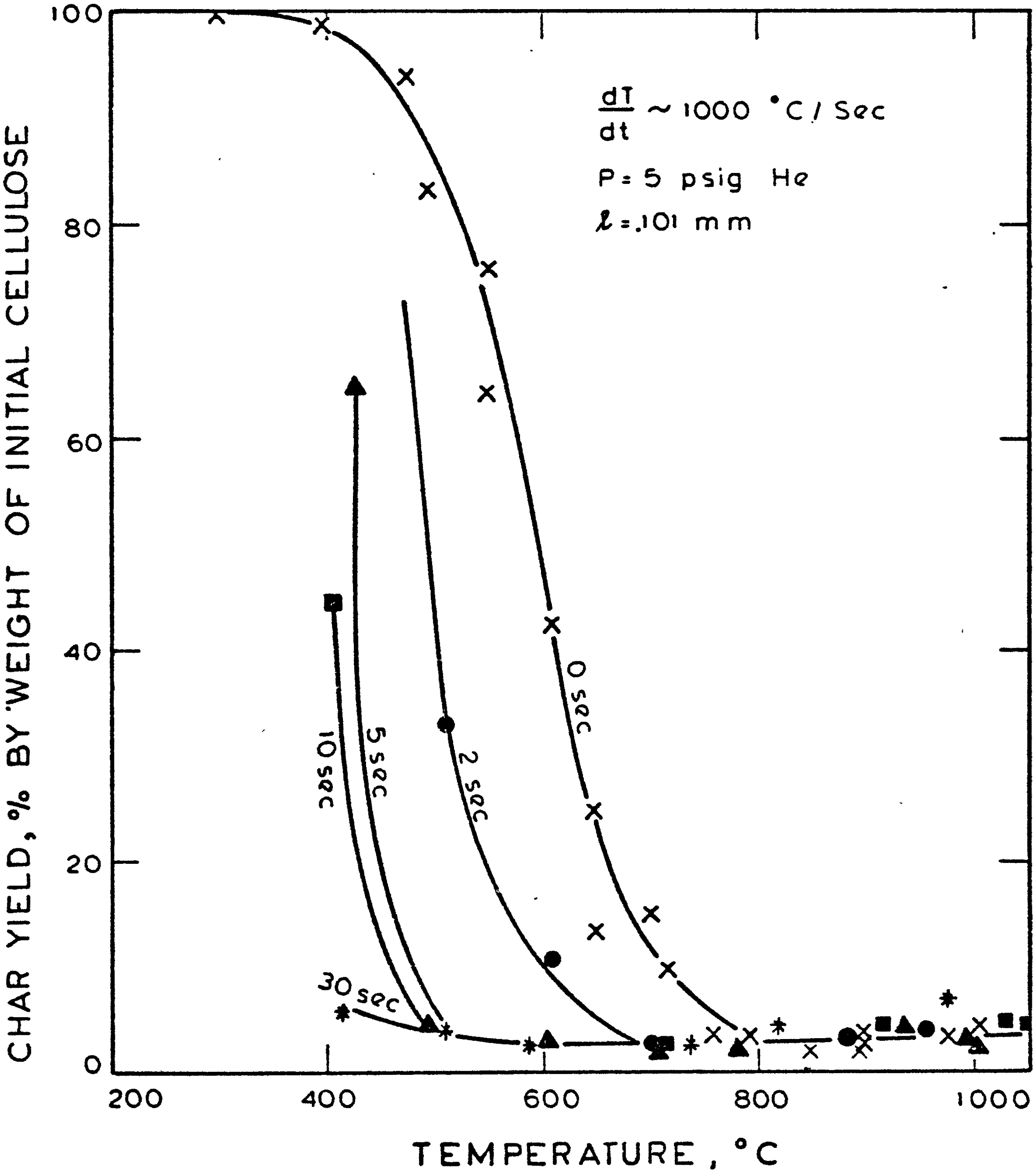


Figure 12. Effect of Holding Time on Yields of Char at 5 psig He Pressure.

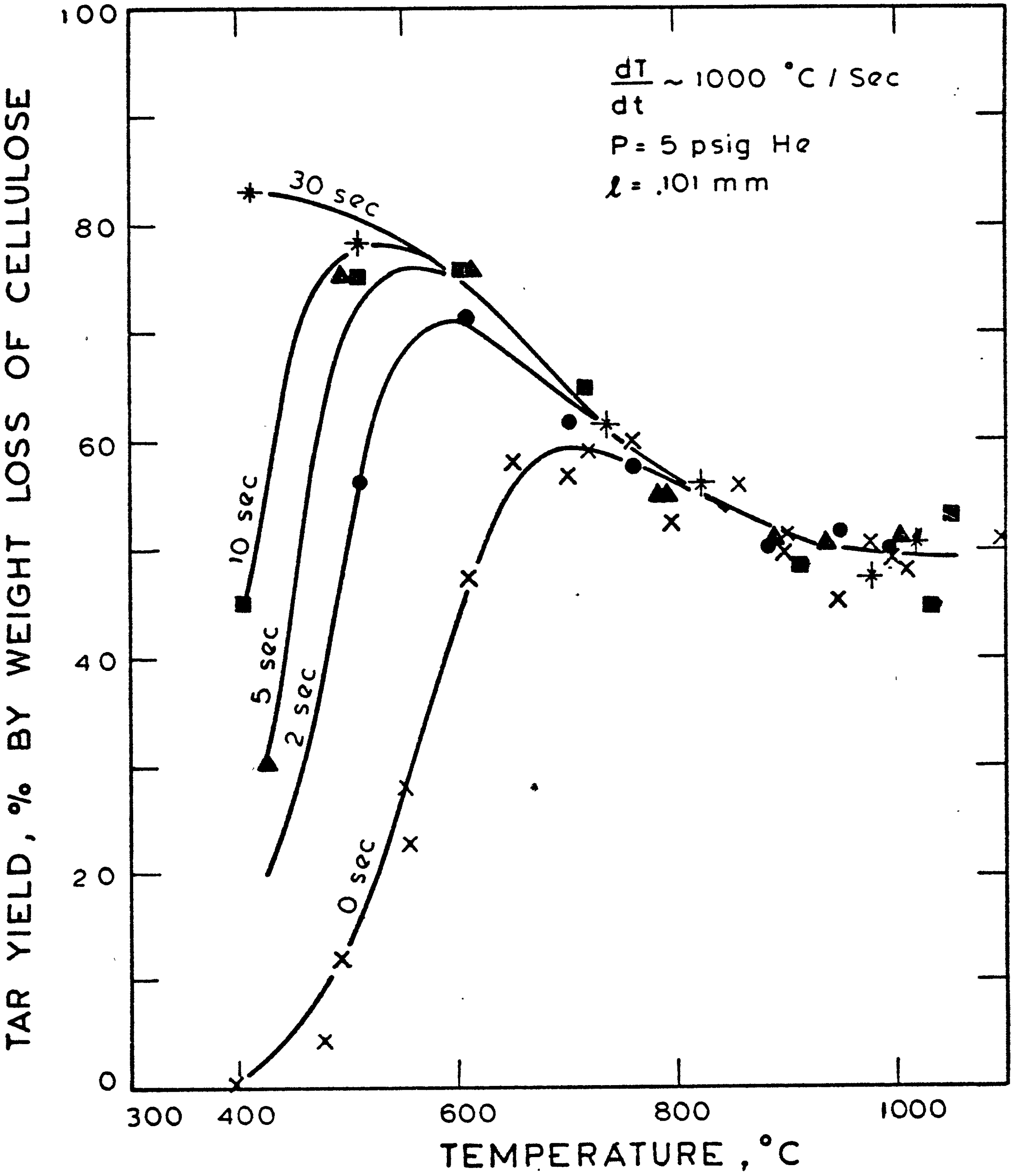


Figure 13. Effect of Holding Time on Yields of Tar at 5 psig He Pressure.

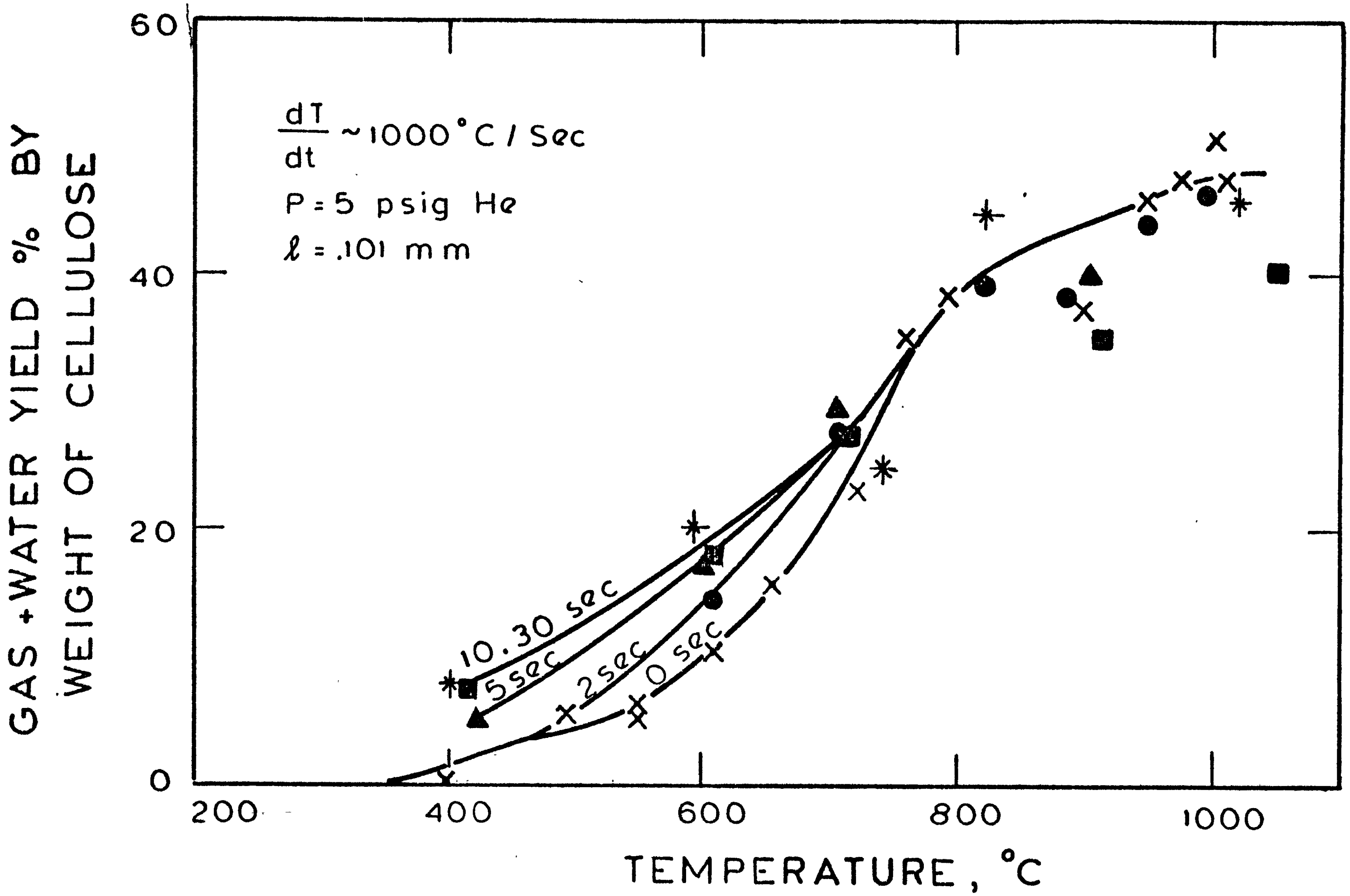


Figure 14. Effect of Holding Time On Yields of Total Gases at 5 psig He Pressure.

low temperatures, the curves for the vacuum runs follow the same path as the curves for the 5 psig runs, but at higher temperatures (>800°C), the effect of holding time becomes significant. Holding time at high temperatures, in vacuum, causes a decrease in tar yield (Figure 15), an increase in char yield (Figure 16) and an increase in total gas yield (Figure 17) because of more secondary cracking of the tar, partly to char but mostly to gases.

A possible explanation for this behavior is that, at vacuum, certain products which could autocatalyze the primary decomposition of the cellulose leave the sample matrix as soon as they are produced. At higher pressure these products stay in the cellulose matrix long enough to autocatalyze further reactions of the unreacted cellulose. Therefore, at vacuum the primary decomposition can't be complete during heating period even at temperature as high as 850°C for zero holding time, and must continue into the cooling period. This means that some of the tar evolved during this period encounters lower and lower temperatures within and in the neighborhood of the decomposing (heat and cooling) sample. This tar will therefore have less probability of cracking and the observed tar yield will be higher. However, in runs with a longer holding time, where the final temperature is held at 800°C or more for a few seconds, cellulose decomposition becomes complete at this high temperature. Under these conditions the evolving tar does encounter temperatures sufficiently high for cracking and some of it decomposes to give additional gases and char. A further point is that in vacuum, because the volatiles which leave the cellulose matrix could leave in any direction, the coke arising from secondary reactions should be more evently distributed on the surface of the screen compared to the 5 psig He runs, and more gases and coke should be produced. This is in fact observed experimentally. Another possible explanation for the

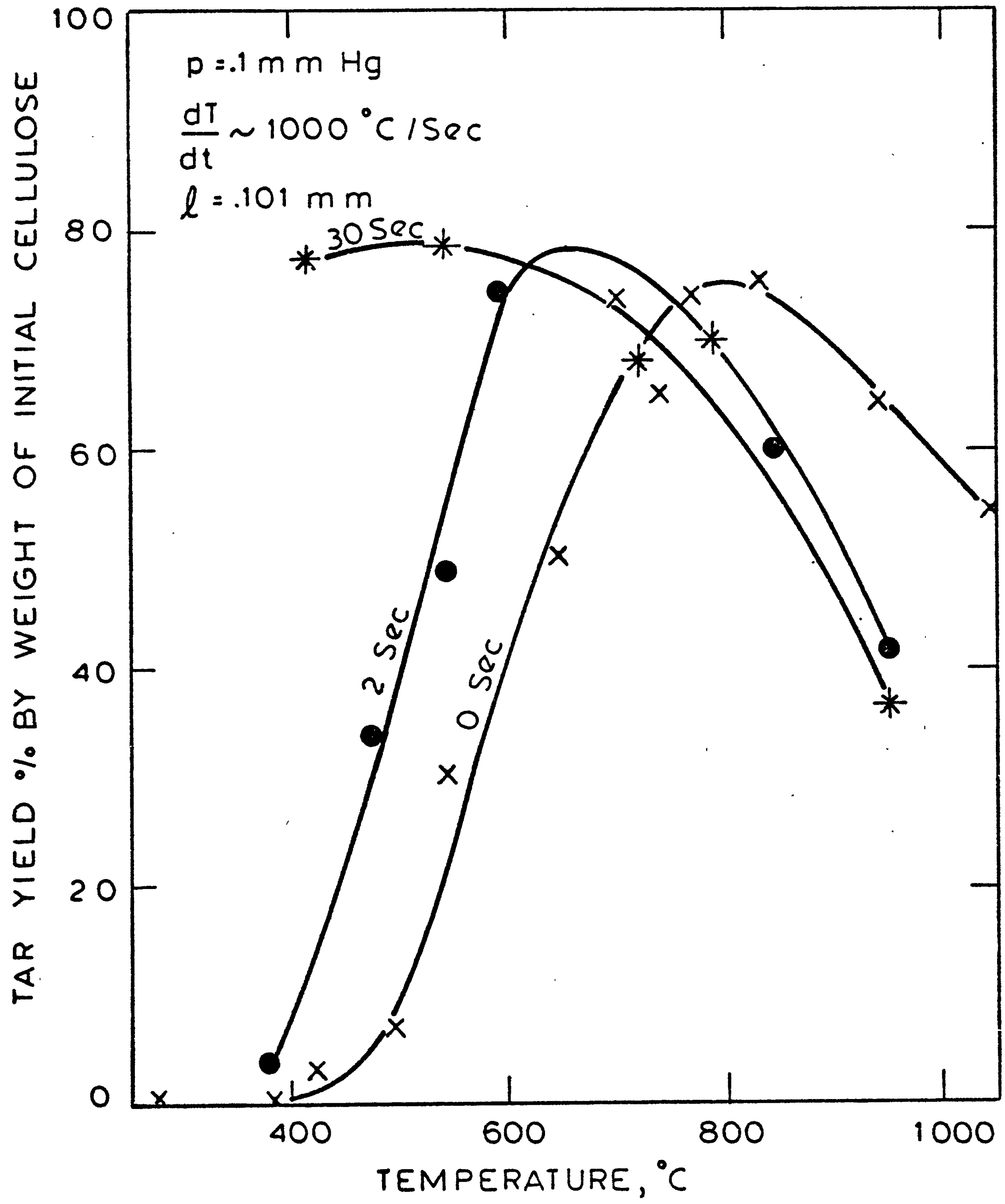


Figure 15. Effect of Holding Time on Yields of Tar at 0.1 mm Hg Pressure.

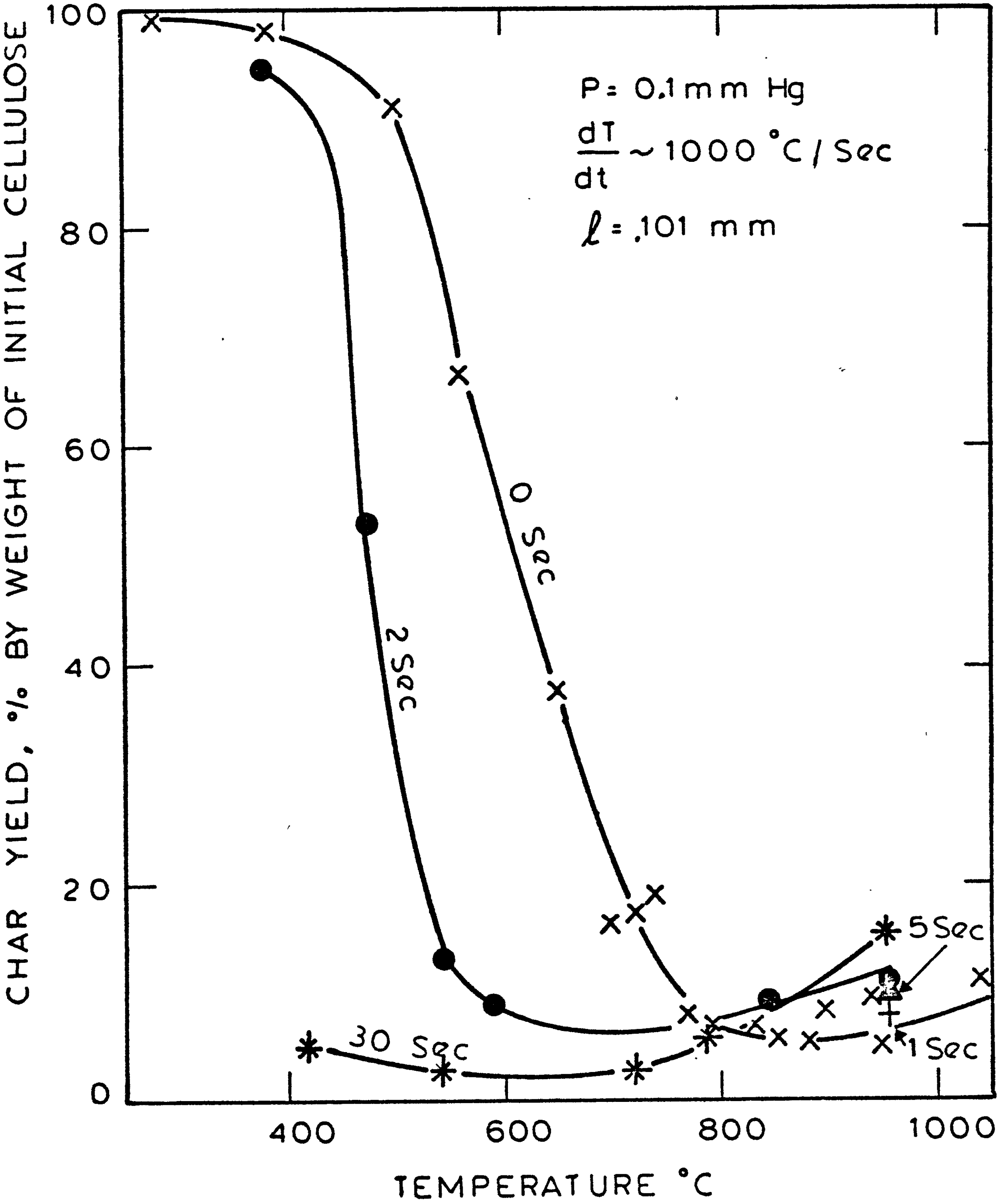


Figure 16. Effect of Holding Time on Yields of Char at 0.1 mm Hg Pressure.

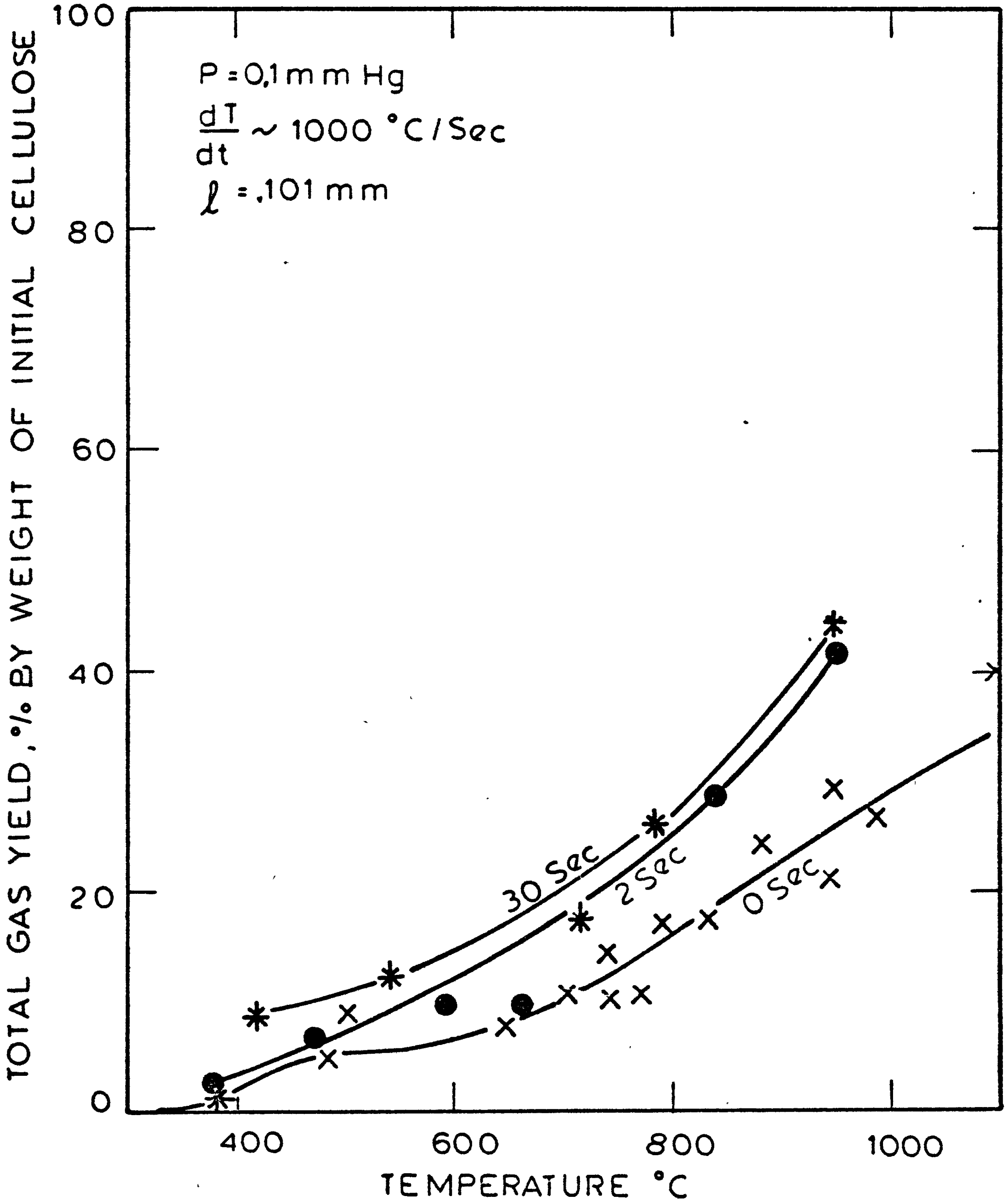


Figure 17. Effect of Holding Time on Yields of Total Gases at 0.1 mm Hg Pressure.

vacuum effects is that at these low pressures volatiles are rapidly transported through the region between the sample and the screen layers. However, under vacuum free convection does little to augment volatiles transport away from the outer layer of screen and into the main volume of the reactor (very small Grashof Number). Therefore the volatiles spend more time in the region outside of but relatively close to the screen than they do at pressures of 5 psig and higher. In zero holding time runs there is minimal opportunity for heating these outside regions, so the freshly formed volatiles passing through them are not significantly heated. However, as holding time increases the fluid in these zones undergoes more and more heating by the hot screen, and under these conditions volatiles passing through them will be heated and thus have better opportunity to be cracked. This behavior is in fact found in the data on tar yield at vacuum.

At 5 psig He, holding time affects the individual volatiles in the same way it does char, tar, and total gases. Figures 18-20 show these effects for 5 psig He runs. At low temperature, the yield of individual volatiles increases with holding time as long as the cellulose hasn't been completely converted. As temperature increases, even this small effect of holding time on volatiles vanishes.

At vacuum and low temperature, the effect of holding time is the same as it is at 5 psig, but at high temperature (>800°C), the effect is quite different (Figures 21-23). Yield of gases, such as CO_2, CO, CH_4, C_2H_4, C_2H_6 and C_3H_6 increase with holding time. Water yield remains almost constant. Aldehyde, ketone, and alcohol yields first increase to a maximum, then decrease. It is believed that these components are cracked to CO, CO_2, CH_4, C_2H_4, H_2, etc.

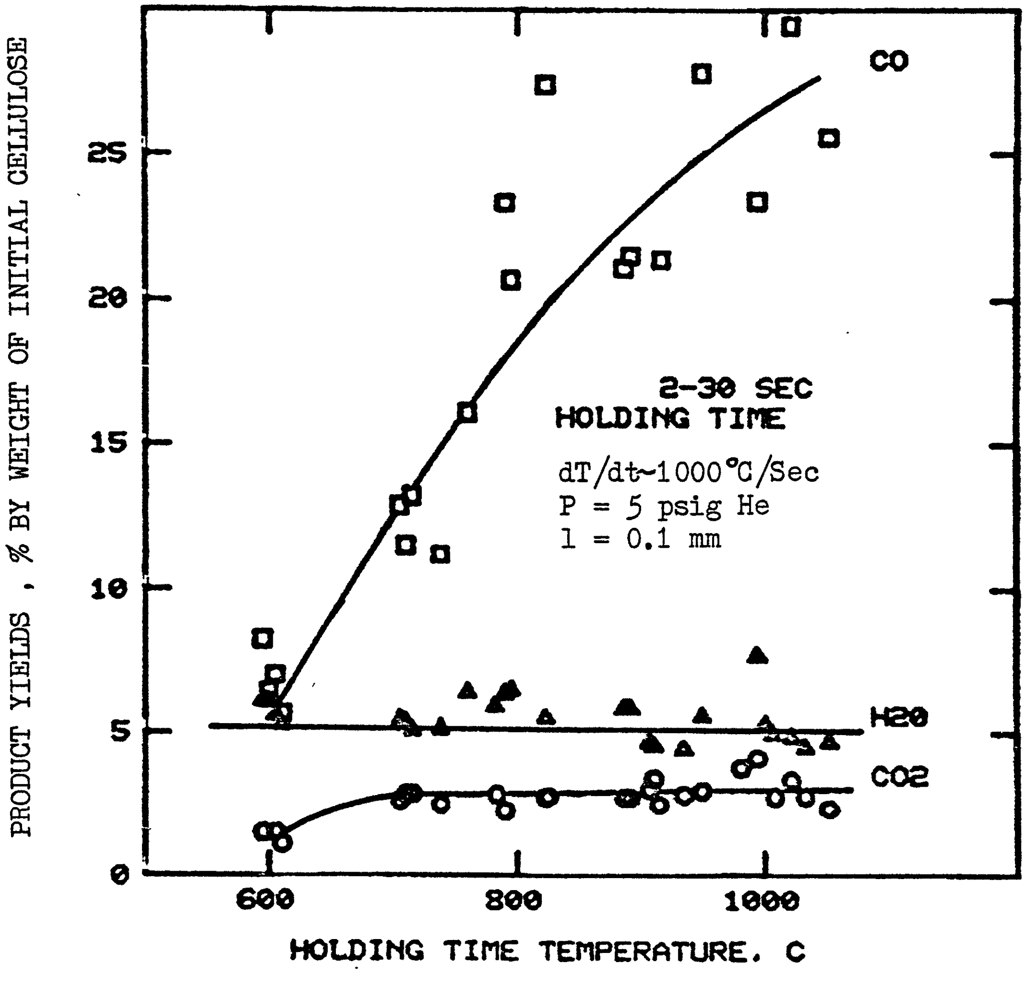


Figure 18. Effect of Holding Time on Yields of CO, CO2, and H2O at 5 psig He Pressure.

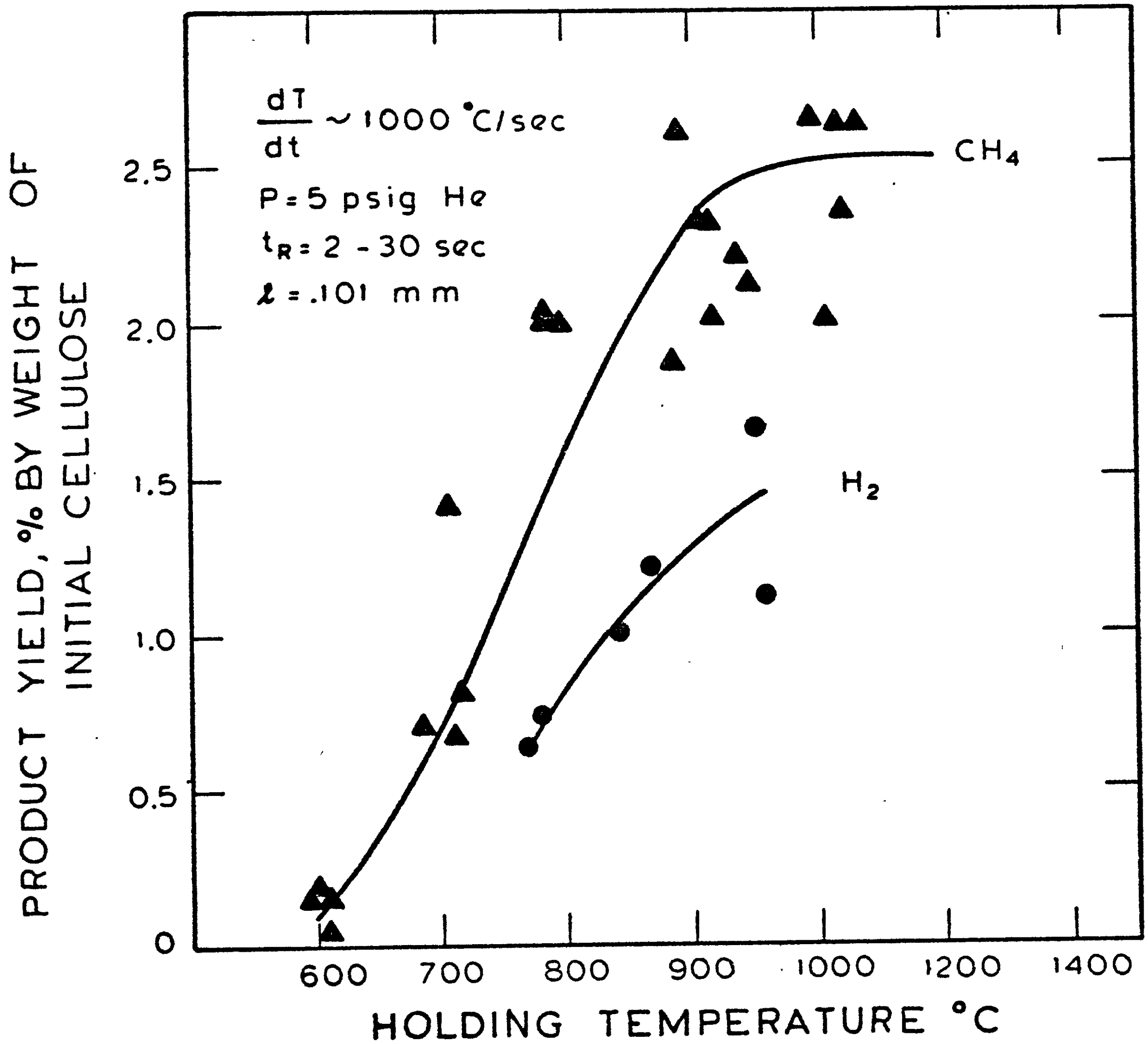


Figure 19. Effect of Holding Time on Yields of CH4, and H2 at 5 psig He Pressure.

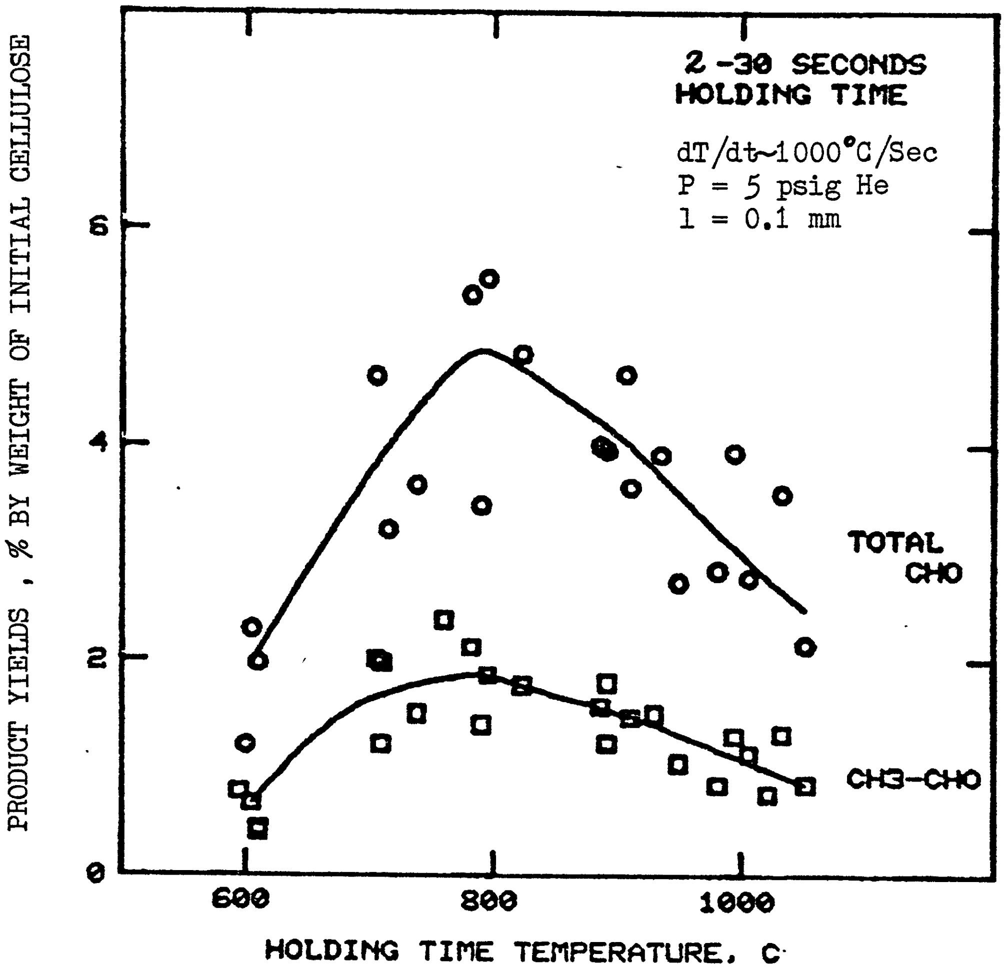


Figure 20. Effect of Holding Time on Yields of Acetaldehyde, and Total Oxygenated Volatiles at 5 psig He Pressure.

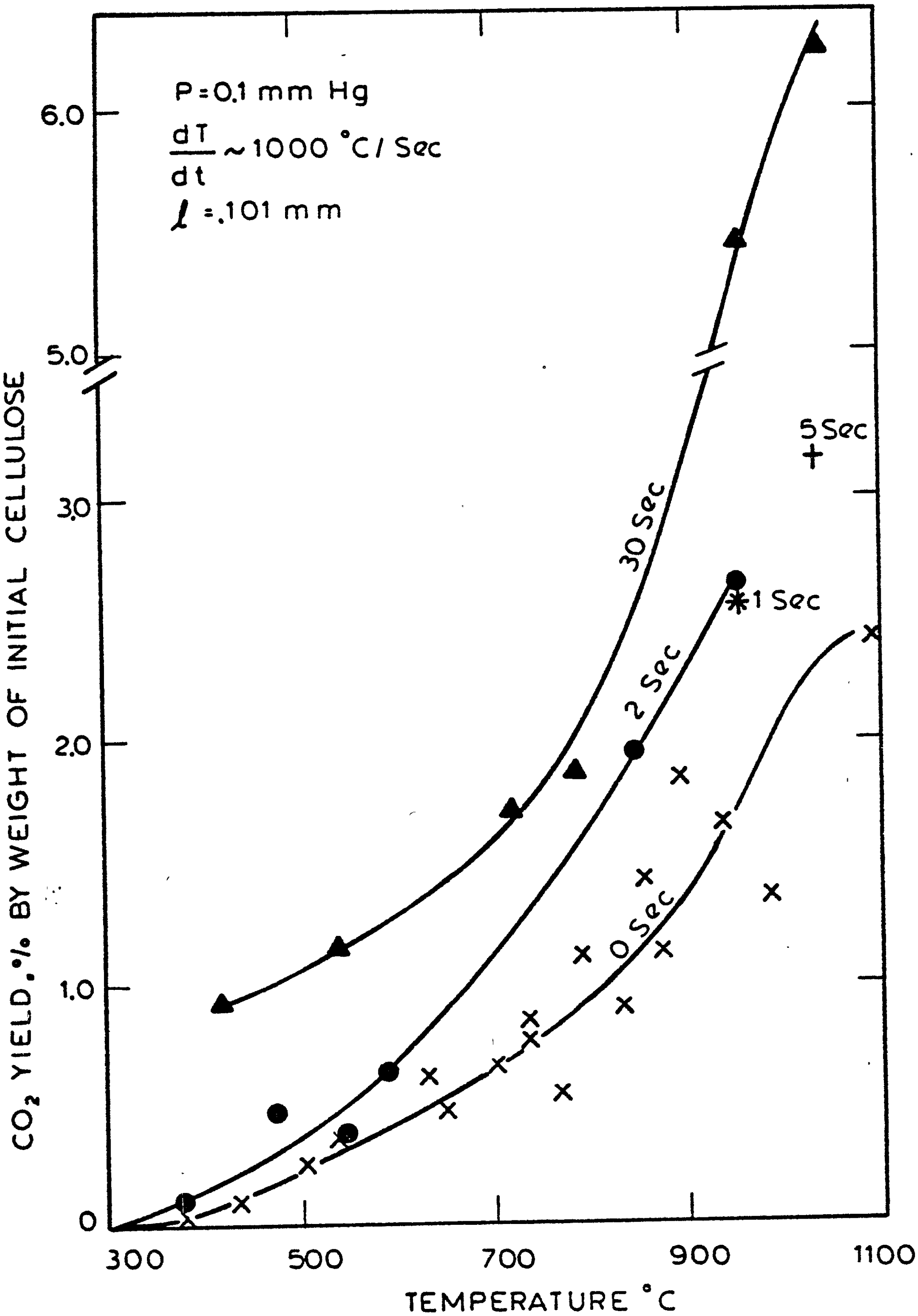


Figure 21. Effect of Holding Time on Yields of CO2 at 0.1 mm Hg Pressure.

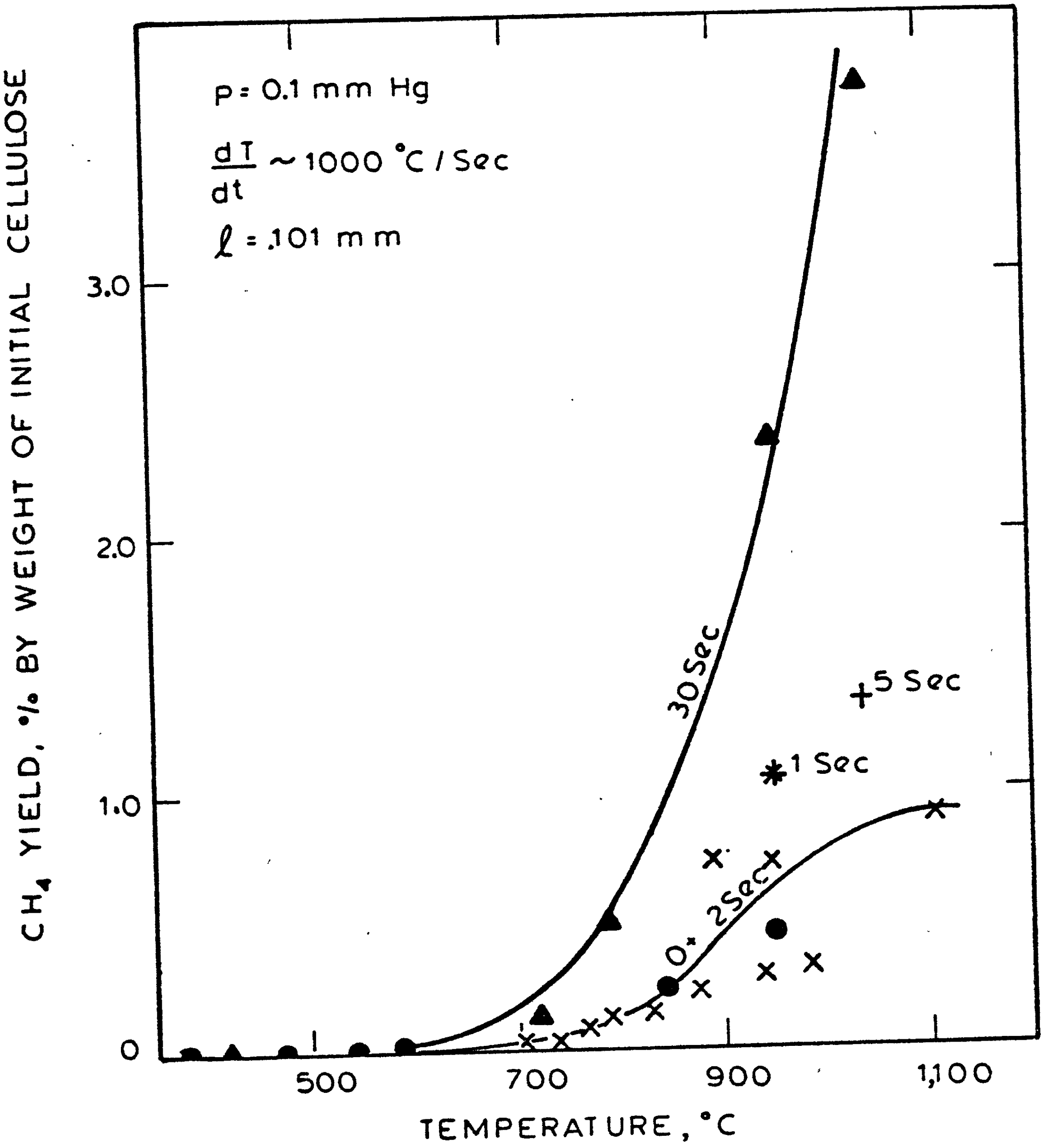


Figure 22. Effect of Holding Time on Yields of CH_4 at 0.1 mm Hg Pressure.

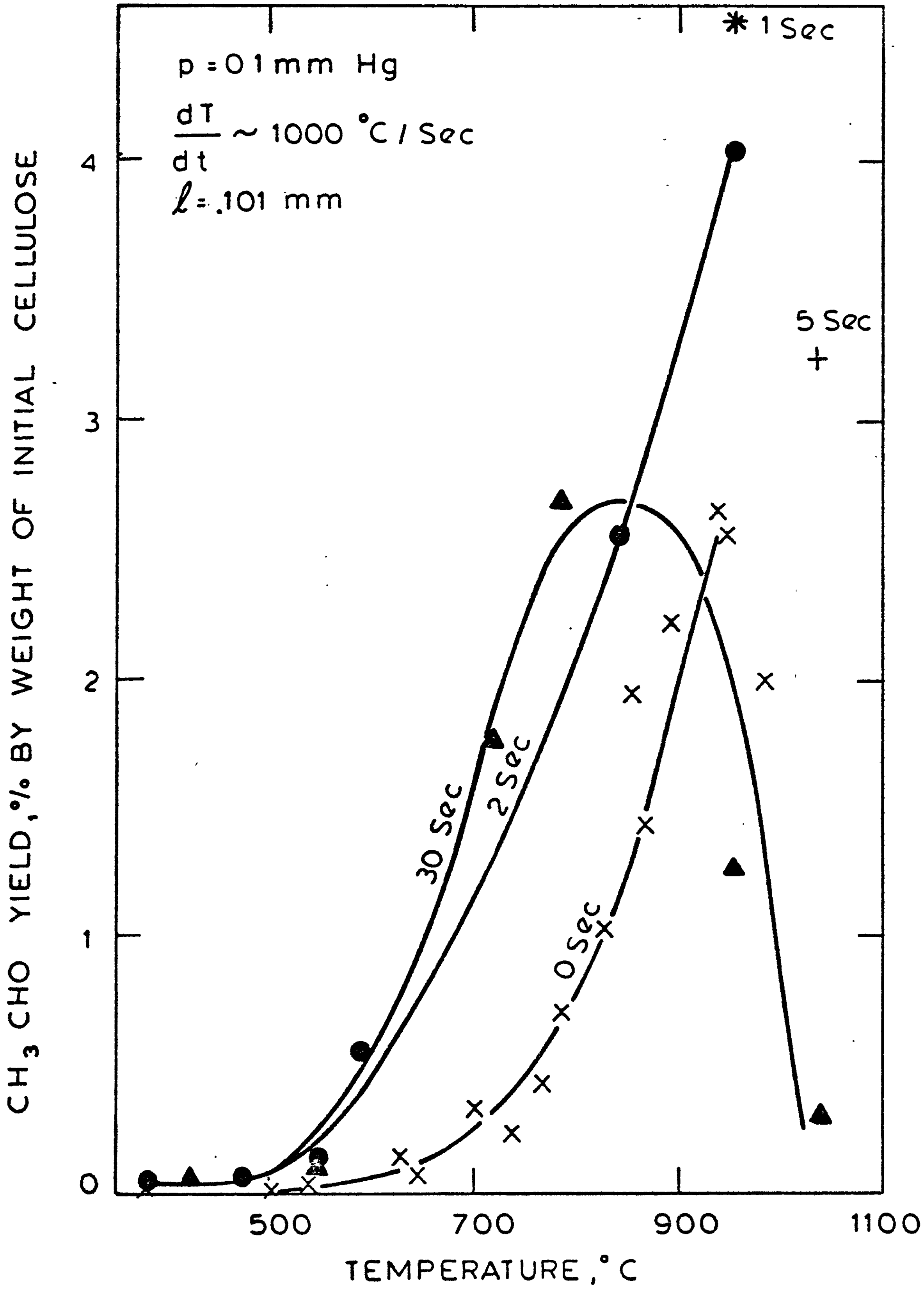


Figure 23. Effect of Holding Time on Yields of Acetaldehyde at 0.1 mm Hg Pressure.

5.2.3. Heating Rate

Another important factor in the pyrolysis of biomass is heating rate. The effects of this parameter on the pyrolysis of cellulose were determined and some of the results are shown in Figure 24-29. The effect of variations in heating rate over the range $\leq$ 100°C/sec to 10,000 - 15,000°C/sec, on yield of char, tar and total gas are shown in Figures 24-26 respectively. At a given peak temperature total conversion of the cellulose to volatiles increases as heating rate decreases. Similar behavior is exhibited by the yields of total gas and tar, below about 750°C. These effects undoubtedly arise because more time is available for conversion reactions during the heatup period, at the lower heating rates. Tar yields approach 85 wt.% of the cellulose at heating rates of $\leq$ 100°C/s and the maximum in the tar yield vs. temperature curve disappears at heating rates of 350°C/s and lower. These maxima have been interpreted as reflecting competition between: (a) escape of freshly formed tar from the elevated temperature environment of the hot stage and decomposing sample, and (b) cracking of the tar in that environment. The disappearance of the maxima at the lower heating rates is believed to occur because there is adequate time during the heatup period for most of the tar to be formed and escape the immediate neighborhood of the screen before temperatures sufficiently high for extensive cracking to occur are attained. Some of the data on the effects of heating rate on the yields of specific volatile are shown in Figures 27-29. Data on oxygenated volatiles (Figure 27) indicates as heating rate increases the maximum yields of these products increases, but the effect is slight. Yields of hydrocarbons and CO show a maximum with a heating rate at approximately 1000°C/sec (Figure 28). The maximum yield of CO_2 and H_2O remain unaffected by heating rate (Figure 29).

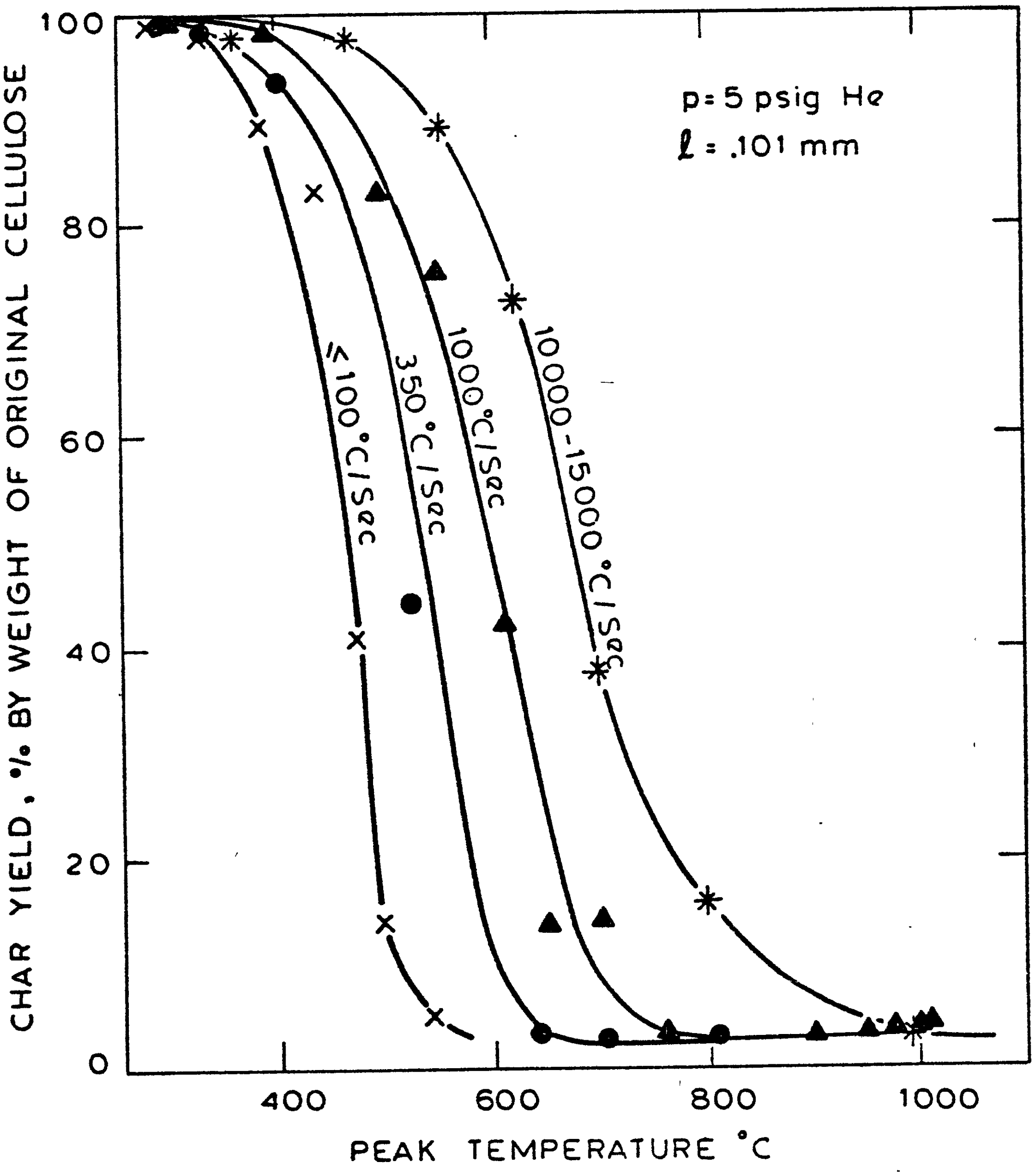


Figure 24. Effect of Heating Rate on Yields of Char at 5 psig He Pressure.

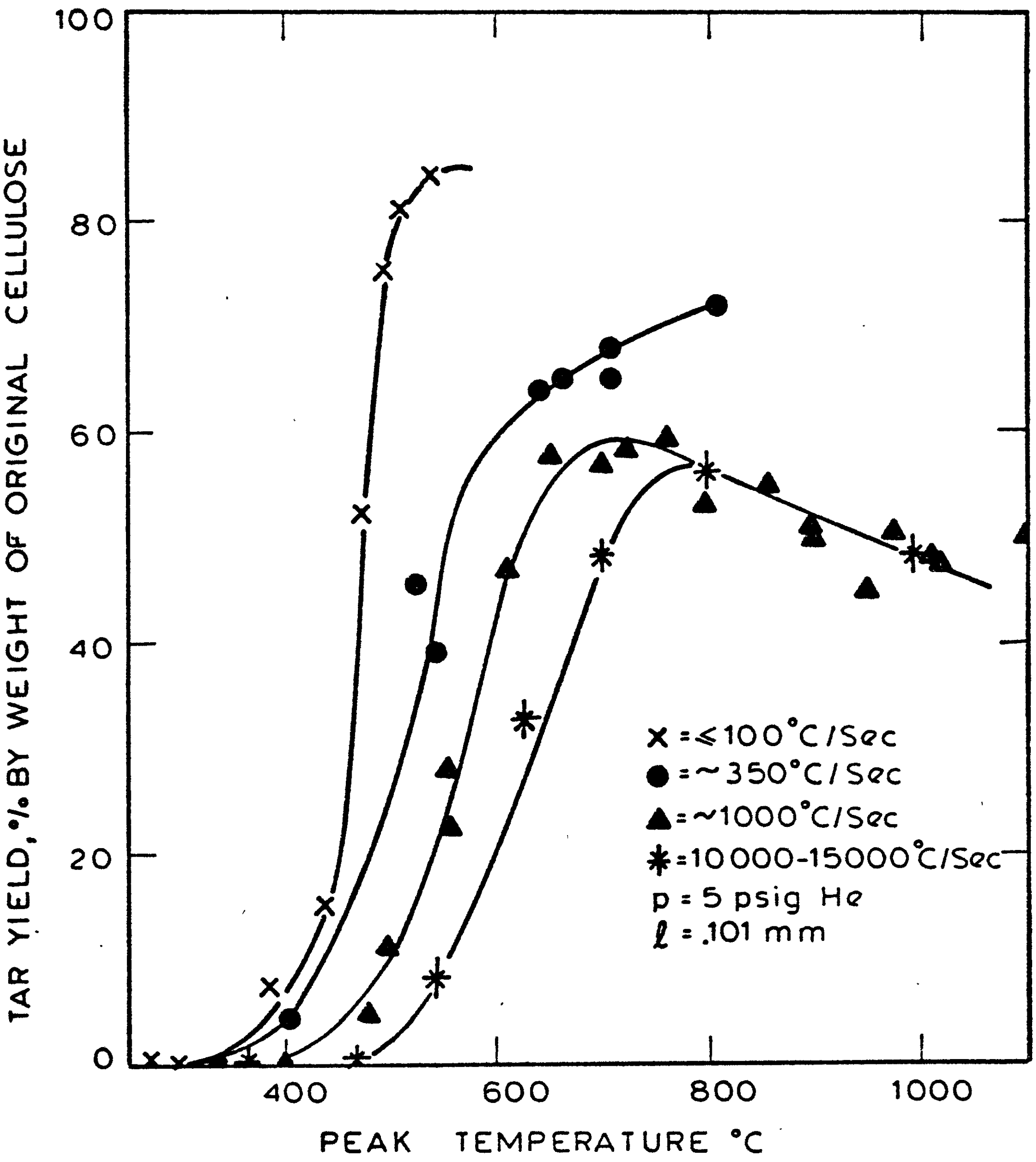


Figure 25. Effect of Heating Rate on Yields of Tar at 5 psig He Pressure.

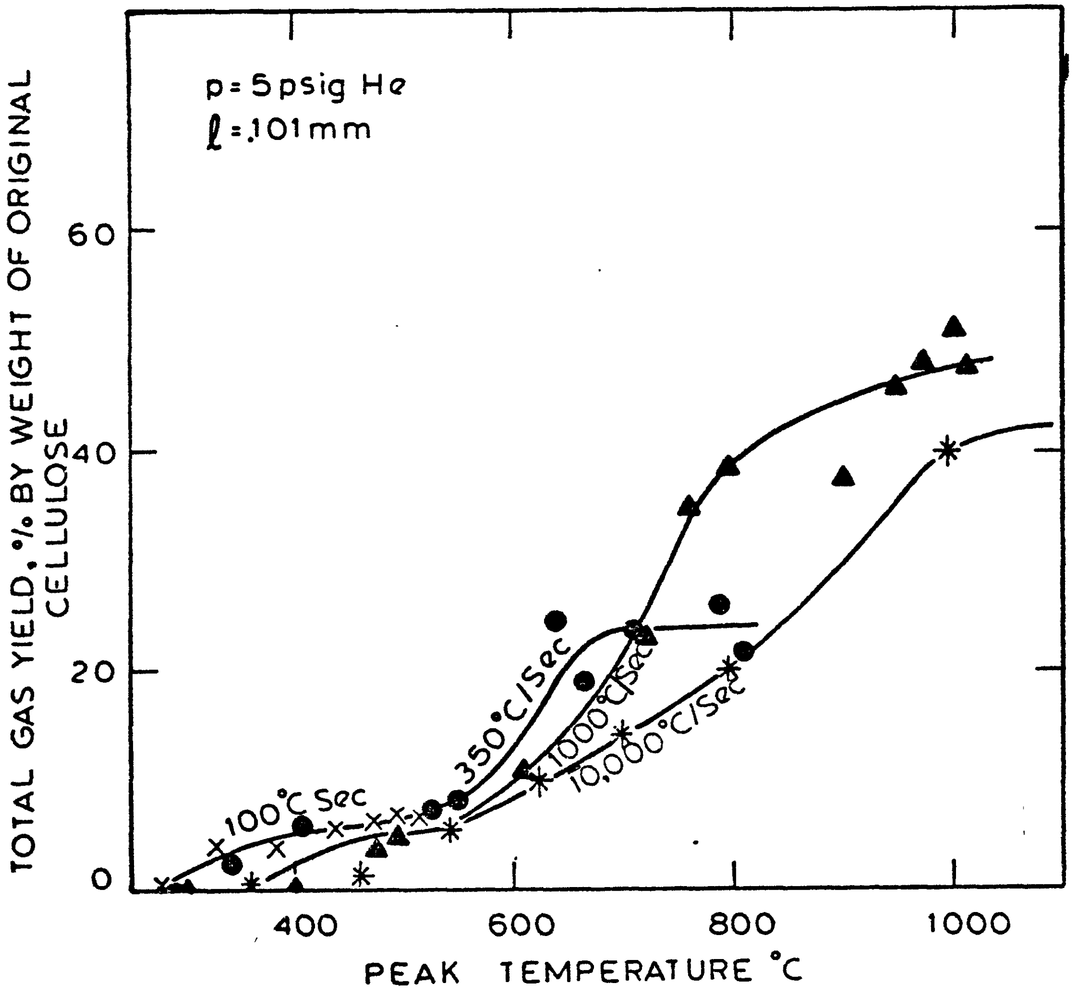


Figure 26. Effect of Heating Rate on Yields of Total Gases at 5 psig He Pressure.

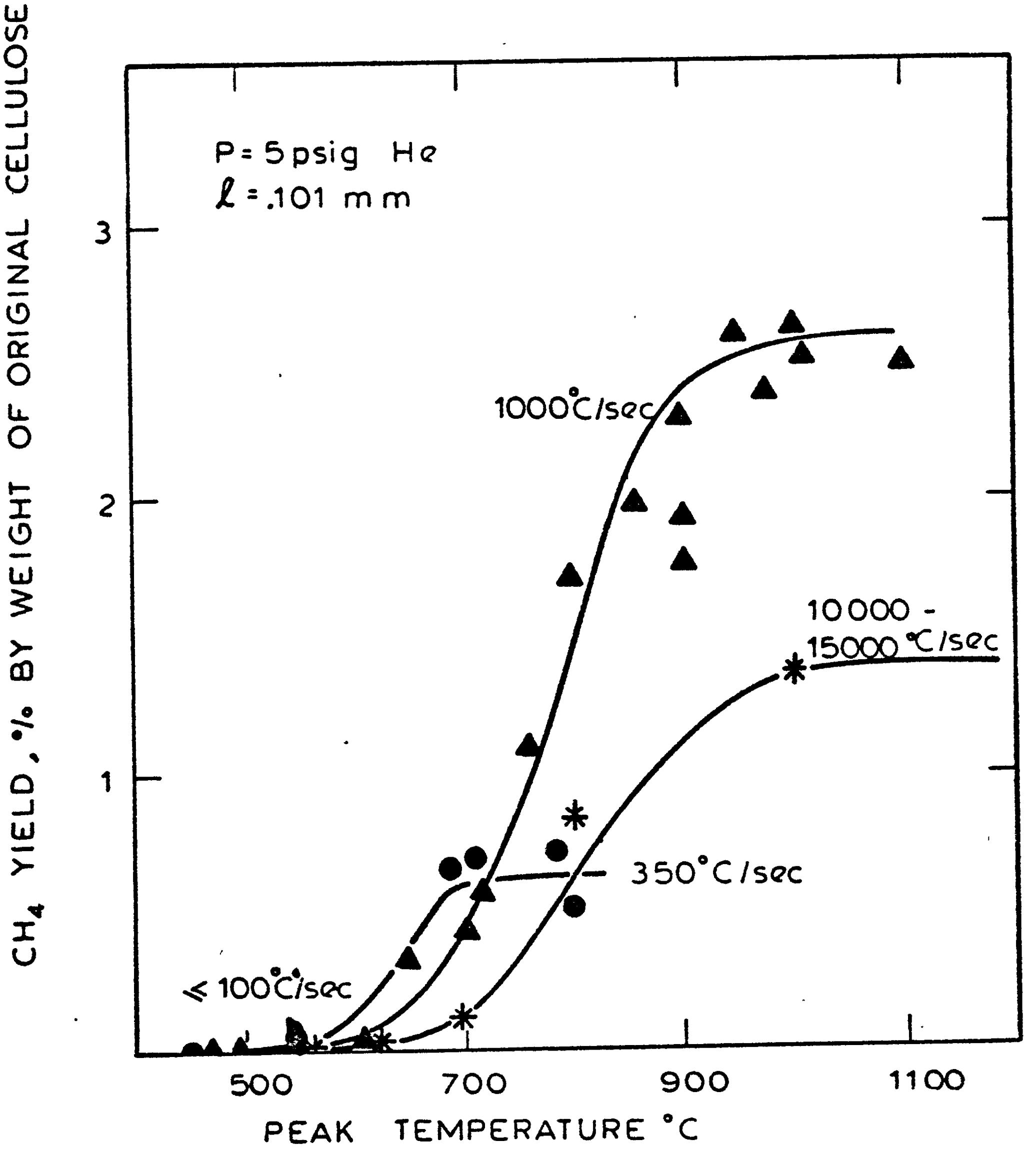


Figure 27. Effect of Heating Rate on Yields of CH_4 at 5 psig He Pressure.

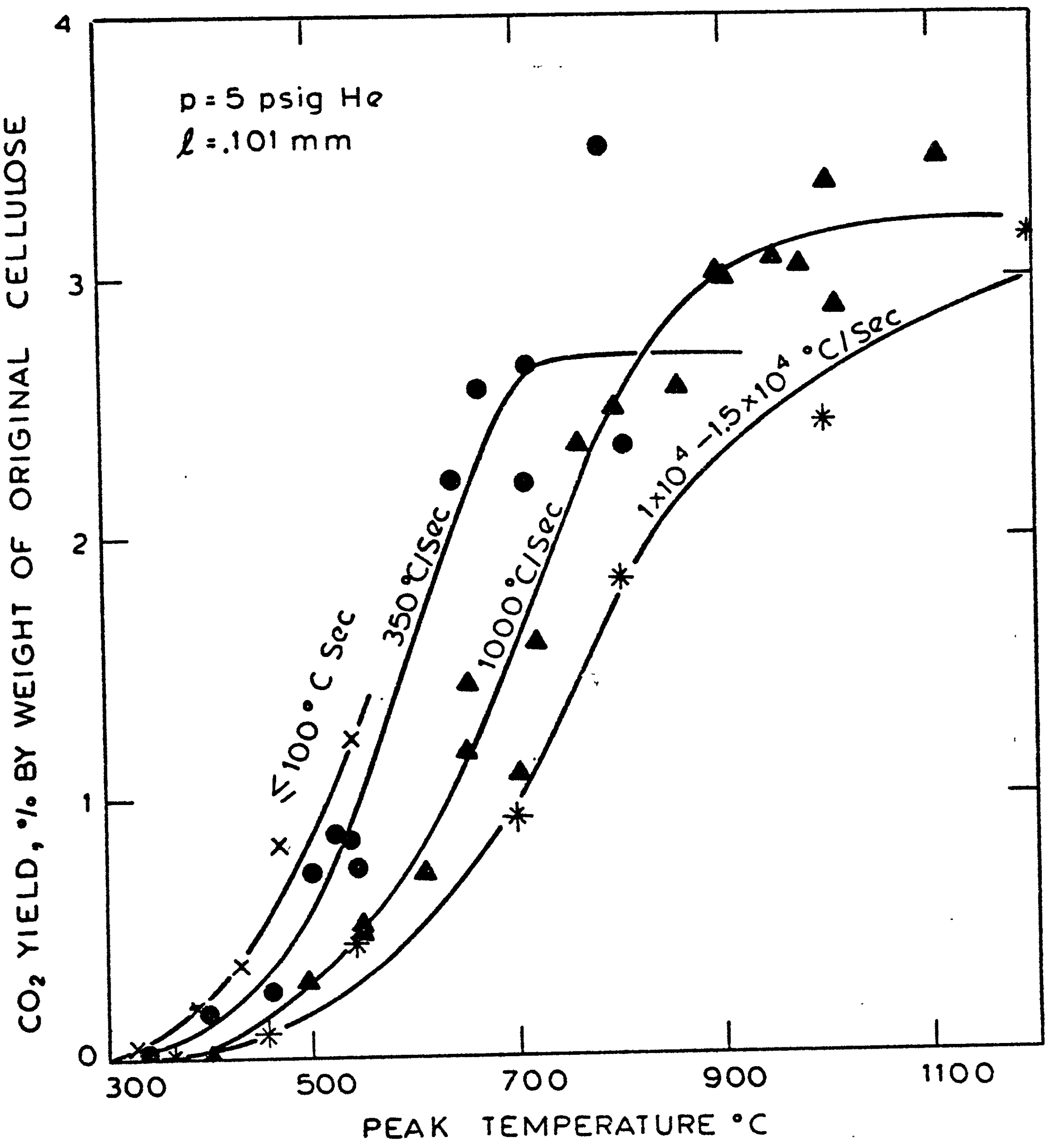


Figure 28.Effect of Heating Rate on Yields of CO2 at 5 psig He Pressure.

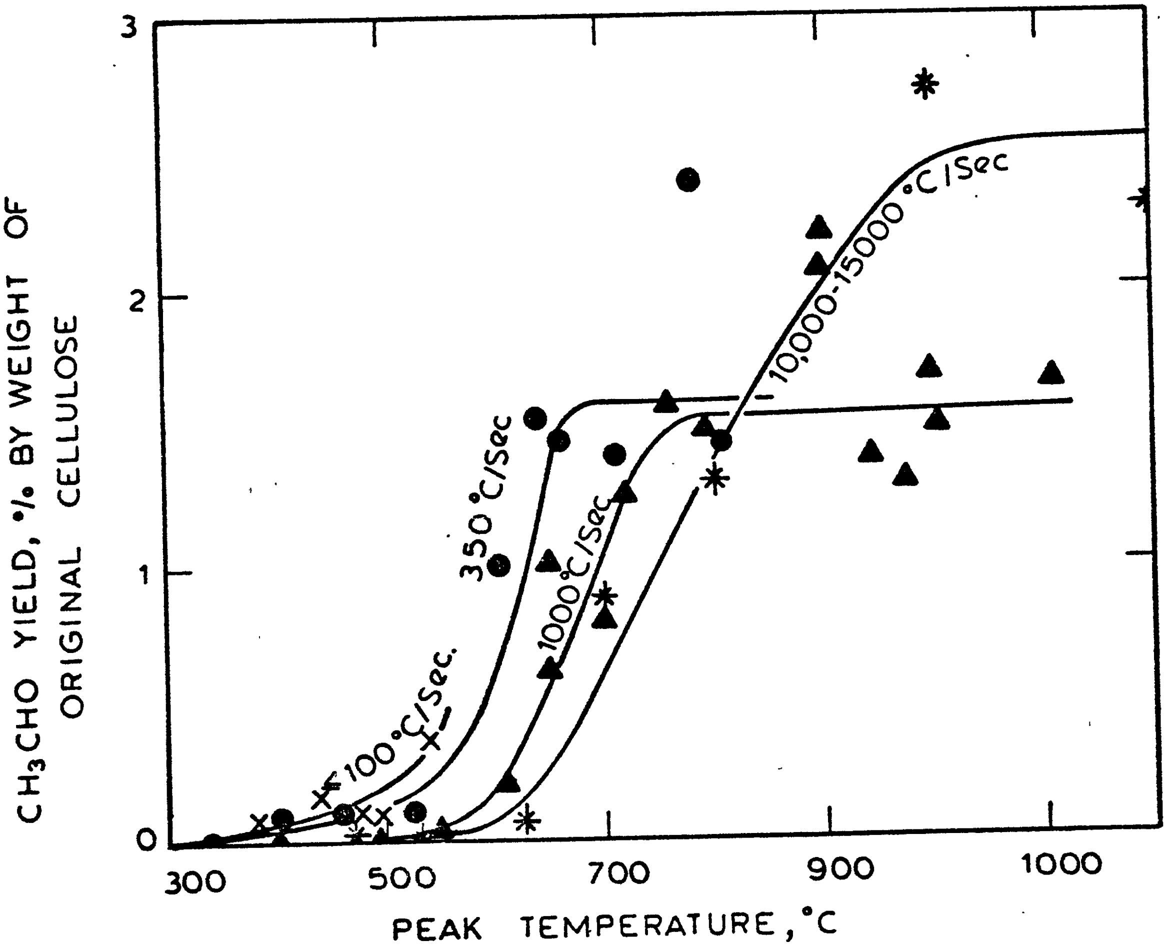


Figure 29. Effect of Heating Rate on Yields of Acetaldehyde at 5 psig He Pressure.

5.2.4. Pressure

Some of the results on the effects of variations in total reactor pressure over the range 1.31 x 10^{-4} to 69 atm, on yields of products for heating rate of 1000°C/sec are shown in Figures 30-34. At a given peak temperature, as pressure decreases from 5 psig He, the tar yield increases, while increasing pressure to 1000 psig He, gives decreased tar yield (Figure 30). Char yield is higher at 1000 psig He than at 5 psig He. This is because more of the tar, which is produced, participates in coke formation reactions. At the same time decreasing the pressure from 5 psig He to vacuum cause increase in char yield at high temperature (Figure 31). Since at vacuum under zero holding time conditions tar cracking is diminished the gas yield drops sharply. At high pressure, where more tar cracking occurs, the total gas yield is higher (Figure 32).

Results on the yields of individual volatiles show, except for oxygenated products such as acetaldehyde, methanol, and acetone which go through a maximum, yields of most of gases increase as pressure is increased (Figure 33-34). This behavior undoubtedly refects secondary cracking of tar and, at elevated temperatures, of these oxygenated light volatiles, and also implies that at higher temperatures, the latter compounds can contribute to the net make of hydrogen, CO, CO_2 and hydrocarbon gases.

5.2.5. Sample Thickness

The effect of sample thickness was determined by using samples of 0.01, 0.019, and 0.04 cm thickness. A comparison of some of the results are presented in Figure 35. It is obvious from the results that doubling the thickness of the sample has no significant effect on the total cellulose decomposition, or on yields of tar or total gases. Increasing the sample

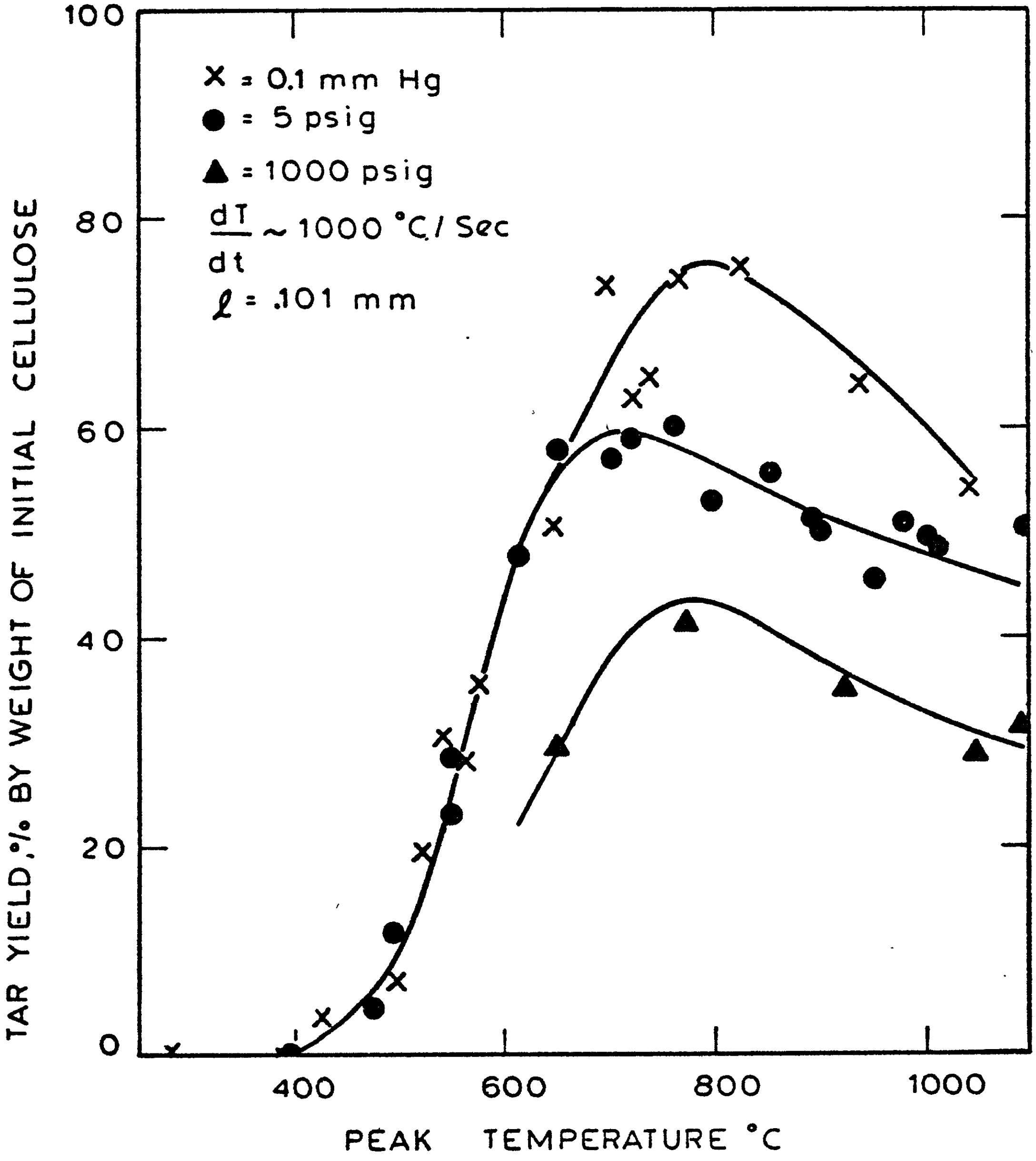


Figure 30. Effect of Pressure on Yields of Tar at 1000°C/Sec Heating Rate.

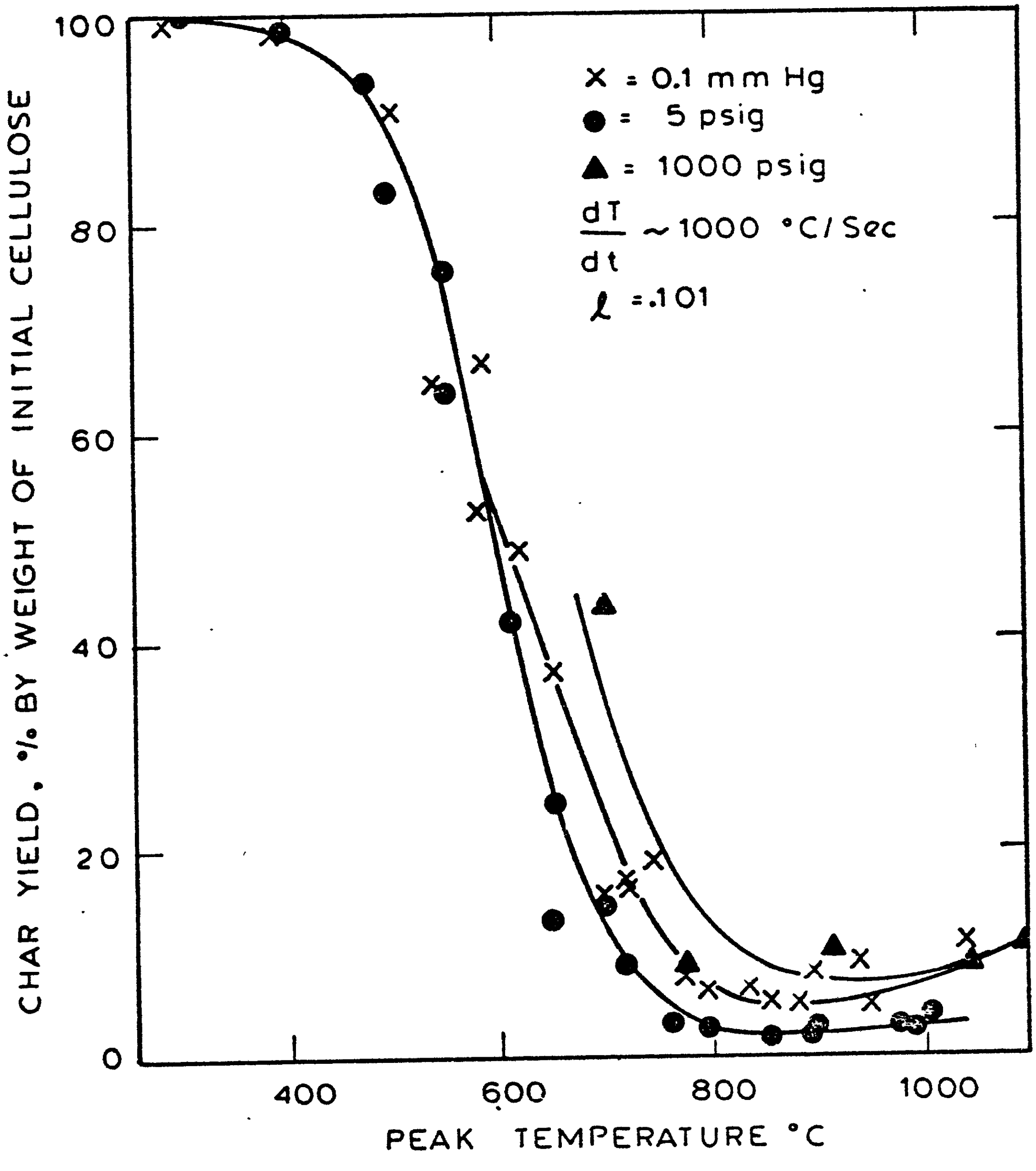


Figure 31. Effect of Pressure on Yields of Char at 1000°C/Sec Heating Rate.

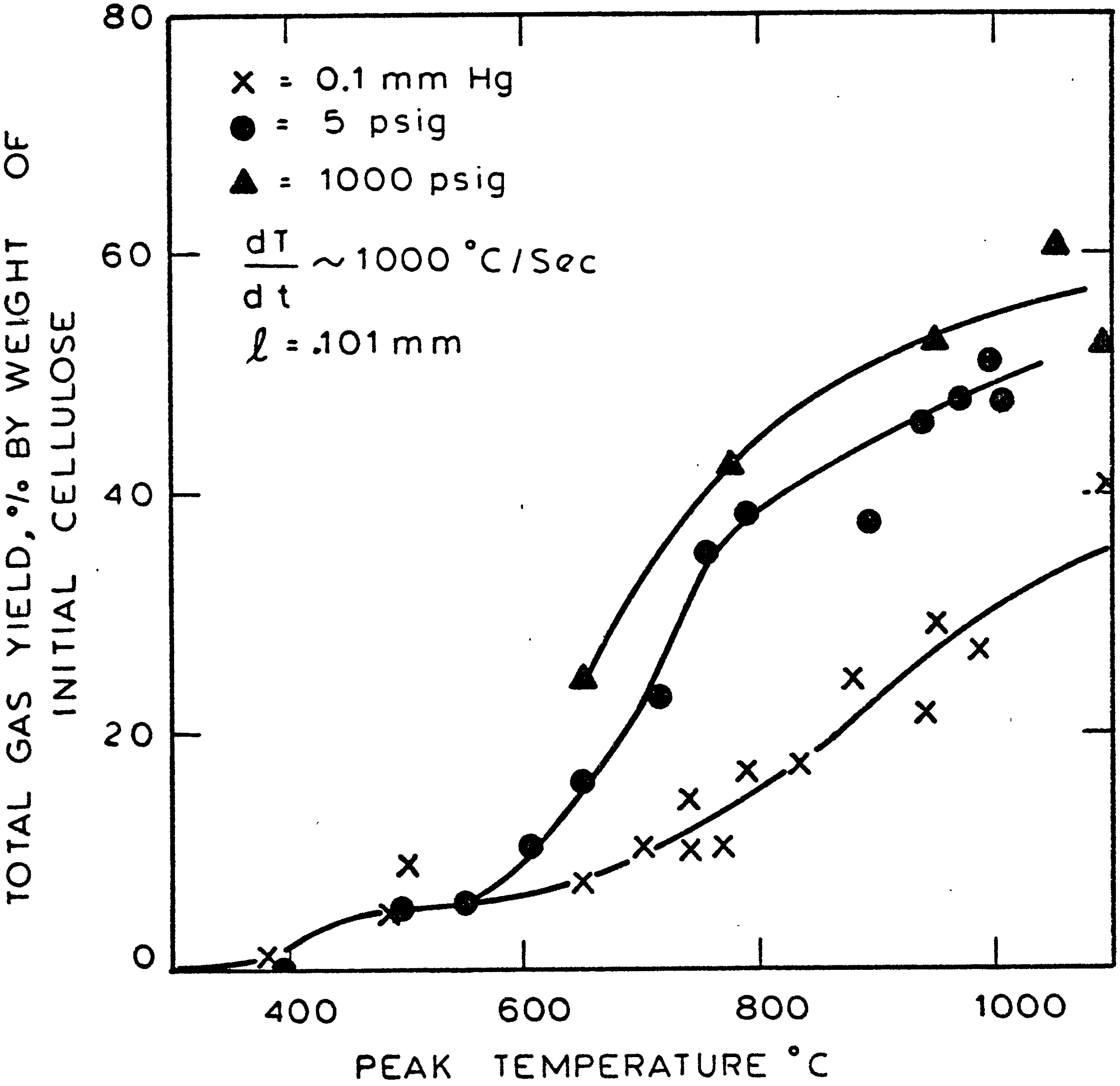


Figure 32. Effect of Pressure on Yields of Total Gases at 1000°C/Sec Heating Rate.

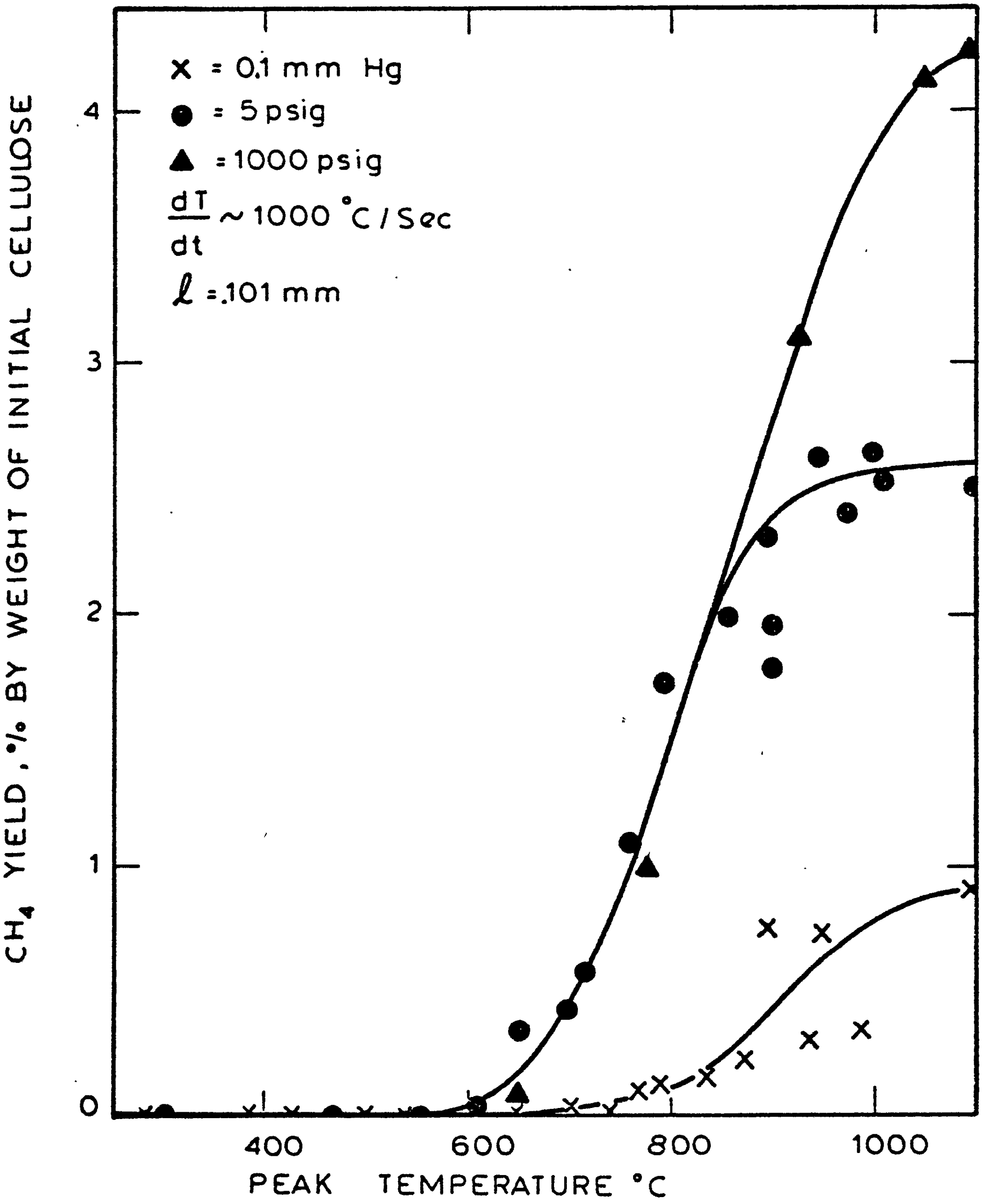


Figure 33. Effect of Pressure on Yields of CH4 at 1000°C/Sec Heating Rate.

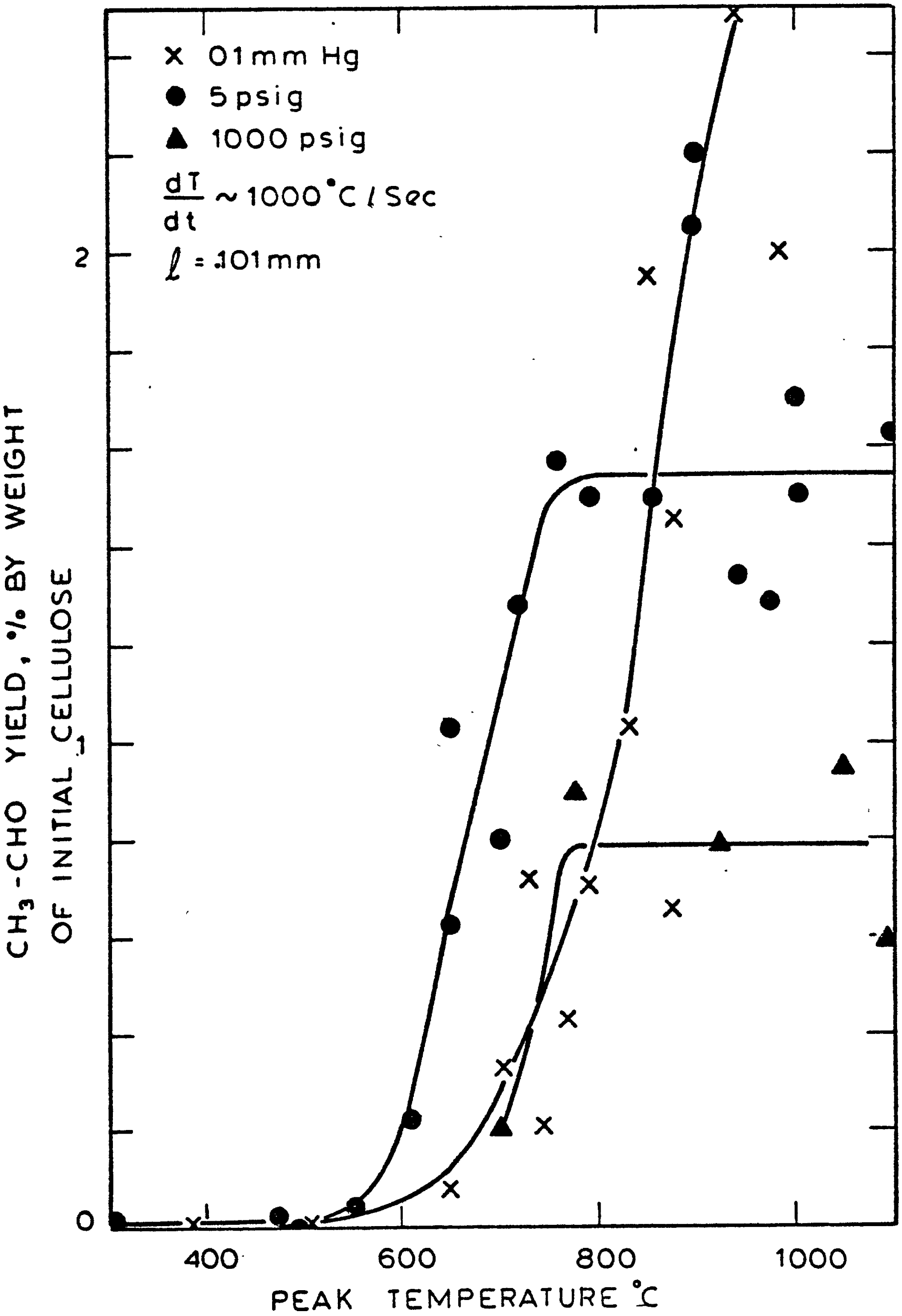


Figure 34. Effect of Pressure on Yields of Acetaldehyde at 1000°C/Sec Heating Rate.

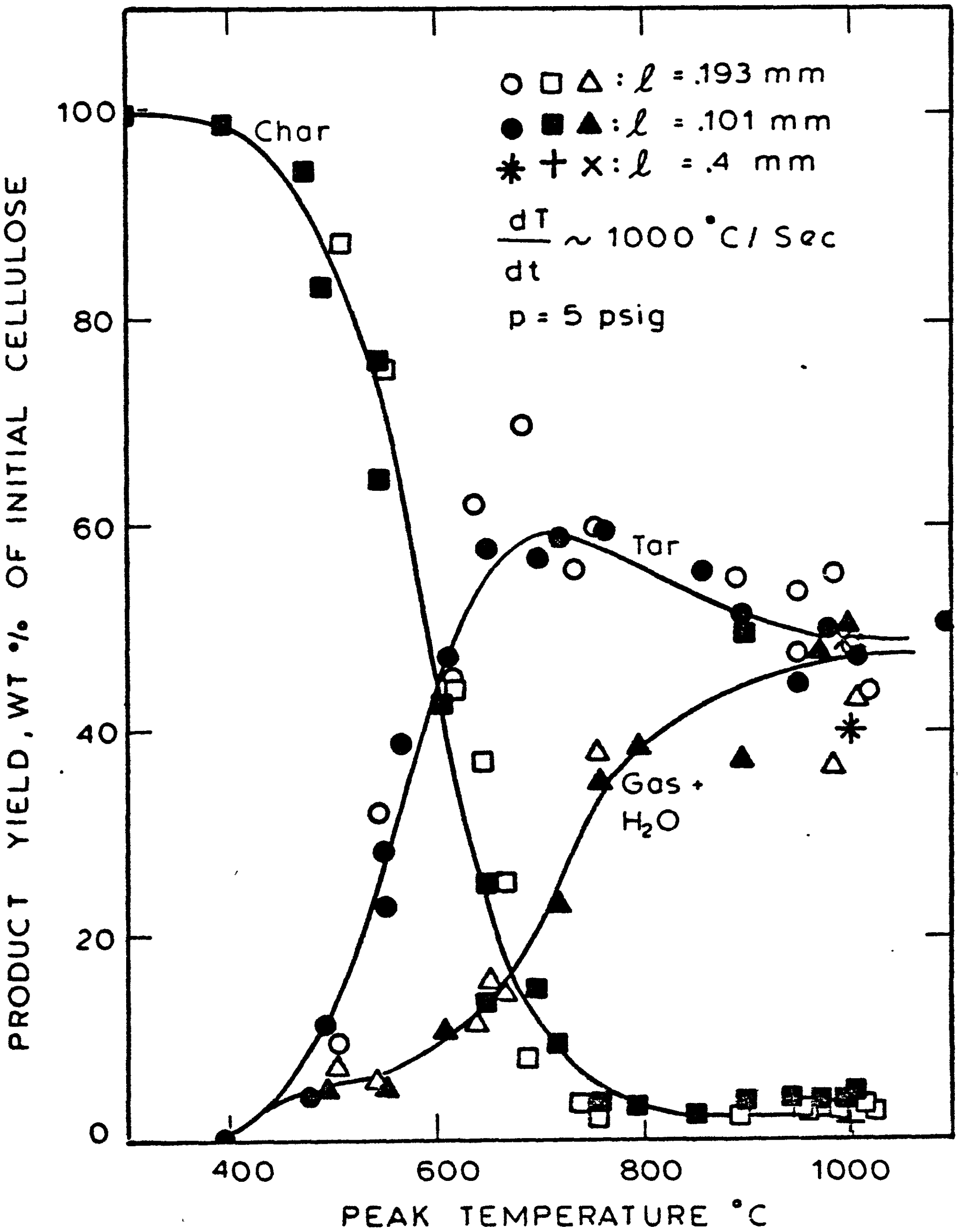


Figure 35. Effect of Sample Thickness on Yields of Char, Tar, and Total Gases at 5 psig He Pressure.

thickness to four times has some effect on the results obtained. The results show 10-15 wt.% decrease in tar yield and a proportional increase in total gas yield. Since the residence time of tar and the probability for its contacting hot surfaces are both increased by increasing the sample thickness, more of it is cracked to lighter volatiles such as CO, CO_2, CH_4, etc.

5.3 Modeling

The development of a kinetic model to account for the behavior shown by data collected in this study is very important. One straightforward approach that has proved useful in the past for correlating similar data on the rapid pyrolysis of coal[26] and cellulose[6] is the single first-order reaction model for total pyrolysis (total weight loss) of cellulose. Thus:

$$\text{Cellullose} \xrightarrow{K_i} \text{product}_i$$

$$\frac{dV_i}{dt} = K_{oi}{}^{-E_i/RT}\,(V_i^* - V_i) \qquad (5.3.1.)$$

Since the time-temperature history and the final yield in each experiment are known, it is possible to obtain a best fit for kinetic parameters. The best fitting kinetic parameters were obtained and summarized in Table 4 for different conditions. Experimental data are tabulated along with the predictions of the model in Figure 36. It can be seen that the results are in good agreement. The ease and accuracy with which the first order reaction model fits the data leads to some important conclusions. A comparison of the kinetic parameters obtained in this study with those obtained in previous investigation (Figure 2), show considerable agreement. Further, the kinetic results obtained here from a single reaction model fitted to data from one set of conditions can

Table 4. Kinetic Parameters for Cellulose Pyrolysis by a Single First-Order Model[1]

Temperature Range	Heating Rate(°C/sec)	Pressure (atm)	E(kcal/ gmole)	$\log_{10} k_o$	V*(%)
400-900	1,000	1.34	31.79	8.30	94.08
300-800	350	1.34	33.21	9.475	95.31
250-540	100	"	33.39	9.567	96.17
400-850	10,000	"	16.37	4.12	99.47
400-900	1000	1.31×10^{-4}	31.25	7.93	86.09
300-750	250	"	32.94	9.135	95.26

[1] It should be noted that first-order reaction model can be only used for those components which at least at a given pressure their yields don't go through a maximum such as weight loss, CO_2 and CO but not tar.

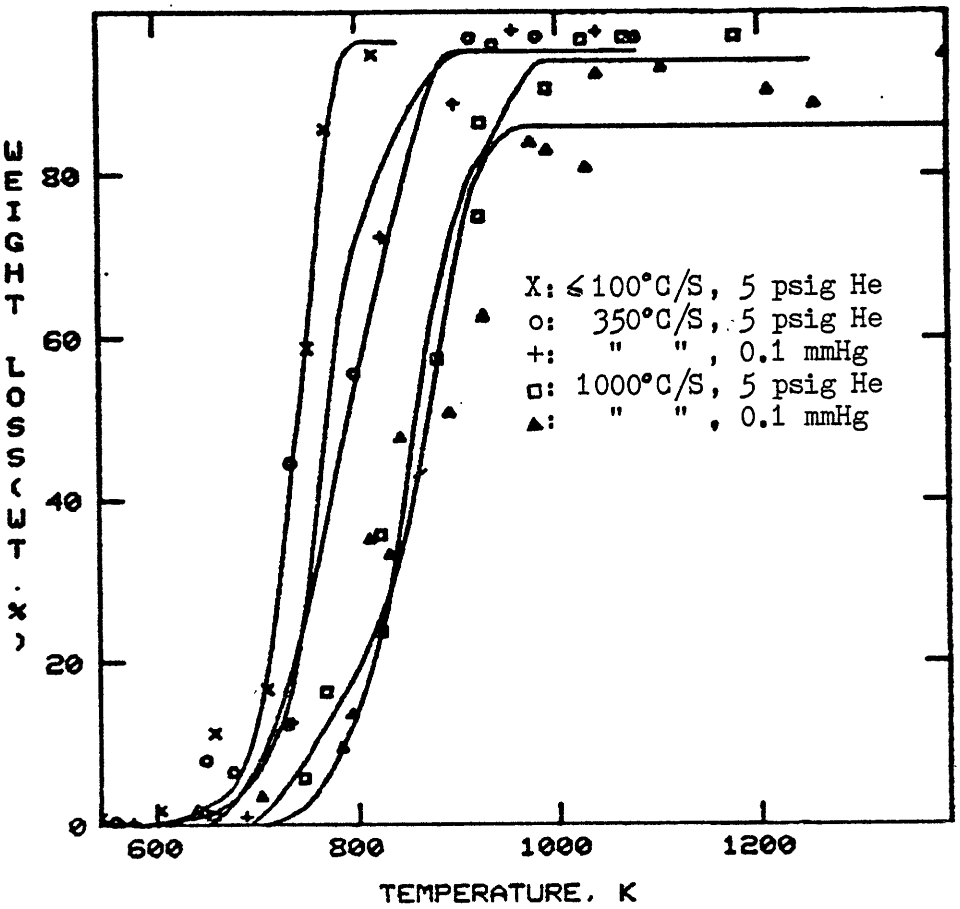


Figure 36. Comparison of Calculated and Experimental Weight Loss of Cellulose at Different Conditions. Prameter values for each set of conditions are those in Table 4.

predict the rate of pyrolysis for a variety of other conditions (Figure 37). This indicates that the basic reactions involved, in the initial pyrolysis of cellulose, are similar. The exception is for very low temperatures of about 250°C.

Although the single reaction model provides a good fit to the experimental data, a model based on the assumption that the decomposition proceeds by many independent parallel reactions might be more realistic, since cellulose pyrolysis is obviously not a simple, single step reaction. In the multiple parallel reaction model, the rate constants are assumed to be represented by a distribution of activation energies with identical frequency factors. The predicted Kinetic parameters for such a model and for the Conditions given in Figure 37R, for total weight loss are: $E = 40.3$ kcal/gmole, $\sigma = 3.25$ kcal/gmole, $\log K_0 = 10.44$ sec^{-1}, and $V^* - 95.73$ wt%. Comparison of the results from single and multiple first-order reaction model are shown in Fig. 37R.

The rate of formation of each volatile species can also be modeled by single first-order reaction model. Table 5 presents the kinetic parameters for these products formation under the experimental conditions given at the bottom of the table. For many of the products the values derived for the activation energy and preexponential factor are reasonable for typical organic decomposition reactions[25,26].

Neither single first-order reaction nor multiple first-order reactions model offers explanation for the observed influence of total reactor pressure on the yield of volatiles from the cellulose pyrolysis. Consequently the cellulose pyrolysis data could only be correlated by models previously described for a given pressure. The results on pressure especially indicate that secondary reactions of tar and to some extent of light oxygenated liquids such as acetaldehyde, contribute extensively to the rates and extent of formation of light volatiles during the rapid

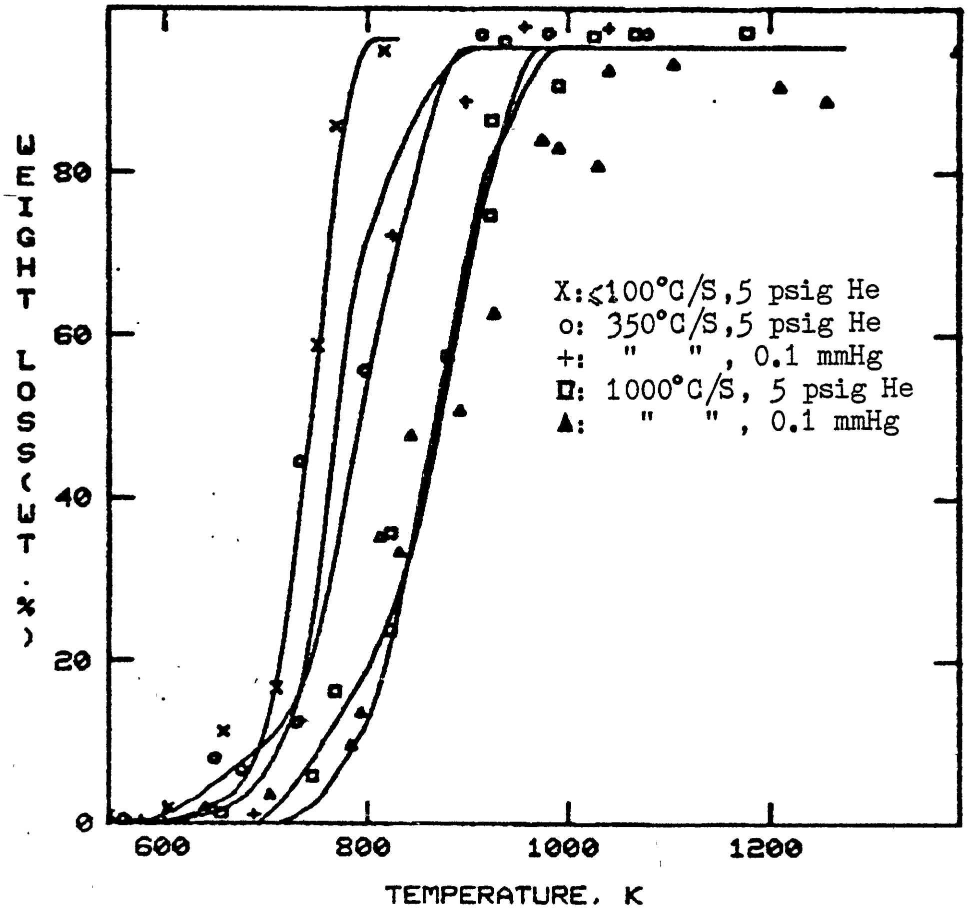


Figure 37. Comparison of Calculated and Experimental Weight Loss of Cellulose at Different Conditions When One Set of Kinetic Parameters are Used for all Conditions(E= 33.21 Kcal/gmole; $\log_{10} k_0$=9.475 Sec^{-1}; V^*=95.31 wt.%).

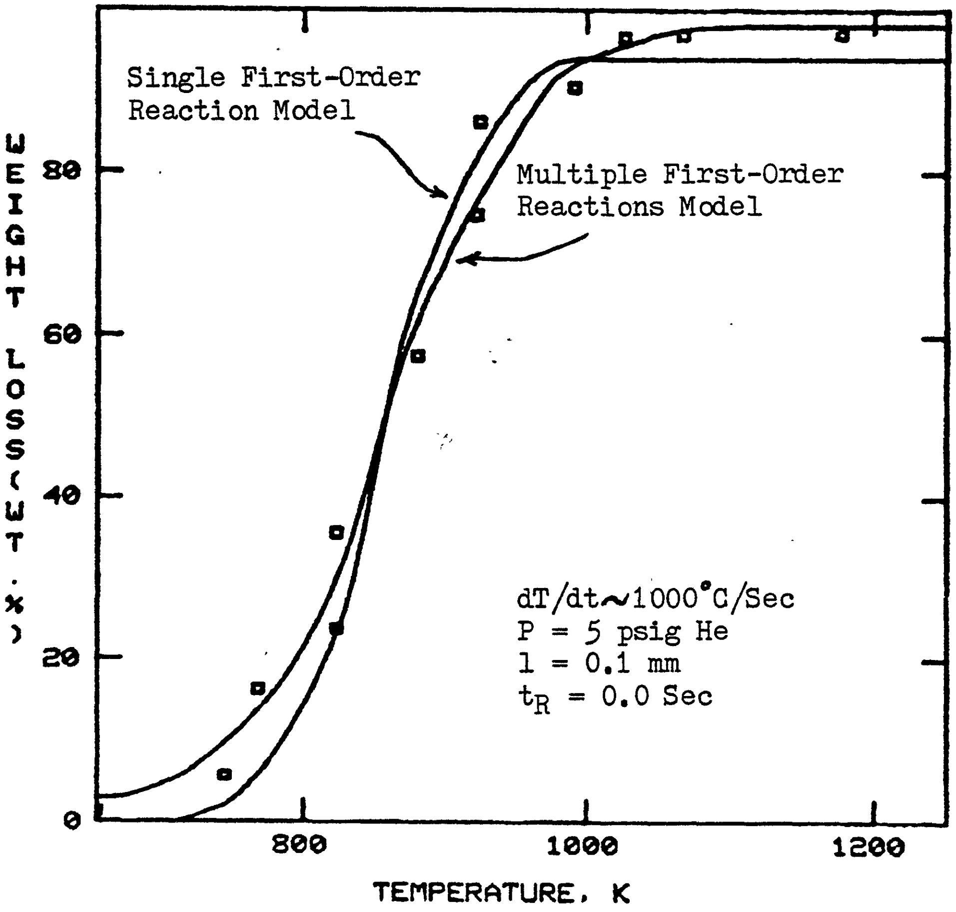


Figure 37R. Comparison of Measured Cellulose Weight Loss with Calculated Values from Single First-Order Reaction Model and Multiple First-Order Reactions Model.

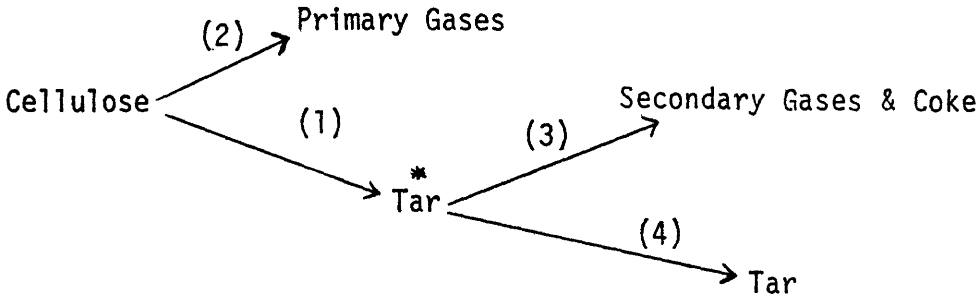
Table 5. Kinetic Parameters for Individual Products in Cellulose Pyrolysis by a Sigle First-Order Reaction Model

Product	E,kcal/g-mole	$\mathrm{Log}_{10}k_o, s^{-1}$	V*,wt.%
Total Weight Loss	31.79	8.30	94.08
CH_4	60.04	13.00	2.41
C_2H_4	49.82	10.82	2.07
C_2H_6	41.55	9.06	0.26
C_3H_6	60.67	14.93	0.67
H_2	27.29	6.17	1.16
CH_3OH	49.35	13.42	0.92
CH_3CHO	55.1	13.56	1.54
Butene & Ethanol	42.54	9.9	0.32
Acetone & Furan	43.04	11.07	0.81
CHO (Mainly Acetic Acid)	58.18	12.8	1.19
H_2O	24.62	6.71	8.04
CO	52.74	11.75	21.64
CO_2	23.42	5.39	3.08

---

[1] Data are for the temperature range 300-1000°C, a nominal heating rate of 1000°C/s, solid residence time of 0 sec and a total pressure of 5 psig. Sample size was 6 cm × 2 cm × 0.0101 cm thick.

pyrolysis of cellulose. Therefore, to extend the applicability of the model, the effects of pressure on the coupled mass-transfer chemical reaction process must be considered. Figure 38 graphically presents such a model. At atmospheric and higher pressure, the amount of secondary reaction in Zone II is important, while at vacuum secondary reaction in Zone III is important. On a more quantitative basis an approximate model is developed in order to consider the simultaneous mass-transfer and secondary reactions of tar presented in Figure 38. The reaction scheme for such a model is as follows:



Assuming that (1) in reaction zone the rate of generation (step 1) and cracking (step 3) of tar are first-order in concentration of tar in this zone, (2) tar cracking occurs in vapor-phase, (3) the rate of mass-transfer is proportional to the concentration of tar in reaction zone, and (4) concentration of tar in ambient gas is negligible. Thus a mass balance on the vapor-phase over reaction zone for tar with a pseudo steady state assumption gives:

$$\dot{Q} - K_C C - K_T C \overset{\sim}{=} 0 \qquad (5.3.2)$$

$$\frac{dV_T}{dt} = K_T C$$

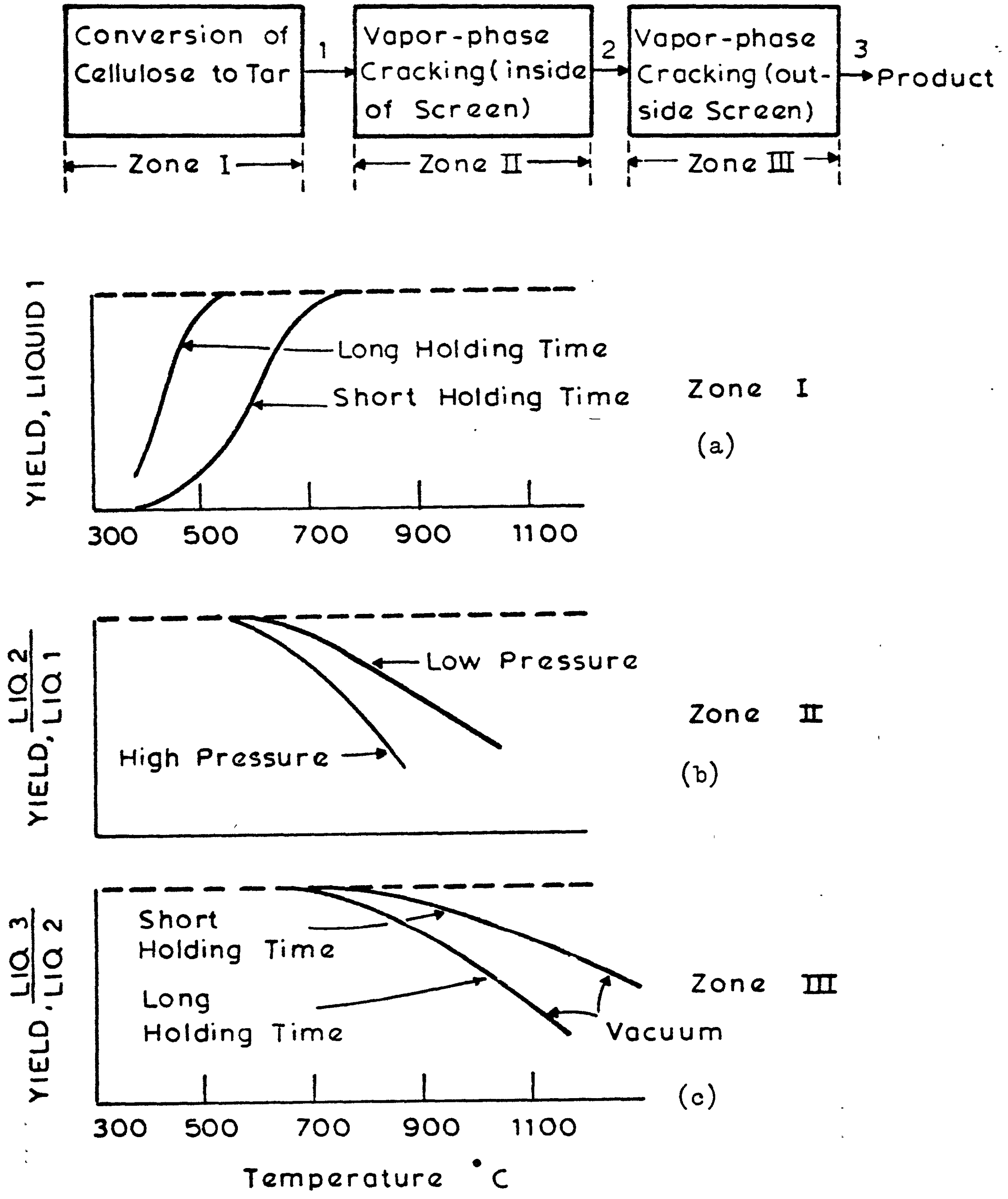


Figure 38. Graphical Presentation of Secondary Reactions with Mass Transport Limitation Model.

where $\dot{Q}$ is the rate of generation of tar $\left(\frac{\text{gr sec}^{-1}}{\text{gr. initial cellulose}}\right)$, K_C is rate constant of secondary reaction (sec^{-1}), K_T is overall mass transfer coefficient (sec^{-1}), C is tar concentration in reaction zone, and V_T is the net yield of tar which is measured experimentally. Since from Equation 5.3.2., $\dot{Q} = (K_C + K_T)C$, therefore:

$$\frac{dV_T}{dt} / \dot{Q} = \frac{K_T C}{(K_T + K_C)C} \qquad (5.3.3)$$

Integration of Equation 5.3.3 for a period of time t gives:

$$V_T = \int_0^t \frac{\dot{Q}}{1 + \frac{K_C}{K_T}} \, dt \qquad (5.3.4)$$

Kinetic parameters for rate of generation of tar (step 1) can be calculated from the temperature region (<650°C) in which secondary reactions are not important, using a single first-order model. The rate constant for secondary reactions was assumed to have the Arrhenius form: $K_C = K_{oC} \exp(-E_C/RT)$. Further, the overall mass-transfer coefficient is assumed to be a function of only temperature and pressure, and to have the form

$$K_T = (\alpha \text{ sec}^{-1}) \, (T/273°K)^{\beta} \left(\frac{1.34 \text{ atm}}{P}\right)^{\gamma}$$

Since for a molecular diffusion process this coefficient is proportional to

$$K_T \propto \frac{T^{\beta = 1.5}}{P^{\gamma = 1}}$$

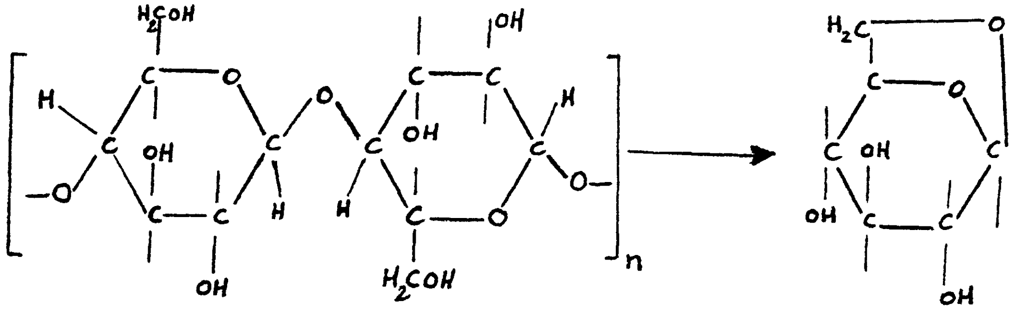
and as convective flow become more and more important this dependency reduces $\left(K_T \propto \frac{T^{\beta < 1.5}}{P^{\gamma < 1.0}}\right)$, therefore it is a reasonable assumption for mass-transfer coefficient. Substituting for K_C and K_T in Equation 5.3.4., the best fitted parameters from integration of this equation over experimental time-temperature histories for 5 psig He (0,2, and 4 sec holding time) and 1000 psig He (0 holding time) runs are: $E_C = 62.69$ kcal/gmole, $\log_{10}K_{oc} = 14.17\ \text{sec}^{-1}$, $K_T = 0.52\ (T/273)^{0.76}(\frac{1.34}{P})^{0.69}\ \text{sec}^{-1}$, where this mass-transfer coefficient corresponds to the mass-transfer limitation at the boundary of Zone II. Data from vacuum runs (0 and 2 sec holding time) were separately subjected to a best fit analysis and gave:

$E_C = 55.98$ kcal/gmole, $\log_{10}K_{oc} = 12.21\ \text{sec}^{-1}$, $K_T = 0.64\ (T/273)^{0.77}$, where this mass-transfer coefficient refers to limitations on the transfer of volatiles under vacuum at the outer boundary of Zone III. Experimental results along with calculated yields are shown for both cases in Figures 39-40 respectively.

It should be emphasized that the parameters calculated in this section should be considered only as useful tools for correlating the experimental data for the ranges of operating conditions under which they were measured. They do not reflect, however, the detailed chemistry of decomposition to specific volatile products.

5.4. Possible Mechanisms of Product Formation

From the results and discussion presented so far, cellulose primarily decomposes to some intermediates such as levoglucosan, levoglucosanove, D-glucose, and some water and CO_2. Cellulose can be converted to intermediate(s) commonly called tar through number of mechanisms. One of the more probable ones are shown below:



(Levoglucosan)

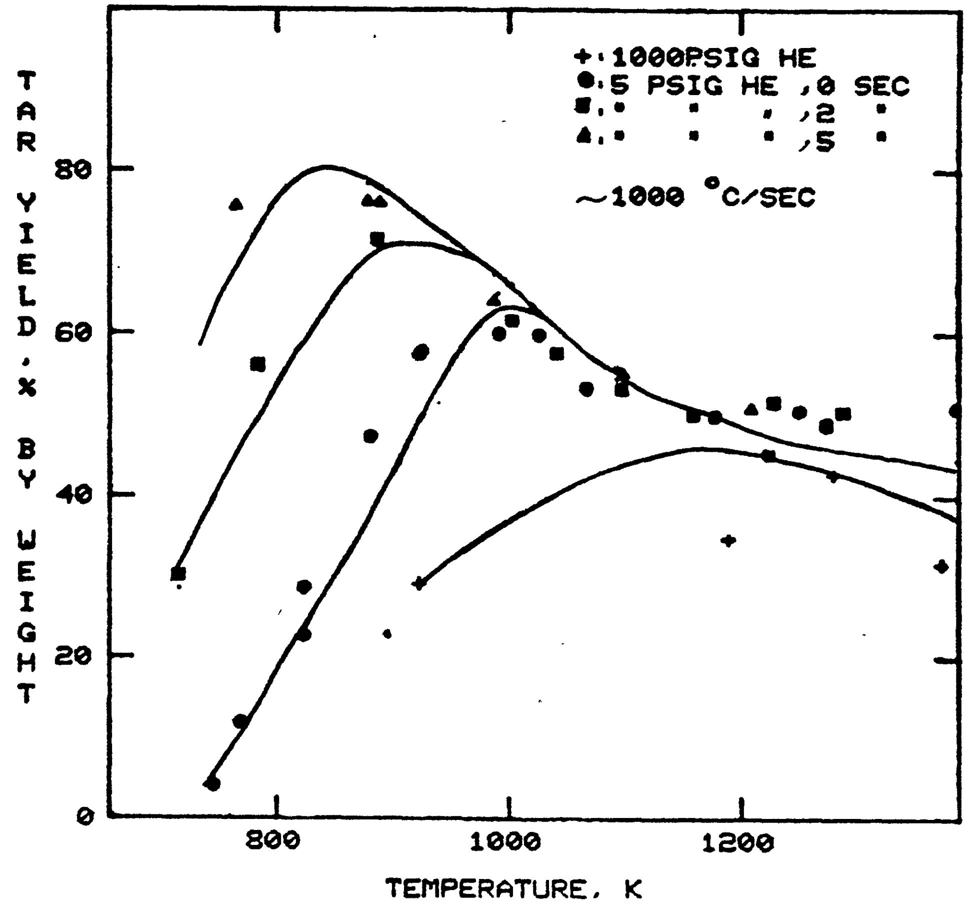


Figure 39. Comparison of Calculated and Experimental Yields of Tar using Secondary Reaction Model for 5 and 1000 psig He Pressures.

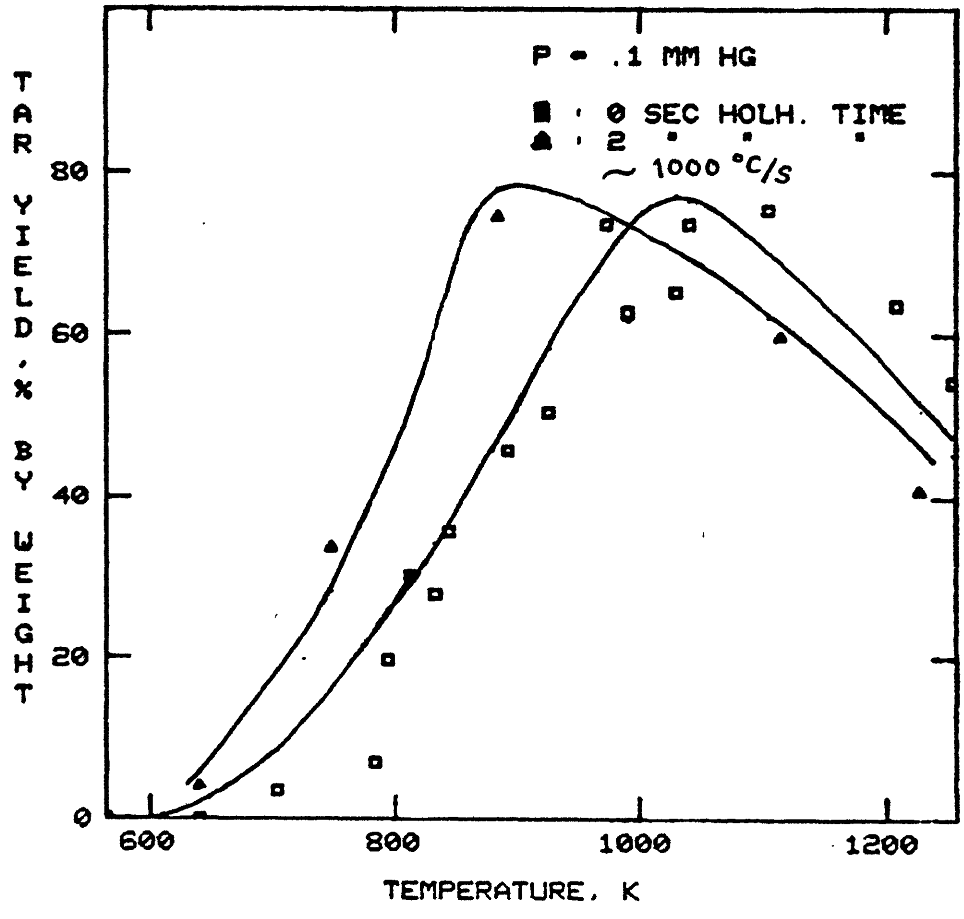
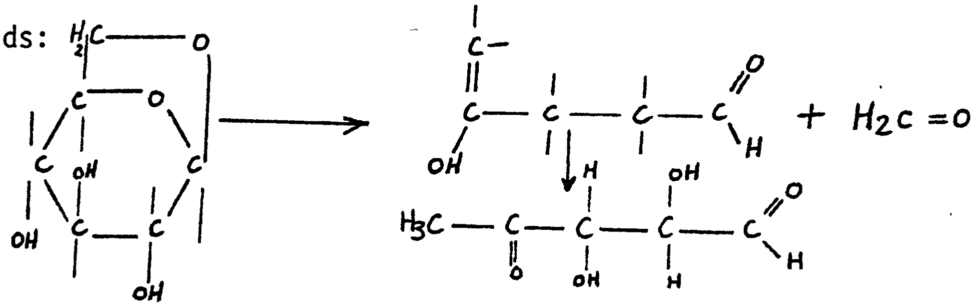
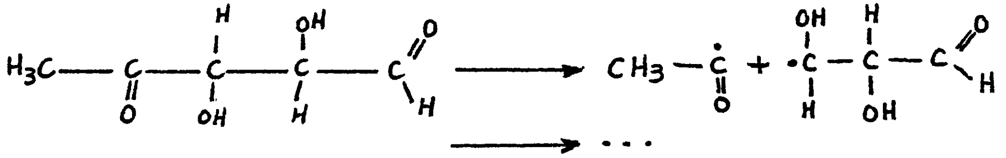


Figure 40. Comparison of Calculated and Experimental Yields of Tar using Secondary Reactin Model for 0.1 mmHg Pressure.

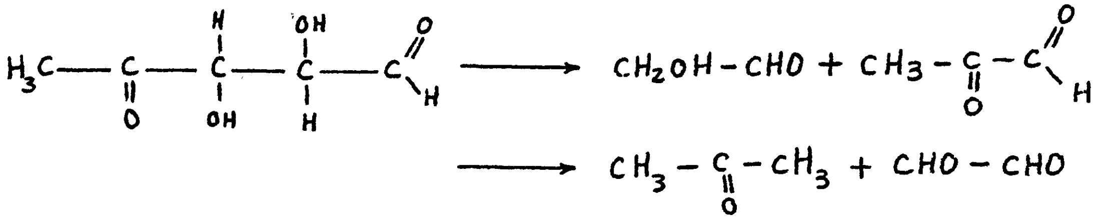
Tar in turn can crack through secondary reaction to lighter compounds. It is established that levoglucosan is one of these intermediate(s). This compound which is structurally an acetol should decompose with formation of an aldehyde. In the scheme proposed by Berkowitz-Mattuck and Noguchi[7] it is assumed that cleavage of the carbon-oxygen bonds involved in the sugar ring leads to the formation of formaldehyde and a di-carbonyl compounds:



The carbonyl groups then weaken the adjacent carbon-carbon bonds leading to scission and formation of free radicals.



Probable rearrangement reactions of the same intermediates are:



The free radicals and molecular species could undergo further reaction and recombination to provide an enormous variety of compounds including: $CH_3\!-\!\overset{O}{\overset{\swarrow}{C}}\!-\!CH_3$, $CH_3\!-\!\overset{O}{\overset{\swarrow}{C}}\!-\!OH$, $CH_3\!-\!CH_2OH$, $HCOOH$, CH_3OH, $CH_3\!-\!CHO$, CO, CO_2, CH_4,... All of the above have been identified in the products of cellulose pyrolysis in this study.

6. Conclusions

The following are the major conclusions of this study:

1) This apparatus provides excellent results at most operating conditions. However, special consideration must be given to the coupled effects of physical transport and chemical reaction in order to interpret data obtained under vacuum (0.1 mm Hg) at high temperatures (> 850°C), because under these conditions secondary reactions are very much effected by apparatus.

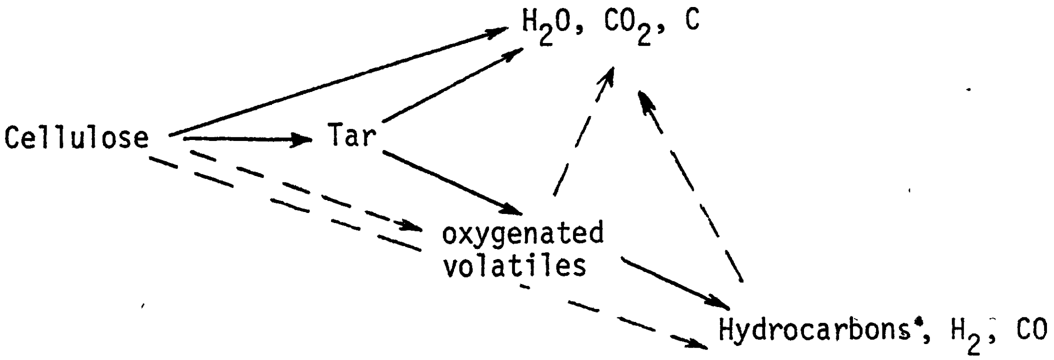
2) Temperature and sample residence time are the two most important parameters in determining the rapid thermal decomposition behavior of cellulose. Heating rate effects can be interpreted in terms of their influence on these two reaction conditions. Pressure is not important as temperature, but its influence on volatiles secondary reaction is important. Sample thickness has less effect on volatiles secondary reactions.

3) Almost 97-98% of cellulose by weight can be converted to volatiles at temperatures of 700 and 800°C at holding times of 2 and 0 sec. respectively. Tar is the major product of cellulose pyrolysis (35-85% by weight of cellulose) and an intermediate that can under some conditions be further converted to lighter compounds and gases such as CH_4, H_2, CO_2, CO, H_2O, acetaldehyde, methanol.

4) CO_2 and H_2O are produced through both primary and secondary reactions. However, the other light volatiles are believed to be produced primarily by secondary reactions of tar. Modest quantities of H_2 ($\sim$ 1 wt.%), CH_4, C_2H_4, C_2H_6, C_3H_6 ($\sim$ 0.2-2.5 wt.% each) and light oxygenated compounds such as acetaldehyde, methanol, acetone + furan ($\sim$ 0.8 - 1.5 wt.% each) are formed primarily over the temperature range 600 - 800°C. Above 750°C CO dominates the gaseous products and attains a yield of above 23 wt.% at 1000°C.

5) The overall pyrolysis of cellulose as well as its pyrolytic decomposition to individual products can each be well described by a single first-order reaction model. Kinetic parameters obtained by fitting a single reaction model at one set of conditions can correlate the rate of total weight loss by pyrolysis for a variety of conditions. However, a model in which secondary reactions as well as mass transport limitations are considered and is needed to obtain tar production for all the conditions studied.

6) The following scheme based on the results obtained in the present study, is proposed as a summary of the most probable steps in cellulose pyrolysis under rapid heating conditions.



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I. Introduction

I.1. Motivating Factors

The urgency of the energy crisis and its critical implications are well known. Finite natural resources such as natural gas and oil continue to be consumed at high rates. Conservation is only a stopgap; any long term solution must involve the discovery of a new energy source.

Renewable resources, commonly known as biomass, offer a great potential as a source of high quality gaseous and liquid fuels. Biomass includes materials specifically grown as a source of fuels, raw materials such as wood kelp and grasses, and waste products such as municipal and industrial wastes, agricultural byproducts, and forest residues. Compared to other alternative energy sources such as shale oil and coal, biomass is not as efficient in BTU's per pound. However, it's easy and relatively rapid renewability add to its attractiveness as an alternate energy source.

The concept of producing fuels and energy from biomass and wastes is a simple one as shown in figure I-1. The simplified form of the natural carbon cycle in figure I-1 shows that it takes many millions of years for the CO2 in the atmosphere to be converted to materials such as oil, gas, and coal which are conventionally used as fuels. Now that fossil supplies are running low, a modified carbon cycle must be utilized if we are to meet the rapidly growing requirements for liquid and gaseous

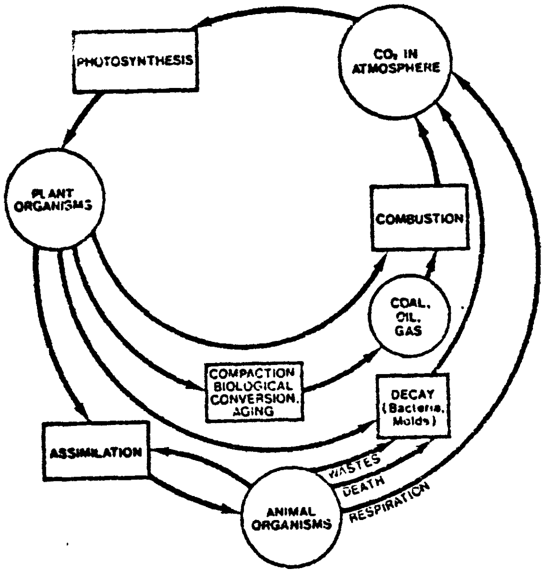

Figure I-1. Natural Carbon Cycle(1).

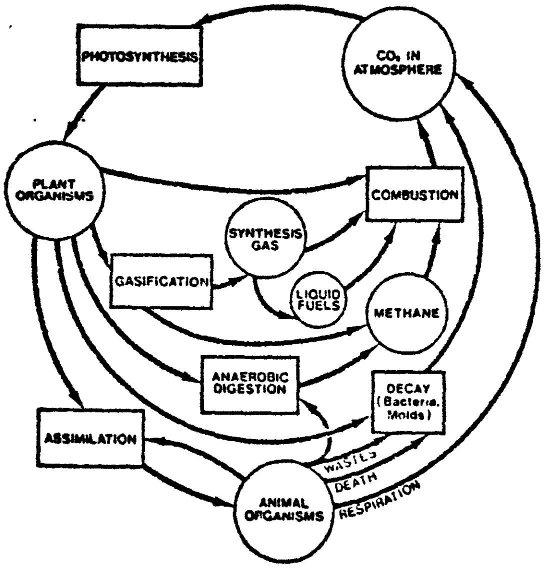

Figure I-2. Modified Carbon Cycle(1).

hydrocarbons for fuels and chemical feed stocks.

The abundance of biomass has sparked a resurgence of interest in biomass pyrolysis as a source of both fuels and chemical feed stocks. Pyrolysis of biomass would provide a more rapid and efficient carbon cycle than that found in nature. Such a cycle is shown in figure I-2, where gasification of biomass is utilized to produce synthetic gas and liquid fuels.

The pyrolysis of biomass is a destructive distillation process effected by the application of heat to the biomass in the absence of air (oxygen). The solid then decomposes into gaseous, liquid, and solid products. This method has a long industrial history (2-6) dating back to ancient China and Egypt. In more recent years, it has been used to obtain several major products including charcoal, acetic acid, methanol, tar and gas(3). The late 1960's and early 1970's was resurgence of interest in the pyrolysis of wood and wood related compounds to yield clean gas and liquid fuels.

Of the many types of biomass, cellulosic materials are of special interest because of their widespread utilization in fibers, textiles, construction materials, in the fabrication of temperature resistant materials, and as binders for solid propellants. About 42-45% of wood is composed of cellulose; also about half of the municipal waste is composed of cellulosic materials, particularly the paper products (table I-1). Other materials, however, such as lignin, rubber, wood, and rich

Table I-1. Typical Municipal Solid Waste Composition[1]

Paper products	48%
Glass and ceramics	8
Metals	9
Food waste	19
Garden waste	4
Plastic, rubber, leather	4
Textiles	3
Wood	2
Ash, rocks, dirt	3
	100%

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[1] Data of Shafizadeh, McIntyre, Lundstrom, and Fu: Chemical Conversion of Wood and Cellulosic Wastes (9).

hydrocarbon plants, are important as well because of their value in the production of specific products. Lignin, for example, is important because its pyrolysis produces valuable phenolic compounds. Unlike cellulose and a few other substances which appear as pure compounds in nature, most types of biomass, such as urban refuse and industrial waste, appear as a mixture of substances. Therefore it would be helpful if the pyrolysis behavior of a mixture of compounds could be predicted from the pyrolysis behavior of the individual constituent components. Wood, which is composed of cellulose, hemicellulose, and lignin, is a clear example of this. There is evidence that its thermal behavior might be predicted from the behavior of its individual compounds. Thus the systematic study of cellulose pyrolysis is important in the future study of heterogeneous materials.

One of the reasons for the growing interest in solid waste pyrolysis process is that it promises to simultaneously solve two of the problems facing our society: energy and waste disposal. Pyrolysis could be used to reduce the large volumes of solid waste which are discarded daily.

Pyrolysis doesn't require a large volume reactor, as do aerobic and anaerobic fermentation processes. The rapid rate of volatilization in the pyrolysis process promises that a large volume reactor is unnecessary, unlike incineration. Thus the cost of effluent cleaning equipment would be reduced. By optimizing the pyrolysis process at its most efficient reaction conditions, the amount of pollution could be substantially reduced.

Research into biomass pyrolysis would have applications to other areas as well. Knowledge of the pyrolysis behavior of cellulosic materials can shed light on ignition, flame propagation, and other flame related phenomena of importance in fire research. For example, a better understanding of the pyrolytic processes might lead to better methods of controlling flame propagation. This is immediately applicable to research into fire proofing of clothing and building materials. Since flammable pyrolysis products sustain the early stages of flaming combustion, the most obvious way to increase fire resistance is to prevent the production of combustible volatiles. Thus, knowledge of pyrolysis reaction mechanisms and rates of formation of pyrolysis products would help in the development of improved fire resistant materials.

Pyrolysis of biomass is only one of a myriad of methods useful for the conversion of biomass to fuels. These methods are summarized in table I-2. They include hydrogenation of biomass to fuel oil, a relatively new technique, and microbial digestion of biomass to produce a single cell protein fodder (11) or compost (12). Hydrolysis to glucose and destructive distillation are two of the chemical processes attempted in the past but these methods failed because of certain deficiencies and problems (2), such as poor product selectivity and poor economy. Among the options for converting coal or biomass to synthetic fuels, pyrolysis has the highest inherent thermal efficiency, but has

Table I-2. Summary of Nonfossil Carbon-to-Energy Processes and Primary Energy Products[1]

Conversion Process	Primary Energy Products	
Incineration	**Energy**	**Thermal**
Separation		**Steam**
Pyrolysis		**Electric**
Hydrogenation	**Solid Fuels**	**Char**
Anaerobic Fermentation		**Combustibles**
Aerobic Fermentation		
Biophotolysis	**Synfuels**	**Methane (SNG)**
Partial Oxidation		**Hydrogen**
Steam Reforming		**Low-Btu Gas**
Chemical Hydrolysis		**Methanol**
Enzyme Hydrolysis		**Ethanol**
Other Chemical Conversions		**Hydrocarbons**
	Energy-Intensive Products	**Ammonia**
		Steel*
		Copper*
		Aluminum*
		Glass*
		Other Chemicals

* **Pertains to urban refuse and certain industrial wastes.**

[1] Data of Klass(101).

been plagued with the disadvantages of poor control of product composition and selectivity. This is because of the high reaction temperatures, the number of reactions taking place, and the existence of secondary reactions.

The pyrolysis process is approximated by primary and secondary reactions. The primary reactions generally produce large molecular weight tars which are volatile at the temperature of the reaction. These tars are collected in greater yield under conditions where they can escape rapidly from the reaction zone (conditions of small sample size and vacuum). During their passage through this zone, the highly reactive components undergo more reaction. Under these conditions, secondary pyrolysis of these materials is believed to occur heterogeniously and/or homogeneously to produce smaller volatile fragments (Fig. I-3).

When the cellulose is heated to approximately 250 degrees C, its molecular structure begins to degrade. The initial volatile products of this reaction are largely water with a small amount of CO2 and other organics. As the temperature is increased further, the pyrolysis reactions become more rapid and the chain of the cellulose molecules is fragmented into smaller molecules, some of which are volatile under the conditions of the reaction, and flow out of the reaction region because of concentration and pressure gradients. Those fragments which are still in the reaction region could undergo further decomposition and give low molecular weight combustible products. Table I-3 shows a typical analysis of products from cellulose pyrolysis at 600 degrees C

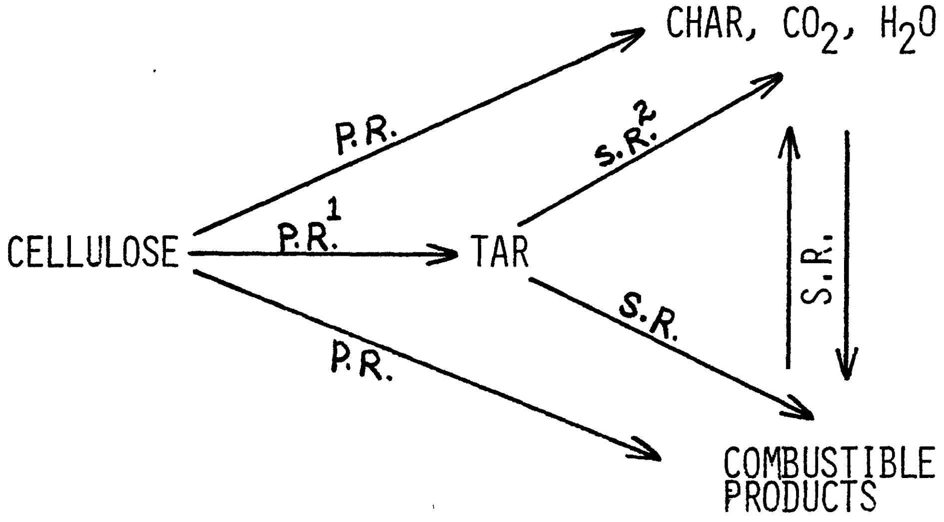

FIGURE I-3 GENERAL SCHEME OF CELLULOSE PYROLYSIS

[1] P.R. REFERS TO PRIMARY REACTIONS

[2] S.R. REFERS TO SECONDARY REACTIONS

Table I-3. Pyrolysis Products of Cellulose and Treated Cellulose at 600°C[1]

Product	Neat	+5% H_3PO_4	+5% $(NH_4)_2HPO_4$	+5% $ZnCl_2$
Acetaldehyde	1.5[a]	0.9	0.4	1.0
Furan	0.7	0.7	0.5	3.2
Propenal	0.8	0.4	0.2	T
Methanol	1.1	0.7	0.9	0.5
2-Methylfuran	T	0.5	0.5	2.1
2,3-Butanedione	2.0	2.0	1.6	1.2
1-Hydroxy-2-propanone Glyoxal	2.8	0.2	T	0.4
Acetic acid	1.0	1.0	0.9	0.8
2-Furaldehyde	1.3	1.3	1.3	2.1
5-Methyl-2-furaldehyde	0.5	1.1	1.0	0.3
Carbon dioxide	6	5	6	3
Water	11	21	26	23
Char	5	24	35	31
Balance (tar)	66	41	26	31

[a] Percentage, yield based on the weight of the sample; T = trace amounts.

[1] Data of Shafizadeh and Chin(15).

using the TGA approach and with long holding time. Analysis of tar from cellulose pyrolysis at approximately 300 degrees C, under similar conditions, is shown in table I-4.

Previous work on the thermal degradation of cellulose materials is extensive. Most studies of cellulosic material pyrolysis is characterized by long heat up times, with periods at final temperature extending to several hours or days. In some work the volatile products were separated into fractions condensable between selected temperatures, such as between liquid nitrogen, dry ice and ambient temperature, and then subjected to further chemical characterization. Solid residue was found in all studies and ranged from a few percent to over 50% of the original sample by weight. Lewellen et.al. appears to be the only worker who reported essentially complete conversion (ca. 99%) of pure cellulose to volatiles by pyrolysis. Rapid heating has also been employed in a few other studies. Radiative heating of a thin sample was used to obtain heating rates estimated to approach 60 degrees C per second with cellulose in air, and between 300 and 1500 degrees C per second for treated and untreated cotton in helium.

In addition, kinetic data on cellulose pyrolysis was obtained in several studies, usually assuming a single step, first order reaction with Arrhenius constants. Variation of several factors of 10 are observed in the rate constants over the temperature range of 200 to 600 degrees C, while activation energies range from 19 kcal/mole to above 50 kcal/mole.

Table I-4. Pyrolsis Products of Cellulose at 300°C Under Nitrogen[1,2]

	Yield, Wt % of Original Cellulose			
	Pressure, mm Hg			
	760		1.5	
Char	34.2		17.8	
Tar	19.1		55.8	
Levoglucosan		3.6		28.1
1,6-Anhydro-β-D-glucofuranose		0.4		5.6
Other materials hydrolyzable to glucose		6.1		20.9
Total materials hydrolyzable to glucose		10.1		54.6

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[1] Data of Shafizadeh and Fu (16)

[2] Thermal Analysis experiment with decomposition occurring mainly from 300-400°C; heating rate believed to be 6°C/min.

I.2. Objectives

Systematic studies of the effect of sample size, heating rate, temperature, residence time, and total pressure on rates and extents of conversion of cellulose have not been reported. However, some general trends which can be recognized from the previous studies on cellulosic materials are:

1. Very large yields of volatile products (60% to 98% by weight) can be obtained from cellulose pyrolysis through proper selection of reaction conditions.

2. Systematic studies of the products composition constituting these large conversions have not, in general, been performed for a wide range of commercially important conditions. There is evidence, however, that:

a) gases of high heating value (200-400 BTU/scf and up to 675 BTU/scf on a CO2 free basis) and

b) liquids low enough in sulfur and of acceptable nitrogen content to be suitable for replacing No.6 fuel oil can be obtained.

3. Kinetic data on the rates of formation of specific products by pyrolysis are virtually nonexistent.

4. A number of very valuable oxygenated compounds including methanol, ketones, furan and its derivatives (which have research octane numbers of 110, 110, and 190 respectively), and furfural,

furfural alcohol, and acetaldehyde which could be employed as a chemical feedstock have been obtained; other intermediaries are obtained in small yields.

Unfortunately, no previous studies have systematically determined if improved product selectivity could be achieved through optimization of the reaction conditions (temperature, pressure, heating rate, residence time, sample size) Therefore, the general approach of this work was:

1. To study the effect of reaction conditions on the yield, composition, and type of products of cellulose pyrolysis.

2. To obtain kinetic data on the rate of formation of individual compounds and of the total weight loss.

3. To obtain a better understanding of the pyrolysis process by extending the range of experimental conditions and measurements previously studied and to develop a model of the thermal decomposition of cellulose.

II. Review of Previous Work

II-1. Effect of Reaction Conditions (temp., press., etc.) on yield and Composition of Products.

The use of nonfossil, renewable carbon as a source of energy is not a new concept. Wood is a well known example of biomass used as a fuel through more of history than any other material. Even today, about half of all wood harvested in the world is for fuel.

Wood carbonization was probably first practiced by the early cavemen to produce the smokeless fuel commonly known as charcoal. Later the ancient egyptians destructively distilled wood to produce not only charcoal, but also tar and pyroligneous acids. The latter are water soluble organic liquids that frequently contain acids, ketones, aldehydes, alcohols, and other oxygenated species, and were employed in embalming (17,18). Most of the investigations in the past generally focused on the yields of major product fractions. Only in the past century has much interest been generated in measuring the rate of pyrolysis and making a more detailed study of product yields and mechanisms of reaction.

However, there is extensive literature on the pyrolysis of biomass and pure cellulose, including several reviews on cellulosic materials (2,19-23). Unfortunately, most of this work, which focused on the effect of reaction conditions on product quality has left a number of important questions unanswered. For example, few studies presented adequate material balances, and frequently the possible cooperative effects of heating rate, temperature, residence time, sample size, and extent of sample dispersion were not examined separately. However, study of some of these results does shed some light on the process of cellulose pyrolysis.

In the early 1900's, Klason (24) reported some information on wood distillation. He stated that wood decomposition begins at 250 deg C, becomes rapid at about 275 deg C, and is complete at 350 deg C. Table II.1-1 shows the results of distillation, at 275 deg C, for birch wood. Klason also reported that the yield of tar and volatiles at high vacuum and at atmospheric pressure differs greatly. For example, formaldehyde yield dropped from 1.27% at vacuum to 0.80% at atmospheric pressure. Bornstein (25), in the distillation of wood, found that non combustible gases were obtained at 165 deg C, water at 180 deg C, combustible gases at 280 deg C, and the first tar at 300 deg C. Later, Palmer and Cloukey (26) reported that increasing the moisture content of yellow birch and maple wood gave increased acid yields and a decreased production of alcohols. Palmer (27) also studied the effect of pressure on wood pyrolysis. He used pressures up to 150 psi and a final temperature of about 335 deg C. Increasing the pressure produced a slight increase of methanol, an increase of charcoal and gas, and a decrease of acetic acid and tar. The effect of raising the pressure up to 60 psi was

Table II.1-1. Thermochemistry of Distillation of Brich Wood for 8 Hours at 275°C and Ordinary Pressure[1].

Products	% by Weight
Charcoal	30.85
Tar	16.94
Acetic Acid	6.77
Formic Acid	0.61
Methanol	1.49
Acetone	.20
Formaldehyde	1.00
CO_2	10.17
CO	3.57
CH_4	.98
C_2H_4	.25
Volatile Oils	3.00
Organic mater., undetermined	3.69
Water	30.48

---

[1] Data of Klason (24).

much greater than higher particularly on the tar. Typical data obtained by Hawley and Palmer over the temperature range from 327 to 415 deg C are summarized in table II.1-2. Selected findings of the numerous studies of this type are also discussed and summarized by Schorger (28), and by Wise and Jahn (6).

Until fairly recently, few systematic studies of the effects of commercially feasible reaction conditions on product quality have been reported. In 1964, Hearon et.al. (29) claimed the production of ethylene or acetylene in very high yield (10% to 20% by weight) from "oxygen containing materials" by very rapid heating of finely ground feed to a temperature between 1000 and 3500 deg F, at residence times of 10^{-4} to 10 seconds. Wen et al. (30) have reported the pyrolysis of sawdust in the temperature range of 1430 to 1500 deg F using a 15 inch inside diameter, fluidized sand bed reactor operated from 0 to 10 psig. The average volatile residence times are estimated to be between 2 and 3 seconds in the bed. Their results are summarized in table II.1-3 by Peters (17) which shows that gases with high heating values (300 to 400 BTU/scf) may be obtained. Overall material balances were not presented, so detailed evaluation of this work is difficult. Application of the occidental flash pyrolysis process to various biomass related materials, have been described by Preston (7) and Boucher et al. (31). This process produces temperatures ranging from 800 to 1600 deg F, with a high heating rate and short residence time, at 2 atm absolute pressure. The process has been studied in a 9 lb/hr, 1 inch I.D.

Table II.1-2. Yields of Products from Destructive Distillation of U.S. Hardwoods[1,4]

Type of Wood	Product Yield, Percent by Wt			
	Methanol	Acetic Acid	Tar	Charcoal
Heart wood	0.90-2.23	4.23-6.89	3.7-13.0	36.4-49.5
Slab wood[1]	0.87-2.09	4.14-8.19	3.7-12.3	37.6-52.9
Limbs and Bark[2]	0.96-2.02	2.98-6.76	--[3]	--[3]

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[1] Beech, birch, maple, red gum, chestnut, tupelo, silver maple, eucalyptus, and various ashes, elms and oaks representing 10 different states.

[2] Beech, maple, chestnut, tupelo, green ash, tanbark oak, and black oak, representing 5 different states.

[3] Not given.

[4] Data taken from Peters(17).

Table II.1-3. Summary of Gas Composition for Fluidized Bed Pyrolysis of Sawdust Using N2/Hot Flue Gas Mixture[1,2]

	Solids Feed Rate		Product Gas Analysis, Mole% Dry Basis							LHV	Production Rate
Feedstock	lb/min. dry	Temperature, °F	H_2	CO_2	CH_4	CO	C_2H_2	C_2H_4	C_2H_6	BTU/SCF	SCF/lb Dry Feed
Sawdust[3]	0.368	1430	25.6	15.0	12.4	43.3	3.05	NM[4]	0.65	398	18.3
" "	0.122	1460	37.5	24.3	3.72	33.8	1.04	NM[4]	0.54	286	18.2
" "	0.682	1450	23.6	14.1	11.9	45.7	3.82	0.29	0.63	412	16.0
" "	0.342	1500	30.0	11.1	10.5	44.5	3.28	0.28	0.32	399	18.6

---

[1] Data taken from Wen *et al.*, (30).

[2] Reactor was a 15" ID fluid bed filled with sand particles (0.025" diameter). Expanded bed depth was 3.5-4 ft.

[3] The sawdust was from an unspecified wood and assayed 2.62% moisture, and (on a dry basis) 47.20% C, 6.49% H, 45.34% O, and 0.97% ash. Particle size was 603 μm (harmonic mean diameter).

[4] Not measured.

bench scale reactor without char recycle. The pyrolysis volatiles exit the reactor very rapidly and undergo rapid quenching to minimize secondary cracking of higher molecular weight products. Some of the results are summarized in tables II.1-4 and II.1-5. Table II.1-4 shows that high total volatile and liquid yields are obtained at moderate temperature from wood, municipal refuse, and straw. It also shows the effect of temperature on liquid and gas yields. Table II.1-5 shows the effect of temperature on the yield of specific gases like hydrogen, methane, carbon dioxide, etc. The table also shows that carbon monoxide and carbon dioxide are prominent products from all feeds, but interesting yields of methane and C2+ compounds can be achieved from tree bark at 784 deg K. It is apparent that there have been few publications of studies that have included specifications of material balances and detailed compositions of all product phases for the pyrolysis of biomass materials as a function of commercially important conditions. One notable exception is data from the occidental flash pyrolysis just discussed.

Although more literature exists for cellulose, much more research is still required for a better understanding of its pyrolysis behavior.

Pictet and Sarasin (32) did some of the earliest pyrolysis on cellulose in 1918. They reported that when cellulose is distilled in vacuum (between 12 and 15 mm Hg) a thick, yellow oil is obtained from which levoglucosan can be crystallized at a 45%

Table II.1-4. Flash Pyrolysis of Biomass. Bench Scale Product Yields[1]

Feed	Temp, K (°F)	Yield, wt% moisture and ash free			
		Oil	Char	Gas	Water
Municipal refuse organics	755 (900)	46	31	10	13
	920 (1200)	40	12	30	18
	1035 (1400)	17	10	57	16
	1145 (1600)	8	8	71	13
Tree bark, sawdust, wood waste	705 (810)	39	46	5	10
	745 (880)	35	49	11	5
	785 (950)	53	21	19	7
	810 (1000)	46	25	15	14
Rice hulls	700 (800)	42	32	8	18
	745 (880)	48	22	6	24
	790 (965)	48	18	16	18
Rye grass straw	755 (900)	56	19	6	19
	785 (950)	52	16	16	16
	810 (1000)	56	10	18	16

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[1] Data taken from Preston(7).

Table II.1-5. Flash Pyrolysis™ of Biomass- Pyrolytic Gas Composition[1]

FEED	WT % MOIST. IN FEED	TEMP K	TEMP (°F)	DRY GAS COMPOSITION, MOL % H_2	CO	CO_2	CH_4	C_2^+	H. HTG. VALUE kJ/NM^3	(BTU/SCF)
MUNICIPAL REFUSE ORGANICS	4	755	(900)	5	34	54	1	6	10,600	(270)
	"	920	(1200)	10	51	19	7	13	25,200	(640)
	"	1035	(1400)	15	50	10	10	15	26,400	(670)
	"	1145	(1600)	20	48	7	12	13	23,600	(600)
TREE BARK	4.7	750	(890)	8	36	48	1	7	8200	(210)
	0.8	785	(950)	14	14	39	15	18	16,000	(410)
	2.7	810	(1000)	2	28	64	3	3	6700	(170)
RICE HULLS	3.2	700	(800)	20	28	46	3	3	9000	(230)
	7.2	755	(900)	2	59	35	3	1	10,300	(260)
	3.0	790	(965)	23	28	41	3	5	9800	(250)
RYE GRASS STRAW	5.6	755	(900)	3	80	10	4	3	13,700	(350)
	1.4	785	(950)	7	51	28	6	8	12,900	(330)
	1.4	810	(1000)	1	44	42	6	7	11,300	(290)

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[1] Data taken from Preston(7).

yield. Schorger (28) summarized some of the work done prior to 1925. Although some of the earlier findings may be of some interest because they indicate what potentially could be obtained by modern day processing techniques, most of these investigations appear to have exerted little, if any, control over important parameters such as sample size, residence time, temperature, and time-temperature history. In fact, in many studies, a large sample was subjected to slow carbonization in massive retorts or the cellulose was boiled in water.

In the 1950's, Schwenker and Pacsu (33) conducted a study on cotton fabric pyrolysis. They pyrolyzed samples of cotton fabric at temperatures between 350 and 375 deg C, in a flow of air. They collected a liquid product composed of 12.5% levoglucosan, 15% carbonyl compounds (including formaldehyde and glyoxal), 7.5% acids (including formic, acetic, lactic, and glycolic acid), and 55% water. In another study (34) under similar conditions at 350 deg C, these investigators showed that oxidations of the primary alcohol groups of the cellulose (with the conversion of cellulose to products at 40% to 47% by weight) resulted in a decrease of the levoglucosan yield from 12.5% to 4.9% on subsequent pyrolysis.

Holmes and Shaw (35) pyrolyzed treated and untreated cotton at 418 deg C under vacuum and in air. Tars from the pyrolysis of untreated cotton samples in vacuum and air yielded 81% and 82% levoglucosan, respectively. The treated cotton samples, pyrolyzed in vacuum, yielded 54% levoglucosan. Martin and

Ramstad (36) in 1961, presented semiquantitative product composition data for cellulose pyrolysis in helium at 250 to 350 deg C, and at 600 deg C. Detailed time-temperature histories were not specified, but the solids residence time for reaction was a few seconds. When the temperature was increased to 600 deg C, carbon monoxide, acetone, acetaldehyde, and acrolein showed significant increases, methanol remained essentially unchanged, and modest amounts of previously unobserved methane, ethylene, acetylene, and ethane appeared. In an extensive study, Schwenker and Beck (37) pyrolyzed cotton by heating it up to 370 deg C in an atmosphere of either air or nitrogen. They identified approximately 30 products from methane to 5-hydroxy-methyl furfural.

Berkowitz-Mattuck and Noguchi (38) radiatively heated 30mg of 1/2 inch O.D., thin, circular samples of treated and untreated cotton at heating rates estimated to vary from 300 to 1500 deg C/sec. Final temperatures were not reported. Volatile products were fractioned into three classes: (a) products which condense at room temperature (25 deg C) such as heavy molecular weight materials like levoglucosn and other tars; (b) products which condense at -80 deg C (the temperature of a dry ice-acetone mixture) which are mostly alcohols, aldehydes, and ketones; (c) Products which condense at -190 deg C (the temperature of liquid nitrogen) which are fixed gases like carbon monoxide, methane, hydrogen, and carbon dioxide. Combined yields of carbon dioxide, carbon monoxide, methane, ethylene, and hydrogen increased linearly with a heat flux from 5% to 18% for untreated cotton. Eighteen compounds were identified, but no quantitative data for liquid yields were reported. In another investigation by Martin et.al. (39), cellulose samples were exposed to intense thermal radiation at flux densities of 4.4 and 11.6 cal/cm2-sec for periods from 0.4 to 8 seconds, at temperatures between 250 and 350 deg C, and 600 deg C, respectively. The volatile products were analyzed chromatographically and the identity of each compound was determined by mass-spectroscopy.

Glassner and Pierce (40) pyrolysed cellulose and levoglucosan in helium, over a temperature range between 170 and 360 deg C for various periods of time, and analyzed certain products quantitatively. Results from cellulose and levoglucosan were similar, and finally it was concluded that levoglucosan is the primary product of cellulose pyrolysis and acts as an intermediate in further decomposition. In another investigation, Byrne, Gardiner, and Holmes (41) pyrolyzed pure and flame retardent cotton under vacuum in temperatures ranging from 350 to 500 deg C. They analyzed major products and determined the levoglucosan yield in the tar fraction.

Lipska and Parker (42) studied the pyrolysis of disks of alpha cellulose (2cm O.D., 0.30 inch thick) at temperatures between 250 and 300 deg C in an atmospheric pressure, fluidized sand bed reactor using nitrogen as a fluidizing gas. Char yields decreased as temperature and time increased, but were still quite high (66% by weight at 298 deg C with one hour of heating).

Preheating the sample at 250 deg C for 90 minutes followed by pyrolysis at 298 deg C for one hour gave an increase in char yields to 72.3% by weight. In a later study, Lipska and Wodley (43), using similar fluidized sand bed equipment and sample sizes, pyrolyzed alpha cellulose. Temperatures were in the range of 315 to 360 deg C, and residence times between 0.5 and 360 minutes. Products were characterized by gas chromatography, mass spectroscopy, and gas chromatographic / mass spectroscopy. Positively identified products included carbon monoxide, carbon dioxide, methane, ethane, acetaldehyde, furan, acetone, 2-methy furan, 2,3-butane-dione, acetol, furfural, furfural alcohol, and butyrolacetone. Unfortunately, no quantitative results on the yields of products were reported.

Among the investigations which have given quantitative data is one done by Tsuchiya and Sumi (44), where Whatman, No. 40 filter paper was thermally decomposed in a pyrex tube reactor connected to a vacuum pump. A sample of cellulose weighing 1.6 grams was placed in the reactor, which was positions at an angle of about five degrees from the horizontal so that the tar flowed out of the reactor. Temperatures ranged from 320 to 520 deg C and residence times were 20 minutes at a pressure of 10^{-4} mmHg. Products were quantitatively analyzed by gas chromatography. The results showed that the yields of heavy products (tar) and water increased with temperature to a maximum at 450 deg C and then started to decrease with a further increase in temperature. On the other hand, yields of fixed gases and volatiles increased continuously as temperature increased. These results are shown in table II.1-6 and figure II.1-1. Unfortunately, detailed analysis of the gaseous volatiles were not reported and the total mass balance is poor.

Some of the most important contributions to improve the understanding of thermal degradation of biomass related materials, especially cellulose, has been made by Shafizadeh and his associates. Some of the results obtained by the vacuum pyrolysis of small captive samples of cellulose over the temperature range of 300 to 425 deg C are given in figures II.1-2 and II.1-3 and table II.1-7. This data shows that by increasing the temperature, not only could the time required for a given extent of reaction be reduced, but also the production of tar could be substantially increased. Table II-1-7 shows that the percentage of levoglucosan, glucose, and all reducing sugars in tar is relatively independent of the temperature used to produce the tar, although absolute tar yield does increase with temperature. Results from the Shafizadeh group on the pyrolysis of pure cellulose at 600 deg C, under one atmosphere of nitrogen, and long residence times are shown in table I.3. A comparison of results for cellulose pyrolysis at 300 deg C for 2.5 hours, under vacuum, and at one atmosphere of nitrogen is shown in table I-4. It can be seen that decreasing the pressure leads to significant increases in the tar yields, which is consistent with previous work. However, despite the extensive work performed by this group and the large number of run where quantitative data was

Table II.1-6. Thermal Decomposition Products of Cellulose[a,1]

Products	Yield, wt-%				
	320°C	370°C	420°C	470°C	520°C
Hydrocarbons	—	0.001	0.04	0.05	0.3
Furan	0.03	0.04	0.03	0.04	0.04
2-Methylfuran	0.02	0.04	0.03	0.05	0.05
Furfural	0.06	0.11	0.10	0.10	0.08
5-Methylfurfural	0.007	0.02	0.02	0.02	0.02
Unknown (R:I. 2270)[b]	0.12	0.3	0.17	0.06	0.08
5-Hydroxymethylfurfural[b]	0.01	0.09	0.09	0.05	0.08
Levoglucosan[b]	3.8	10.1	20.2	21.6	18.2
1,6-Anhydro-β-D-glucofuranose[b]	0.2	0.7	2.5	2.4	2.2
α-D-Glucose[b]	0.03	0.09	0.2	0.2	0.2
β-D-Glucose[b]	0.04	0.1	0.2	0.3	0.3
Dimers of anhydroglucose[b]	0.2	0.3	0.5	0.7	0.4
Unanalyzed tar[b]	5.9	6.5	1.9	14.7	7.0
Carbon monoxide	0.5	1.4	1.5	1.7	2.6
Carbon dioxide	1.5	3.3	2.8	2.5	2.9
Water	9.3	24.8	26.6	18.7	20.7
Char	67.8	24.8	17.5	14.4	12.8
Total	89.5	72.7	74.4	77.6	68.0

[a] Figures in columns are weight percentages of sample at indicated pyrolysis temperatures.

[b] Tar fraction.

[1] Data of Tsuchyia and Sumi(44).

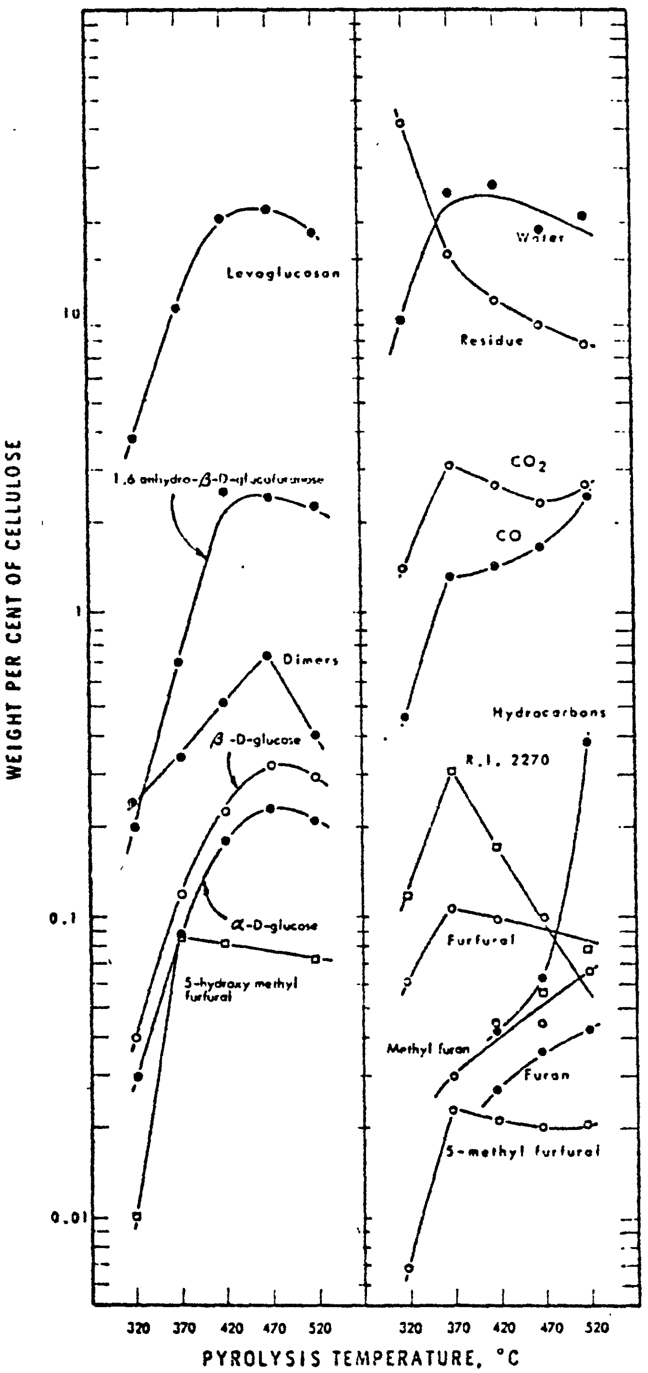

Figure II.1-1. Decomposition Products of Cellulose at Various Temperature (44).

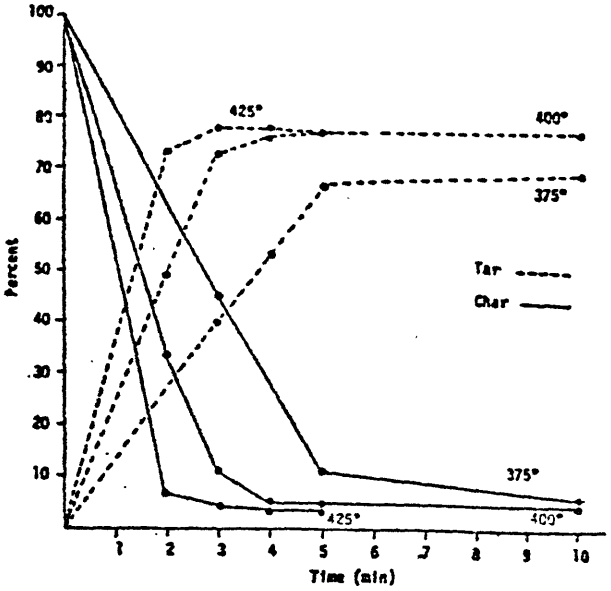

Figure II.1-2. Formation of Tar and Char from Cellulose Pyrolysis: 300-375°C. Data of Shafizadeh (45).

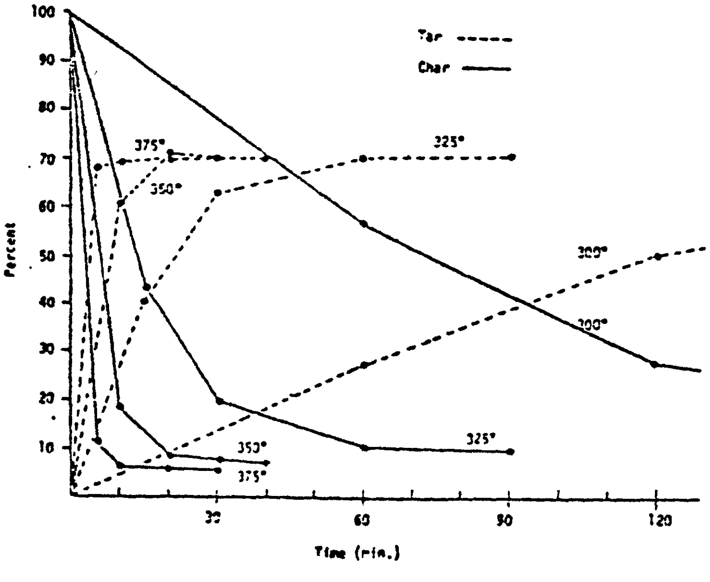

Figure II.1-3. Formation of Tar and Char From the Pyrolysis of Cellulose ; 375-425°C. Data of Shafizadeh(45).

Table II.1-7. Effect of Temperature on the Composition of Tars from the Vacuum Pyrolysis of Cellulose[1,2]

Pyrolysis Conditions Temp, C°	 Time, Min	% Levoglucosan In Tar	 From Cellulose	% Reducing Sugar[3] In Tar	 From Cellulose	% Glucose[3] In Tar	 From Cellulose
300	150			82	49	67	40
320	60			82	57	72	50
325	60	53	37				
340	45			80	55	74	51
350	20	53	38				
360	30			85	63	79	58
375	10	52	37				
400	5			85	67		
425	3			83	64		

---

[1] Data of Shafizadeh et al., see Shafizadeh (45).

[2] 0.5 g samples at 1.5 mm Hg.

[3] After hydrolysis.

reported, several important questions on cellulose pyrolysis remain unanswered.

In recent years, some work has been performed by Howard and his colleagues (Lewellan et.al. (13)). Conversion to volatiles (as defined by total weight loss) of 0.01cm thick single strips of cellulose, weighing approximately 10mg, was measured for controlled variations in selected reaction conditions of commercial interest including final temperatures between 250 and 1000 deg C, heating rates from 400 to 10,000 deg C/sec, residence times between 0.2 and 30 seconds, and ambient pressure between 0.0005 and 1.0 atmosphere). Unfortunately, information on the yields, composition and production kinetics of tar and gaseous products was not obtained. A significant finding of this research was that virtually total conversion of cellulose to volatiles (ca.99%) with no char formation, could be achieved by pyrolysis under one atmosphere of helium, at solids residence times ranging from 0.2 sec above 800 deg C to 30 seconds below 400 deg C.

Very recently, Antal (83) reported on the effect of residence time, temperature, and pressure on the steam gasification of biomass. In this study, stationary 0.25mg samples of cellulose (Whatman #1 filter paper) were pyrolyzed in a tubular, plug flow reactor. A heating rate of 100 deg C/min, with a gas phase residence time of up to 11 seconds, at a peak temperature between 500 and 750 deg C was employed. This study indicated that gas phase cracking becomes very rapid above 650 deg C, and these reactions generate a hydrocarbon rich, synthetic gas, containing a commercially interesting amount of ethylene, propylene, and methane. The results also indicate that above 650 deg C the yield of gases goes through a maximum with increasing gas phase residence time. The author believes, however, that increasing pressure appears to inhibit the gasification process.

From this discussion it should be evident that a lot of qualitative and semi-quantitative information has been reported on the affect of reaction conditions on cellulose pyrolysis, and some general qualitative trends have been discussed. However, much more work needs to be done with an emphasis on systematic studies of the effects of controlled variations in reaction conditions of commercial interest on product yield, composition, and formation kinetics. Such information would shed new light on the fundamental mechanisms of cellulose pyrolysis and could provide some guidance for the design and selection of commercial scale operations to thermally convert biomass to valuable fuels and chemicals.

II.2. Chemical Structure of Cellulose

Cellulose is a polydisperse polymer of high molecular weight. Its primary chemical structure is that of a linear polymer of glucopyranose units; this structure is described more accurately as poly-(β-1,4-glucopyranose). Carbohydrates other than D-glucose, and chain branching may occur to a very minor extent in natural cellulose. This structure of cellulose is based on the following facts (50):

1) Combustion analysis shows the elemental composition of cellulose to be $C_6H_{10}O_5$.

2) Hydrolysis yields at least 95% glucose.

3) Partial hydrolysis experiments yield cellobiose and higher members of the homologous series up to cellahexulose.

4) Acetolysis experiments lead to cellobiose octoacetate.

5) Optical rotation and kinetics of acid hydrolysis indicate that at least 99.9% of the bonds are of the Beta configuration.

6) The formation of various derivatives of cellulose proves that three alcoholic hydroxyl groups are free and readily undergo substitution.

7) Further analysis of cellulose derivatives shows that two of the hydroxyl groups are secondary and one is primary.

8) The nonreducing terminal group on the left in formula (1), figure II.2-1, has been identified by the isolation of 2,3,4,6-tetramethyl - glucose from the hydrolysis of fully methylated cellulose.

9) On the basis of conformational analysis, a better structural presentation is probably given by formula (2), Figure II 2-2.

The degree of polymerization (DP) varies widely according to the cellulose source and the method of its isolation. Typical molecular weights, values, and DP for various types of cellulose are shown in table II 2-2. Native (natural) cellulose may have a DP between 3,500 and 10,000 while treated chemical cottons are significantly degraded with a DP between 500 and 2,100. Apart from the wide variation in the DP of various forms of cellulose, there are also major differences in the degree of crystallinity and crystal orientation in different samples. Basch and Lewin (51) have shown in a very thorough study, that many of the reported literature differences in the behavior of cellulose on pyrolysis may be attributed to the differences in crystal structure and crystal orientation as well as to the variations in the DP. The purity of the cellulose is of critical importance. It plays an important role in the reaction mechanisms involved in pyrolysis and in determining the products' distribution and yields.

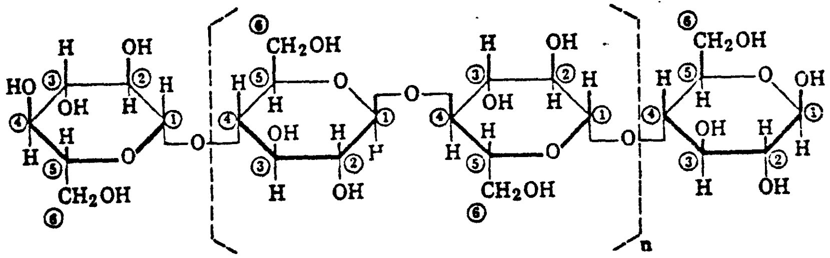

Figure II.2-1. Cellulose Structure (60).

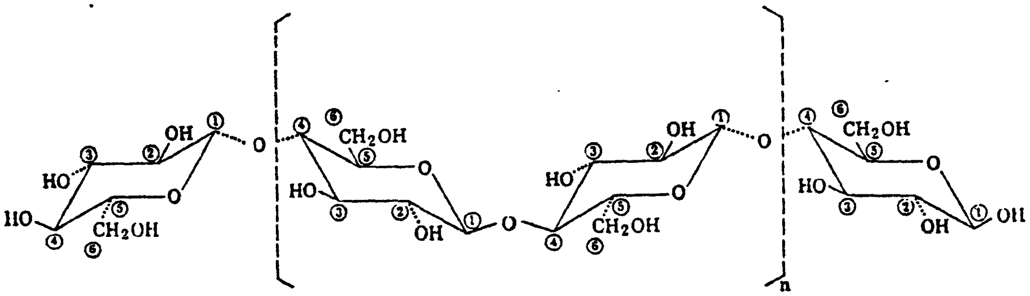

Figure II.2-2. Cellulose Structure (60).

Table II.2-1. Representative Molecular Weight Values for Cellulose and Cellulose Derivatives[1]

Material tested	Molecular weight	Approximate degree of polymerization
native cellulose	600,000–1,500,000	3,500–10,000
chemical cottons	80,000–500,000	500–3,000
wood pulps	80,000–340,000	500–2,100
regenerated celluloses		
tire cord (regular to Super III)	65,000–89,000	400–550
staple fiber and rayon filament	57,000–73,000	350–450
cellophane	45,000–57,000	280–350
commercial nitrocelluloses	16,200–875,000	100–3,500
commercial cellulose acetates	28,000–58,000	175–360

[1] Data of Hamilton and Mitchell (50).

II.3. Products of Cellulose Pyrolysis

Knowledge of the products from the thermal degradation of the complex structured cellulose material is essential for the full understanding of the mechanism or mechanisms involved. Unfortunately, at the elevated temperatures characteristic of the decomposition process, the mechanisms become extremely complex due to intramolecular rearrangements and the occurrences of secondary interactions between the degradation products. Nonetheless, knowledge of the types of products and their compositions can shed light on the types of reactions occurring and is thus helpful in finding the reaction mechanisms.

The products formed on pyrolysis or destructive distillation of cellulose and related compounds have been investigated by a number of authors. In the earlier studies, which were reviewed by Heuser (46), it was recognized that cellulose pyrolysis provides a large variety of primary and secondary products which could be isolated as the gas, as an aqueous solution, and as residual or char fractions. An early paper by Goos (47) has presented a large list of over 200 compounds found in the liquid fraction from the distillation of wood and wood compounds. It was not specified in the paper how the fractions were analyzed and some of the analysis was apparently not confirmed.

In an extensive study by Schwenker and Beck (37), Cellulose was pyrolyzed and the products analyzed quantitatively. Purified cotton fabric was pyrolysed in a conventional pyrolysis apparatus by preheating the samples (ca. 0.10g) at 110 deg C, followed by heating the samples at a heating rate of 15 deg C/min to a temperature of 370 deg C in an atmosphere of air or pure nitrogen. The products were trapped at -78 deg C and 75 deg C, and several gas chromatograph columns were used for the analysis of the products. A total of 34 peaks were eluted from the best column; of these, 15 were identified. Levoglucosan, a major product from cellulose pyrolysis, was not found among the fifteen peaks identified before. However, results on a column containing 3% by weight of polyethylene glycol (carbowax-20M) as the liquid phase, instead of the 10% by weight (which was used before this investigation), have indicated a product that has been tentatively identified as levoglucosan.

In another study by Lipska and Wodley (43), cellulose was pyrolyzed in a fluidized sand bath. The products were analyzed by separating the components on a gas chromatograph and analyzing the separate peaks with a mass spectrometer. From the total of 36 peaks separated by the gas chromatograph, only 17 could be identified on the mass spectrometer. With this system, levoglucosan was not identified, but when cellulose was pyrolyzed directly within the mass spectrometer, a mass peak at 73, corresponding to levoglucosan, was observed.

Several other groups (16,33,36,38,41,48,49) have used chromatographic methods including: gas chromatography, paper chromatography, gas-liquid chromatography, liquid chromatography, thin layer chromatography, and gel permeation chromatography. Martin and co-workers (39) analyzed products of cellulose pyrolysis by the gas chromatography / Mass Spectrometer method and found that the gas phase contains mostly CO_2, CO, and minor proportions of H_2, CH_4, C_2H_6, and C_3H_8. The liquid fraction consisted mainly of water with small portions of acetaldehyde, furan, acetone, butadione, methanol, 3-butene-2-one, and ethanol. In addition to these sixteen products that were positively identified and quantitatively measured, there was a relatively large proportion of tar which appeared to be mainly levoglucosan.

These studies indicate the limitation of gas chromatography for analyzing high molecular weight substances. The number of compounds identified in cellulose pyrolysis has been further expanded through the application of Thin Layer Chromatography and Gel Permeation Chromatography. Molton (22) recently summarized all non-carbohydrate products formed in the pyrolysis of cellulose in the list in table II-3-1.

Table II.3.1 Non-Carbohydrate Materials Formed in the Pyrolysis of Cellulose[1]

Product Identified	Reference	Product Identified	Reference
Furan	43-44,49,81-82	Cyclooctatetraene	81-82
2-Methylfuran	43-44,49	Pentene	81-82
2,5-Dimethylfuran	81-82	'Hydrocarbons'	44
2-Furaldehyde (Furfural)	37,40,43,44, 81-82	Formaldehyde	34,37,40,48
		Acetaldehyde	37,41,43,48-49, 77,81-82
5-Hydroxymethyl-2-furaldehyde	37,41,44,48,81-82	Glyoxal	34,37,40-41,48
2-Furyl Hydroxymethyl ketone	41,48	Propanal (Propionaldehyde)	37,40,49,81-82
3-Hydroxymethylfuran	77	Butanal (n-Butyraldehyde)	37,40-41,48, 81-82
5-Methyl-2-furaldehyde	43-44, 81-82		
2-Hydroxymethylfuran (Furfuryl alcohol)	43, 81-82		
2-Hydroxy-3-methyl-3-cyclopentene-1-one	81-82	2-Butenal (Crotonaldehyde)	81-82
Cyclopentanone	81-82	2-Methyl-2-butenal (Tiglaldehyde)	43
Cyclohexanone	43	cis-4,5-Expoxy-2-pentene	49
Butyrolactone	43,81-82	Glyceraldehyde	41,48
		2-Ketopropandial (Mesoxaldehyde)	41,48
2-Ketopropanal (Pyruvaldehyde)	41,48,77,81	Methanol	37,40,49
		Methyl formate	43
Hydroxyethanal (Glycolaldehyde)	41,48	Hydroxypropanone (Acetol)	43,81-82
Propenal (Acrolein)	37,40-41,43, 48-49,81	Formic acid	34,37,40,81
		Acetic acid	34,37,40, 81-82
Acetone	37,40-41,43, 48-49, 81	Propanoic acid	43
2-Butanone (Ethyl methyl ketone)	37,41,48, 81-82		

Table II.3.1 Non-Carbohydrate Materials Formed in the Pyrolysis of Cellulose[1] (continued)

Product Identified	Reference	Product Identified	Reference
2-Pentanone (Diethyl ketone)	41		
		Glycolic acid	34
		Lactic acid	34,37
Butenone (Methyl vinyl ketone)	81-82	Pyruvic acid	41,48
		Dilactic acid	34
2,3-Butandione (Diacetyl)	43,81-82	4-Ketopentanoic acid (Levulinic acid)	41,48
Dihydroxyacetone	41-48	3-Hydroxy-2-ketopropanal (Hydroxypyruvaldehyde)	48

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[1] Data taken from Molton (22).

II.4. Kinetics

The overall rate and kinetics of the thermal degradation of cellulose has been investigated under a variety of conditions. However, the studies often relate to one of the physical effects produced by the overall process of heating or pyrolysis instead of the kinetics of the chemical reactions involved in producing individual products. Consequently, the large amount of data generated in this area has often not correlated.

Some reviews (19-21) published in recent years discuss some of these results. It will be profitable to briefly examine selected previous studies to get an idea of the approximate kinetics and perhaps to better understand the process of pyrolysis.

Welker (21), in a brief review of the pyrolysis of cellulosic materials, pointed out that many investigations have been reported where the data on the pyrolysis of cellulosic materials has been analyzed with the emphasis on overall reaction kinetics. Most investigators have successfully correlated isothermal weight loss results with single, first order reaction kinetics. Welker indicates, that for cellulose, the Arrhenius pre-exponential factors have been reported as ranging from 5×10^8 sec^{-1} to 5×10^{11} sec^{-1}, and the activation energies have been reported as ranging from 23 kcal/gmole up to 46 kcal/gmole. While this variation could be because of the different reaction conditions, types of sample, and apparatus employed, it may also be an indication of a complex series of reactions which are involved in cellulosic materials pyrolysis.

The first measurements of pyrolysis rates were done by Bamford, Crank, and Malan (52), who pyrolyzed sheets of pear wood. They assumed first order, Arrhenius expressions for weight loss. The values of the kinetic constants which best fit the data were $k_o = 5.3\text{x}10^8 \text{sec}^{-1}$, and $E=33.16$ Kcal/gmole. These values are somewhat affected by the physical properties of the wood such as density, heat capacity, and thermal conductivity.

The next work appeared ten years later, when Stamm (53) reported the kinetic results collected by himself and MacLean (54) on wood and wood components. Their results are presented in table II.4-1. An interesting observation that Stamm made was that the three major constituents of wood reacted at different rates. He also determined the rates and activation energies for the thermal degradation of alpha cellulose, cotton, rayon, and paper, all of which were found to be well correlated by a first order reaction model.

An indication of the complexity of the problem of wood pyrolysis was obtained when Akita (55) reported that cellulose reacted more slowly than lignin in the temperature range between 270 deg C and 370 deg C. This data was contrary to Stamm's results. Akita studied the decomposition of the Japanese cypress and its constituents in air. He reported an activation energy of 17kcal/gmole for hemicellulose, and 26 kcal/gmole for lignin

Table II.4-1.

Kinetics of Weight Loss of Wood and Cellulose[1]

Material	Heating Condition	Temp Range (°C)	Activation Energy kcal/gmole	k sec^{-1}
Coniferous Wood	oven	93.5-250	29.5	6.1×10^{7}
Sitka Spruce Veneer	under molten metal	167-300	29.8	2.7×10^{7}
Douglas Fir Sawdust	oven	110-220	25.0	2.3×10^{5}
α-Cellulose from Douglas Fir	oven	110-220	26.0	6.0×10^{5}
Hemicellulose from Douglas Fir	oven	110-220	26.7	6.9×10^{6}
Lignin from Douglas Fir	oven	110-220	23.0	1.1×10^{4}
Coniferous Wood	steam	121-177	15.8	8.1×10^{1}

[1] Data of Stamm and MacLean(54).

between the temperatures of 270 and 340 deg C. For cellulose, he reported 36kcal/gmole between 270 and 340 deg C, and 24kcal/gmole between 340 and 370 deg C. The activation energy of wood similarly decreased from 26kcal/gmole, in the lower temperature range, to 23kcal/gmole between 340 deg C and 370 deg C. However, this data follows the first order reaction law throughout this temperature range.

Several investigations of the pyrolysis of cellulose (42,56,57) have yielded data where the initial stages of pyrolysis didn't follow a first order reaction law, even though the latter stages did. Tang's (56) data follows a zero order reaction law for the first 2% to 3% of weight loss. The data of Lipska and Parker (42), where they studied pyrolytic reactions of very thin samples of alpha cellulose (0.0762 cm thick, 2cm in diameter) in a nitrogen atmosphere, at temperatures ranging from 250 to 300 deg C, showed a zero order reaction which shifted to a first order reaction at 50% weight loss with an activation energy of 42kcal/gmole and a frequency factor between 0.9×10^{11} sec^{-1} and 2.0×10^{11} sec^{-1}. They also measured the kinetic constants by measuring the glucosan units remaining after a period of exposure, and the results were about the same. Even with these precautions, these authors observed an initial, rapid decrease in weight between 2% at 250 deg C to 6.5% at 298 deg C which they couldn't explain. They were forced to attribute it to a chemical reaction of the cellulose rather than moisture loss since the material had been pre-dried.

The data of Madorsky et.al. (57) shows the rate of weight loss rising to a maximum of about 20% weight loss before decreasing by a first order rate law. He heated small samples (between 5 and 85mg) of purified cotton cellulose in a vacuum at a temperature between 261 and 291 deg C. He correlated his data and found an activation energy of 50kcal/gmole and a preexponential factor of 5.6×10^{15} $\sec^{-1}$. There has been some discussion in the literature that activation energies of this magnitude have only been observed in small samples of high purity. It should be noted that only small differences in experimental results would have altered the kinetic constants greatly.

In a series of papers discussing the same experimental results, Blackshear and Kanury (58-61) show how various interpretations of experimental data could lead to greatly different kinetic constants. Unfortunately, most previous kinetic studies were generally carried out on large samples in which there were temperature gradients across the specimen. There are some reported results in which the activation energy changes with the position in the sample. For example, the activation energy changes from 22kcal/gmole near the surface to 13kcal/gmole at the center line (58-61).

Comparison of the activation energy obtained by Lipska and Parker (42) for alpha cellulose with the data obtained by Madorsky et.al. (57) for cotton cellulose is interesting. Using the same method of computation, Lipska and Parker found the activation energy to be 50kcal/gmole, the same value determined by Madorsky. Thus, Lipska and Parker concluded that the kinetics of uncatalyzed pyrolysis of cellulose, in an inert atmosphere, are essentially the same regardless of whether the cellulose is in the form of cotton or paper, or whether the experiment is performed under vacuum or in a nitrogen atmosphere. The latter conclusion, however, is at variance with the results of Lewellen, et.al. (13).

Golova and Krylova (62) pyrolyzed cotton cellulose and measured the decrease in the D-glucose residue instead of the total weight loss as a function of time. They found that the reaction follows a zero ordered model.

Recently, Lewellen et.al.(13) studied cellulose pyrolysis with an apparatus similar to that used in this work. They measured the total weight loss at various temperatures, heating rates, atmospheric pressure of helium, and under vacuum. The resulting integral yield data were analyzed using a non isothermal kinetic model to provide parameters for the cellulose pyrolysis. They reported that a simple, single, first order reaction model correlated the decomposition data quite successfully. However, a multiple, first order reaction model previously developed (63) to describe the complex decomposition of coal was also successfully applied to the data in this research.

Despite the disagreement between the order of the kinetics, there is justification for assuming that they represent a useful approach to the problem of modelling cellulose pyrolysis since global kinetic schemes have been used successfully to describe the behavior of cellulose pyrolysis in a variety of circumstances. A formal expression for correlating the overall pyrolysis rates, or the yield of any specific species from pyrolysis by a single step, first order expression with an Arrhenius rate constant equation may be derived as follows:

$$dv/dt = k(v^{*}-v) \qquad \text{II.1}$$

where: $$k = k_o \exp(-E/RT) \qquad \text{II.2}$$

v: mass of a species per mass of original material evolved at time t, or fractional weight loss for the overall reaction

v^{*}: value of v at a long time where t=infinity

k: rate constant

k_o: frequency factor in the Arrhenius rate expression

E: apparent Arrhenius activation energy

R: gas constant

T: absolute temperature

By integration of equation II-1 over an arbitrary time-temperature history (T(t)), total yield could be obtained.

$$v/v^{*} = 1-\exp(-{}_o\!\int^{t} k_o \exp(-E/RT(t))dt \qquad \text{II.3}$$

In a more sophisticated pyrolysis model (multiple reaction), based on the concept that thermal decomposition of a complex compound or mixture of compounds consists of a large number of independent, parallel, first order, decomposition reactions, each species i will have a rate of production of:

$$dv_i/dt = K_i(V_i^* - V_i) \tag{II.4}$$

where:

$$k_i = k_{oi}\exp(-E_i/RT) \tag{II.5}$$

and

thus:

$$dv_i/dt = k_{oi}(V_i^* - V_i)\exp(-E_i/RT) \tag{II.6}$$

Here, instead of single, first order reactions, a set of multiple, independent, first order reactions was used.

The activation energies Ei are further assumed to be distributed continuously according to the function:

$$f(E_i) = \frac{1}{\sqrt{2\pi}\,\sigma}\exp[-(E_i-E_o)^2/2\sigma^2] \tag{II.7}$$

Which is a Gaussian distribution, with mean activation energy Eo and standard deviation (σ) sigma (in units of kcal/gmole). The contribution of each reaction i to the total yield is then:

$$dv^* = v^* f(E)\,dE \tag{II.8}$$

since for a normalized Gaussian distribution,

$$\int_{-\infty}^{+\infty} f(E)dE = 1$$

one can integrate equation II.6, and with the substitution of the

Gaussian functions obtain a final, formal, expression for either the overall pyrolysis yield (total weight loss) or for the yield of a specific product:

$$V^* - V = \frac{V^*}{\sqrt{2\pi}\ \sigma} \int_{-\infty}^{+\infty} \exp[-k_o \int_o^t \exp(-E/RT)dt - \frac{(E-E_o)^2}{2\sigma^2}]dE \qquad \text{II.9}$$

In general, if a linear heating rate, $dT/dt = m$, is imposed, the expression for a single reaction can be further simplified to:

$$(V_i^* - V_i)/V_i^* = \exp[-\frac{k_{io}RT^2}{mE_i} \exp(-\frac{E_i}{RT})] \qquad \text{II.10}$$

Where it has also been assumed that $Ei/RT << 1$. Which means only the first two terms in the expansion of the exponential integral have been retained. The rate of weight loss or production of a specific species in this approximation is then given by:

$$dV_i/dt = V_i^* k_{io} \exp[\frac{E_i}{RT} - \frac{k_{io}RT^2}{mE_i} \exp(-\frac{E_i}{RT})] \qquad \text{II.11}$$

It should be noted that these equations are correct only for those runs where there is zero residence time at the final temperature T followed by infinitely rapid quenching of the sample at a temperature too low for further reactions. For instance, in a process in which a sample is heated to a final temperature T and held there for a time τ, and then evenly cooled from T at a finite rate, equations II.10 and II.11 must be modified to:

$$(V_i^*-V_i)/V_i^* = \exp[-k_{io}(\frac{RT^2}{mE_i} + \tau)\ \exp(-\frac{E_i}{RT})] \qquad \text{II.12}$$

$$x\ t \quad \frac{dV_i}{dt} = V_i^*\ k_{io}\ \exp[-\frac{E_i}{RT} - (\frac{k_{io}RT^2}{mE_i} - k_{io}\tau)\ \exp(-\frac{E_i}{RT})] \qquad \text{II.13}$$

A finite, linear cooling rate, m, can be accounted for in equations II.10 and II.12 by analogy with equations II.10 and II.11 respectively.

We now return to the kinetics model which has been proposed by different investigators. The concept that pyrolysis of wood related materials involves more than a single reaction was studied and treated by Tinny (64). He showed that he could improve the correlation between experiment and theory if the kinetic constants changed at arbitrary points during the reaction. Several investigations have used this approach. For example, Akita (55), whose results were mentioned earlier in this section, used this method of analysis.

Further evidence of a multi-step process of thermal degradation was presented by Arseneau (65). He used thin (0.46mm thick) sheets of Whatman No. 1 filter paper (0.1% ash) in nitrogen, and reported evidence of four reactions.

A more sophisticated and perhaps more realistic approach to the concept of multiple reactions during thermal degradation was advanced by Panton and Rittmann(66). They proposed that cellulose decomposes by three first order reactions, two competing and one consecutive, to form solid and gaseous products.

$$S_1 \xrightarrow{r_1} S_2 + G_1$$

$$S_1 \xrightarrow{r_2} G_2$$

$$S_2 \xrightarrow{r_3} S_3 + G_3$$

The constants which are reported for the reactions are:

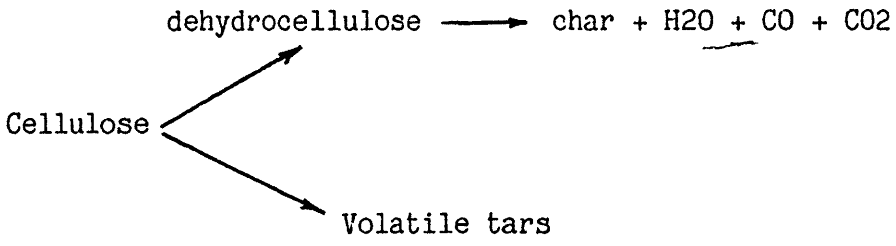
E_1 = 23.8kcal/gmole $K_1 = 8.7 \times 10^{4}\ \text{sec}^{-1}$

E_2 = 31.0kcal/gmole $K_2 = 8.7 \times 10^{6}\ \text{sec}^{-1}$

E_3 = 35.8kcal/gmole $K_3 = 8.7 \times 10^{-2}\ \text{sec}^{-1}$

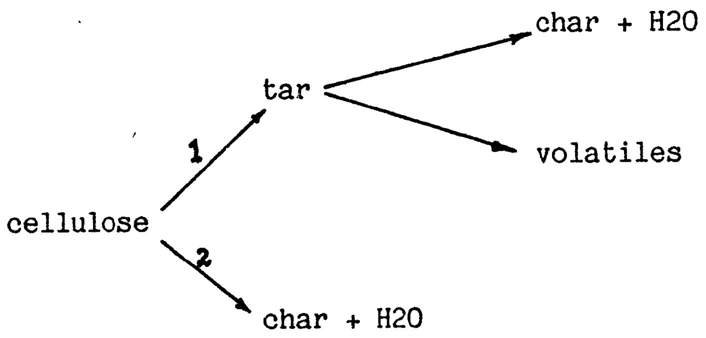
However, no justification or reasons for proposing this scheme were advanced.

The concept of multiple reactions was further advanced by Broido and Weinstein (67). They used samples of 90mg, 3cm x 5cm sheets of Whitman No. 541 filter paper (0.0008% ash) in an evacuated (10-3 to 10-4 mmHg) Cahn Electrobalance at 226 deg C. Starting with this simple reaction scheme:



All reactions were hypothesized to be first order. The results which fit the experimentally measured weight loss were consistent with the authors' previously (68) determined value of frequency factor of $K_o = 5.25 \times 10^{17}$ sec^{-1} and an activation energy of E = 54.9 kcal/gmole.

Aldrich (19) used a multiple reaction approach in his study of alpha cellulose decomposition. In his study, samples of alpha cellulose, 4.25cm in diameter, 0.47 to 1.96cm long, and insulated at the back and circumferential surfaces, to approximate one half of a symmetrically heated cylinder, were exposed to an incident radiant heat flux of between 0.408 and 1.11 $cal/cm^2 sec$. This exposure was done under a nitrogen atmosphere. A reaction scheme was proposed as follows:

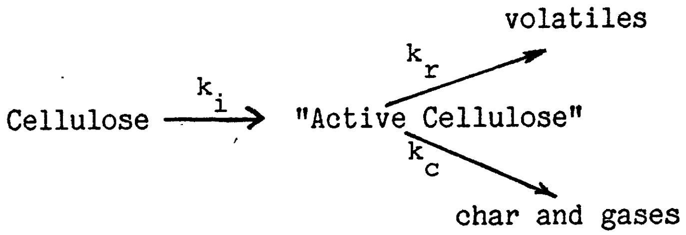


The rate constants and activation energies for the reactions were assumed to follow a first order, Arrhenius expression. The kinetic parameters for the first two reactions of the proposed reaction model have been determined by comparing predicted weight losses and final char yield with measured values. The parameters are as follows:

$E_1 = 31$ kcal/gmole $\qquad K_1 = 5 \times 10^7$ sec^{-1}

$E_2 = 26.5$ kcal/gmole $\qquad K_2 = 1 \times 10^6$ sec^{-1}

Very recently, this approach was employed by Bradbury et.al. (69). Their apparatus consisted of a horizontal, cylindrical, electrically heated furnace, 25cm long, containing a pyrex tube, in which another pyrex tube was placed. One end was connected to a vacuum pump and the other was connected to a nitrogen tank. Samples of powdered cellulose (ca. 250mg of Whatman CF11) were placed in aluminum boats and moved to the pyrolysis area. The reaction temperature used in this kinetic analysis was taken at the center of the sample, 2mm above the floor of the boat. They reported pyrolysis of cellulose at low pressure (1.5 torr) can be described by a three step model:



In this model it is assumed that an initiation reaction leads to the formation of an "active cellulose" unit which subsequently decomposes by two competitive, first order reactions, over the temperature range of 259 to 341 deg C. Rate constants were reported to be:

$K_i = 1.7 \times 10^{21}$ sec^{-1} $\qquad E_i = 58$ kcal/gmole

$K_v = 1.9 \times 10^{16}$ sec^{-1} $\qquad E_v = 47.3$ kcal/gmole

$K_c = 7.9 \times 10^{11}$ sec^{-1} $\qquad E_c = 36.6$ kcal/gmole

Which have somewhat higher activation energies and frequency factors than those usually reported for cellulose pyrolysis.

A summary of the works discussed in this section are shown in table II.4-1. The large variation in kinetic constants are obvious. The plot of the natural log of the rate constant versus the reciprocal of the temperature for cellulose pyrolysis, in figure II.4-1, shows this variation.

From the discussion in this section it should be evident that, although the thermal degradation of cellulose has been studied extensively, there still is no method of a priori predicting reaction rates. The past results can yield approximate kinetic constants, but more important, the lack of agreement among the many investigations show that pyrolysis is an extremely complex combination of chemical and physical processes, especially at elevated temperatures, where enough energy is available to allow many reaction pathways to contribute to the observed decomposition behavior.

II.5. Mechanisms of Pyrolysis

The pyrolysis of cellulose and cellulosic materials have been investigated under a variety of conditions. These investigations have produced several theories and considerable discussion about the mechanisms of pyrolytic reactions. The large number of products, ranging from high to low molecular weights, which are formed in this process gives an indication of the complexity of the reaction mechanism. Not surprisingly, the

Table II-4.2 Summary of Kinetic Constants for Cellulose Pyrolysis

Investigator	Material	Atmosphere	k_o sec^{-1}	E kcal/gmole	Temperature Range, °C	Comments
Stamm (53)	α-Cellulose from Douglas Fir	Air	6×10^5	26	110 - 220	Weight after exposure
Akita (55)	Cellolose from Japanese Cypress	Air	-	36	270 - 340	Weight after exposure
			-	24	340 - 370	
Madorsky (92)	Cotton Cellulose	Vacuum	5.6×10^{15}	50	261 - 291	Arrhenius plot-rate of small samples
Blackshear & Kanury (59-61)	α-Cellulose	Air	1.7×10^4	19	- 600	Local temperature and density measurements during exposure
Lipska & Parker (42)	α-Cellulose	Nitrogen	$k/C_o \simeq 2.5 \times 10^{11}$	42	250 - 298	Measured remaining glucosan units
			$k/W_o \simeq 1.5 \times 10^{11}$	42	250 - 298	Weight - Zero order
Arseneau (65)	Filter Paper	Nitrogen	1×10^9	36.2	250 - 282	T.G.A. of small samples
			4×10^{12}	45.4	282 - 320	
Phillips et al. (93)	Cotton Cellulose	Nitrogen	2×10^8	30	- 400	Local density and temperature after exposure
			1.5×10^8	30	- 500	
			1×10^8	30	- 600	

(con't)

Table II-4.2 Summary of Kinetics Constants for Cellulose Pyrolysis (continued)

Investigator	Material	Atmosphere	k sec^{-1}	E kcal/gmole	Temperature Range, °C	Comments
Broido & Weinstein (11)	Filter Paper	Vacuum	At 226°C $\frac{dw}{wdt} \approx 4.3 \times 10^{-7}$ sec^{-1}			Continuous weight for long exposure
Lewellen et al. (13)	Filter Paper	Helium	6.79×10^{9}	33.4	200 - 800	single first-order
			7.67×10^{10}	37.0(σ=1.10)	"	multiple order
Broido & Weinstein (67)	Filter Paper	Vacuum	5.25×10^{17}	54.9	226	continuous weight for long exposure
Aldrich (19)	α-Cellulose	Nitrogen	$\{ k_1 = 5 \times 10^{7}$ $k_2 = 1 \times 10^{6}$	$\{ E_1 = 31$ $E_2 = 26.5$	25 - 550	weight-loss after exposure, first-order

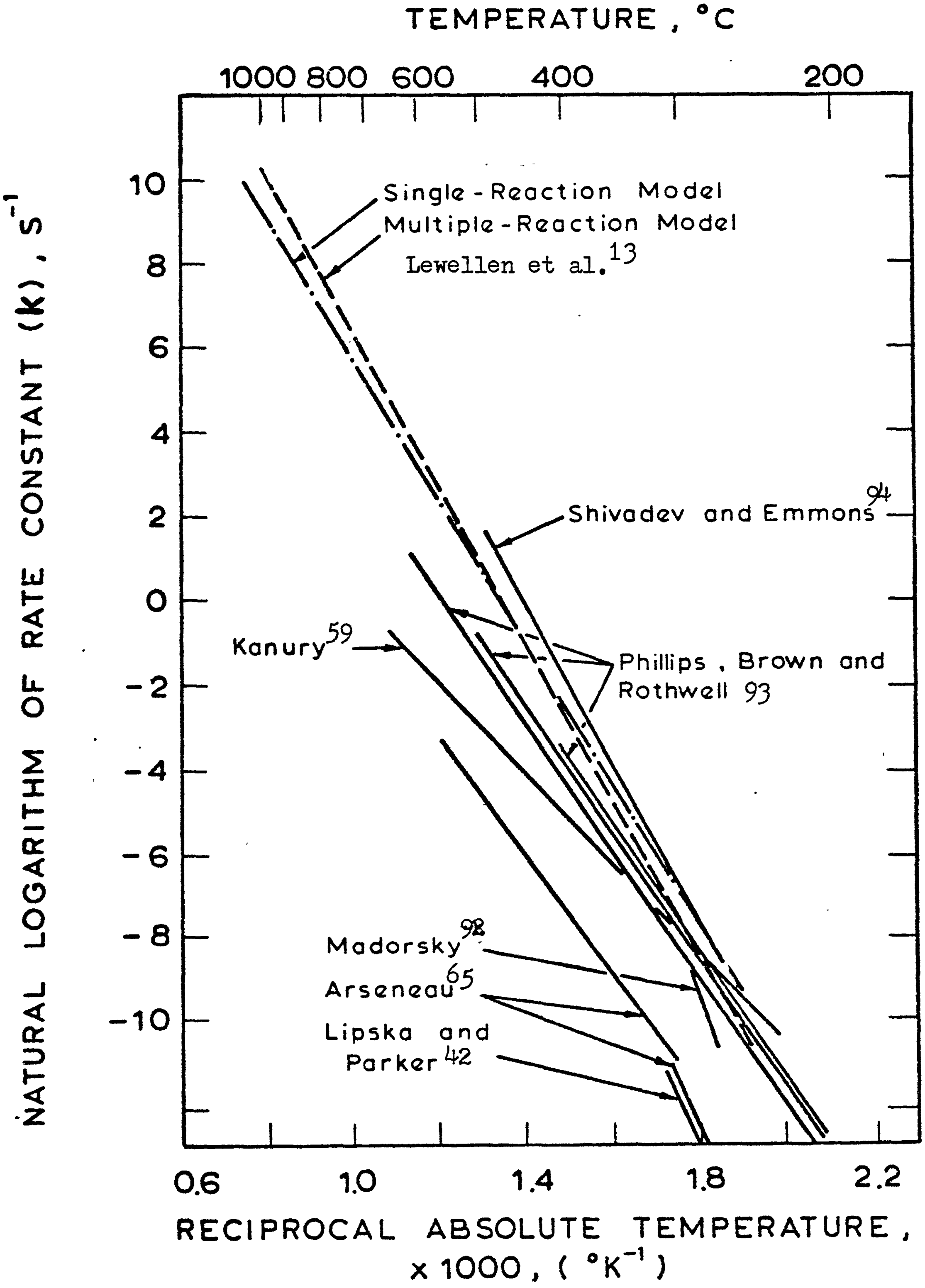


Figure II.4-1. Rate Constant of Cellulose Pyrolysis Measured by Various Investigators (13).

exact courses of the reactions are still not known. Nevertheless, a discussion of some of the mechanisms reported is useful in a more thorough understanding of the problem.

Much of the evidence in the literature strongly suggests that, when cellulose is heated the following sequence of reactions occur:

1) Dehydration and char formation reactions at low temperatures. These reactions begin at temperatures as low as 180-210 deg C and result in water, carbon dioxide, and char. This water is not absorbed water, but apparently results from the dehydration of random glucosan units along the cellulose molecule.

2) Depolymerization reactions at higher temperatures. These reactions which become significant at about 300 deg C, yield anhydro sugars, such as levoglucosan, and the so called tars, which are volatile at the reaction temperature, but condense when the temperature drops.

3) Decomposition reaction. The tar which is produced in the previous step and the cellulose could undergo decomposition to produce volatile, low molecular weight compounds.

However, at higher temperatures, dehydration, depolymerization, and decomposition occur simultaneously. With different reaction conditions, different reactions dominate the process.

In 1955, Parks et.al. (70) advanced the theory of the degradation of cellulose through an intermediate, levoglucosan, an anhydro monosaccharide, which subsequently undergoes two competing reactions: further degradation to combustible, volatile, low molecular weight compounds, and repolymerization and aromatization to form char.

Golova et.al. (71) reported that during the decomposition of the first 5-10% by weight of the cellulose, the pyrolysis process yields no levogluscosan. Madorksy and co-workers (57,72,73) have reported the rate controlling step in low temperature cellulose pyrolysis to be the formation of levoglucosan, which is then postulated to follow two reaction paths: dehydration and polymerization to produce water and char, and decomposition to more volatile species.

Berkowitz-Mattuck and Noguchi (38) in their very rapid pyrolysis of cotton, identified levoglucosan as an important product and presented a detailed molecular mechanism demonstrating how low molecular weight esters, aldehydes, ketones, acids, alcohols, and free radicals could all be produced by its further decomposition.

Glassner and Pierce (40) analyzed the products from the controlled application of heat to cellulose and levoglucosan. Their results revealed that at 242 deg C and above, the degradation products were essentially the same for the two substances, but data obtained at 190 deg C and 215 deg C did not correlate well, figure II.5-1. The explanation may be that cellulose degrades in this lower temperature range by a mechanism not involving levoglucosan as an intermediate.

Reported yields (57,16,23,32) of levoglucosan are increased by the rapid heating of cellulose under vacuum to the temperature required for volatilization. Rapid heating quickly moves the sample through the region of dehydration and charring into the range where depolymerization occurs rapidly and is the dominant reaction. Vacuum draws the product out of the reaction zone quickly, thereby minimizing further degradation of tar.

Kilzer and Broido (74) reported that cellulose, held first at 250 deg C for a day, forms about three times as much char at 400 deg C as a sample heated directly to 400 deg C. This preheating allows the early char producing reactions to proceed to a greater extent. The sample directly heated to 400 deg C quickly leaves the range of the char producing reactions and enters the range of the depolymerization and decomposition reactions.

Martin (39) in an extensive study reported that the earliest products appear to be mainly water, carbon dioxide, and carbon monoxide. Aside from a reduction in degrees of polymerization (DP), intermolecular or intramolecular water loss is probably the only significant reaction taking place below 250 deg C. Cellulose which has undergone only 16% volatilization by weight below 250 deg C, exhibits an infrared spectrum virtually

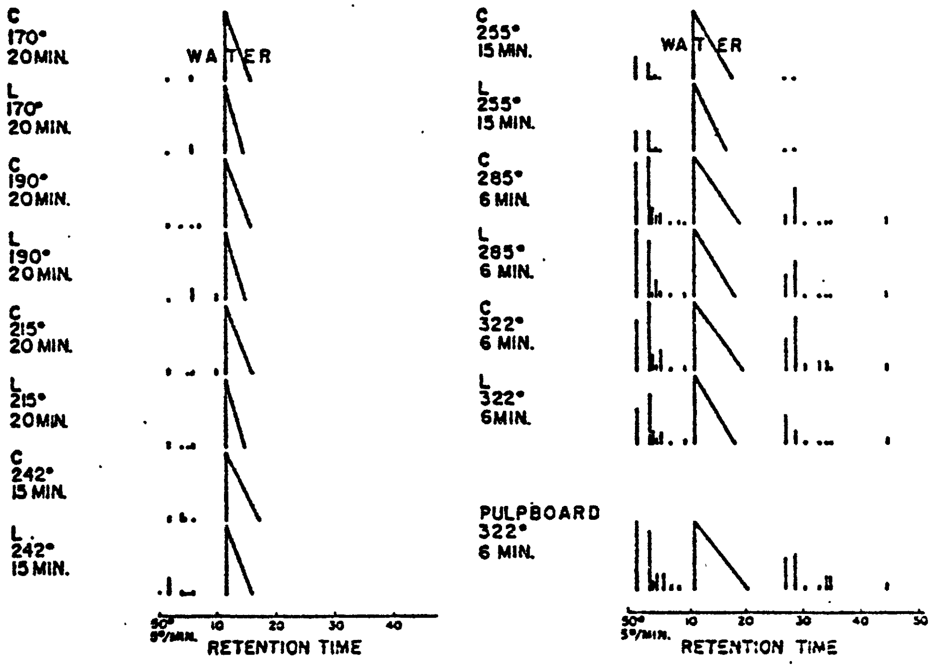


Figure II.5-1. Volatile products of cellulose(C) and levoglucosan (L) at varying temperatures and heating times. Positions of bars indicate elution time and size of bars indicates relative quantities of seperated compounds. Data of Glassner and Pierce (40).

unchanged, except for the appearance of a 5.7 micron absorption band, suggesting the formation of unsaturated or carbonyl groups as a result of the elimination of water from the hydroxyl groups of the glucosan units. The extent to which this dehydration takes place before the higher temperatures are reached will influence the subsequent reactions.

The indicated production of carbon dioxide and carbon monoxide indicates a more drastic type of reaction. There is no reasonable way of generating these compounds (besides secondary reactions) without at least opening the glucosan ring. Before any large amount of weight has been lost, the distribution of products changes sharply, and the volatile products are dominated by the high molecular weight substances, i.e. tars.

Finally, Martin concluded that the reactions competing for cellulose as the common reactant (i.e. the primary reactions) have as products: char, carbon dioxide, and water for the low temperature favored reactions, and tar (i.e. levoglucosan), acetadehyde, acrolein, hydrogen, etc., for the high temperature favored reactions. However, a similar trend from highly oxygenated to carbon and hydrogen rich volatiles (i.e. H2, CH4, C2H4, C2H6, etc.) also can be seen. This trend implies that the low molecular weight, carbon and hydrogen rich compounds are products of secondary reactions.

Arseneau (65) in his work on cellulose and levoglucosan concluded that at low temperatures (210 deg C) dehydration reactions are dominant, even though cellulose could undergo further reaction to form carbon dioxide in addition to water. At higher temperatures, about 270 deg C, depolymerization reactions become dominant. Above this temperature more decomposition of levoglucosan, which is the product of cellulose depolymerization, occurs in addition to the depolymerization reactions. The decomposition of the levoglucosan occurs rather than the decomposition of the so called 'anhydro cellulose' which was suggested by Esteve and workers (70).

Shafizadeh's (15,16,23) results are also indicative of some dehydration, elimination, and breakdown of the sugar molecule. This resulted in the gradual charring at lower temperatures and depolymerization at higher temperatures. His data indicates that these reactions take place very slowly until about 300 deg C, when sufficient energy becomes available for a rapid cleavage of the glycosidic bond, rapid weight loss, formation of levoglucosan, and formation of tarry pyrolysis products.

The mechanism for the thermal degradation of cellulose and the relationship of levoglucosan to this mechanism has been investigated and discussed by several other workers. It has been established that levoglucosan is a major component of the tar portion of cellulose pyrolysis. It is also thought to be the intermediate through which cellulose is thermally degraded to lower molecular weight materials.

It may be surprising if levoglucosan is the major product in the tar, since the direct dehydration of a glucose unit would be expected to give an unsaturated product. However, there are a number of mechanism which could account for these results.

First, the hydrolysis of both carbon-oxygen bonds in one glucosan unit, or bond of a unit at the end of a cellulose chain, will produce a molecule of glucose. Subsequent dehydration of glucose yields 1,2 anhydro-glucosan (figure II.5-2).

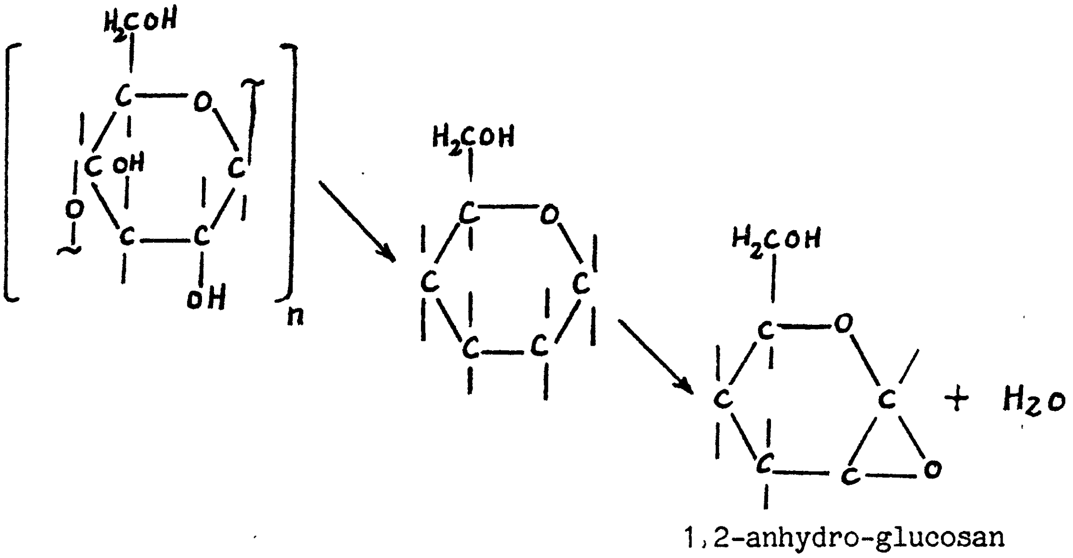


Figure II.5-2

At temperatures above 110 deg C, 1,2-anhydroglucosan rearranges to levoglucosan (figure II.5-3).

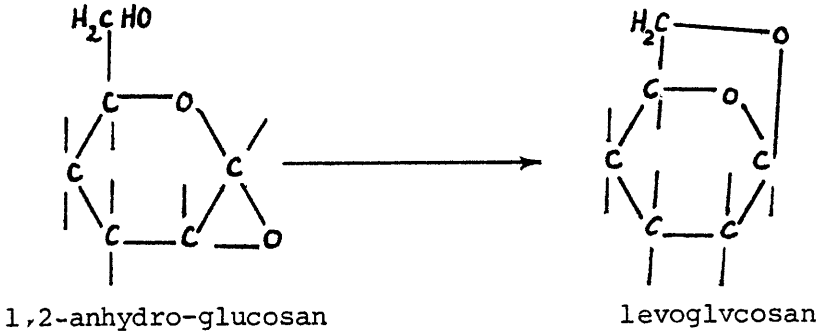


Figure II.5-3

The above mechanism, on the origin of levoglucosan, was originally proposed by Browne (75), and was later discredited by him and Golova et.al. (68,71). They later found that pyrolysis of glucose yields almost no levoglucosan. If hydrolysis is not the route, then the cellulose molecule must decompose by an unzipping reaction which propagates along the chain.

The exact mechanism of the unzipping reaction is not yet well established. However, one proposal (19) indicates direct formation of levoglucosan by an intramolecular chain transfer (fig II.5-4).

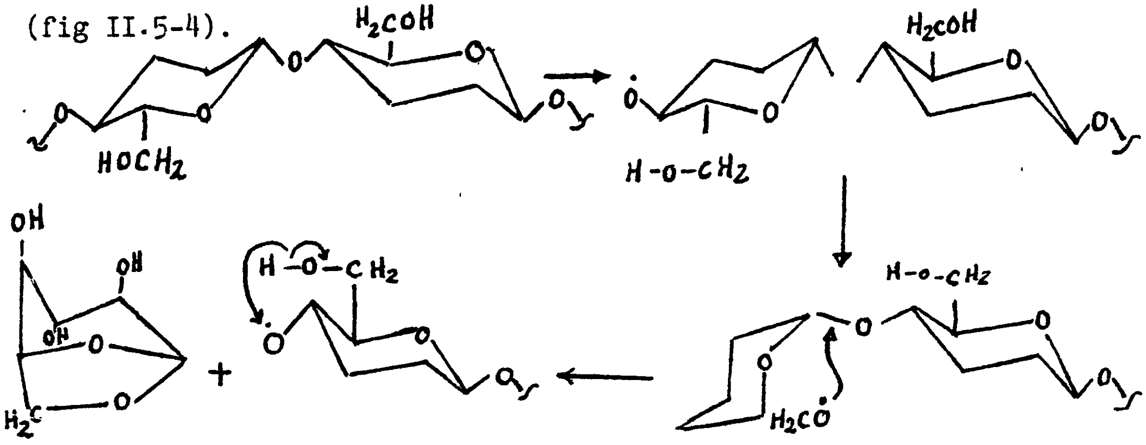
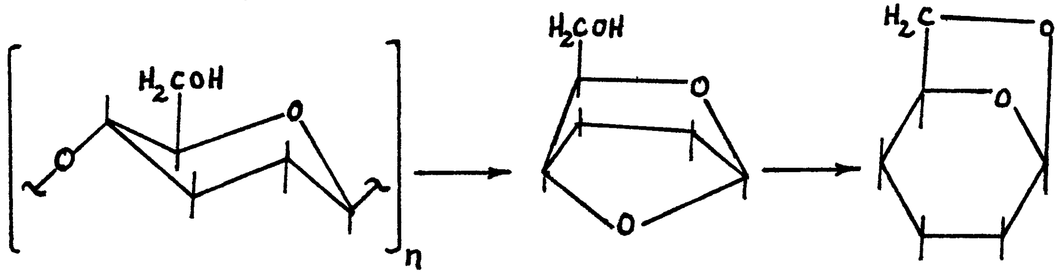


Figure II.5-4

producing one molecule of levoglucosan, and continuing along the chain.

An alternative mechanism of an intramolecular reaction has been proposed which involves direct attack at the carbon-1 position by the oxygen attached to the carbon-4 at the end of the chain. This attack displaces the carbon-1 oxygen and results in a molecule of 1,4 anhydro-alpha-D-glucopyranose (b). Subsequent attack at the carbon-1 position by the hydroxyl attached to the carbon 6 could produce levoglucosan (c).



(a) (b) (c)

Figure II.5-5

Another proposed mechanism (70) involves direct conversion of cellulose into levoglucosan by a concerted displacement reaction.

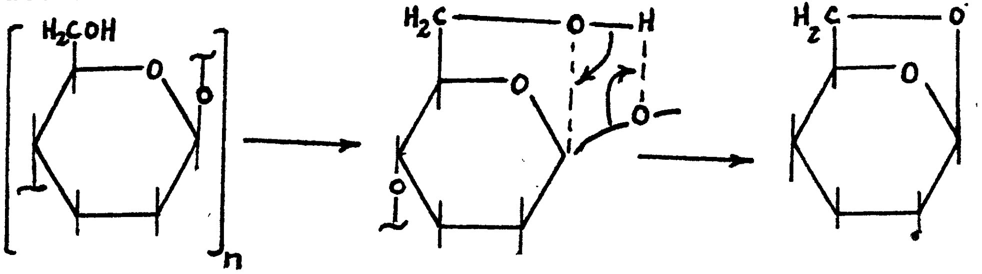


Figure II.5-6

The free radical mechanism proposed (76), involves the initial cleavage of the oxygen bond at the carbon-4, migration of the hydrogen atom from the carbon-6 hydroxyle group to carbon-4, and the formation of an oxygen bridge between carbon-1 and carbon-6.

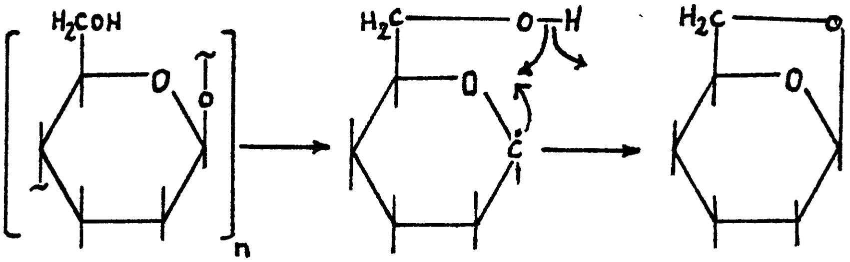


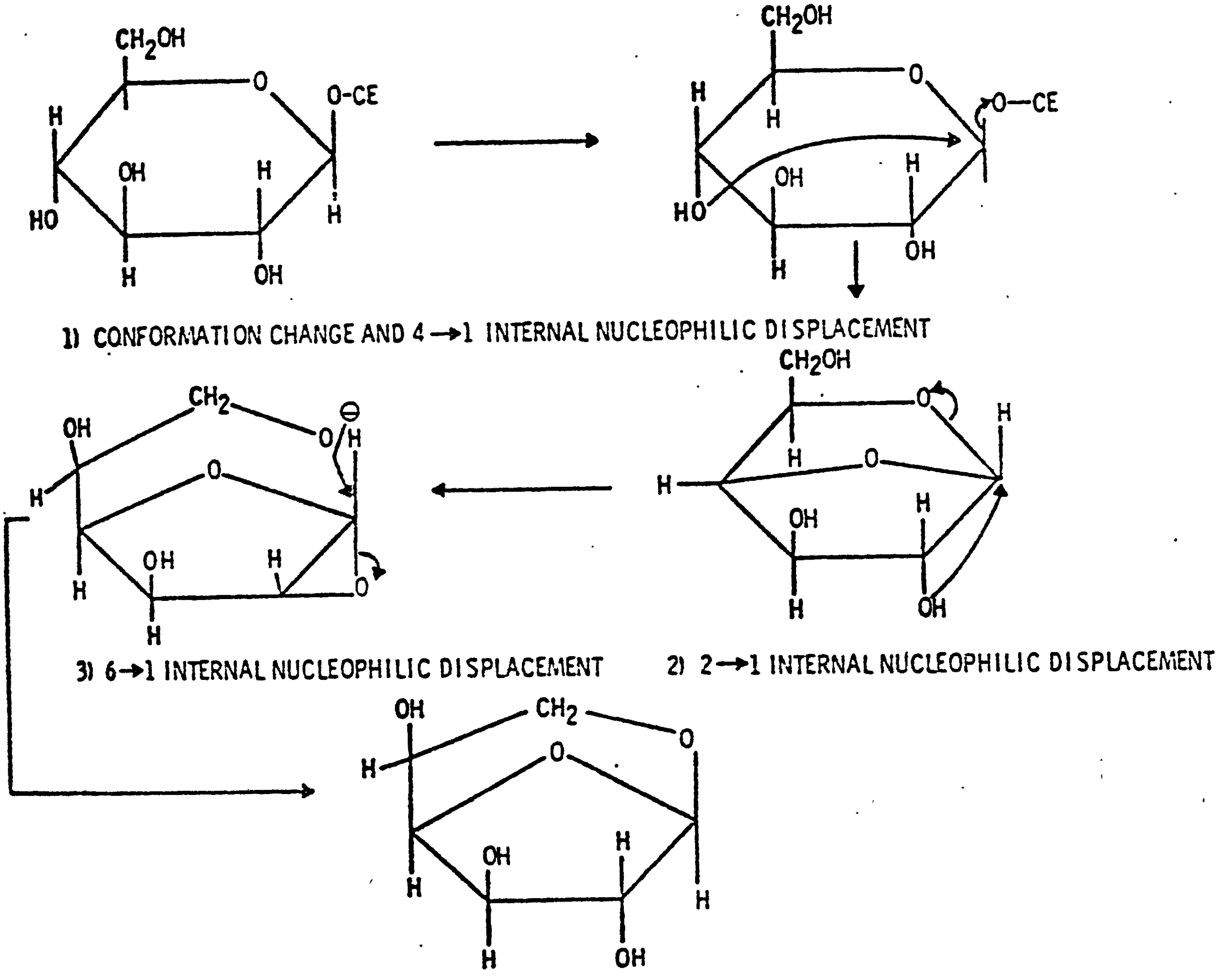
Figure II.5-7

Madorsky and co-workers (57) in explanation of simultaneous decomposition and depolymerization of the cellulose molecule pointed out that the carbon-oxygen bonds are thermally less stable than the carbon-carbon bonds. On heating of cellulose, random breaking of the carbon-5-oxygen, carbon-1-oxygen bonds (involved in the oxygen ring), and the carbon-4-oxygen bond connecting the D glucose residues, result in a more or less complete breakdown of a part of the chain. This yields water, carbon dioxide, carbon monoxide, and char. On the other hand, random cleavage of the glycosidic carbon-1 oxygen link leads to the formation of 1,6-anhydro rings; the subsequent breakage of the glycosidic bond at the next unit yields levoglucosan.

The question of which of these possible mechanisms is the correct mechanism under which circumstances is the subject of great speculation. There is, however, insufficient evidence to draw an accurate conclusion. What is important here is that an intermediate with a structure like levoglucosan can be expected, and that from the complexity of the reactions involved, it is clear that different conditions of temperature, pressure, heating rate, and residence time, all effect the reactions that occur.

II.5.1. Decomposition of Cellulose to Other Compounds

Although levoglucosan is a frequently observed product of cellulose decomposition, it is not the only one. Indeed, in some cases it is not even the primary or the major product. The formation of levoglucosan from cellulose pyrolysis seems beyond doubt, but this doesn't mean that cellulose can't decompose by routes which do not involve levoglucosan. In fact it is possible, though unlikely, that levoglucosan is the major product simply because it is more stable than other products which degrade faster. However, detailed analysis of the tar compounds obtained from the vacuum pyrolysis of pure cellulose (16,48,35,44,41) has shown that other products have been observed. One of these is 1,6-anhydro-beta-D-glucofuranose, which Gardiner (48) believes is formed through an energetically unfavored route involving an initial chair/boat conformation change, followed by a succession of three internal nucleophilic displacements between hydroxyl groups at positions four through one (cleaving the glucose residue from the cellulose chain). The changes of 2 ⟶ 1 and 6 ⟶ 1, respectively, are shown in figure II.5-8. Perhaps not surprisingly, 1,6-anhydro-beta-D-glucofuranose, is a minor product from cellulose pyrolysis. Its formation seems to be beyond doubt. It has been isolated and identified by: gas chromatography, as a chemical derivate, and by mass spectroscopy (41,44,48,16). Other carbohydrate derivatives are formed from cellulose and have been identified by various means. They include both alpha and beta-D-glucose (16,44,23), 1,4 and 3,6-dianhydro-alpha-D-glucopyranose (41,48), 3-deoxy-D-erythro-hexoseulose (16,77), other dehydration products of D-glucose, and a variety of poly and oligo saccharides (16,44).



1,6-ANHYDRO-β-D-GLUCOFURANOSE

Figure II.5-8. Mechanism of Formation of 1,6-Anhydro- -D-Glucofuranose from the Nonreducing End Group of Cellulose(22).

However, the fate of the anhydro sugars which are formed from the cleavage of the glycosidic linkage in cellulose pyrolysis depends on the relative stability of the compound and the prevailing conditions. The 1,2 and 1,4- anhydro sugars are easily converted into the more stable 1,6-anhydro sugars. Under high vacuum, the anhydro sugars are readily removed from the heated reaction zone before extensive degradation and decomposition of the sugar units can occur. Consequently, the tar fractions of pyrolysis products contain a mixture of different anhydro sugars as well as various oligo and poly saccharides. Partial decomposition and dehydration of these compounds, at higher temperatures or higher pressures, could lead to alpha and beta-D-glucose, 3-deoxy-D-erythro- hexosulose, and various furan derivatives.

Investigations which have been conducted by Shafizadeh's group on model compounds which have been identified in cellulose pyrolysis prove that not only are they a product of cellulose pyrolysis but behave as intermediates for the production of light products in cellulose decomposition. Some of this data is shown in tables II.5-1,2,3. This data, which was obtained from the pyrolysis of cellulose, levoglucosan, levoglucosanone, and 3-deoxy-D-erythrohexoseulose, respectively, shows the importance of each in the production of lower molecular weight compounds.

II.5.2. Secondary Reactions

Reactions of cellulose pyrolysis in general can be divided

Table II.5-1. Pyrolysis Products of Cellulose and Treated Cellulose at 600°C[1]

Product	Neat	+5% H_3PO_4	+5% $(NH_4)_2HPO_4$	+5% $ZnCl_2$
Acetaldehyde	1.5[a]	0.9	0.4	1.0
Furan	0.7	0.7	0.5	3.2
Propenal	0.8	0.4	0.2	T
Methanol	1.1	0.7	0.9	0.5
2-Methylfuran	T	0.5	0.5	2.1
2,3-Butanedione	2.0	2.0	1.6	1.2
1-Hydroxy-2-propanone Glyoxal	2.8	0.2	T	0.4
Acetic acid	1.0	1.0	0.9	0.8
2-Furaldehyde	1.3	1.3	1.3	2.1
5-Methyl-2-furaldehyde	0.5	1.1	1.0	0.3
Carbon dioxide	6	5	6	3
Water	11	21	26	23
Char	5	24	35	31
Balance (tar)	66	41	26	31

[a] Percentage, yield based on the weight of the sample; T = trace amounts.

[1] Data of Shfizadeh and Chin (15).

Table II.5-2. Pyrolysis Products of 1,6-Anhydro- - D-Glucopyranose(Levoglucosan) at 600°C[1]

Pyrolysis product	Yield		
	Neat	$+ZnCl_2$	+NaOH
Acetaldehyde	1.1	0.3	7.3
Furan	1.0	1.3	1.6
Acrolein	1.7	<0.1	2.6
Methanol	0.3	0.4	0.7
2,3-Butanedione	0.5	0.8	1.6
2-Butenal	0.7	0.2	2.2
1-Hydroxy-2-propanone	0.8	<0.1	1.1
Glyoxal	1.4	<0.1	4.9
Acetic acid	1.7	0.7	1.5
2-Furaldehyde	0.9	3.0	0.4
5-Methyl-2-furaldehyde	0.1	0.3	--
Carbon dioxide	2.9	6.8	5.7
Water	8.7	20.1	14.1
Char	3.9	29.0	16.0
Balance (tar)	74.3	36.8	40.3

[1] Data of Shafizadeh (23).

Pyrolysis Products of 3-Deoxy-D-erythro-Hexosulose at 500°C[1]

Pyrolysis Product	Yield (%)		
	Neat	+ZnCl$_2$	+Na$_2$CO$_3$
Acetaldehyde	1.5	0.5	2.1
Furan	0.6	0.2	0.5
Acrylaldehyde	T[a]	T	0.6
2-Methylfuran	2.0	5.8	1.1
2,3-Butanedione	T	T	1.3
2-Butenal	0.8	0.4	1.0
1-Hydroxy-2-propanone	0.8	0.1	2.6
Glyoxal			
Acetic acid	0.2	0.1	0.6
2-Furaldehyde	3.1	6.5	0.1
5-Methyl-2-furaldehyde	0.8	0.9	0.6
2-Furfuryl alcohol	0.1	T	T
Carbon monoxide	4.0	3.3	4.4
Carbon dioxide	12.4	8.1	16.1
Water	18.4	22.3	16.8
Char	38.2	45.1	35.2
Balance (tar)	17.1	6.7	17.0
Composition of the tar after sodium borohydride reduction	(65.0)[b]		
3-Deoxy-D-hexitols	(24.7)		
Glycerol	(8.3)		
3,6-Anhydro-D-glucose	(2.6)		
2-Deoxy-D-*erythro*-pentitol	(1.3)		
2,5-Dihydroxymethylfuran	(0.5)		
Glucometasaccharinic acid 1,4-lactone	(T)		
3,6-Anhydro-D-glucitol	(T)		

---

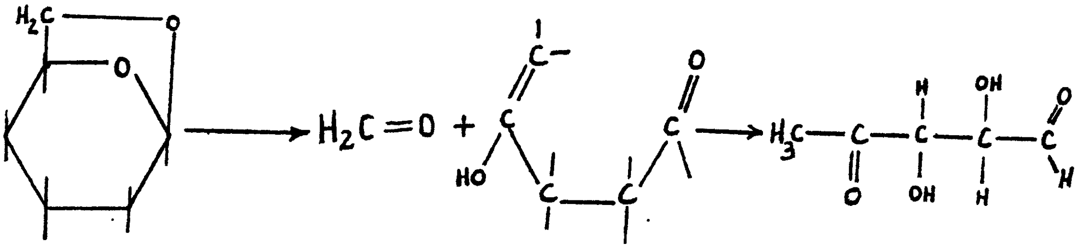
[1] Data of Shafizadeh (23).

into two sets, primary or secondary reactions, according to whether they directly affected the cellulose substrate, or one of the intermediate degradation products.

Products of the primary reactions, if not rapidly removed from the heated environment, could further react and decompose to a series of secondary compounds of low molecular weight. With the exception of scattered information on the products formed from the pyrolysis of cellulose (reviewed in the previous sections) and some isolated experiments, there is very little definitive information on the nature, sequence, and mechanism of the secondary reactions.

The discussions thus far presented have indicated that secondary reactions, at least in part, involve further decomposition of intermediates. Therefore, in order to obtain a better understanding of the nature and sequence of the secondary reactions and products, an insight into the various mechanisms that could yield these products would be helpful.

Levoglucosan, the major component of cellulose pyrolysis, is structurally an acetal and should decompose with the formation of an aldehyde. In the scheme proposed by Berkowitz-Mattuck and Noguchi (38), it is assumed that cleavage of the carbon oxygen bonds involved in the sugar ring leads to the formation of formaldehyde and a dicarbonyl compound.



The carbonyl groups then weaken adjacent to the carbon carbon bonds, which break with the formation of free radicals.

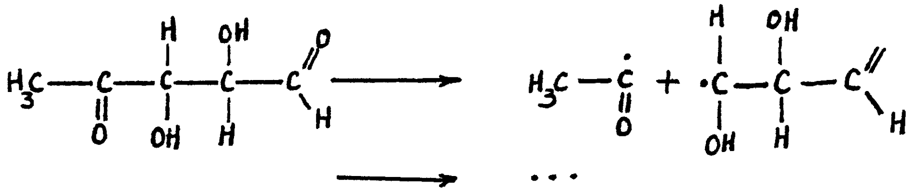


Figure II.5-9

Probably rearrangement reaction of the same intermediate are:

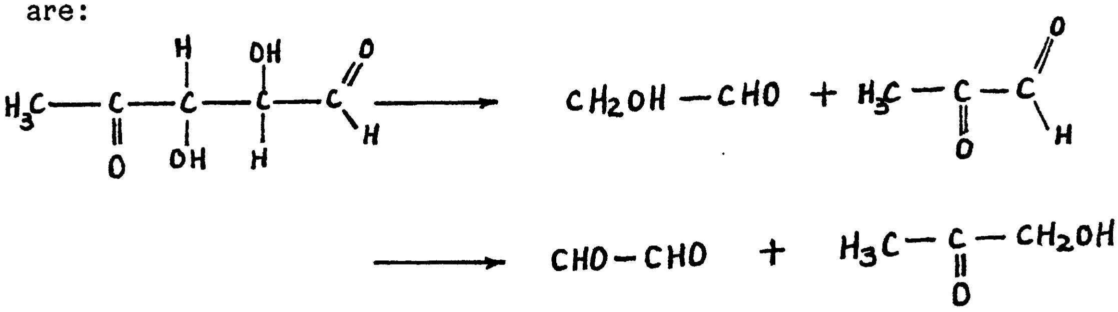


Figure II.5-10

The free radicals and molecular species could then undergo further reaction and recombination to provide an enormous variety of compounds including:

$cH_3-\overset{O}{c}-cH_3$

$cH_3-\overset{O}{c}-oH$

cH_3-cH_2oH

H-c"°-H

cH_3OH

$cH_3-\overset{O}{c}-H$

CO, CO_2, CH_4

c_2H_4 $H_2, \ldots$

All of the above have been identified in the products of cellulose pyrolysis.

Alternative mechanisms have been postulated (41), which account for the direct conversion of cellulose into a variety of carbonyl compounds, and a carbon rich char through a carbonium ion intermediate (figure II.5-11). According to this mechanism, the intermediate carbonium ion is derived from the breakdown of cellulose and its subsequent decomposition to form unsaturated products containing aldehyde and enol groups. These products yield carbonyl compounds or undergo aldol reactions, with the elimination of water, to provide a carbon rich char.

Another possible mechanism is through 3-deoxy-D-erythro-hexosulose, which, as data by Shafizadeh indicated, plays a significant role as an intermediate in the production of furan derivatives. As is shown in figure II.5-12, it could undergo a variety of reactions to produce volatiles and char.

It is stated by Martin (39) that during the radiative heating of cellulose, hydrogen, methane, ethane, and propane (hydrocarbon gases) are formed at the later stages of pyrolysis, when the char layer becomes hot enough (above 600 deg C) to react endothermally with the pyrolysis products. Whether there is enough evidence to validate this mechanism for the production of hydrocarbon gases, is a point of contention. There is evidence that reactive products, which are obtained from either the decomposition of intermediates or from the direct decomposition of cellulose, could pyrolyze to hydrogen, hydrocarbon gases, and carbon monoxide. These reactive compounds include alcohols, aldehydes, and ketones which even at low temperatures, pyrolyze

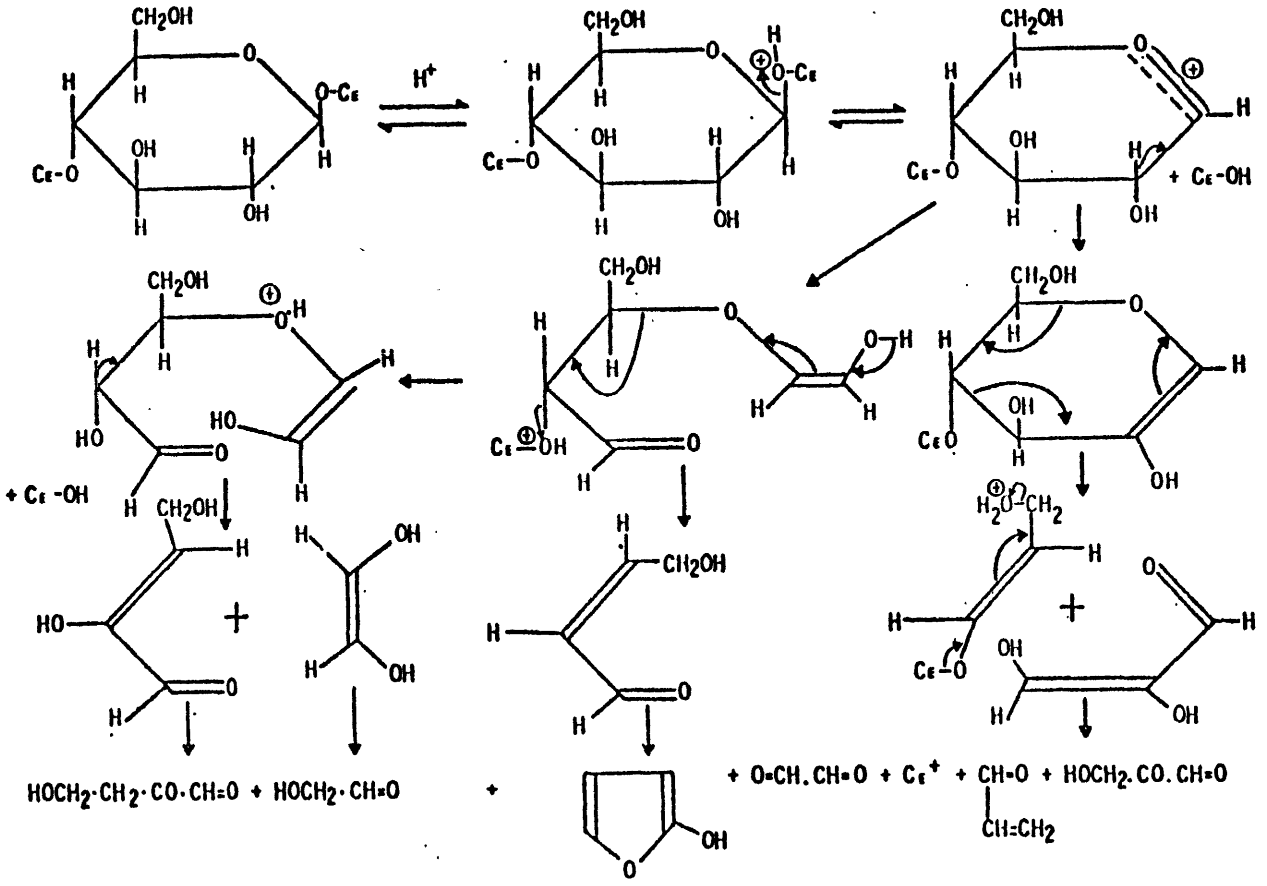


Figure II.5-11. Mechanism of Formation of Carbonyl Compounds from Cellulose (22).

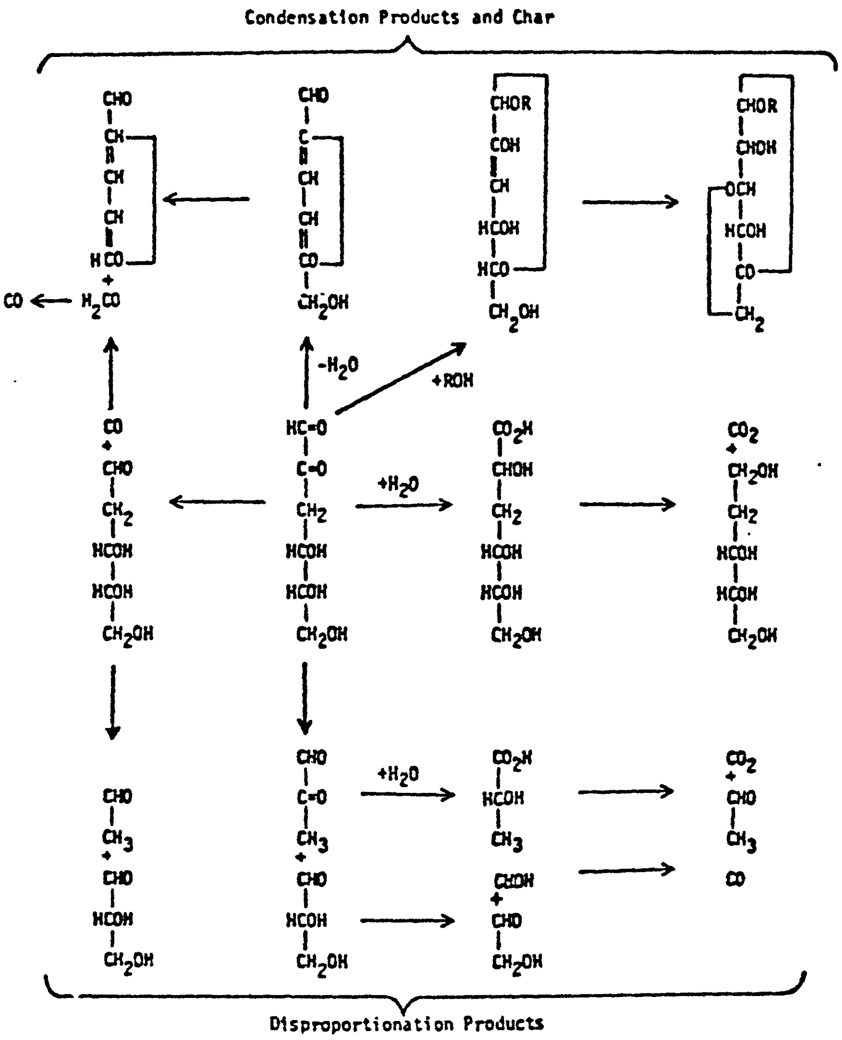


Figure II.5-12. The Pyroltic Reactions of 3-Deoxy-D-erythro-Hexosulose(23).

to hydrocarbons (39).

Whether or not it is accepted that hydrocarbons and hydrogen comes from the autocatalytic reaction of some products and char, Lewellen et.al. (13) suggested that the occurrence of autocatalytic and secondary inhibition reactions could qualitatively explain their observations on the effects of increasing the heating rate and reducing pressure on the rapid decomposition of pure cellulose. In the experiments with high heating rate (10,000 deg C/sec) or low pressure (0.5 torr), the observed reaction rates were slower than at one atmosphere pressure and a heating rate of 400 deg C/sec. They found that this behavior is consistent with the existence of an autocatalytic step or steps in the overall decomposition process, even though this is not unequivocally proved by existing data. The data in Figure II.5-13 shows that the kinetic parameters obtained at 400 deg C/sec and 1 atmosphere pressure, gives over the predicted yield for lower pressure and higher heating rate. It was explained that these conditions facilitate the escape of freshly formed volatile products from the cellulose matrix. Hence, any catalytic effect associated with the presence of these materials in the cellulose substrate would be reduced in magnitude relative to the one atmosphere and low heating rate case, which leads to the decrease in the observed reaction rate.

All of the reactions thus far considered have been those yielding volatile products. The mechanism of char formation is even less well understood. It is not clear whether it occurs at

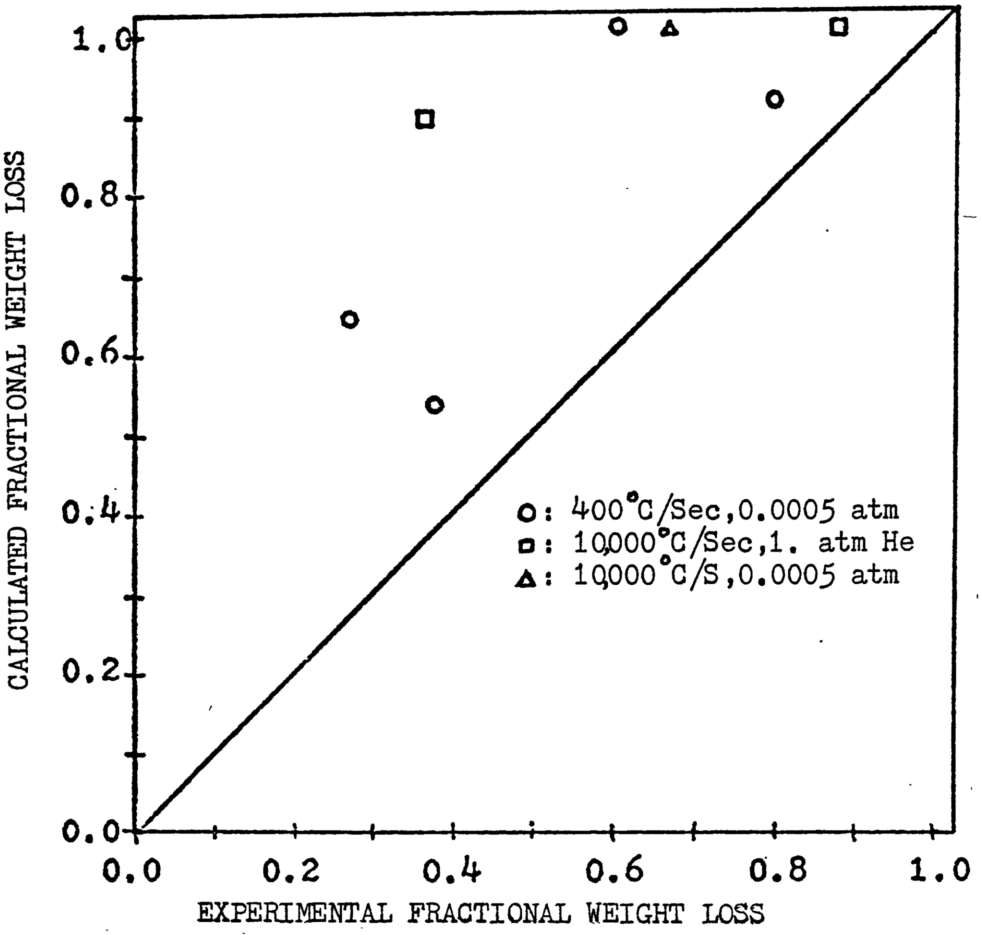


Figure II.5-13. Comparison of Calculated and Measured Cellulose Fractional Weight Losses(13).

the location of the initial break in the glucose chain, from the glucosan units, through a furan structure, if it results from cross linking and repolymerization of cellulose, or if it comes from the cracking of the pyrolysis products.

II.5.3. The Pyrolysis of Oxygenated Volatiles

Even low molecular weight oxygenated compounds from cellulose pyrolysis, such as the lower boiling aldehydes, ketones, and alcohols could be pyrolyzed to fixed gases or other lower molecular weight compounds, even at relatively low temperatures. A good example of these is acetone, a compound identified in cellulose pyrolysis. When acetone undergoes photolysis or pyrolysis, the overall reaction sequence can be presented by the following sets of equations (84):

$$\begin{aligned}
\mathrm{CH3\text{-}CO\text{-}CH3} &\longrightarrow \mathrm{C2H6 + CO} \\
&\longrightarrow \mathrm{1/2CH4 + (CH3\text{-}CO\text{-}CH2)_2 + CO} \\
&\longrightarrow \mathrm{1/2C2H6 + (CH3CO)_2} \quad \text{below 120 deg C} \\
&\longrightarrow \mathrm{CH4 + CH2CO} \quad \text{above 200 deg C} \\
&\longrightarrow \mathrm{1/2\ CH4 + C2H4 + 2CO} \quad \text{above 300 deg C}
\end{aligned}$$

Figure II.5-14

The absorption of heat or light by acetone causes a chemical reaction whose products are ethane, carbon monoxide, methane, CH3COCOCH3, CH3COC2H5, CH2CO, and (CH3COCH2)2. Biacetyl seems to be an important product only at temperatures below 100 deg C (84), it has been found only in pyrolysis (87,88). Methane yields depend markedly on temperature (85), pressure, and, in photolysis, light intensity. The ethyl methyl ketone yield is comparable to that of methane at temperatures below 180 deg C, but the yield decreases with increasing temperature (86). Above 200 deg C, ketones become an important product (89), and above 300 deg C, ethylene also begins to appear in increasing quantity.

Another example is pyrolysis of acetaldehyde. This pyrolysis seems to be simpler than acetone pyrolysis. The products of acetaldehyde pyrolysis are carbon monoxide and methane, along with very small amounts of ethane and hydrogen, at temperatures near 500 deg C. (90). The pyrolysis reaction for acetaldehyde can be represented by:

$$\begin{aligned} CH3\text{-}CHO &\longrightarrow CH4 + CO \\ &\longrightarrow 1/2C2H6 + H2 + CO \quad \text{near 500 deg C} \end{aligned}$$

Figure II.5-15

Finally, the materials discussed in this section could be summarized in the following manner (as shown in figure II.5-16). Cellulose could decompose rapidly to an intermediate (tar). Tar, which is a mixture of many different compounds, may then: (1) be transported from the cellulose matrix to give a tar product, (2) repolymerize, crack, or be cross linked to yield char, and (3) be pyrolyzed to lighter volatile products including carbon monoxide, carbon dioxide, fixed gases, organic acids, ketones, esters,

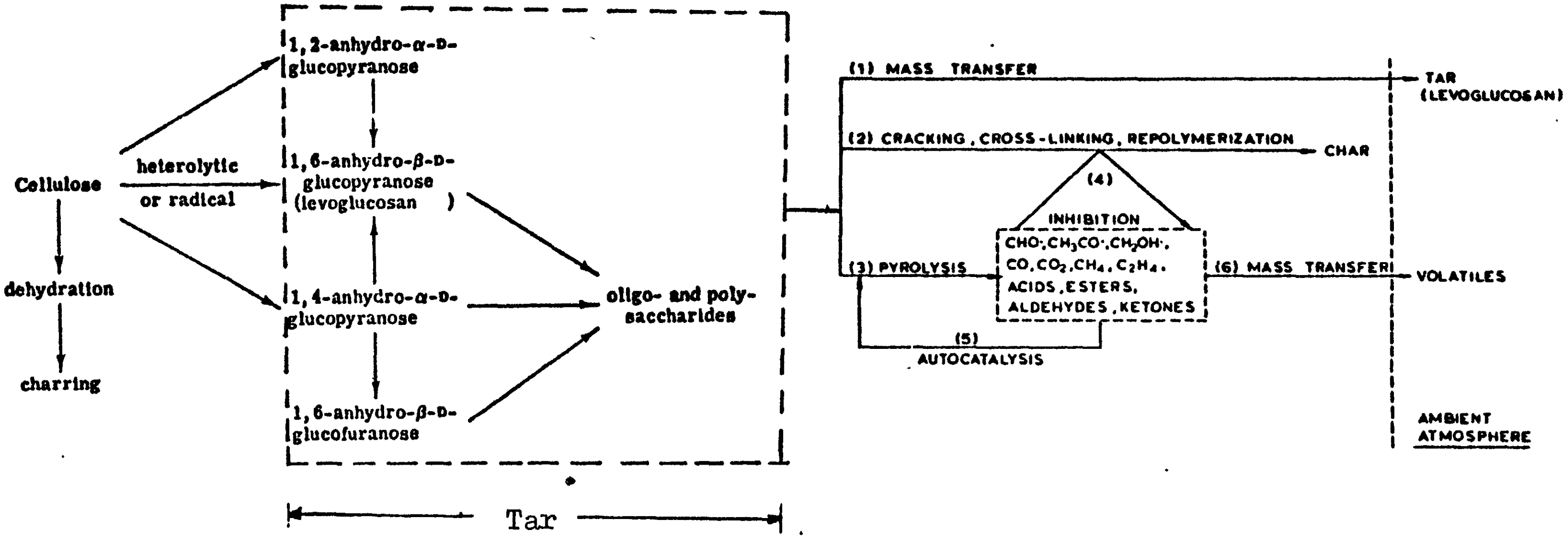


Figure II.5-16. Possible Reaction Pathways for Thermal Degradation of Cellulose.

aldehydes, and free radicals. Some of these volatile products could (4) inhibit char formation, or (5) autocatalyze step (3). Lighter, stable products could also (6) escape the matrix to yield volatiles. However, pyrolysis at low temperature could dehydrate the cellulose to yield water and char.

Therefore, the discussion here merely provides an insight into the problem and gives an indication of the various, possible reaction pathways and the complexity of the reaction mechanisms. It is not appropriate to favor one of the pathways over the others in the absence of definitive information. In fact, under the conditions in which the molecule is physically torn into fragments, it is very possible that more than one mechanism or set of reactions could be involved. This is especially true when the effect of temperature, heating rate, pressure, and the residence time of volatiles in the heating zone is not well known.

III. Apparatus and Procedure

The apparatus which was employed is the captive sample apparatus first designed by Anthony (78) for pyrolysis studies on coal. Later, this apparatus was used by Lewellen et al. (13) for investigations on pure cellulose pyrolysis, and with further modifications to allow determination of product compositions by Suuberg (79), for studies in coal pyrolysis and hydropyrolysis. Experiments with this apparatus showed that with total pyrolysis weight loss of coal and pure cellulose, good kinetic data could be obtained. Kinetic parameters for the yields of specific products from coal pyrolysis have also been studied.

This system has a number of distinct advantages:

- Independent control of heating rate, final temperature, and holding time at the final temperature.

- Good heat transfer between the hot stage and the sample.

- Accurate measurement of the entire time / temperature history of the sample.

- Near zero residence time of volatile products at elevated temperatures.

- Rapid quenching of volatiles, which leads to less cracking of the products.

- Operating capability for a wide range of pressures, from vacuum up to 100 atmospheres.

- Operating capability for a wide range of temperatures, from 100 to 1100 deg C.

- Operating capability for a wide range of heating rates, from 50 to 100,000 deg C/sec.

- Operating capability for a wide range of solids residence time, from virtually zero seconds to infinity.

Nevertheless, the effect of secondary reactions between fresh volatiles and the non-decomposing solid cannot be studied very well in this apparatus because products exit the decomposing solid matrix and its hot surroundings very rapidly. With the large volume reactor, there is also rapid quenching of the products, and little opportunity for vapor phase cracking. Also, the sample size was so small that only a small quantity of products was available for analysis. Another disadvantage is the possible cracking of products on the screen. The problem of sample size was solved by constructing a large scale reactor. This reactor was designed and built by Richard Caron (80) and accomadates a sample size ten times larger than the previous reactors.

III.1. Apparatus Description

A schematic view of the apparatus is shown in figure III.1-1. The apparatus consists of five components: the reactor, designed to contain the sample in a gaseous environment of known pressure and composition; the electrical system, used to subject the sample to a controlled time-temperature history; the time-temperature monitoring system; the product collection system; and the product analysis system.

III.1.1. The Reactor Vessel

The specific reactor used in this study is designed for pyrolysis measurements at atmospheric pressure and also vacuum. It is a Corning Pyrex, cylindrical pipe, nine inches in diameter and nine inches long. It is closed at each end with 3/8 inch

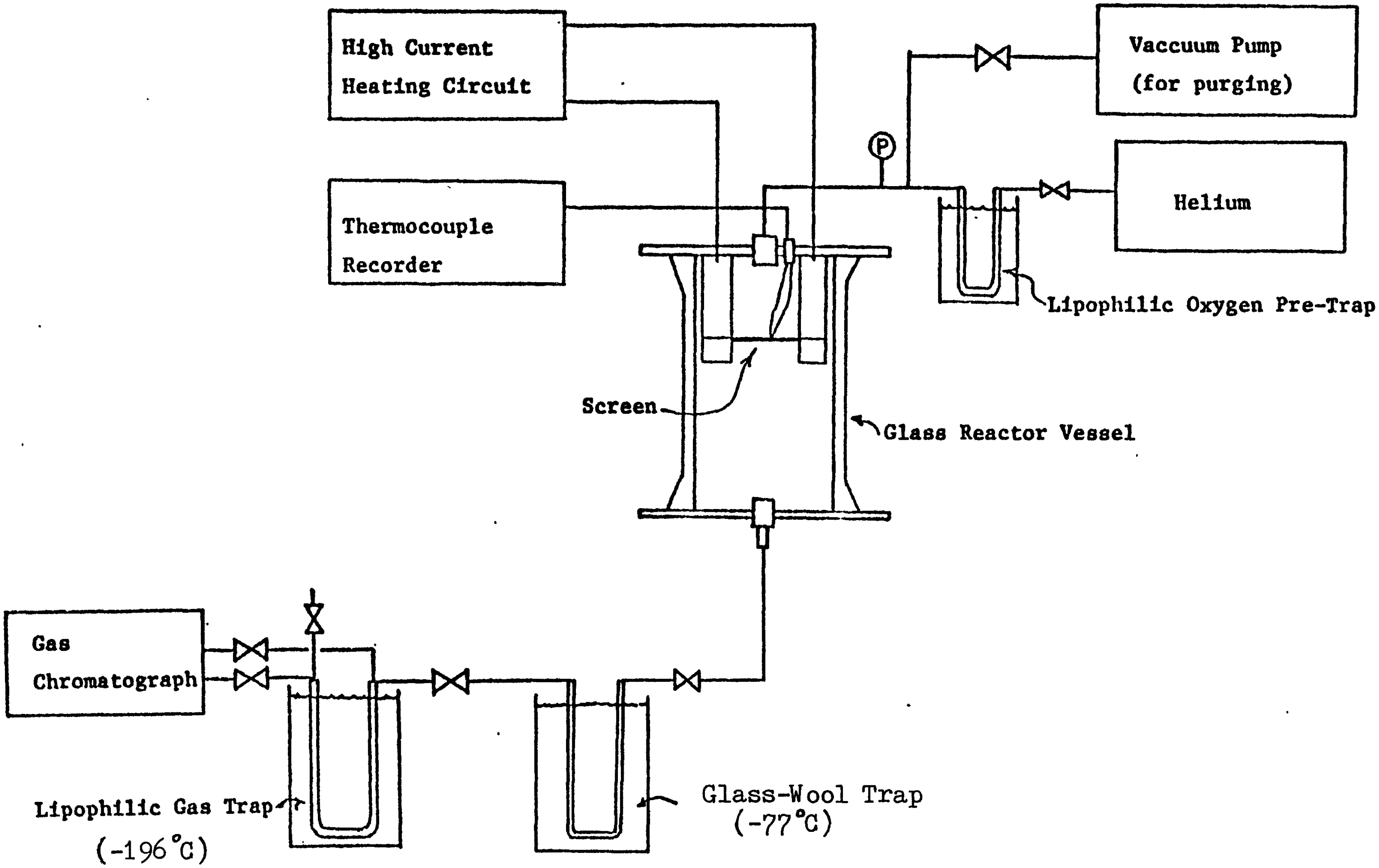
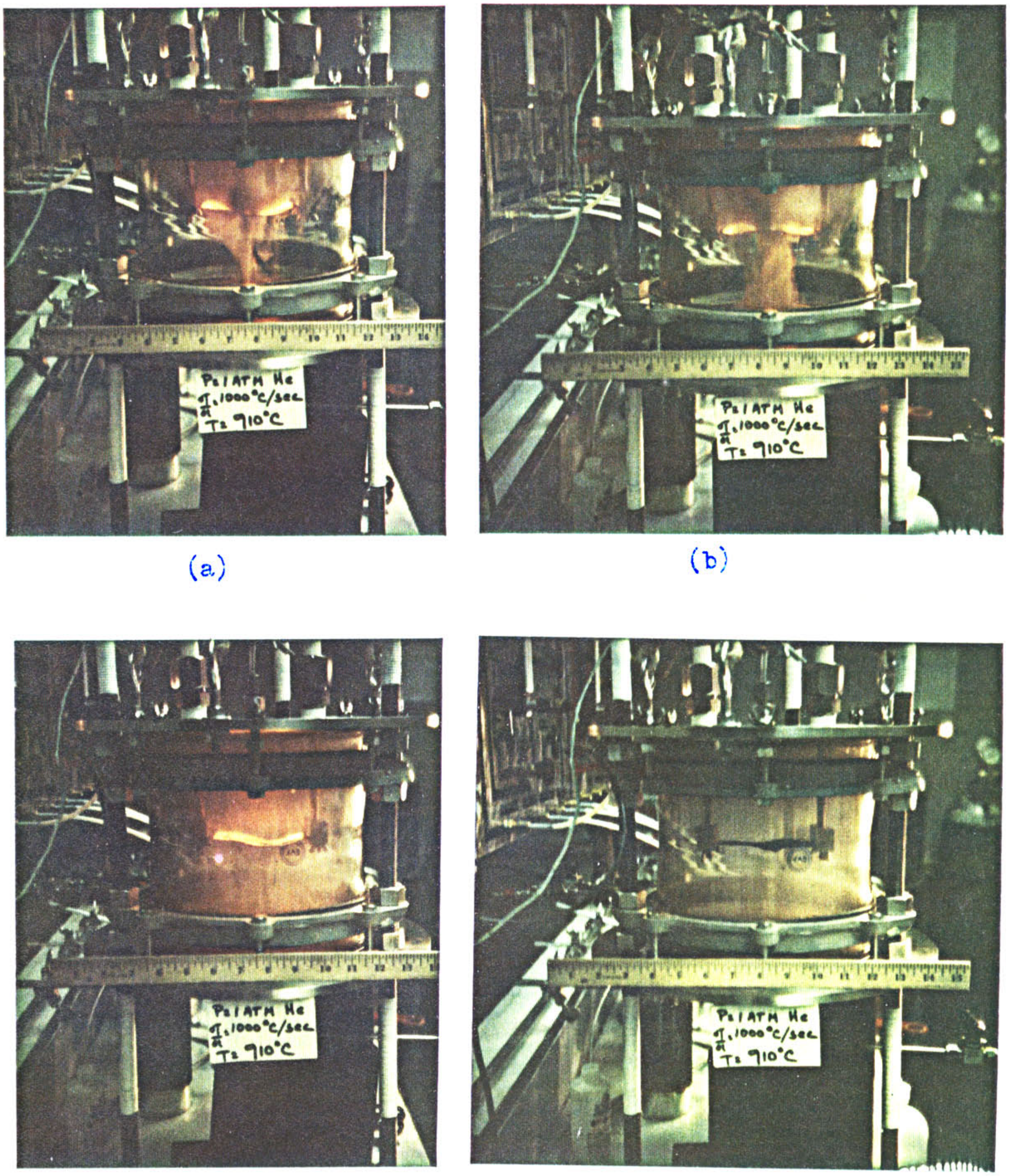


Figure III.1-1. Captive Sample Apparatus Flow Diagram stainless steel plate flanges, sealed to the pipe with wing nuts and O rings. The plates are fitted with conax EGT-375 electrical feed throughs and gas inlet and outlet ports. The pyrex reactor shell permits visual observation of the thermal decomposition process and of the condensation of the higher boiling reaction products on its inner walls. The photograph in figure III.1-2 shows the outflow of volatile matter produced by the pyrolysis of coal. The maximum pressure and temperature that the vessel itself can withstand is 15 psig and 250 deg C, respectively. However, another reactor which can withstand pressures up to 100atm, is available for use in this work.

The top flange of the reactor consists of an O ring groove, two electrical feed through holes, a gas inlet/outlet port, a sample introduction port, and one thermocouple, feed through orifice. The bottom plate has one 1 1/2 inch pipe threaded in the center in which a 2.6 inch pipe nipple is threaded. The pipe nipple supports a perforated plate upon which the a filter and cap which secures the filter are placed.

The sample is held on a 13cm (5.25 inch) by 14cm (5.5 inch), 325 mesh (45 micron), stainless steel screen, folded over twice to give a 14cm x 4.33cm x 0.0254cm sandwich. The screen is held between two massive brass electrodes, Figure III.1-3. The 45 micron square openings in the screen allow for the outflow of volatile matter as the sample is heated. Each run begins with a fresh screen. Screens are always prefired at over 1000 deg C for five seconds, in the apparatus, under one atmosphere of Helium,



(a) (b)

(c) (d)

Figure III.1-2. The outflow of volatile matter produced by the pyrolysis of coal, (a) right at the peak temperature, (b) after 2-3 seconds holding at the peak temperature , (c) after long holding time, and (d) after circuit is broken.

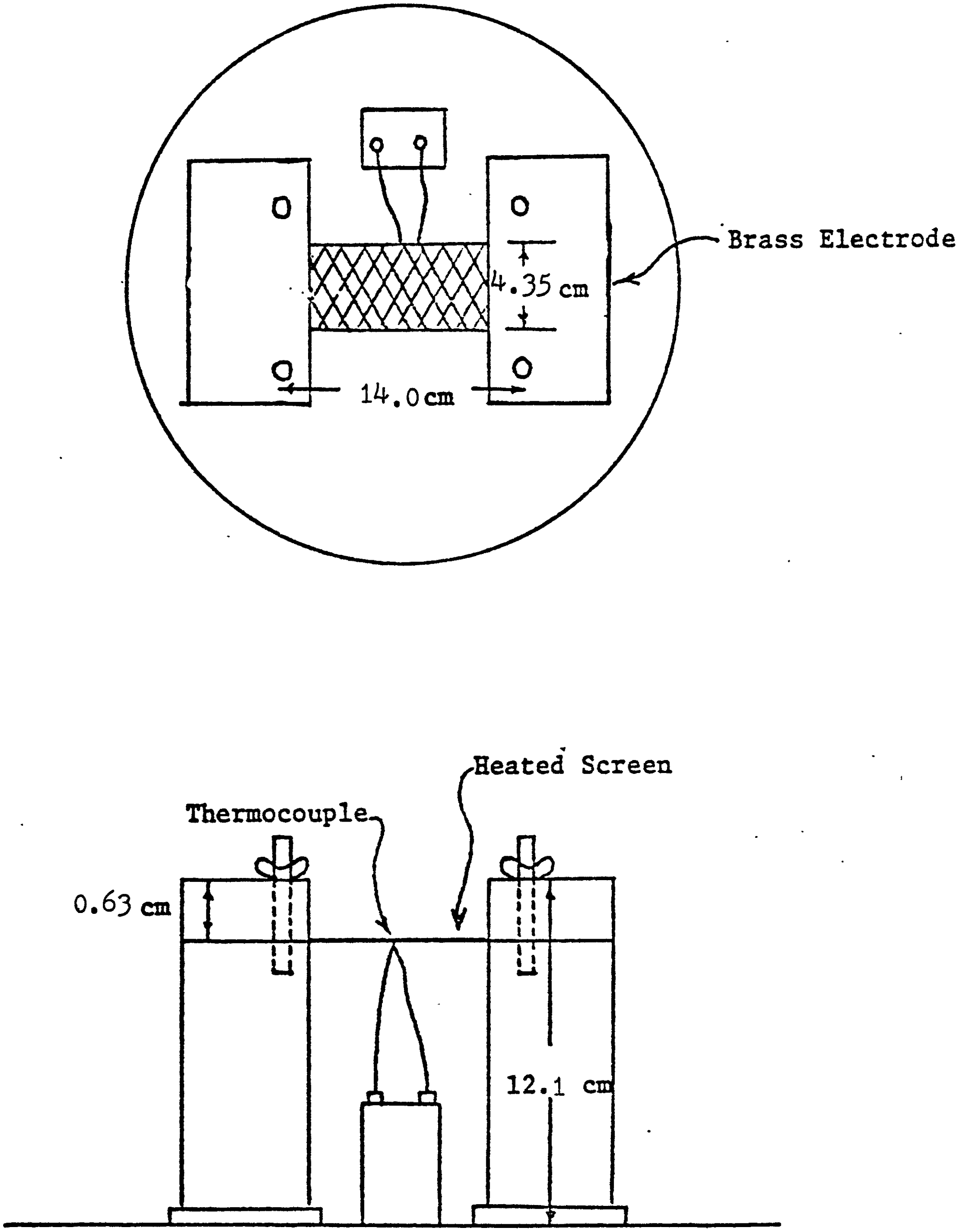


Figure III.1-3. Captive Sample Reactor Details.

to ensure cleanliness. It is believed that the Helium contains sufficient oxygen impurities to form a thin layer of chromia on the screen mesh by reacting with the chromium in the stainless steel of the screen (91). After such treatment, the screen never loses additional weight under experimental conditions.

All tubing, through which products flow, is either standard 1/4 inch stainless steel, or 1/4 inch teflon. The reactor can be charged with filtered or unfiltered helium. The filtered helium is used for the runs, the unfiltered helium is only used for the prefiring operation. Reactor vacuum readings are taken with a McLeod gauge.

III-1-2 The Electrical System

The heating circuit consists of 100 and 50 amp variable transformers (variacs), connected as shown in Figure III.1-4, which are controlled by two 100 amp relays, a one second industrial timer, and a 60 second industrial timer. A 100 amp service is the primary of the 100 amp, double ganged, variable transformer (hereafter referred to as the heating variac). Its secondary is branched to the heating relay and the primary side of the 50 amp variable transformer (hereafter referred to as the holding variac). The secondary of the holding variac is connected directly to the holding relay. The two hot wires on the load side of each relay form a junction with the load going to the hot side of the screen electrode. Similarly, the neutral wires from each variac are joined and connected to the neutral of

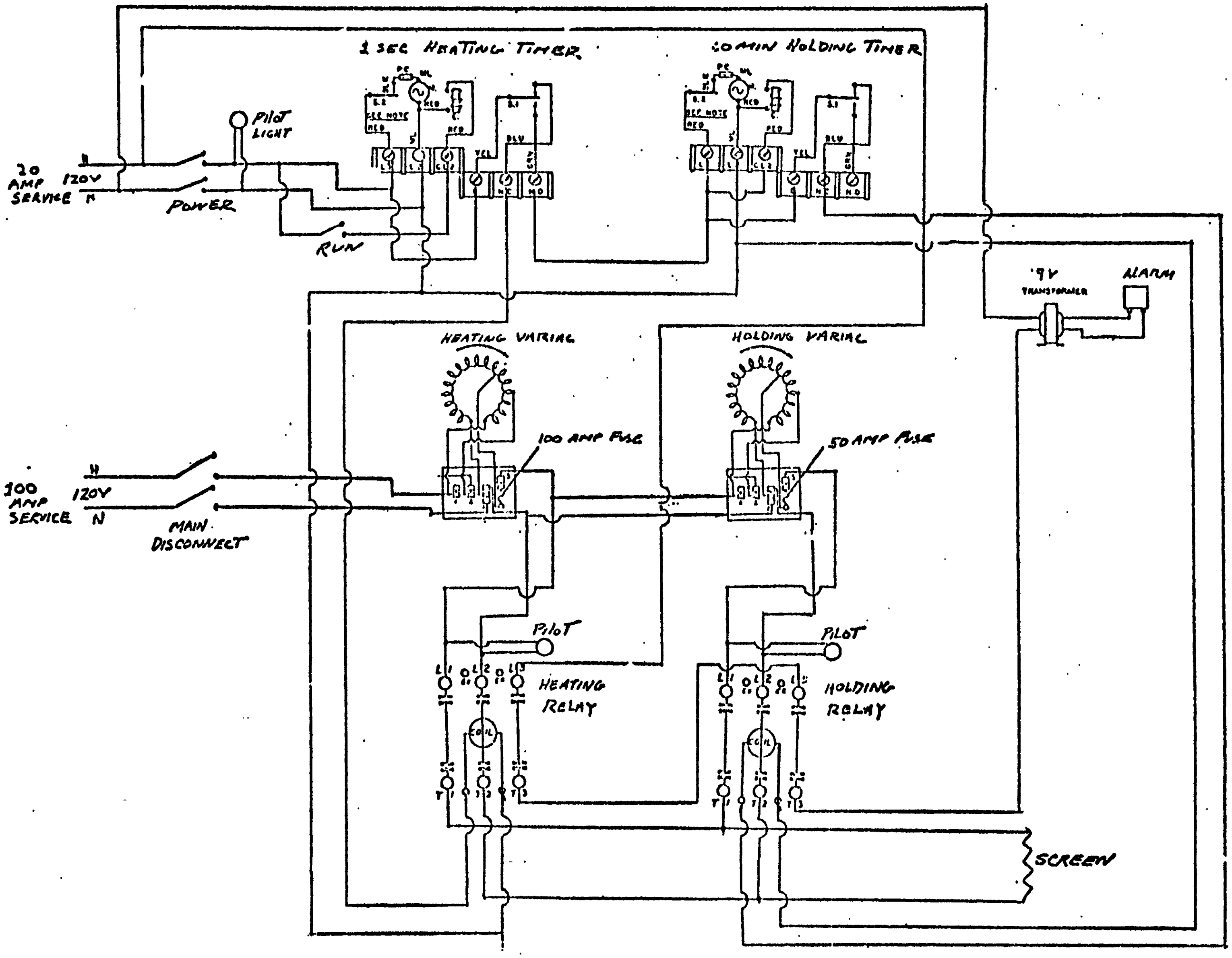


Figure III.1-4. Captive Sample Reactor Wiring Diagram(80).

the electrodes.

When the heating relay is closed and the holding variac is open, the heating variac is directly heating the screen. In the reverse situation, the screen is being heated by the holding variac, the primary of which is driven by the output voltage of the heating variac. The heating voltage necessary for the rapid heating rates desired (between 100 and 100,000 deg C/sec) is always higher than the holding voltage because the energy needed to hold the screen at a given temperature is less than the energy required to raise the screen to that temperature. Thus the holding voltage need only be some fraction of the heating voltage. By this wiring method, increased sensitivity is obtained since the holding variac only delivers a fraction of the heating voltage during the isothermal period of the run.

The peak temperature and holding time at that temperature are controlled by time relay, industrial timers. The heating timer is a one second timer with 1/60 second gradations. The power switch on the control panel operates only the synchronous motor of this timer. The synchronous motor should be run for 2 to 3 seconds before the run switch is closed to begin the time cycle. When the time cycle is initiated, the heating relay is closed. At the end of the time cycle, the heating relay is opened and a second timer, the holding timer, which is graduated in one second intervals to 60 seconds and controls the holding relay, is activated. This closes the heating relay for the duration that was set on the holding timer.

The heating rate is controlled by changing the setting on the heating variac. A setting of 20 corresponds to a heating rate of 1000 deg C/sec. Once the heating rate is established, the peak temperature is varied by changing the length of time that power is supplied to the screen. This is done by adjusting the heating timer. The holding temperature is determined by the setting on the holding variac. The setting must be changed to match the peak temperature obtained during the heating to give a smooth, time - temperature history. The control system is also capable of overriding the timers and manually controlling the heating and holding relays. The calibration curve of peak temperatures versus heating time for the 1000 deg C/sec heating rate is presented in figure III.1-5. The curve provides the timer setting to achieve a desired maximum temperature for an experiment conducted with no holding time. Figure III.1-6 is another calibration curve indicating the final equilibrium temperature which will be achieved for a given setting on the holding variac.

III.1.3. Time-Temperature Monitoring System

A type K (chromel/alumel) thermocouple fabricated from 0.001 inch diameter bare wires to give an approximately 0.003 inch diameter bead, was used to monitor the rapid heat up of the sample. The small thermal mass of the thermocouple bead allows for a very high response (time constant = 0.003 sec). The thermocouple is placed within the folded screen and the millivolt signal is monitored by a fast response recorder.

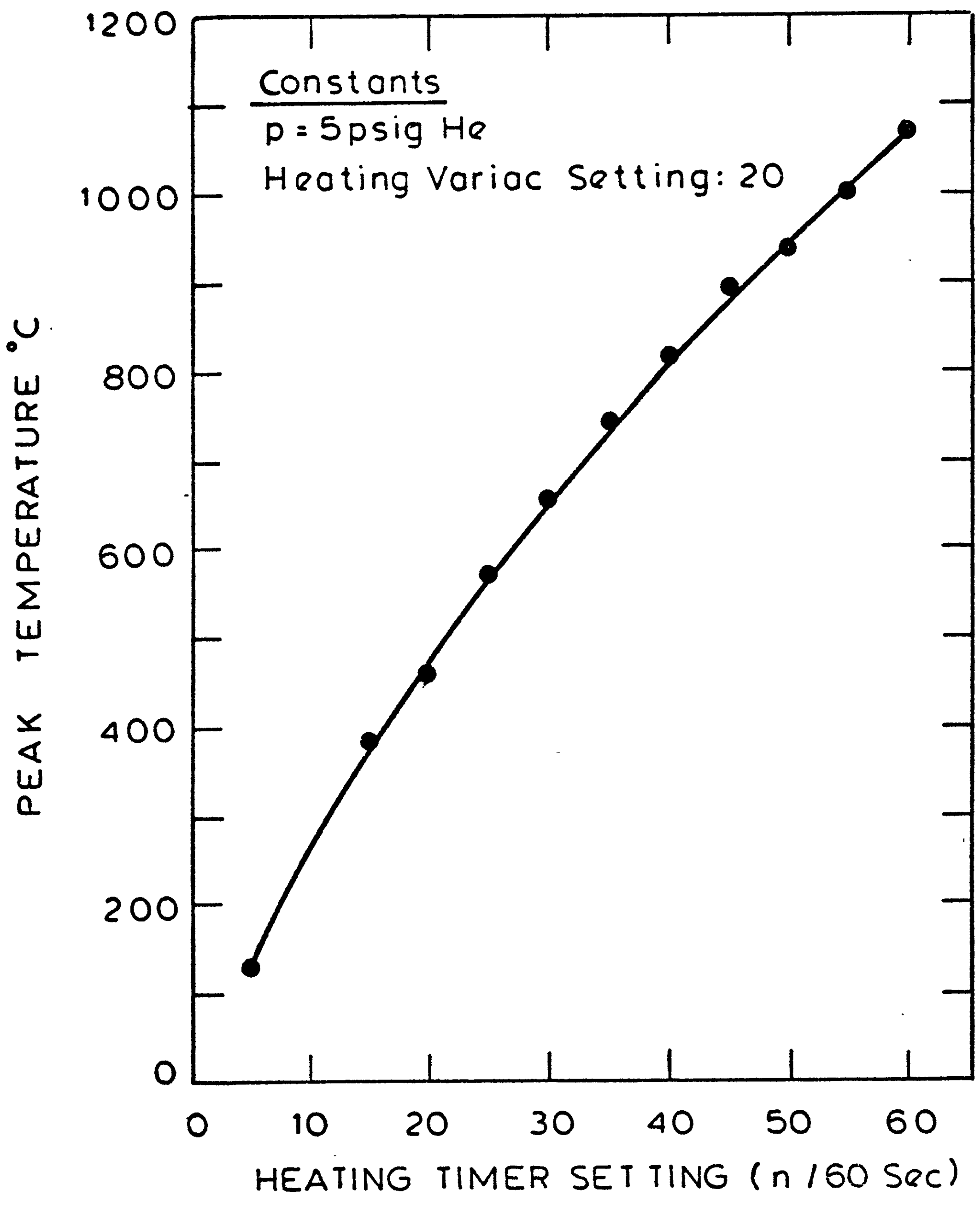


Figure III.1-5. Calibration Curve of Peak Temperature vs Heating Timer Setting.

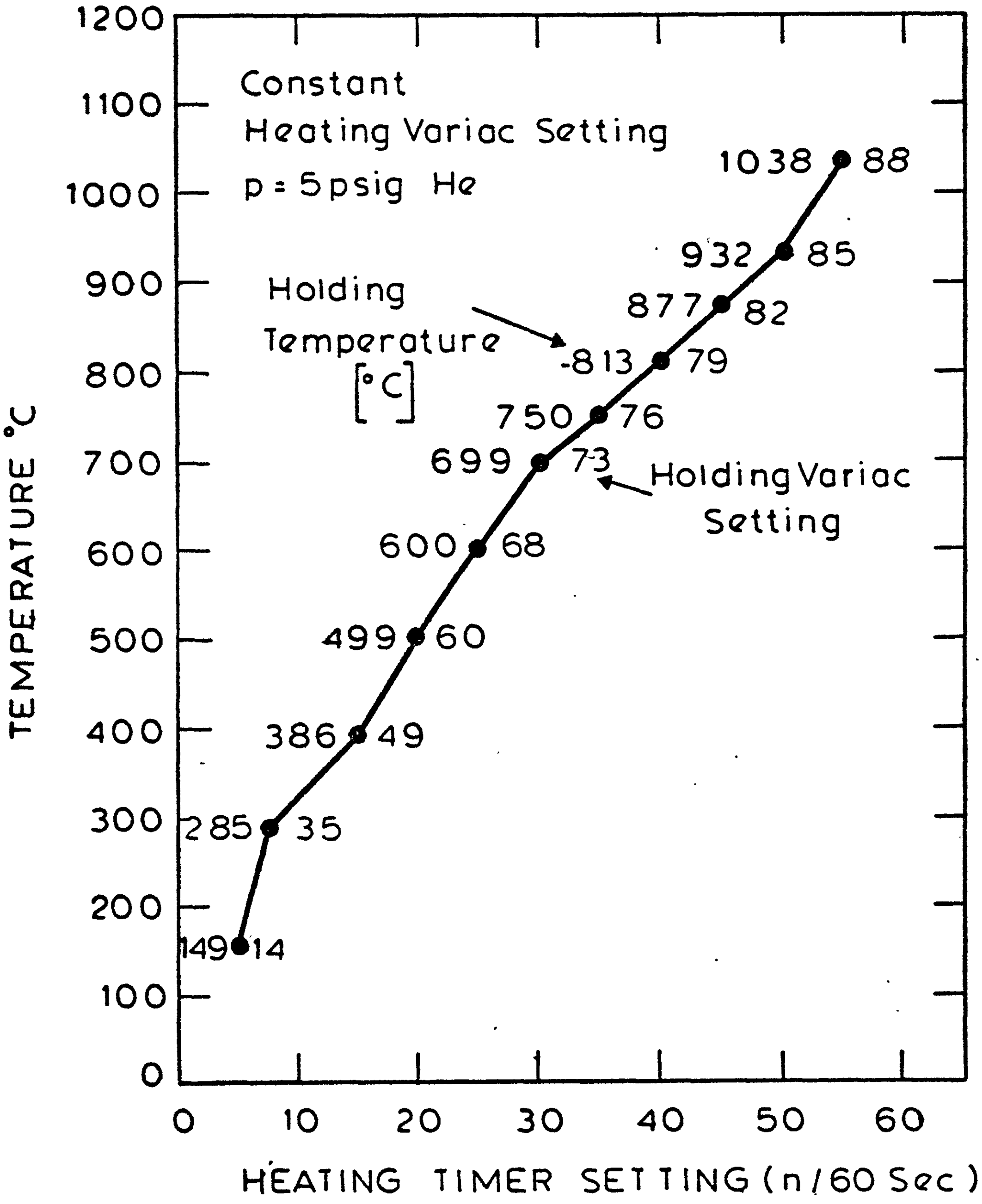


Figure III.1-6. Calibration Curve of Holding Temperature vs Heating Timer Setting and Heating Varic.

Figure III.1-7 shows some typical time - temperature histories obtained by using this system. Since the quenching of the sample occurs by natural cooling (radiative, conductive, and convective), there is a slight variation in the cooling behavior from run to run. This is especially true when comparing vacuum runs to runs performed at higher pressure. On the average, the cooling rate of the sample, in helium at atmospheric pressure is on the order of 200 deg C/sec. However, the actual time temperature history of the solid is always recorded in each run and accounted for in the kinetic analysis.

III.1.4. Products Collection System

The pyrolysis products are collected in three locations within the reactor vessel,(on the walls or the foil liners adjacent to them, on the screen, and on the filter) and also downstream of the reactor vessel, in a dry ice/alcohol trap cooled in a -77 deg C bath, and a lipophilic gas trap cooled to -196 deg C in a liquid nitrogen bath.

The char remains on the screen and the total yield is determined gravimetrically. The tar which deposits on the reactor walls is recovered by washing the reactor walls and electrodes with a preweighed tissue soaked in a 2/1 (V/V) mixture of methanol and acetone. Total tar yield is measured gravimetrically by weighing: a) the residue remaining after evaporating the solvent from the tissue and b) the preweighed foil liner and exit filter used in the reactor. The more volatile tar exits the reactor,

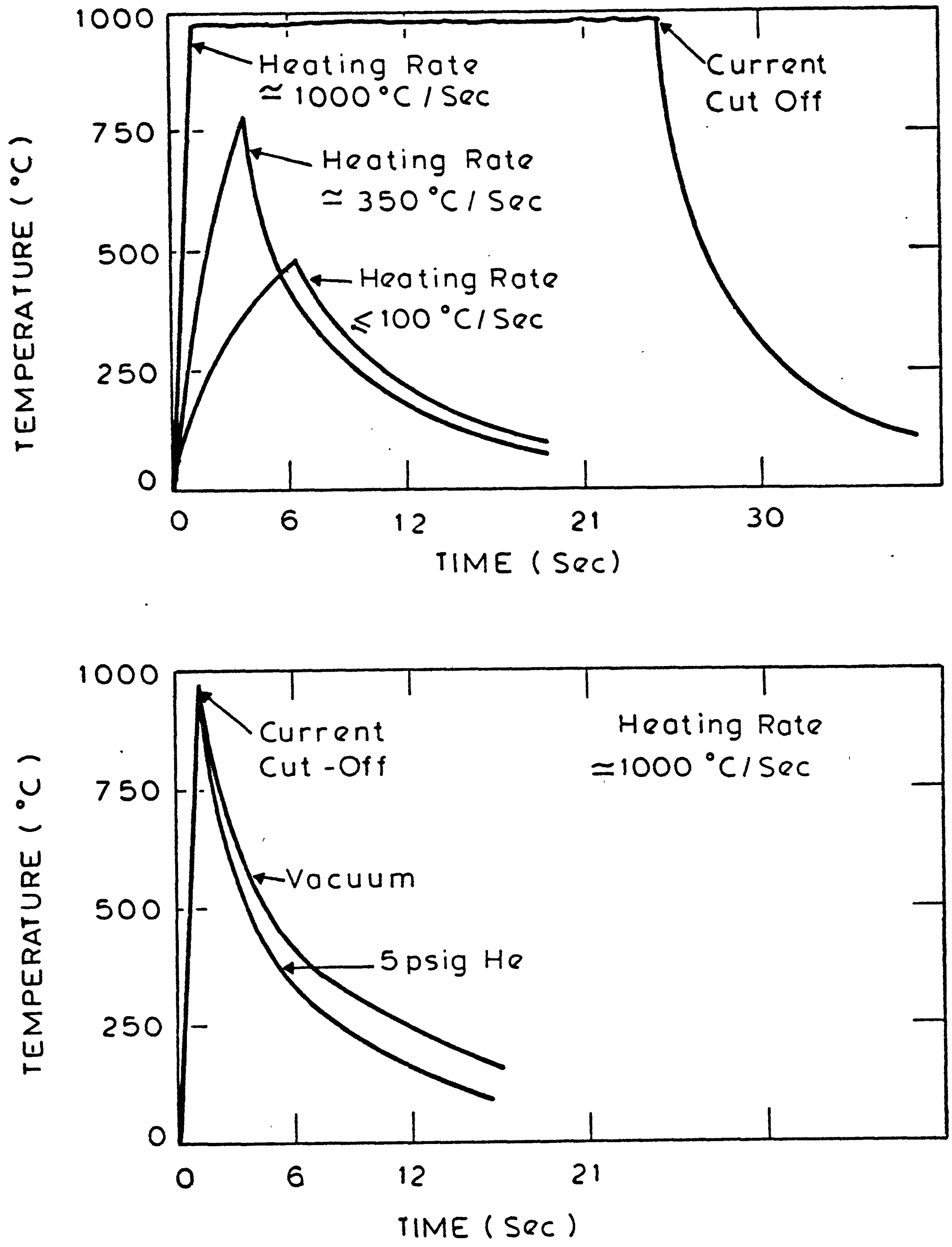


Figure III.1-7. Examples of " Typical " Time-Temperature Histories.

but is trapped in the condensable product trap. The entire trap is immersed in a -77 deg C bath filled with a slurry of dry ice in alcohol. The trap consists of a 14 inch, 3/8 inch O.D. U shaped, 325 stainless steel tube packed with finely divided glass wool of high surface area to promote adsorption and bulk condensation on its surface. Water, acetone, acetaldehyde, some methanol, and some intermediate molecular weight oxygenated products are trapped here. The products are recovered from the tar trap by heating it to 100 deg C, then washing it with a 2/1(V/V), acetone/methanol mixture.

The lighter products (carbon monoxide, carbon dioxide, hydrocarbons, and oxygenated volatiles), which pass through the glass wool trap, are collected in a cryogenic trap, with a similar geometry to the condensable trap, except that the stainless steel tube is packed with 50/80 mesh Poropak QS chromatographic column packing. This trap is immersed in liquid nitrogen at a temperature of -196 deg C, and all of the remaining product gases, except hydrogen are partitioned onto the sorbent.

Hydrogen, as a product of pyrolysis, cannot be collected quantitatively by the above traps. Therefore, it was recovered for analysis by direct sampling of the gases inside the reactor, by the insertion of a precision syringe through a small rubber septum on the top plate of the reactor.

III.1.5. Products Analysis System

In-house product analysis makes extensive use of gas chromatography. A Perkin Elmer Model 3920 chromatograph with dual thermal conductivity / flame ionization detectors, and a Perkin Elmer Model 1 integrator are used routinely in the analysis of products trapped in the glass wool trap and lipophylic trap.

Products trapped on the glass wool and lipophylic trap are analyzed on a 12 feet by 1/4 inch, 50/80 mesh (366cm x 0.635cm, 177/297 micron), Porapak QS column, temperature programmed from -70 deg C to 240 deg C at a rate of 16 deg C/min. Helium is used as a carrier gas at a 60 m.L./min flow rate.

Hydrogen is analyzed on a 10ft by 1/8 inch, 80/100 mesh (305cm x 0.318cm, 150/170 micron), spherocarb column, isothermally at 0 deg C with nitrogen used as a carrier gas at a flow rate of 30 m.L./min.

Some attempts have been made to analyze the oxygenated products trapped on the traps in more detail. Results are reported in Appendix I.

III.2. Run Procedure

Approximately 100mg of cellulose in the form of single rectangular strips, 2cm x 6cm x 0.0101cm thick, of low ash content (it has a chemical composition of 43.96% carbon, 6.23% hydrogen, 49.82% oxygen, and 0.007% ash, nitrogen, and sulfur), cut from S & S No.507 filter paper, are placed inside a screen which is reweighed to get the precise initial weight of the sample. Each end of the screen is then inserted between the two sections of the corresponding brass electrodes of the reactor. The screen is then secured in place by tightening the wing nuts which force the sections of each electrode together. The reactor is then evacuated to 0.1 mmHg and flushed 3 to 5 times with helium first filtered by passing it through a lipophilic trap immersed in liquid nitrogen. The vessel is then brought to the desired pressure for the run. The sample temperature is then raised at the desired rate to the final temperature. The sample is maintained at this final temperature for the desired holding time, and then the circuit is broken. The sample is cooled by convection, conduction to the screen, and radiation. The cooling occurs rapidly since the vessel, the electrodes, and the atmosphere in the vessel remains at approximately room temperature during the experiment. This cooling, however, is not so rapid as to avoid the occurrence of significant weight loss during this period for at least some conditions.

Upon completion of the heating and cooling cycle, products in the vapor phase at room temperature are removed from the reactor by passing 5 to 7 reactor volumes of filtered helium through the vessel and on into the -77 deg C and -196 deg C traps, where they are collected.

The yield of char, which remains on the screen, is determined gravimetrically. The yield of tar, which is mainly condensed material inside the reactor at room temperature, is collected primarily on the foil liner on the bottom of the reactor and on the filter paper at the exit port of the reactor. Any tar condensed on non lined reactor surfaces is collected by washing the surface with a methanol/acetone mixture (2:1 ratio) on a preweighed tissue paper.

The traps contents are then analyzed by gas-chromatography. Since, except for hydrogen, the entire volume of gas produced during the pyrolysis process is trapped and analyzed, and since the initial sample is about 100mg, components present in quantities of 0.1mg, representing about 0.01% of the original sample, could be easily quantified. The chromatographic response factor used for the calculation of vapor phase yield (both gases and oxygenated compounds), together with a sample calculation of the quantitative yield of a typical gaseous product, are shown in Appendix II.

Elemental analysis of the cellulose, selected tar, and char samples, were performed by Huffman Laboratories, Wheatridge, Colorado.

III.3. Experimental Error

The weight of the screen and the cellulose sample was determined to within +/- 0.01mg. The uncertainty of the total weight loss measurement is about 0.01 multiplied by the square root of the number of times that the sample is weighed (97), therefore, this becomes 0.01 x 2 or 0.014% by weight of cellulose. The quantity of char and tar was also measured to within +/- 0.01mg, so the uncertainty here is also 0.014% by weight of cellulose. The method of tar collection gives a greater uncertainty in the total tar weight. The maximum error in tar yield for the 5psig runs is between 1 and 1.5% by weight of cellulose. This error is greater in vacuum runs because the collection of tar is more difficult. In most cases, the tar yield in the vacuum runs has been less than the true yield. This can be seen by comparing the total mass balance for the runs at vacuum to the mass balance for the runs at 5psig. The high pressure runs have the same uncertainty. The products quantified by gas-chromatography are subjected to a calibration uncertainty between 1 and 3% of the mass of the species being measured. In addition to this, the products which appear on the tailing peak of water give a lot of error in analysis. In some cases, this error can be as much as 10 to 20% of the mass of the species being measured. The error by weight of cellulose, however, is less than 0.5% because these products represent a small fraction of the cellulose. Because of the large quantity of carbon monoxide being produced by pyrolysis, and the effect of large air peaks, there is an uncertainty of 5% by weight of carbon monoxide being measured. The gain and loss of moisture by the cellulose sample during the initial weighting is not important. The error, even under high humidity conditions, is not more than 1% by weight of cellulose.

However, the reproducibility of results, by the apparatus, is excellent. This is shown by the results of runs at about the same conditions in App. IV.

It was feared that the screen used to hold the cellulose might be another source of error by catalyzing the primary pyrolysis or secondary cracking reactions. Prefiring the screen coats the screen with a layer of ceramic type material, which undoubtedly diminishes the catalytic activity of the screen. Pyrolysis experiments were also carried out with stainless steel screens, the surfaces of which had been passivated by vaccuum deposition of a layer of gold. The results showed no significant difference in the product yields from the unpassivated screens. There were some differences in the yields of individual components, but these were within the precision of the current data. Screens with two and five layers were used in some of the runs in addition to the normal three layer screens. These runs showed almost no difference from the 3 layer screens, except for the tar yield which, surprisingly, increased with an increase in the number of layers.

Another source of error is the time-temperature monitoring system. The ability of the thermocouple to track the temperature of the sample depends on its placement in the screen. In order to give an accurate reading on the temperature, the thermocouple should ideally be in good thermal contact with the sample. The results from different runs show the uncertainty of the temperature recording system to be in the order of +/- 10 deg C at low temperatures and +/- 15 deg C at high temperatures. At high heating rates (10,000 to 15,000 deg C/sec), however, there is more error in the final temperature, since the recorder isn't as fast as the heating rate and the differences in the response time between the thermo couple and the sample incurs a greater error at higher heating rates.

IV. Results and Discussion

All the data reported in this section is for approximately 100 mg of filter paper #507 S&S, with dimensions of 2cm x 6cm x 0.0101cm. Most of the results in this section are graphed, however all the experimental results are tabulated in Appendix IV. All yields are presented as a percent by weight of initial cellulose, except when otherwise specified.

The elemental analysis of the cellulose used in this study gave an empirical formula of $CH_{1.7}O_{0.85}$ In order to eliminate the effect of humidity on the pyrolysis process, the samples were placed in a dessicator with silical gell for at least a week before use.

In this set of experiments, the total mass balance, or reproducibility of the results, is very good. In most runs the balance was 100% +/- 5%, although in some runs only 90 to 95% of the mass was accounted for. Experiments with mass balances poorer than 90% were not used in the analysis. This is one of the outstanding points of this study which has not been previously reported. Few previous studies reported mass balances this high, and then only for a few of their experiments.

IV.1. The Effect of Temperature

Figure IV.1_1 represents the effect of peak temperature on yields of gases, including water, char, and tar which was produced by the pyrolysis of cellulose. In these experiments, the cellulose was heated to peak temperature at a rate of 1000 deg C/sec, at a pressure of 5psig, then cooled to room temperature by convection and radiation (the initial cooling rate for the atmospheric pressure runs is about 200 deg C/sec). As the results in figure show, at these conditions the decomposition of cellulose begins between 300 and 400 deg C and increases with temperature until most of the sample is converted to volatiles and a few percent to char. It is clear from the graphs that most of the weight loss takes place between 500 and 700 deg C. After 750 deg C, the change in the yield of char is not significant, although it decreases to about 3% between 800 and 900 deg C. Above 900 deg C, the yield of char starts to increase very slowly because of the cracking of volatiles which occurs at very high temperatures. At 1000 deg C, the char yield is about 4%, however a run at 1300 deg C showed no char yield.

Tar yield increases as temperature increases until the maximum production of volatiles from the cellulose is achieved. The maximum yield for tar was obtained at a temperature, close to the lowest temperature which gave the maximum weight loss. However, as it can be seen from the graphs, the tar yield then goes through a maximum with further temperature increases. This is because above this temperature ,the tar yield becomes very high and the rate of evaporation (with a heating rate of 1000 deg

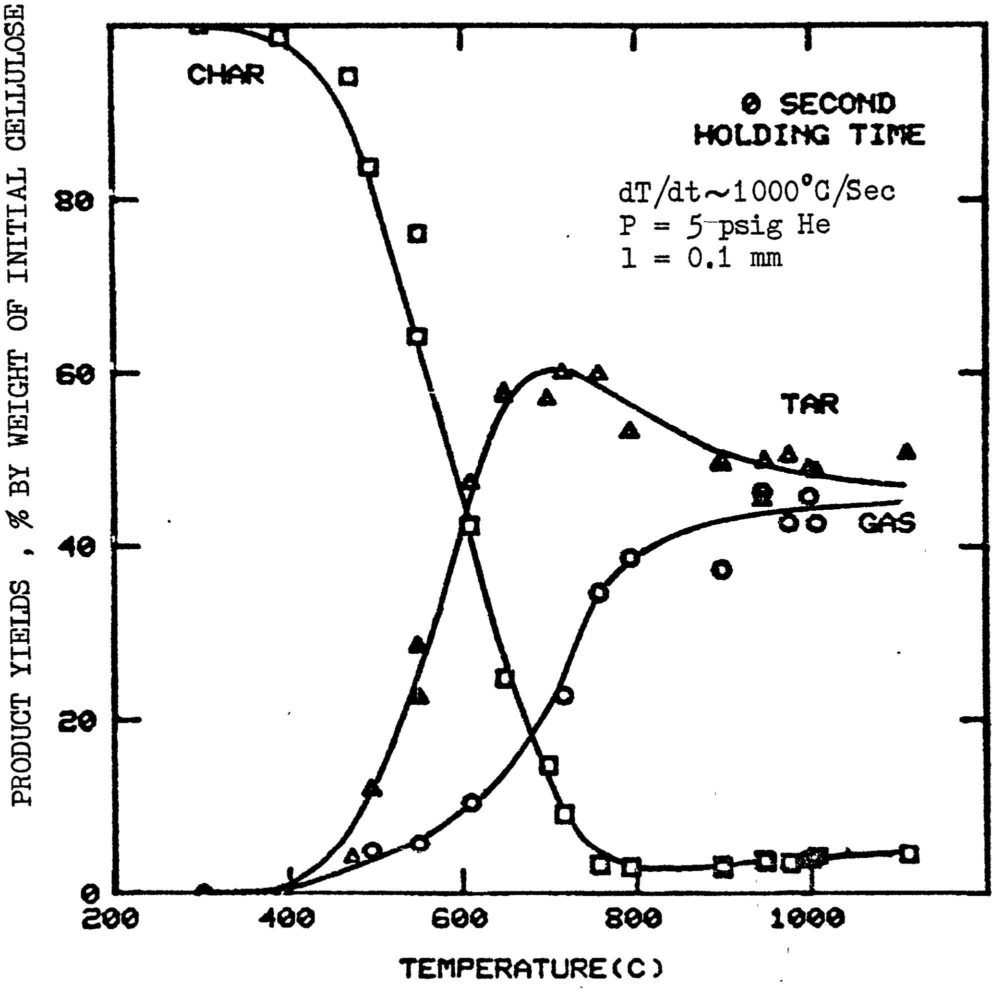


Figure IV.1-1. Effect of Peak Temperature on Yields of Char, Tar, and Total Gases at 5 psig He Pressure.

C/sec and 5psig pressure) is not fast enough to remove the tars from the reaction zone, so some of the tar cracks to give gases, other more volatile materials, and possibly some coke.

It can be seen from the time temperature histories that for significant yields of volatiles by cellulose pyrolysis under these conditions, the sample must remain above its decomposition temperature for a certain amount of time which depends on the heating and cooling rate, and final temperature, as well as the sample size and operating pressure, etc. For zero holding time conditions, complete reaction can be achieved at or above 750 deg C for a 1000 deg C/ sec heating rate. If the temperature is increased further, however, most of the decomposition occurs in the heating period, thus, when peak temperature is reached, tar which could not escape the hot reaction zone during the heating period, could participate in secondary reactions to yield lighter volatiles.

The total gas yield, which includes water, also increases with peak temperature, but at the temperature which tar yield goes through a maximum, the slope of the gas yield curve changes. This is probably because the tar is cracked primarily to gases with little, if any coke being formed.

The effect of peak temperature on such volatile products as methane, ethylene, ethane, propylene, hydrogen , water, carbon monoxide, carbon dioxide, methanol, acetaldehyde, ethanol, acetone and furan, etc., are presented in Figures IV.1-2 through

IV.1-5.

As the results show, all the products are in small yield at low temperatures except water, which has a quite high yield right after decomposition starts. This is not surprising since it is generally believed that the major part of the water comes from dehydration and depolymerization reactions. Oxygenated compounds, such as methanol, acetaldehyde, etc., have a relatively higher yield at lower temperatures than hydrocarbons. Carbon dioxide appears in greater quantities and at a lower temperature, than carbon monoxide. When temperature increases further and maximum tar yield is achieved, however, the yields of the volatiles, except for water, suddenly increases. This is an indication that most of the gases are products of secondary reactions and tar decomposition rather than the result of the direct decomposition of cellulose.

The yield of volatiles become constant after a certain temperature, from 700 deg C for water, to about 800 deg C for carbon dioxide, propylene, acetaldehyde, methanol, and acetone and furan, to 900 to 950 deg C for hydrogen, methane, and ethylene. The data on carbon monoxide yields (Fig. IV.1-2) some scatter which arises from the interferences from air impurities during the gas chromatographic analysis. It is nevertheless believed that a true asymptote for these conditions is attained at around 1000 to 1100 deg C. The yields of the light oxygenated liquids like methanol, acetaldehyde, and acetone and furan may go through a maximum as temperature increases

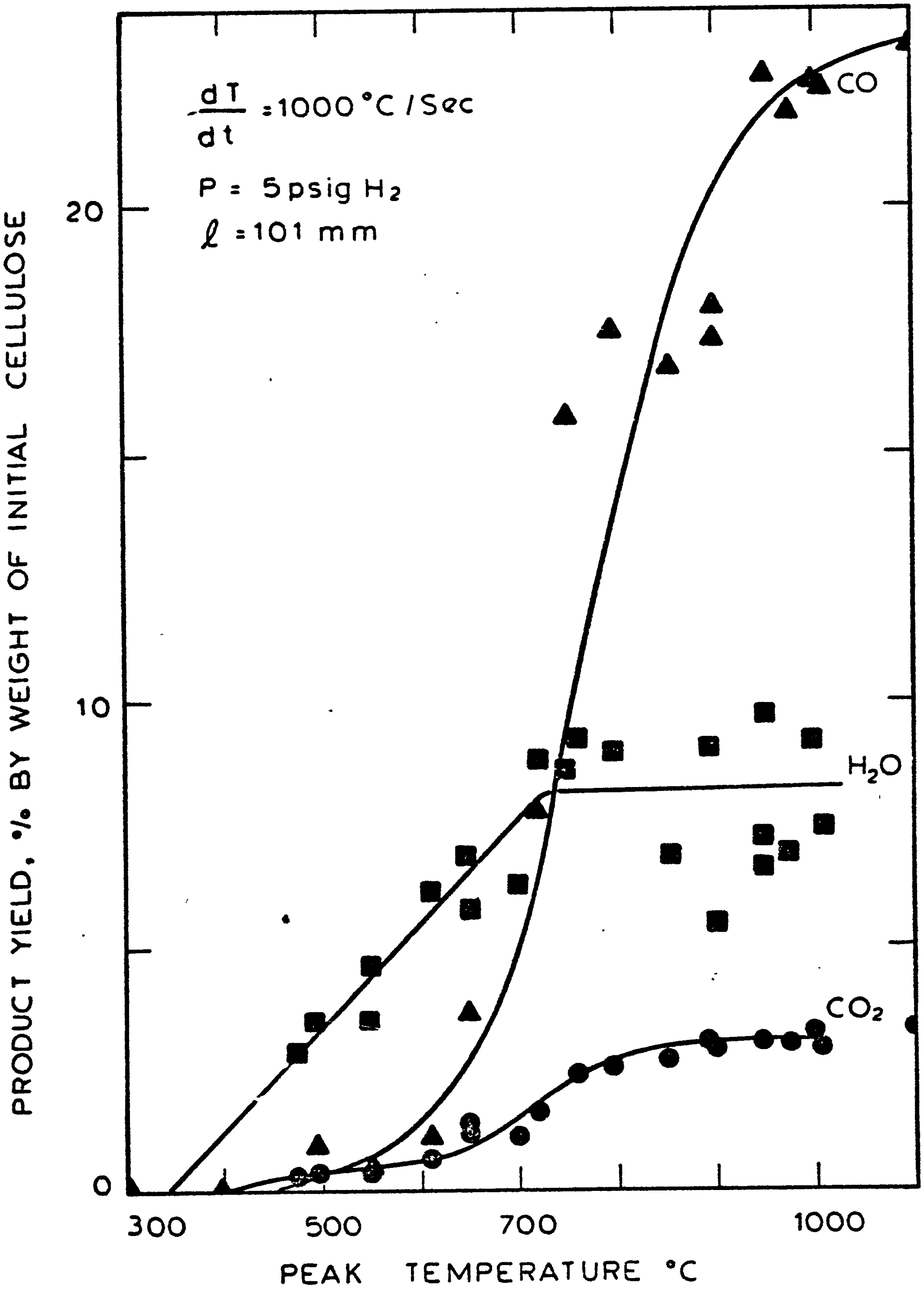


Figure IV.1-2. Effect of Peak Temperature on Yields af Yields CO,CO2,and H20 at 5 psig He Pressure.

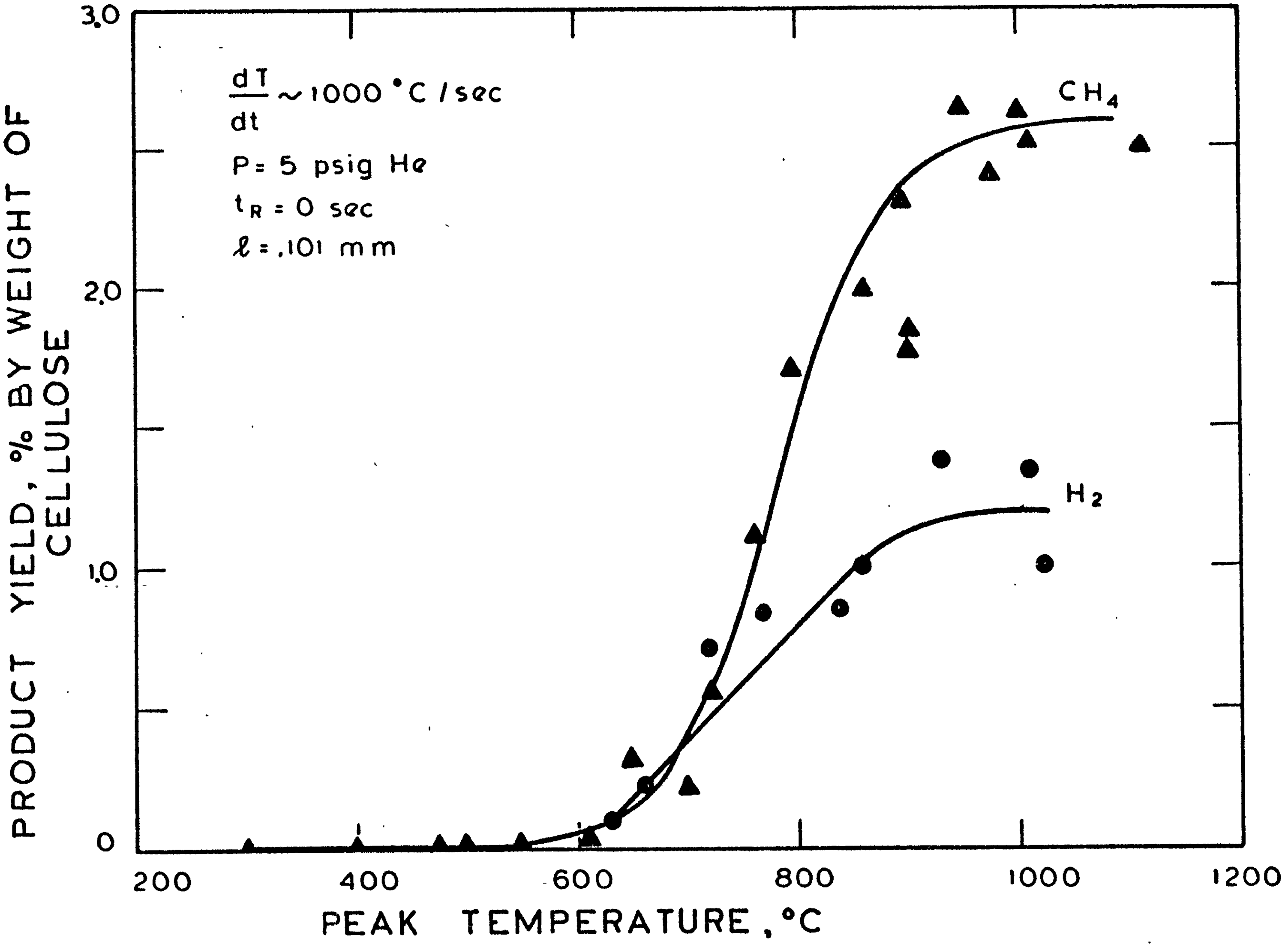


Figure IV.1-3. Effect of Peak Temperature on Yields of CH4, and H2 at 5 psig He Pressure.

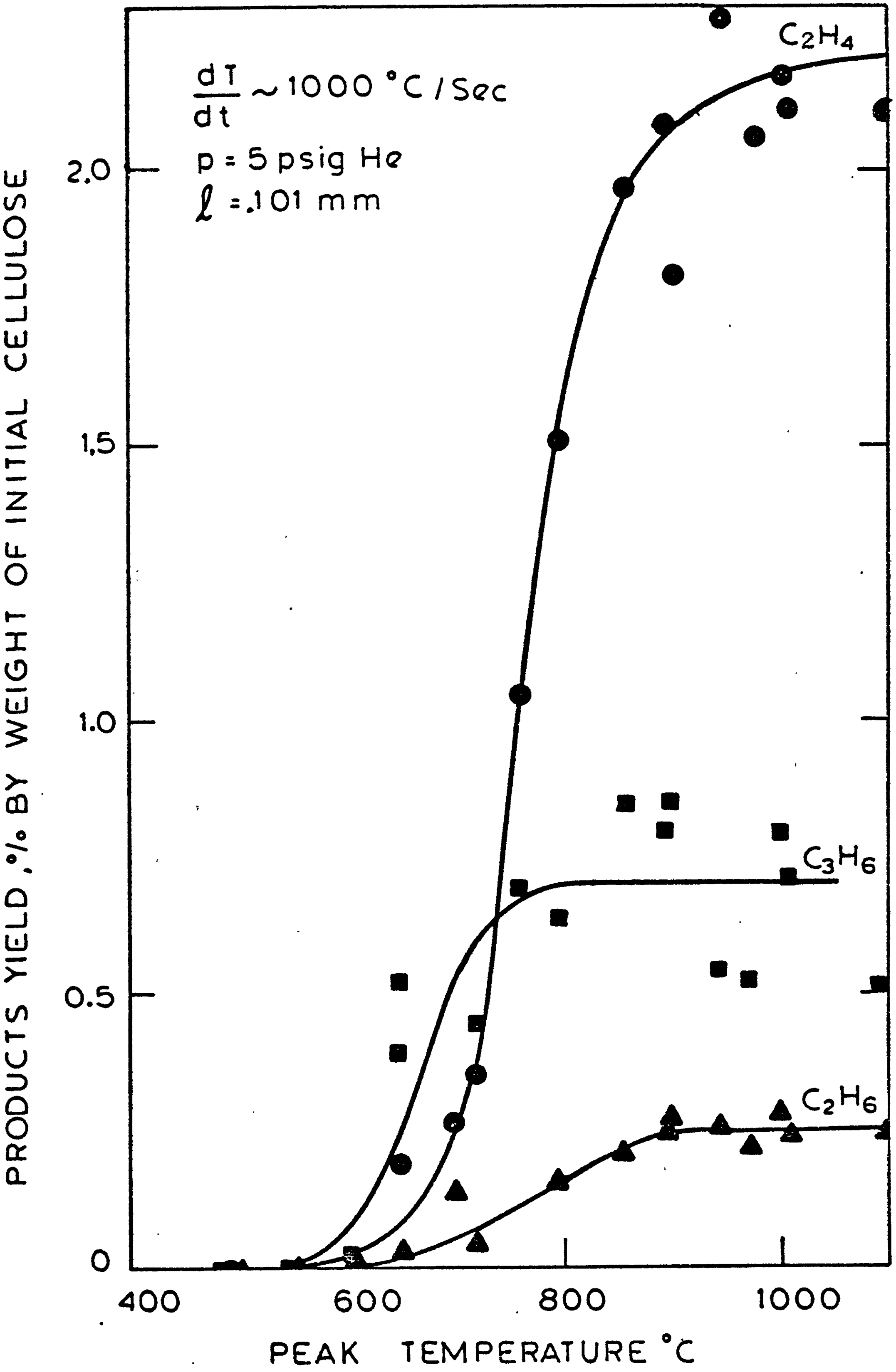


Figure IV.1-4. Effect of Peak Temperature on Yields of C2H4, C2H6, and C3H6 at 5 psig He Pressure.

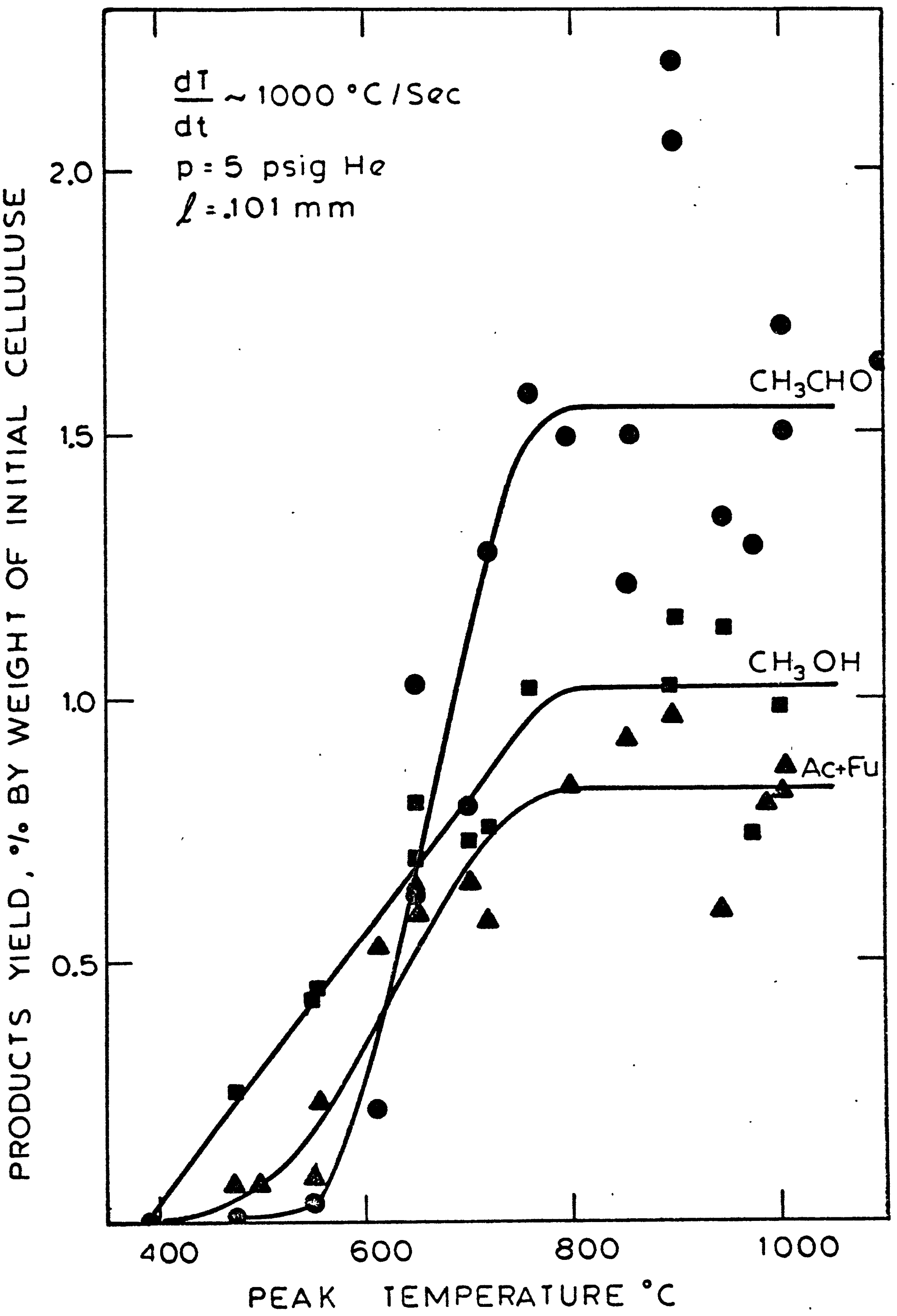


Figure IV.1-5. Effect of Peak Temperature on Yields of Acetaldehyde, Methanol, and Acetone/Furan Mixture at 5 psig He Pressure.

beyond between 800 and 900 deg C but the scatter in the data preclude establishing this unequivocally. The existence of such maxima would not be unreasonable since these products can decompose at temperatures as low as 500 deg C.

The data reported are consistent with previous work. For example, the results reported by Tsuchyia and Sumi (44), Figure II.1-1 shows that an increase in temperature increases hydrocarbons yield and gives a maximum for oxygenated products. However, the difference in quantities arise from differences in conditions and apparatus which were used.

IV.2. Effect of Holding Time

In order to determine the effect of temperature and holding time on cellulose decomposition, samples of cellulose were heated to different peak temperatures at 1000 deg C/sec and then held at that temperature for 2 to 30 seconds at pressures of 0.1 mmHg and 5psig Helium.

The effect of holding time on total weight loss, tar yield, and total gas yield, are presented in Figures IV.2-1 through IV.2-7. At low temperatures, where the pyrolysis is incomplete at peak temperature, holding time is very effective on increasing sample decomposition and tar yield. However, it has a very small effect on the total gas yield because most of the cellulose goes to tar (84%) at this temperature. This is further indication that most of the gases are produced through secondary reactions.

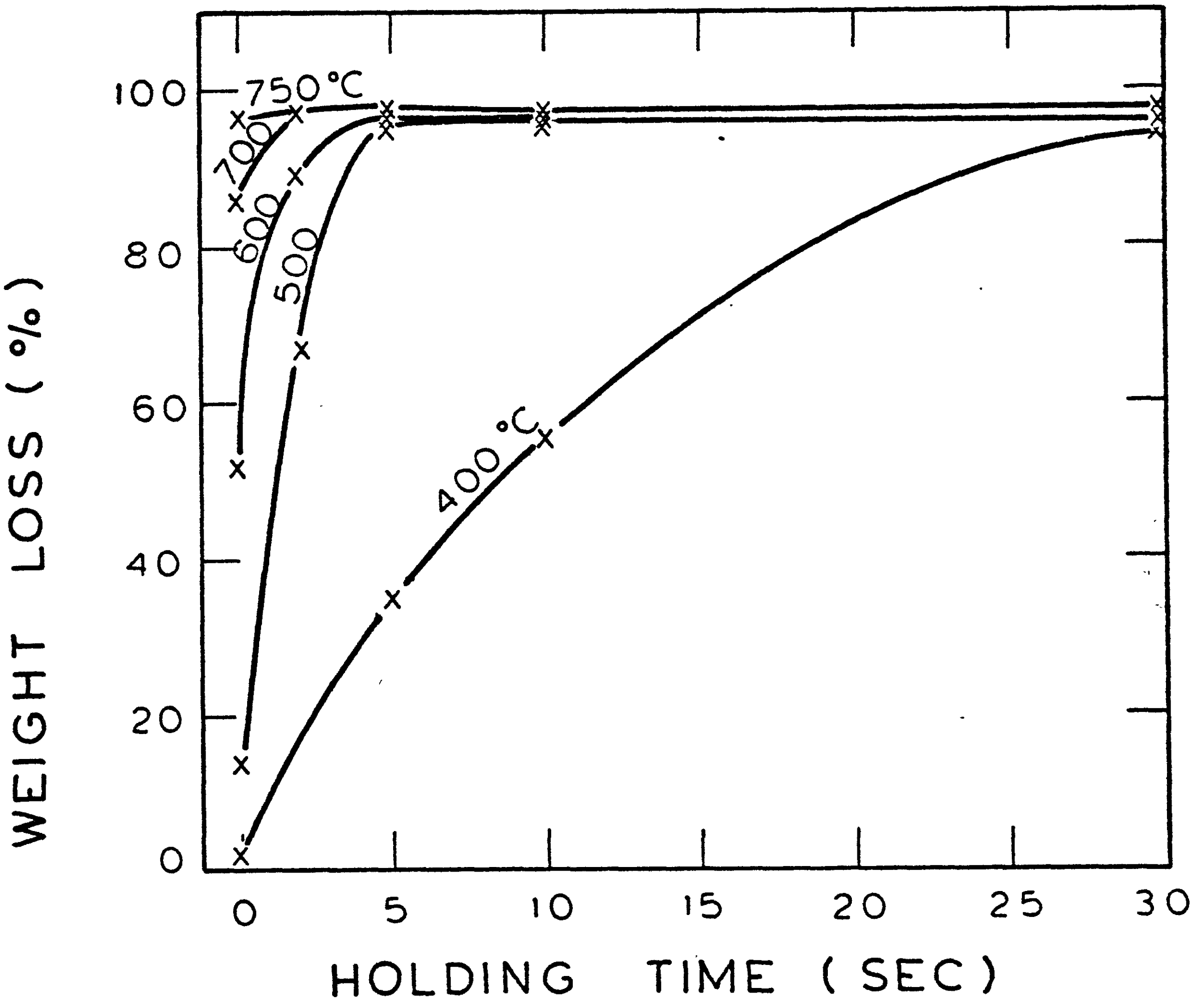


Figure IV.2-1. Effect of Holding Time on Total Weight Loss of Cellulose during Pyrolysis at 5 psig He Pressure and 1000 C/Sec Heating Rate.

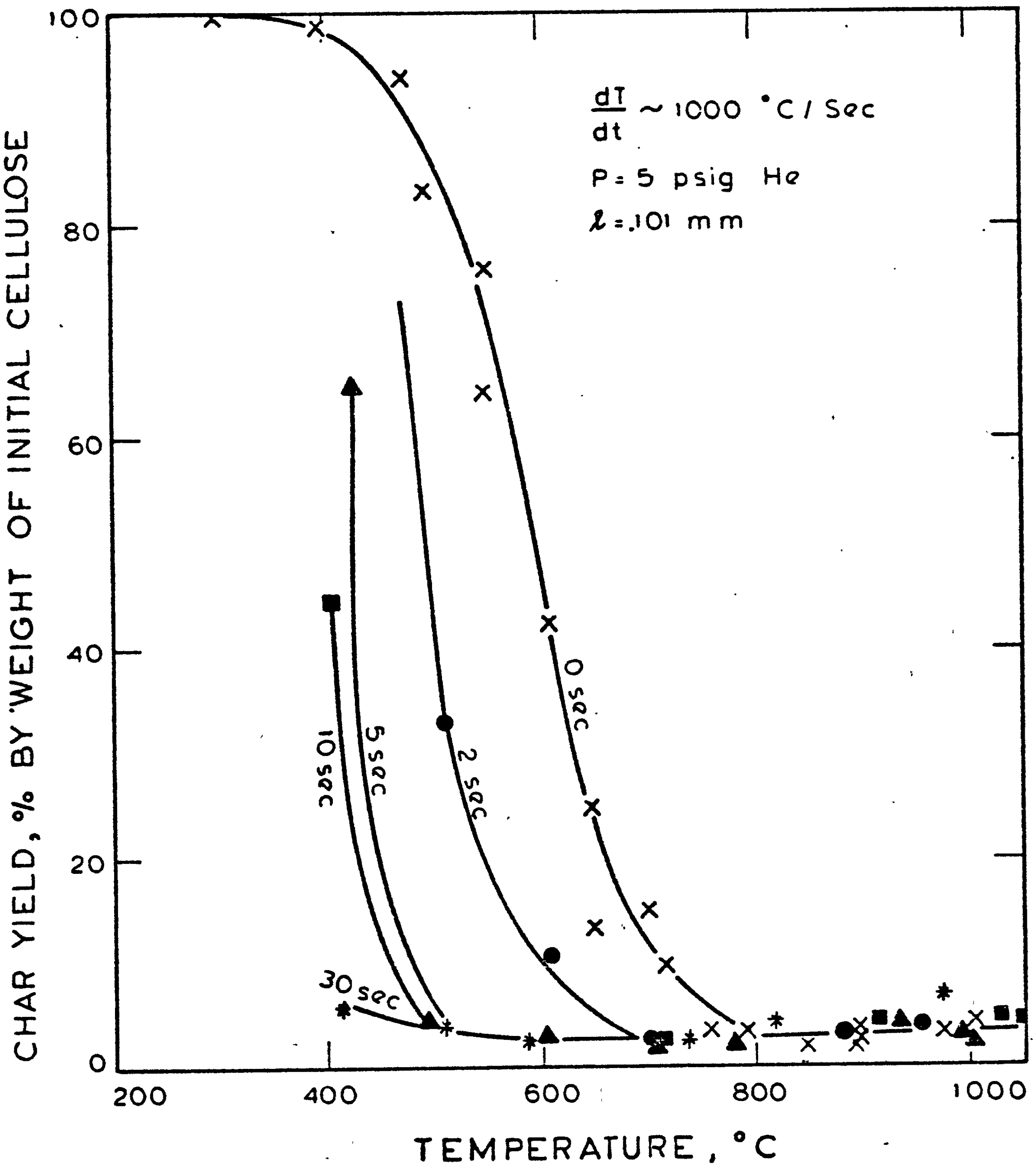


Figure Iv.2-2. Effect of Holding Time on Yields of Char at 5 psig He Pressure.

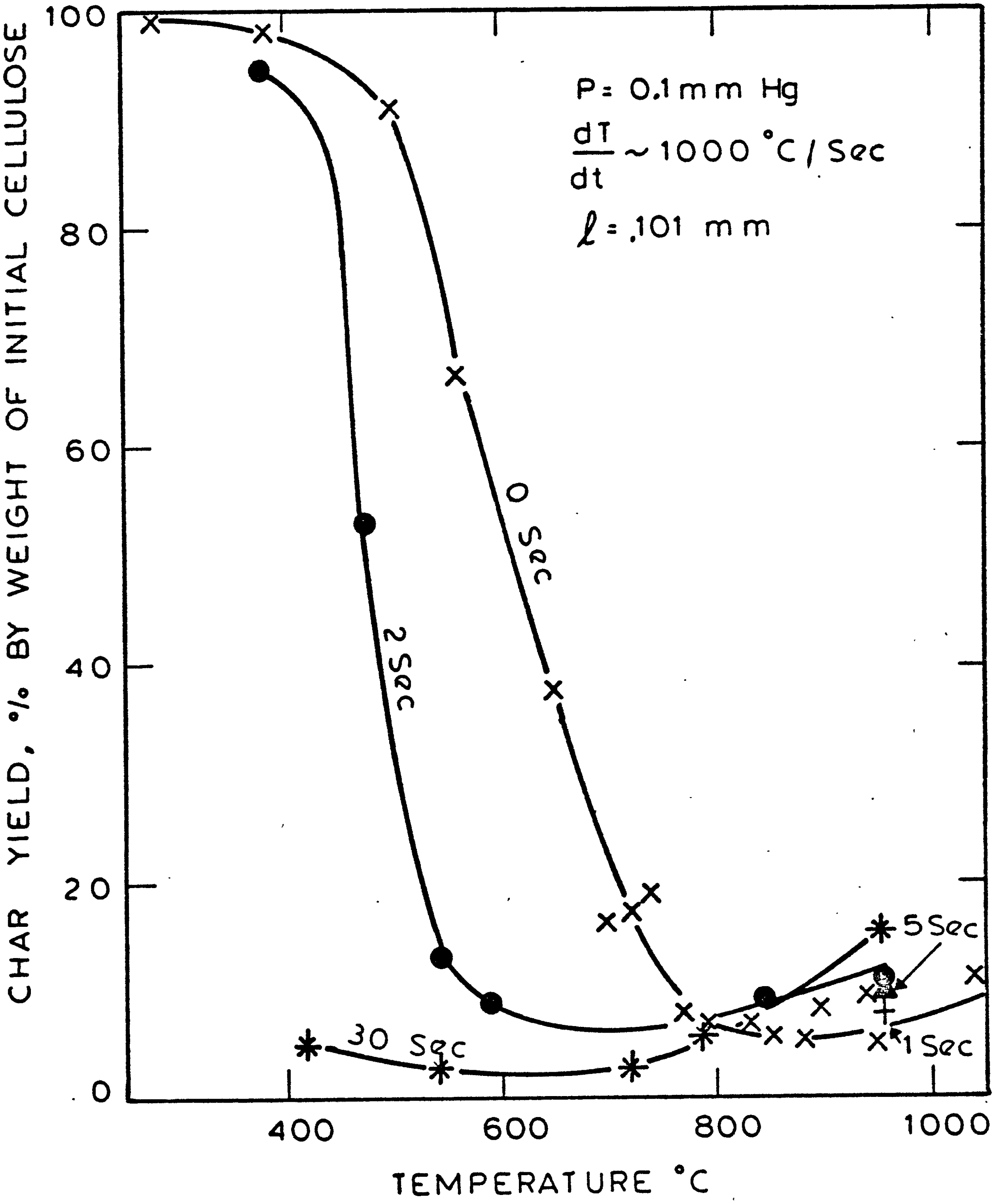


Figure IV.2-3. Effect of Holding Time on Yields of Char at 0.1 mm Hg Pressure.

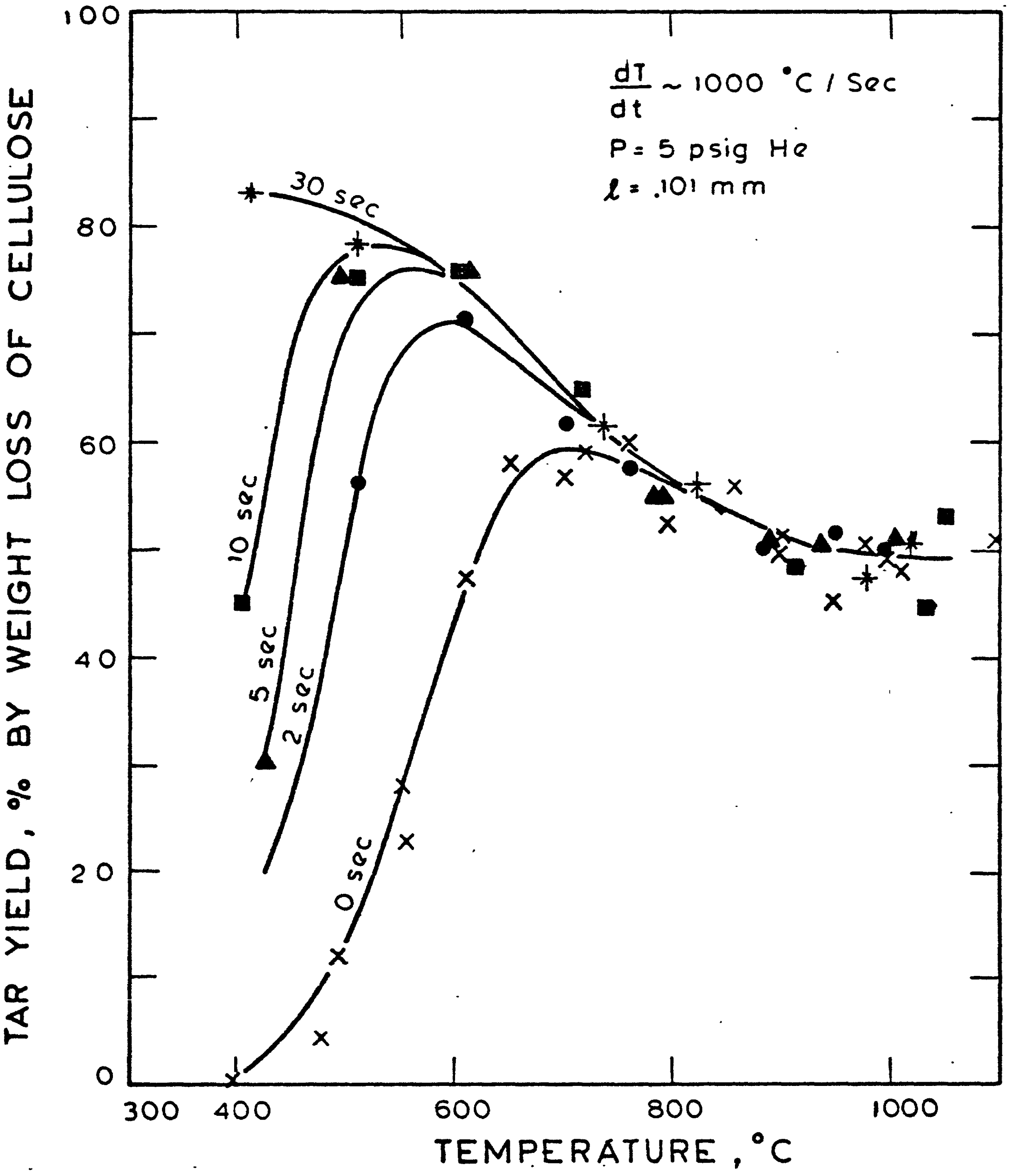


Figure IV.2-4. Effect of Holding Time on Yields of Tar at 5 psig He Pressure.

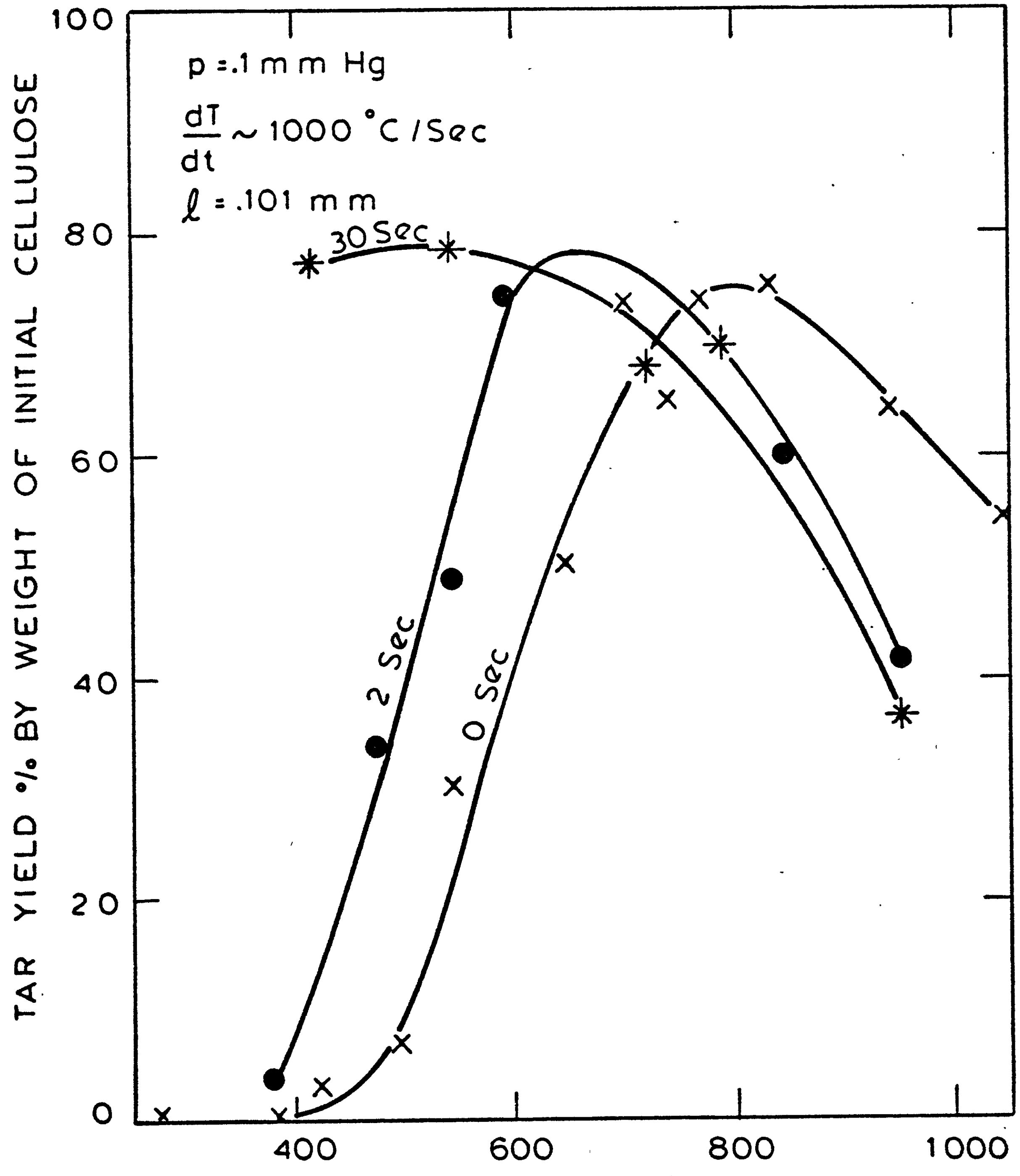


Figure IV.2-5. Effect of Holding Time on Yields of Tar at 0.1 mm Hg Pressure.

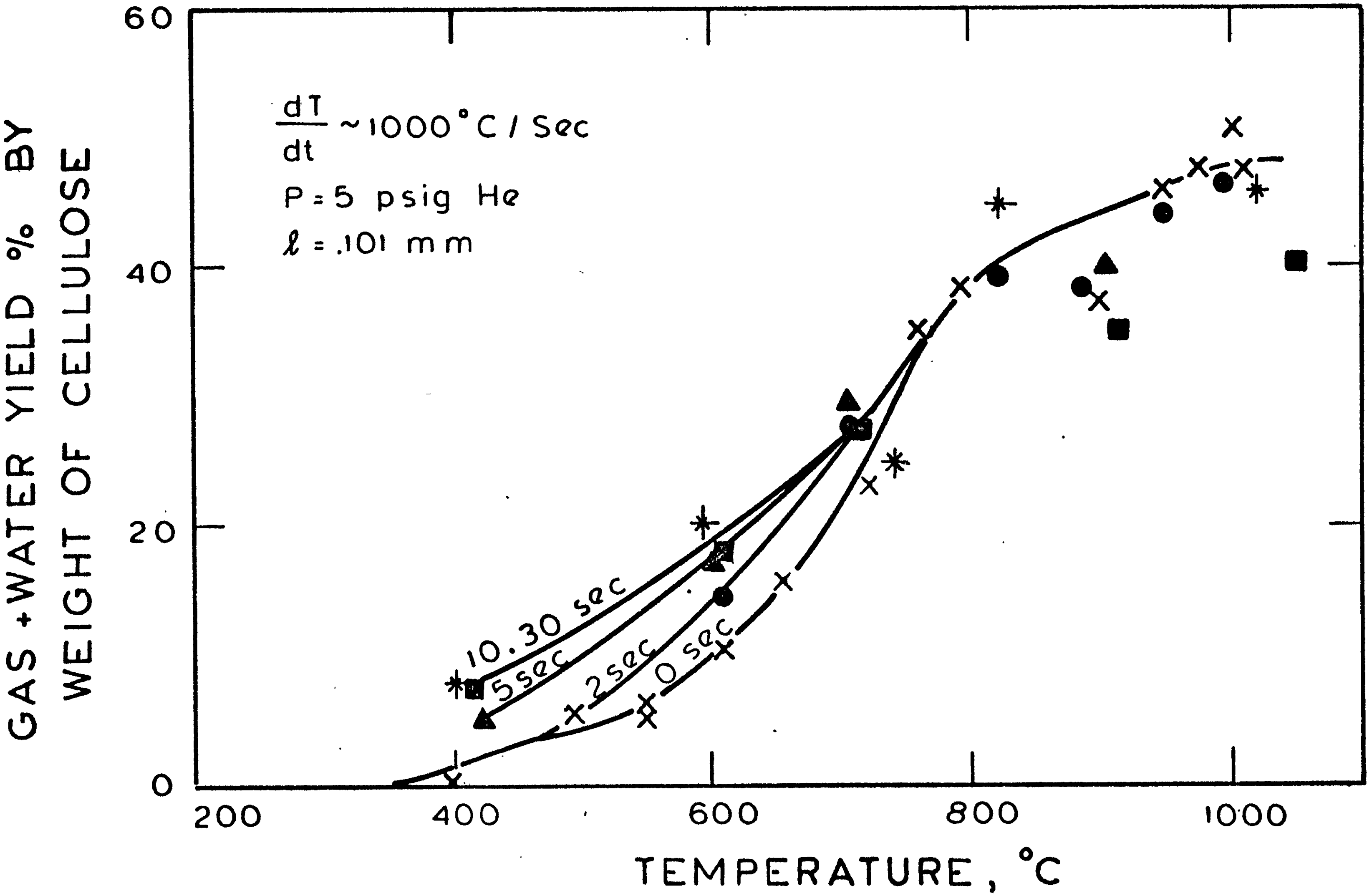


Figure IV.2-6. Effect of Holding Time on Yields of Total Gases at 5 psig He Pressure.

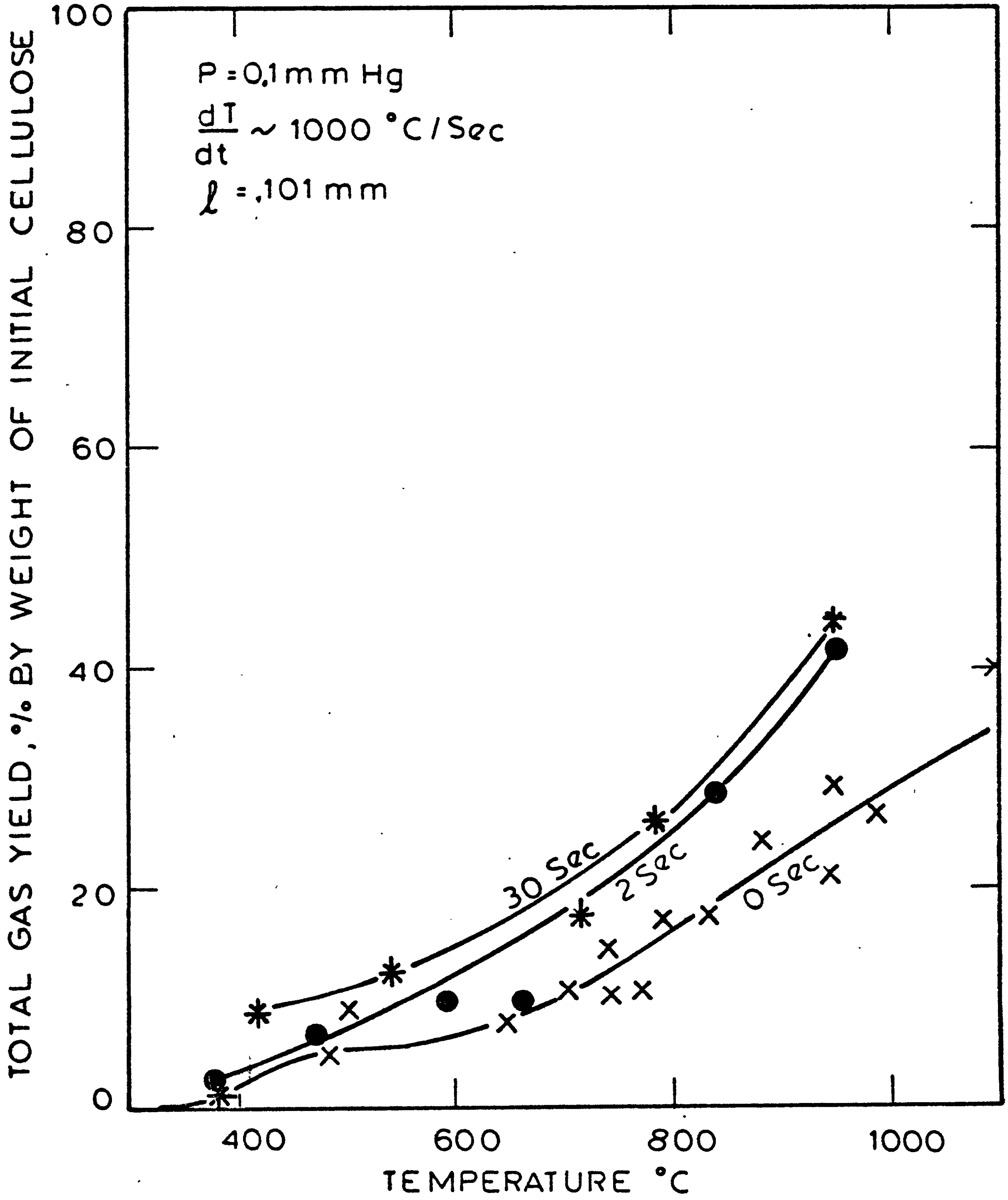


Figure IV.2-7. Effect of Holding Time on Yields of Total Gases at o.1 mm Hg Pressure.

As temperature increases, most of the pyrolysis is complete by the time the cellulose reaches peak temperature. Therefore, holding time has less effect on cellulose decomposition at high peak temperatures because no cellulose remains inside the screen, to be decomposed into tar and gas. At about 750 deg C (for the 5psig runs) holding time has no effect on tar yield and total weight loss, although it has some effect on gas composition. Above this temperature, the slope of the char yield curve shows a slight increase and the slope of the tar yield curve decreases slightly, because the cracking becomes more important. At higher temperatures, however, holding time has no significant effect on the yields of tar, char, and gases, even though free convection flows become more important.

As soon as the screen is heated because of the density difference of hot gas around the screen and cold gas of the reactor, a free convection flow starts in the reactor. This flow could circulate some of the tar and gases through the screen especially in holding time runs. The question is how important is this flow in further decomposition of gases which circulate through the screen.

As the results for 1000 deg C/sec heating rate, and 5psig He runs show, recirculation has no significant effect on secondary reactions. Although it might have some effect at low holding temperature runs because of the existence of a large amount of tar as a dense fog within the reactor. At higher temperatures, the effect is negligible.

This effect at vacuum is even less important. Because rough calculation of Grashof at vacuum and atmospheric case show that free convection at pressures of 0.1mm Hg is very small.

$$G_r = \frac{\bar{\rho}\ g\ b^3\ \Delta\rho}{\mu^2}\text{, Grashof number}$$

where

$$\bar{\rho} = \frac{Mp}{R\bar{T}}\text{, density}$$

$$\Delta\rho = \frac{Mp}{R}\left(\frac{1}{T_C} - \frac{1}{T_H}\right)\text{, density difference}$$

$$g = 980\ \text{cm}^2/\text{sec}$$

$$b = \text{characteristic length} \approx 4.75\ \text{cm}$$

$$\mu = \text{viscosity}$$

For vacuum, gases are assumed to be mainly a mixture of Carbon dioxide, water, and carbon monoxide with an average molecular weight of 28, which is close to carbon monoxide. For the case of atmospheric runs, it is assumed to be helium. The viscosity of helium is very close to carbon monoxide. Therefore, at 5psig He pressure, 1000 deg C/sec heating rate, and 1000 deg k final temperature, $Gr \cong 10^4$. For the same conditions with different pressures:

$$\frac{(G_r)_{p\,=\,5\text{psig}}}{(G_r)_{p\,=\,0.1\text{mmHg}}} = \frac{\dfrac{\bar{\rho}_p\ g b^3 \Delta\rho_p}{\mu_p^2}}{\dfrac{\bar{\rho}_v\ g b^3\ \Delta\rho_v}{\mu_v^2}} \propto \left(\frac{M_p P_p}{M_v P_v}\right)^2 \sim 10^6$$

The results from the vacuum runs differ slightly from the 5psig runs. At low temperatures, the curves for the vacuum runs follow the same path as the curves for the 5psig runs, but at higher temperatures, the effect of holding time becomes significant. Holding time at high temperatures, in vacuum, causes a decrease in tar yield, an increase in char yield and an increase in total gas yield because of more secondary cracking of the tar.

A possible explanation for this behavior is that, at vacuum, certain products which could autocatalyze the primary decomposition of the cellulose leave the sample matrix as soon as they are produced. At higher presure, these products stay in the cellulose matrix long enough to autocatalyze the reactions of the unreacted cellulose further. Therefore, at vacuum, the primary deomposition can't be complete during the heating period even at temperatures as high as 850 deg C for zero holding time, and must continue into the cooling period. This means that some of the tar evolved during this period encounters lower and lower temperatures within and in the neighborhood of the decomposing sample (heating and cooling). This tar will thus have less probability of cracking and the observed tar yield will be higher. However, in runs with a longer holding time, where the final temperature is held at 800 deg C or more, for a few seconds, cellulose decomposition becomes complete at this high temperature. Under these conditions, the evolving tar does encounter temperatures sufficiently high for cracking and some of it decomposes to give additional gases and char. Another point is that in vacuum, because the volatiles which leave the cellulose matrix could leave in any direction, the coke arising from secondary cracking should be more evenly distributed on the surface of the screen when compared to the 5psig He runs, and more gases and coke should be evolved. This result is observed experimentally. Another possible explanation for the vacuum effects is that at these low pressures, volatiels are rapidly transported through the region between the sample and the screen layers. However, under vacuum, free convection does little to augment volatiles' transport away from the outer layer of the screen (very small grashof number) and into the main volume of the reactor. Therefore, the volatiles spend more time in the region outside, but relatively close to the screen than they do at pressures of 5psig and higher. In zero holding time runs, there is minimal opportunity for heating these outside regions, so the freshly formed volatiles passing through them are not significantly heated. However, as holding time increases, the fluid in these zones undergo more heating from the hot screen, and, under these conditions, volatiles passing through them will be heated and thus have more opportunity for cracking. This behavior is in fact found in the data on tar yield at vacuum.

Holding time affects the individual compounds in the same manner. Figures IV.2-8 through IV.2-11 show these effects for 5psig He runs. At low temperatures, the yield of gases increases with holding time as long as the cellulose hasn't been completely converted. At these temperatures, tar cracking is not significant, and the increase in yields is small. At this

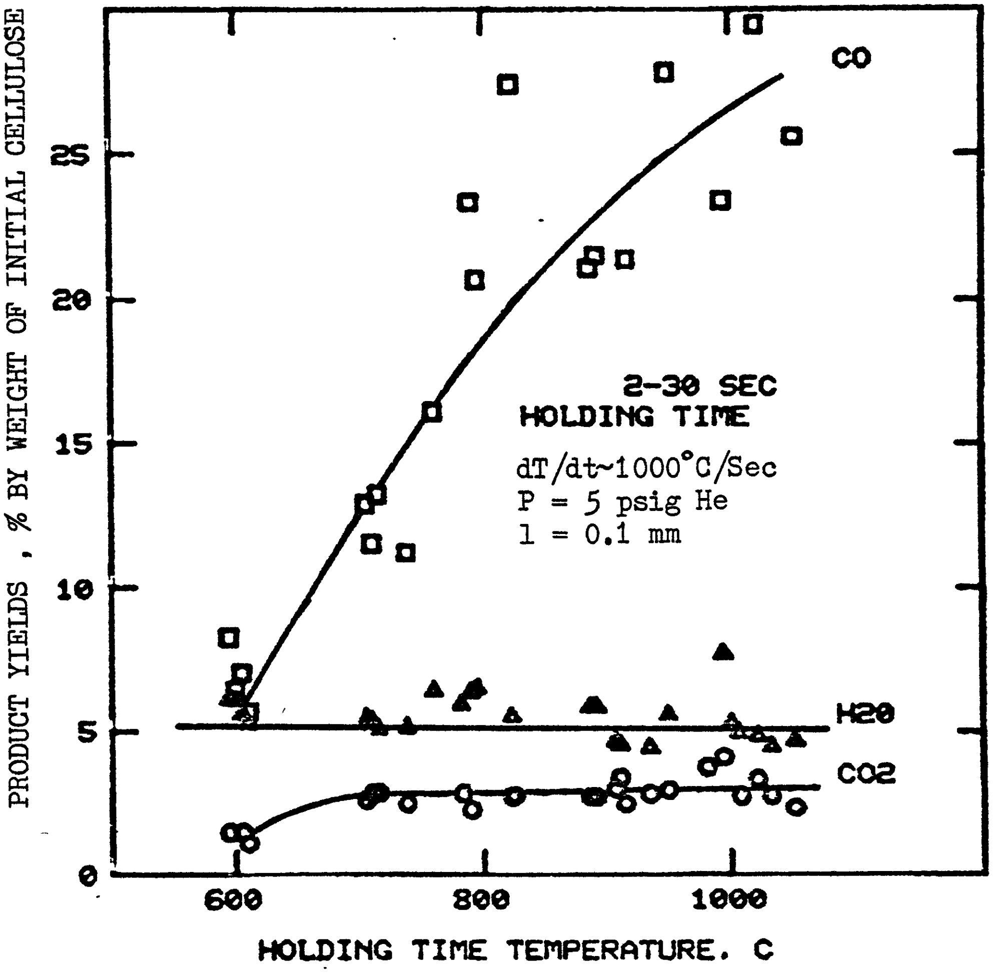


Figure IV.2-8. Effect of Holding Time on Yields of CO, CO2, and H2O at 5 psig He Pressure.

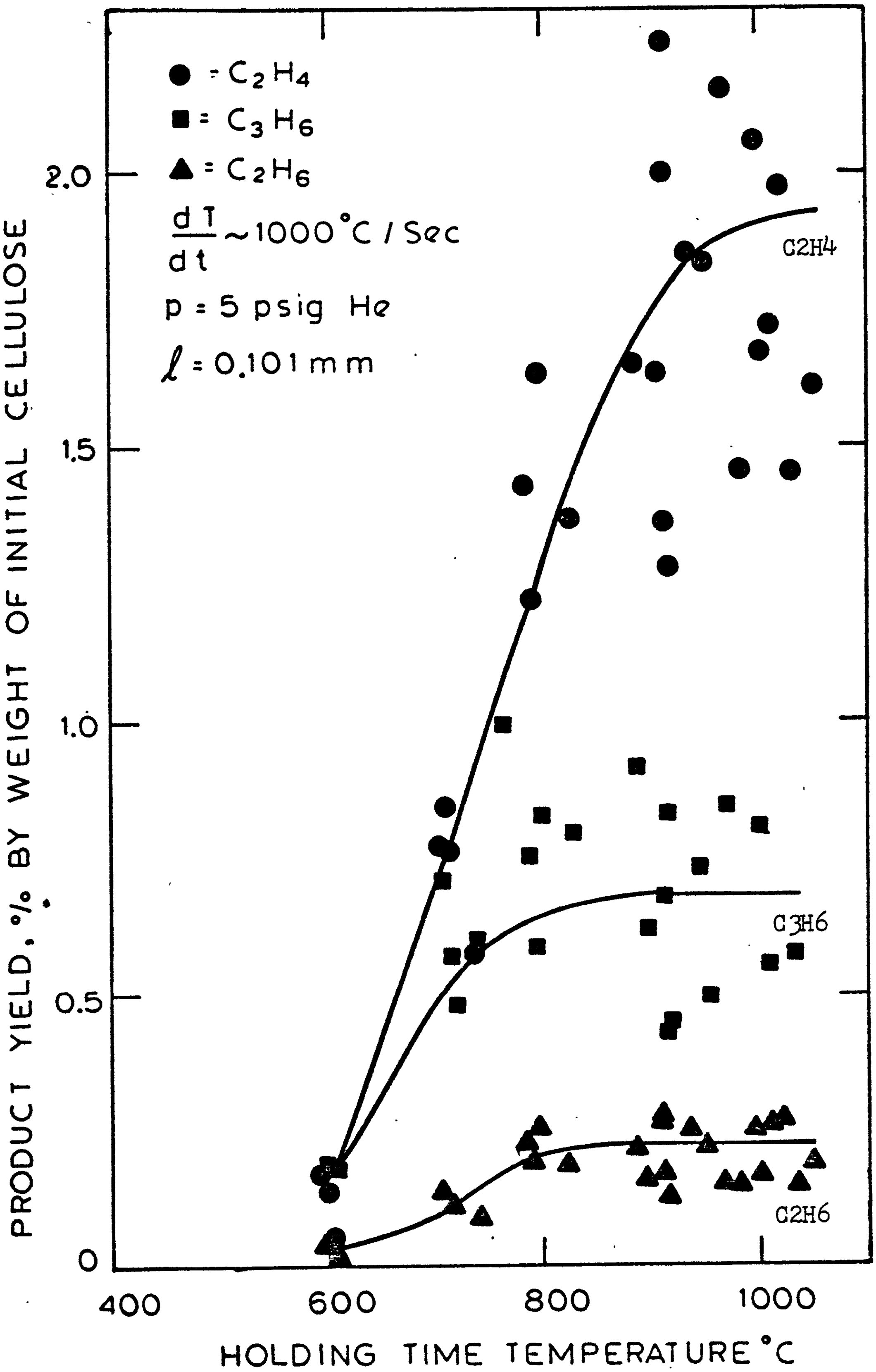


Figure IV.2-9. Effect of Holding Time on Yields of C2H4, C2H6, and C3H6 at 5 psig He Pressure.

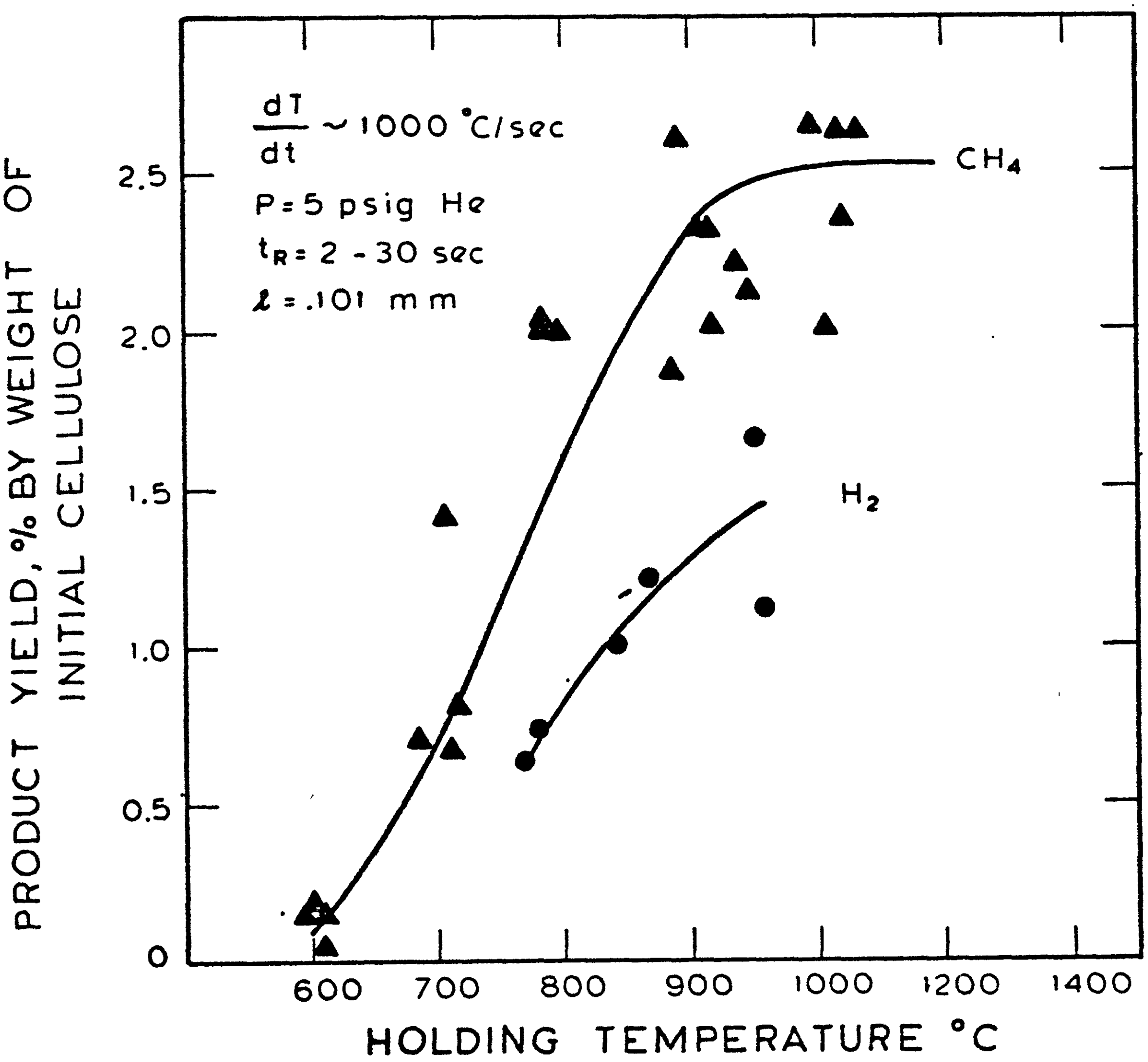


Figure IV.2-10. Effect of Holding Time on Yields of CH4, and H2 at 5 psig He Pressure.

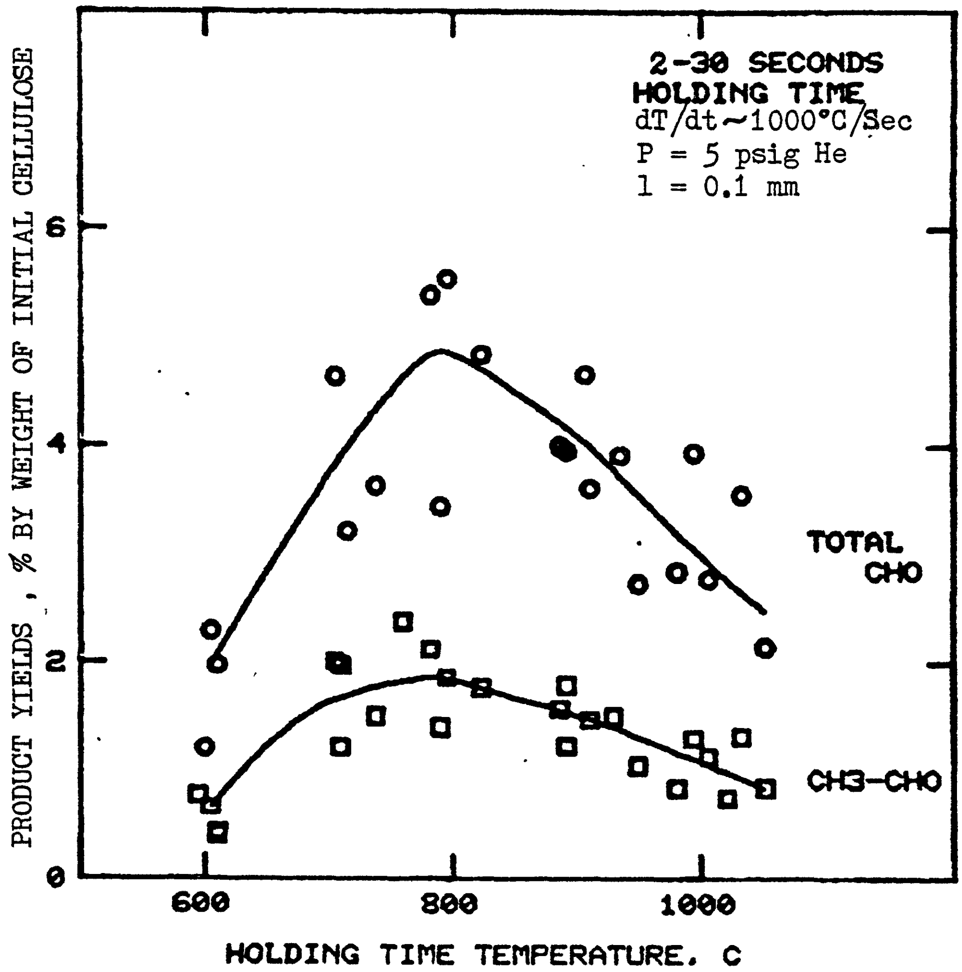


Figure IV.2-11. Effect of Holding Time on Yields of Acetaldhyde, and Total Oxygenated Volatiles at 5 psig He Pressure.

temperatures, the major components of gas are water and carbon dioxide. These two compounds are more affected by holding time than carbon monoxide, oxygenated compounds, and hydrocarbons. Total yields of hydrocarbons, oxygenated compounds and carbon monoxide in this temperature range (400 to 500 deg C) are 0.04, 0.45, and 0.25 respectively. As temperature increases, even the small effect of holding time on gases vanishes. This is because at high temperatures, the pyrolysis process is complete when the screen reaches peak temperature, and no cellulose remains to be pyrolyzed with increasing holding time. Secondary reactions resulting from free convection flows at these conditions (5psig He, 1000 deg C/sec), do not make a significant contribution to gas yields. This shows that the main cracking of tar or oxygenated compounds (aldehydes, alcohols, and ketones) occurs while they are inside the cellulose matrix, or hot zone. Ketones, aldehydes, and alcohols go through a maximum as temperature increases. This phenomena becomes much more evident in runs with a holding time than in runs with zero holding time.

At vacuum and low temperature, the effect of holding time is the same as it is at 5psig, but at high temperatures, the effect is quite different (Figures IV.2-12 through IV.2-23). Yields of gases, such as carbon dioxide, carbon monoxide, methane, ethylene, ethane, and propylene, start to increase with holding time. This effect is especially evident in carbon dioxide. Water yield remains almost constant with different holding times. As temperature increases, aldehyde, ketone, and alcohol yields

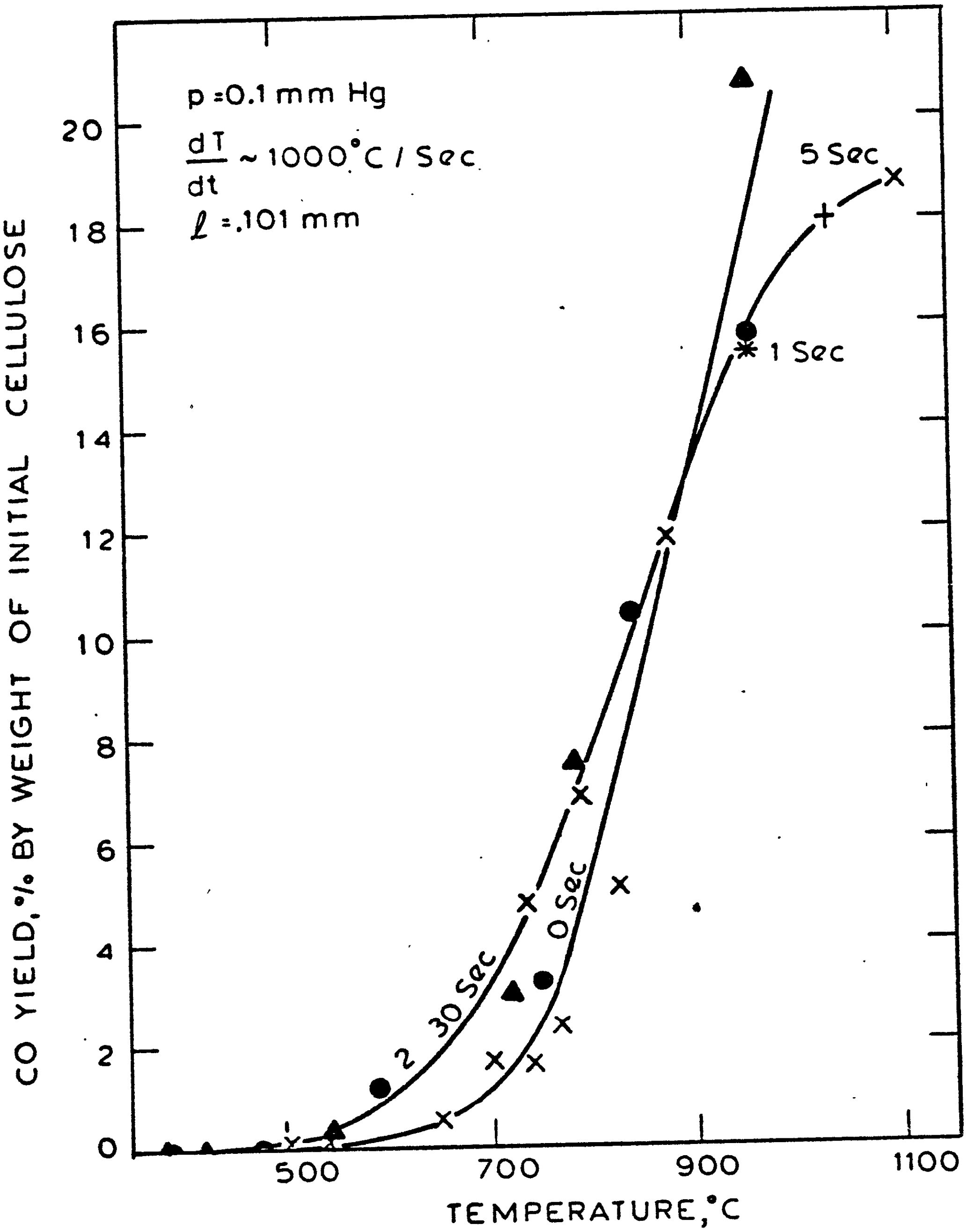


Figure IV.2-12. Effect of Holding Time on Yields of CO at o.1 mm Hg Pressure.

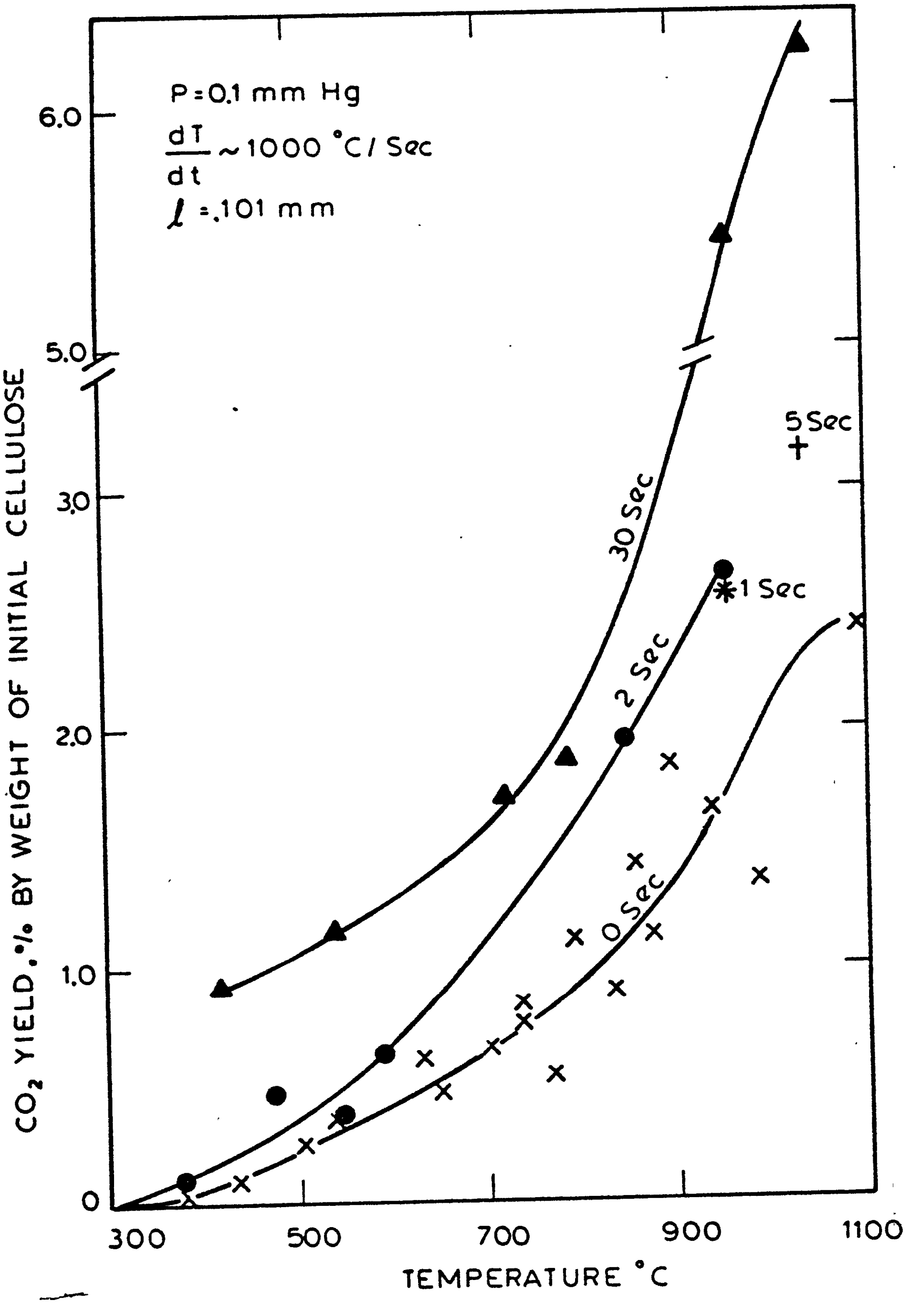


Figure IV.2-13. Effect of Holding Time on Yields of CO2 at 0.1 mm Hg Pressure.

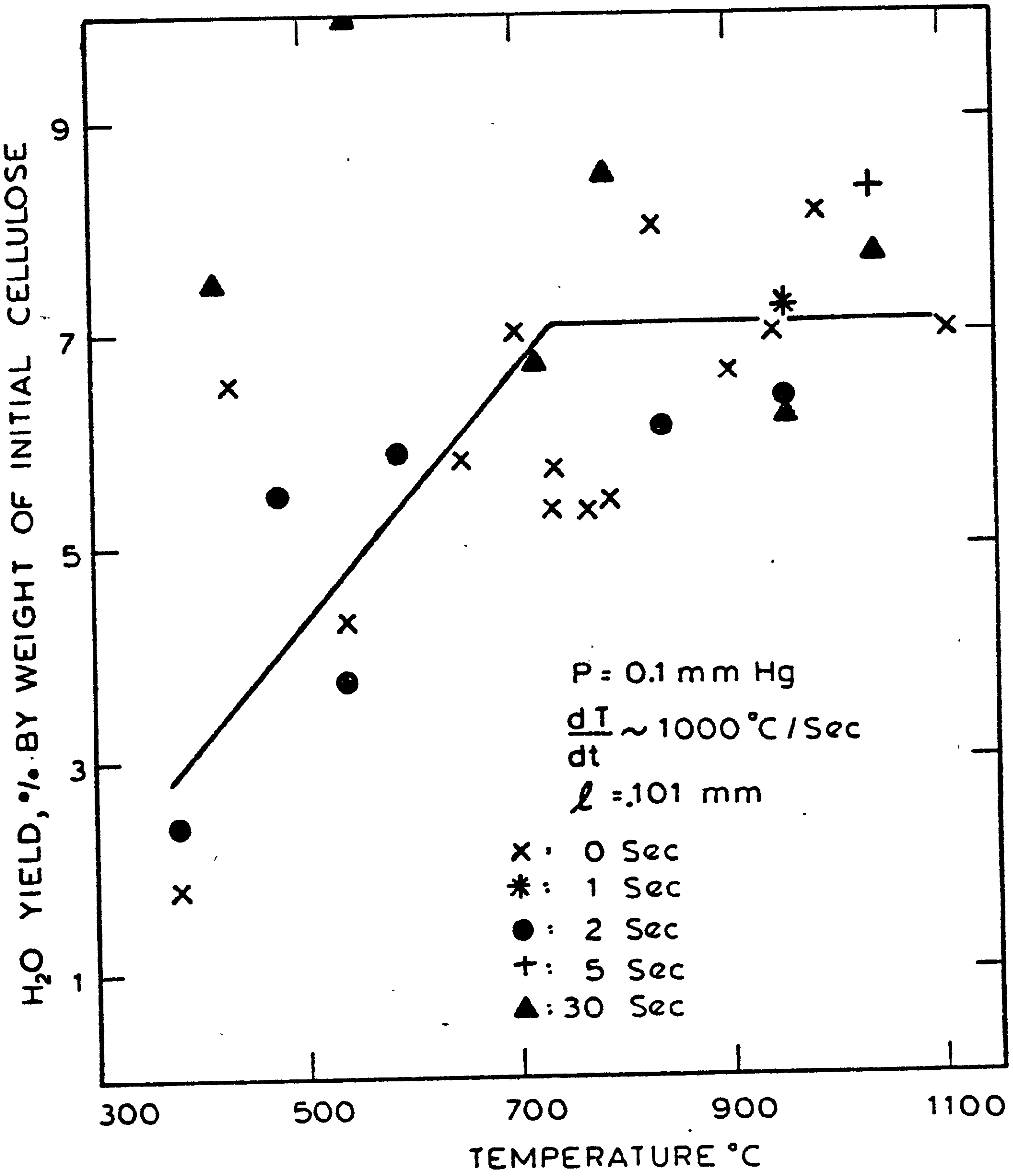


Figure IV.2-14. Effect of Holding Time on Yields of H20 at 0.1 mm Hg Pressure.

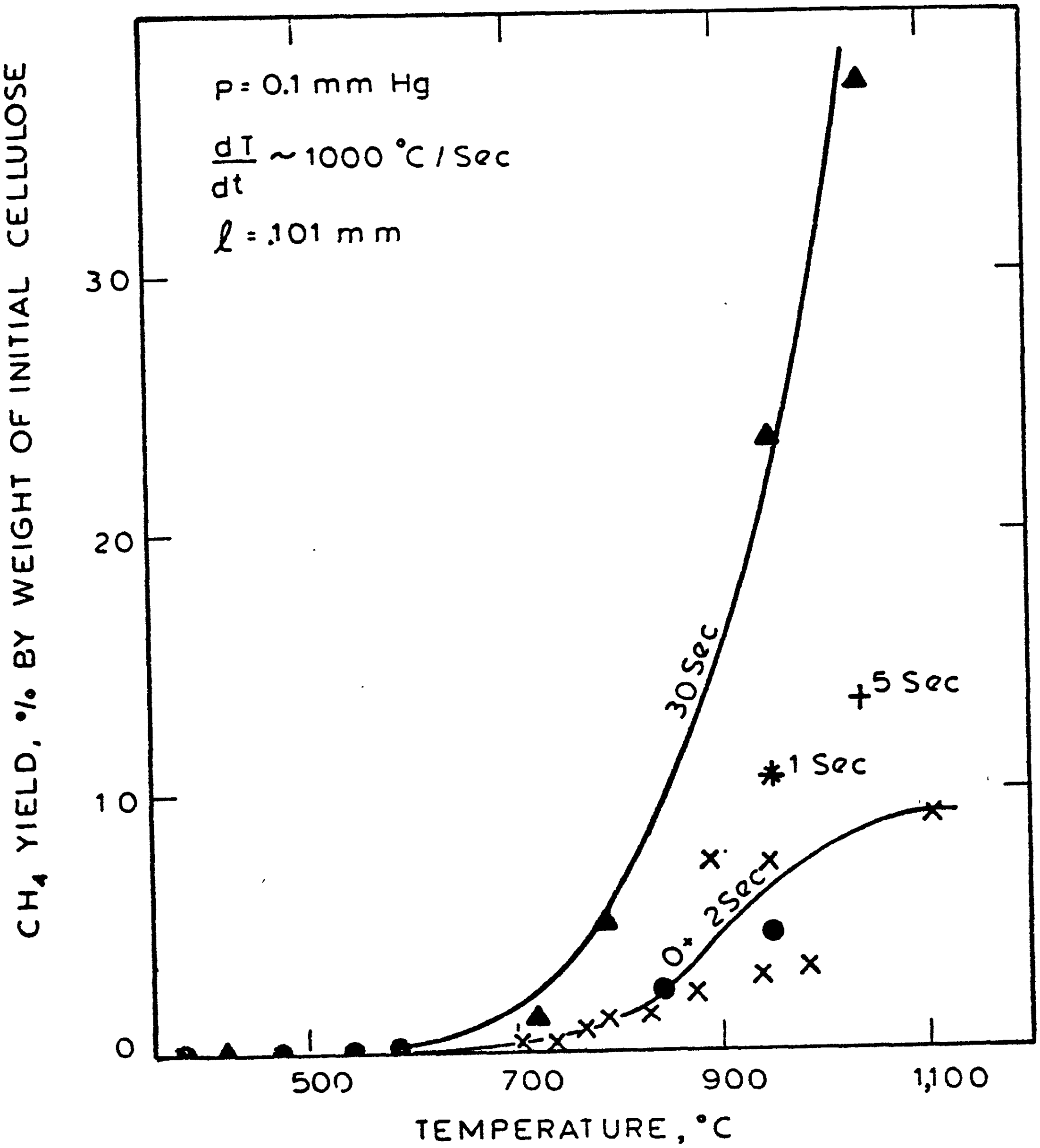


Figure IV.2-15. Effect of Holding Time on Yields of CH4 at 0.1 mm Hg Pressure

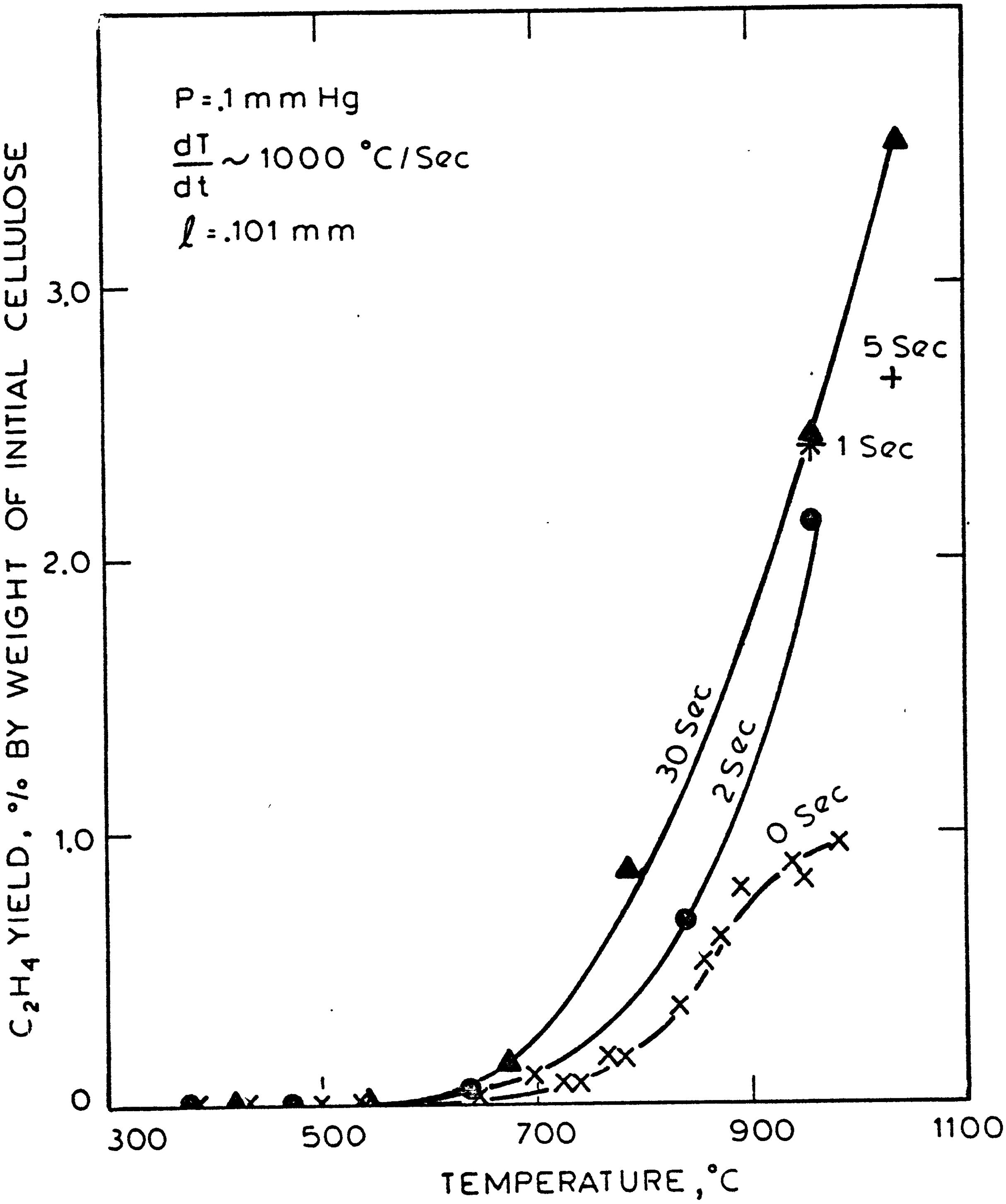


Figure IV.2-16. Effect of Holding Time on Yields of C2H4 at 0.1 mm Hg Pressure.

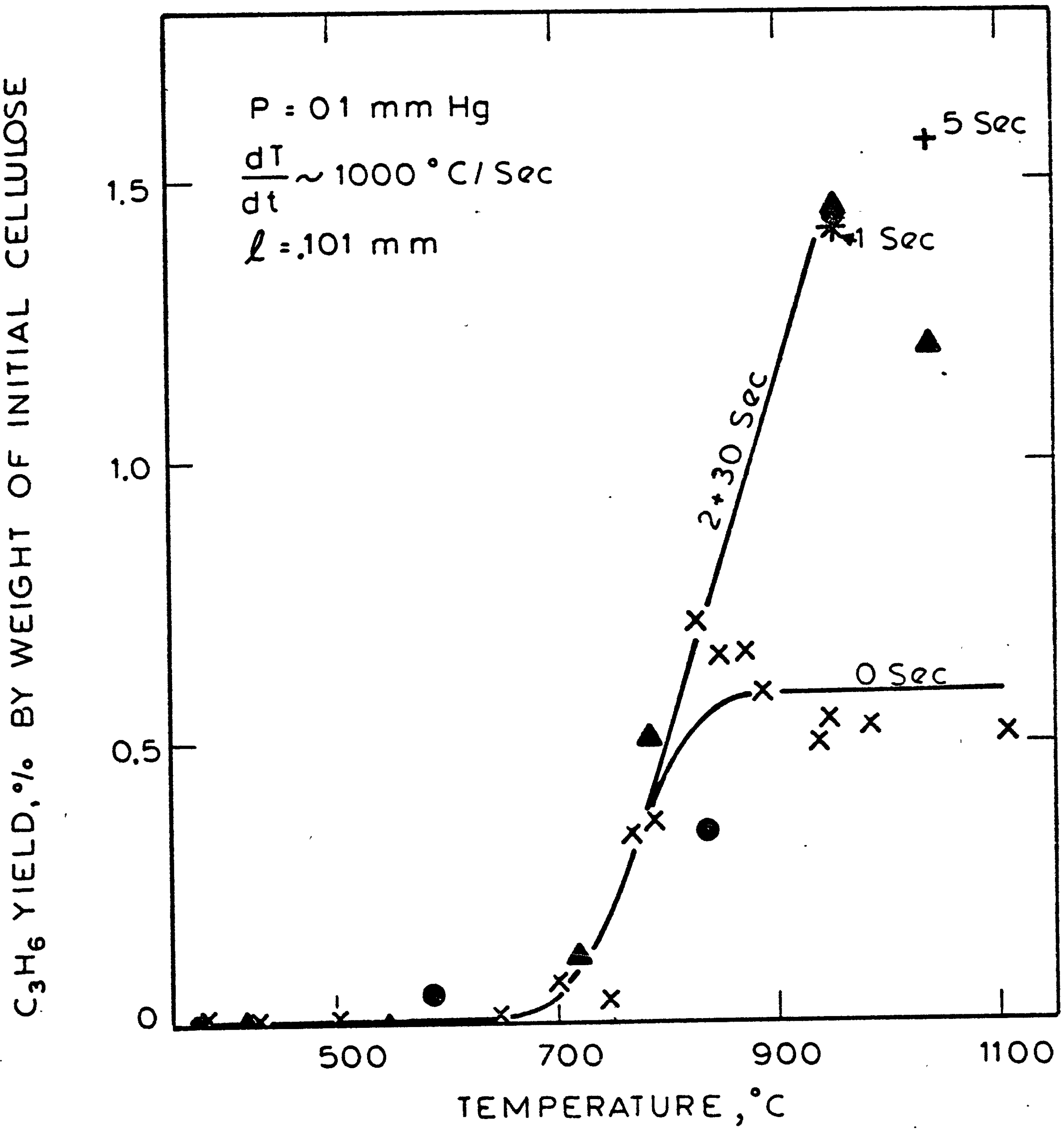


Figure IV.2-17. Effect of Holding Time on Yields of C3H6 at 0.1 mm Hg Pressure.

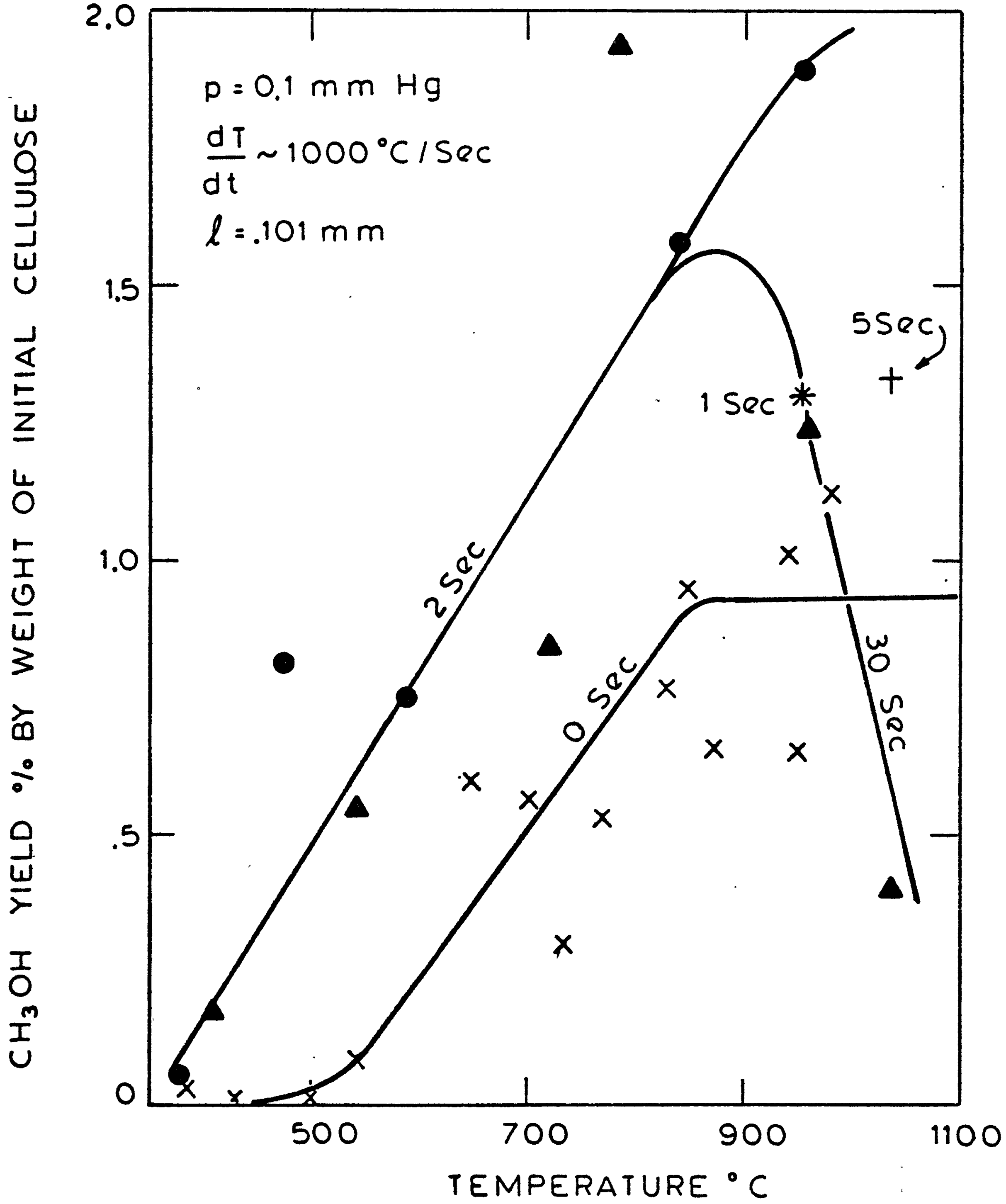


Figure IV.2-18. Effect of Holding Time on Yields of Methanol at 0.1 mm Hg Pressure.

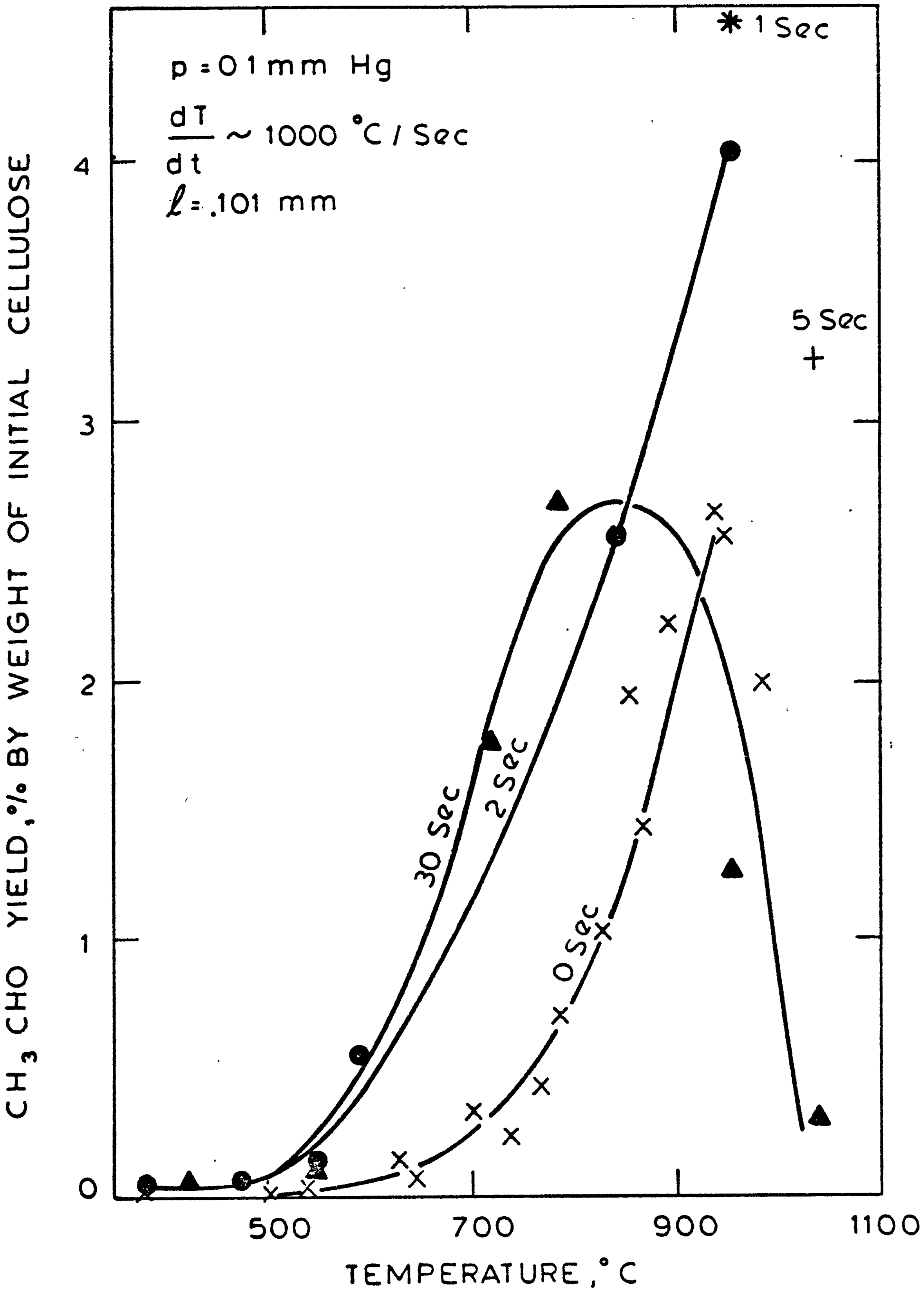


Figure IV.2-19. Effect of Holding Time on Yields of Acetaldehyde at 0.1 mm Hg Pressure.

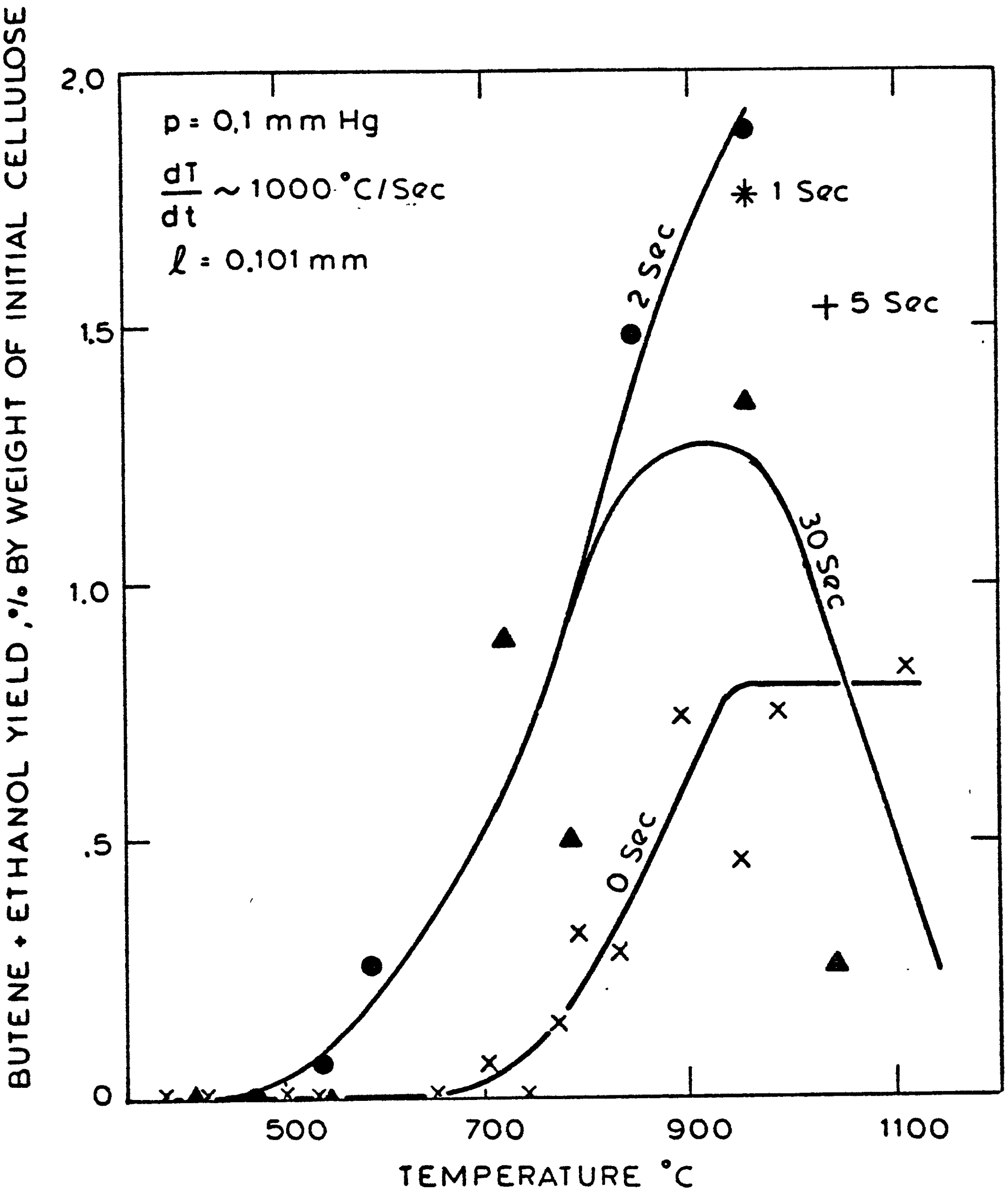


Figure IV.2-20. Effect of Holding Time on Yields of Butene+Ethanol at 0.1 mm Hg Pressure.

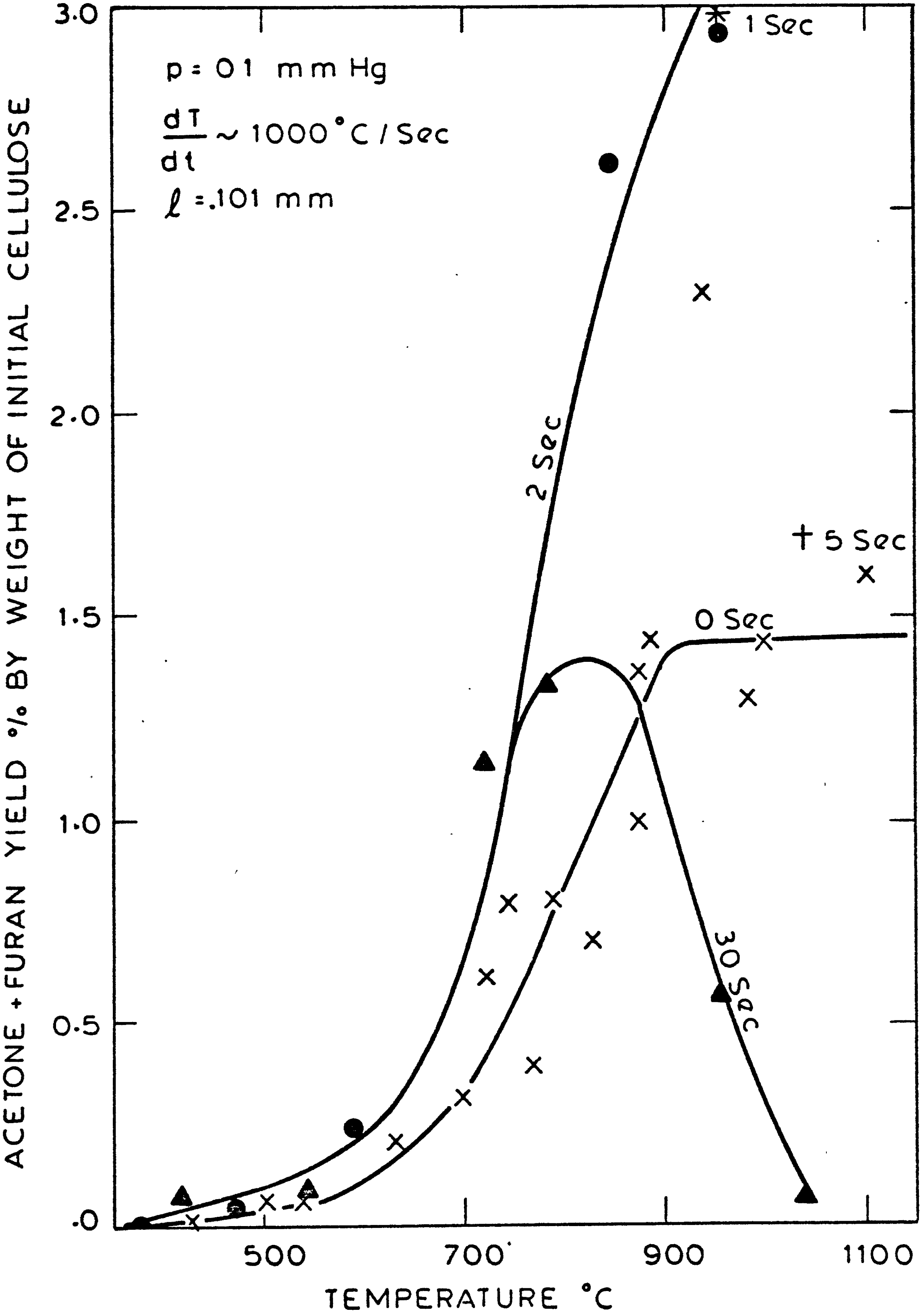


Figure IV.2-21. Effect of Holding Time on Yields of Acetone + Furan at 0.1 mm Hg Pressure.

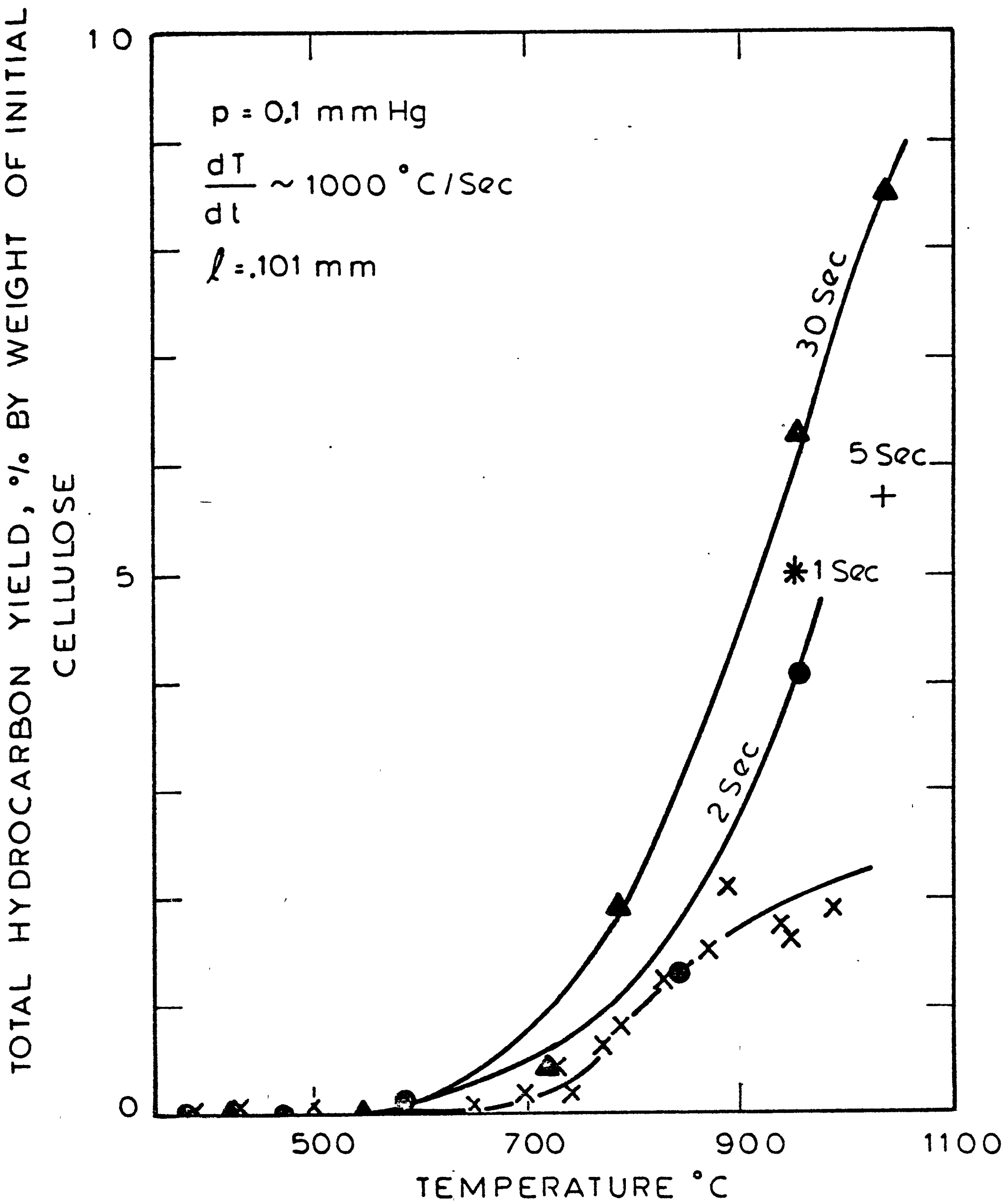


Figure IV.2-22. Effect of Holding Time on Yields of Total Hydrocarbon Gases at o.1 mm Hg Pressure.

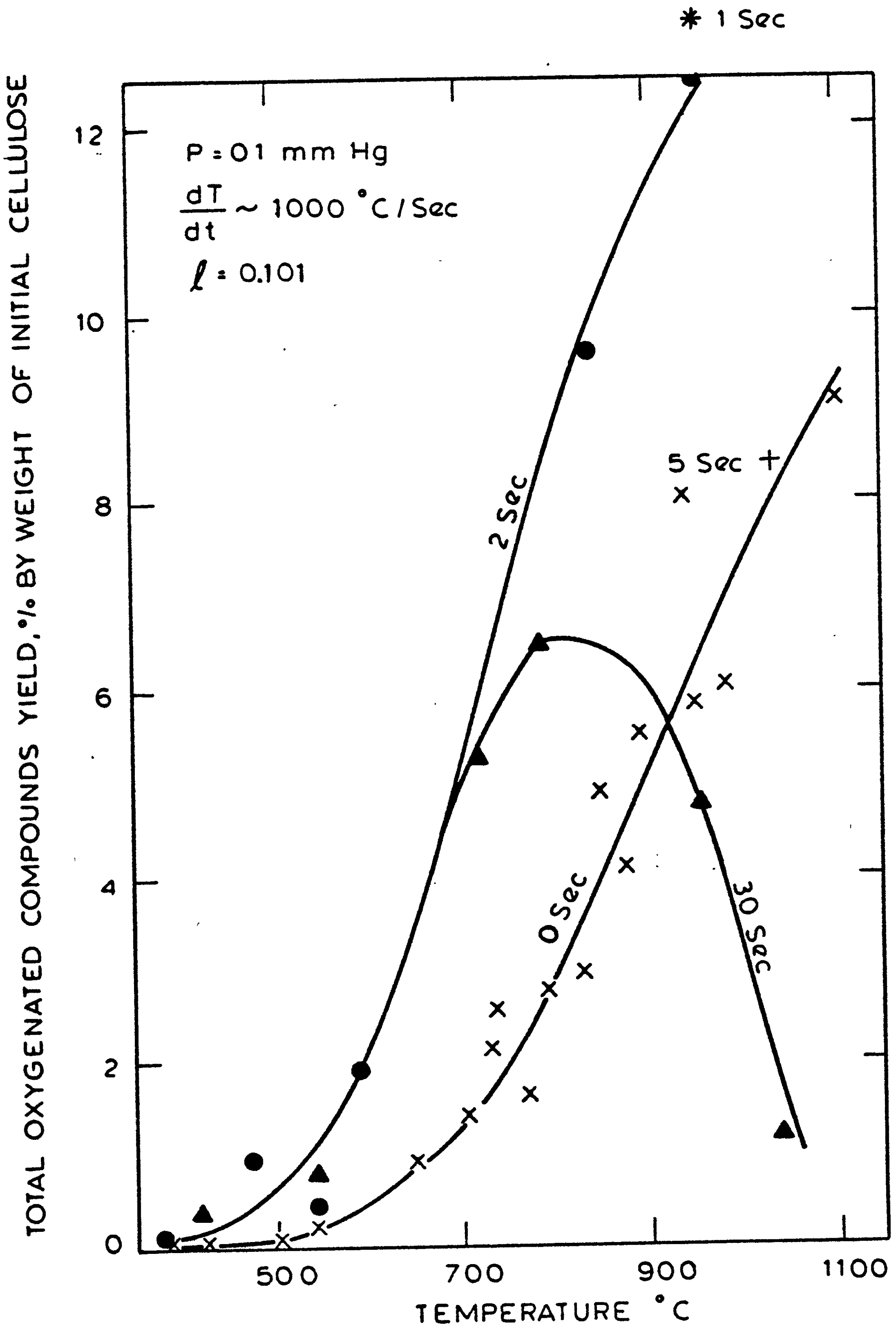


Figure IV.2-23. Effect of Holding Time on Yields of Total Oxygenated Volatiles at 0.1 mm Hg Pressure.

first increase to a maximum, then decrease. It is believed that these components are cracked to carbon monoxide, carbon dioxide, methane, ethylene, hydrogen, etc.

IV.3. Effect of Heating Rate

Another important factor in the pyrolysis of biomass is heating rate. The effects of this parameter on the pyrolysis of cellulose were determined and are shown in Figures IV.3-1 through IV.3-14. Figure IV.3-1 shows the effect of heating rate on the total decompositions of cellulose. As heating rate decreases from 1000 deg C/sec (the base case for this study), the amount of decomposition at a constant peak temperature increases, and vice-versa as heating rate increases. As stated before, peak temperature alone does not determine the amount of decomposition of cellulose, but the time of heating is important as well. Previous studies show that a proper combination of temperature and time, even at low temperatures, between 300 and 400 deg C, could give more than 90% weight loss. Therefore, peak temperature is more important in secondary reactions than in the initial decomposition, although it is also important for this step. At low heating rates, it takes a longer time to achieve a certain peak temperature. Since at this heating rate the cellulose is exposed to heat for a longer time, it is reasonable to observe that the quantity of initial decomposition of cellulose increases as heating rate decreases for a given peak temperature.

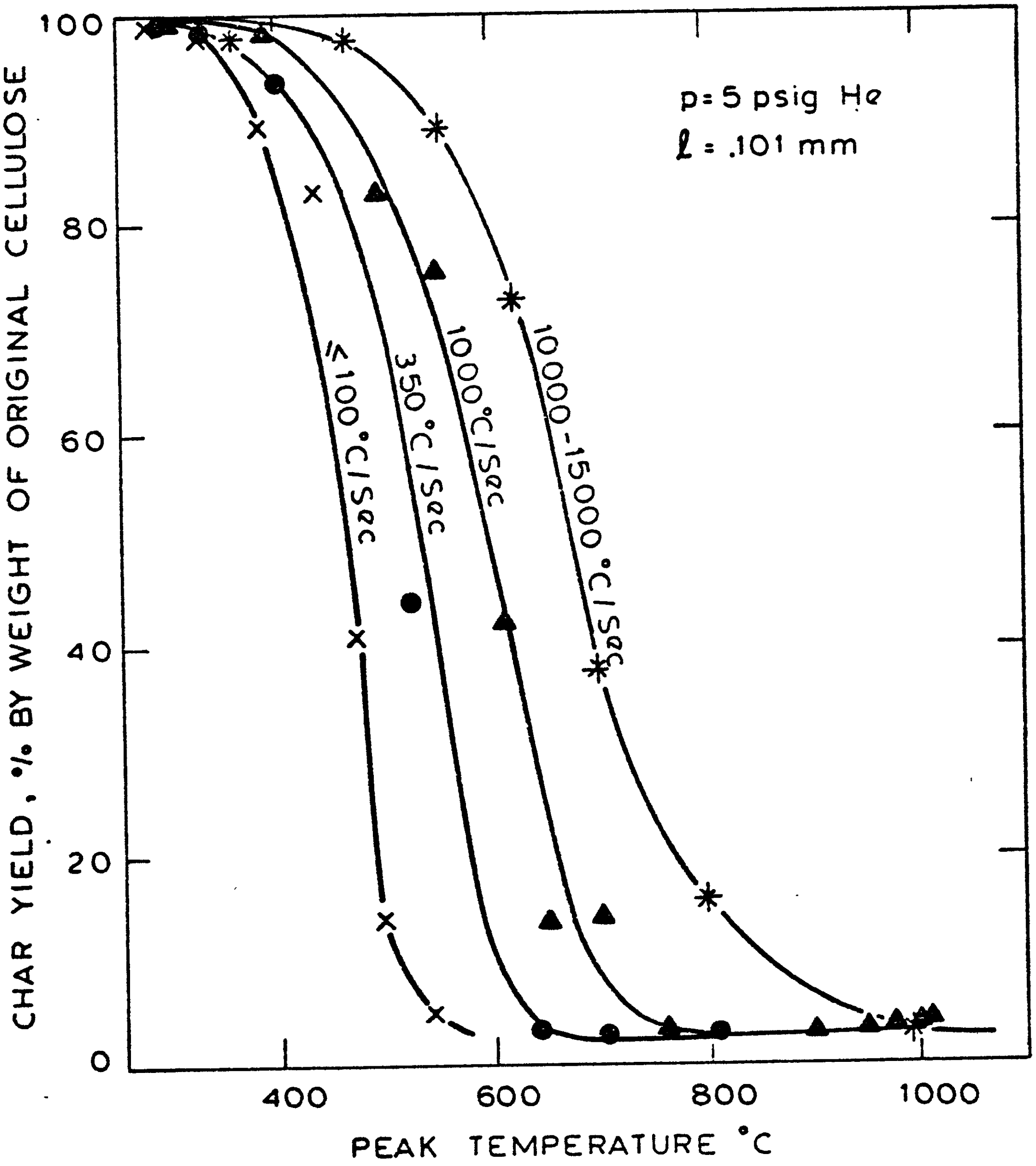


Figure IV.3-1. Effect of Heating Rate on Yields of Char at 5 psig He Pressure.

Tar yield also increases for a constant peak temperature as heating rate decreases (Figure IV.3-2). This is because there is more cellulose decomposition at low heating rates, and as a result of this, more tar production. Another factor is the decrease in secondary reactions on tar. As the results show, as the heating rate decreases, the secondary reactions of tar are gradually eliminated, and the maximum in the tar yield vs. temperature curve becomes much broader. At the lowest heating rate used in this study, approximately 85% of the cellulose was converted to tar. The explanation of this effect is obvious. At higher heating rates, tar production occurs in a shorter time. In this case, mass transfer becomes more important. If the tar is not rapidly removed from the heating zone, which is not possible at 5psig He, high heating rate, and high peak temperature, the tar goes through secondary reactions to yield many low molecular weight compounds. At low heating rate, however, tar production occurs during a longer time interval there is more production of tar at temperatures below the threshold for rapid cracking of tar. Thus, there is minimal effect of mass transfer on tar within the cellulose matrix or screen during this time, and as the higher reaction temperatures are approached, leave less chance for secondary reactions. Therefore, a maximum yield of tar can be obtained at the lowest heating rate, here 100 deg C/sec or less. However, the results of total gas yield at different heating rates (Figure IV.3-3) indicates that the heating rate for maximum gas yield is 1000 deg C/sec. This would be expected based on the previous postulate

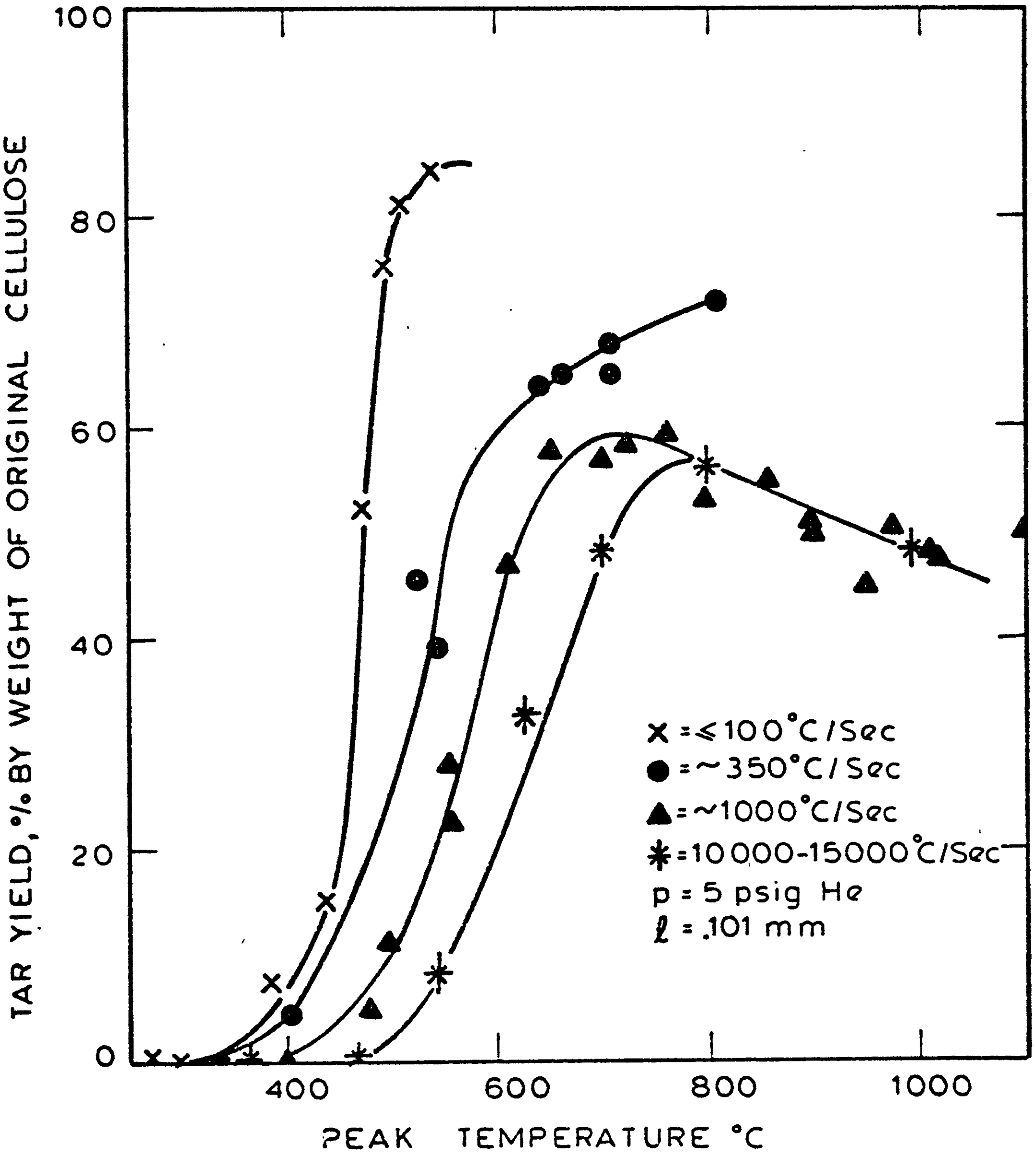


Figure IV.3-2. Effect of Heating Rate on Yields of Tar at 5 psig He pressure.

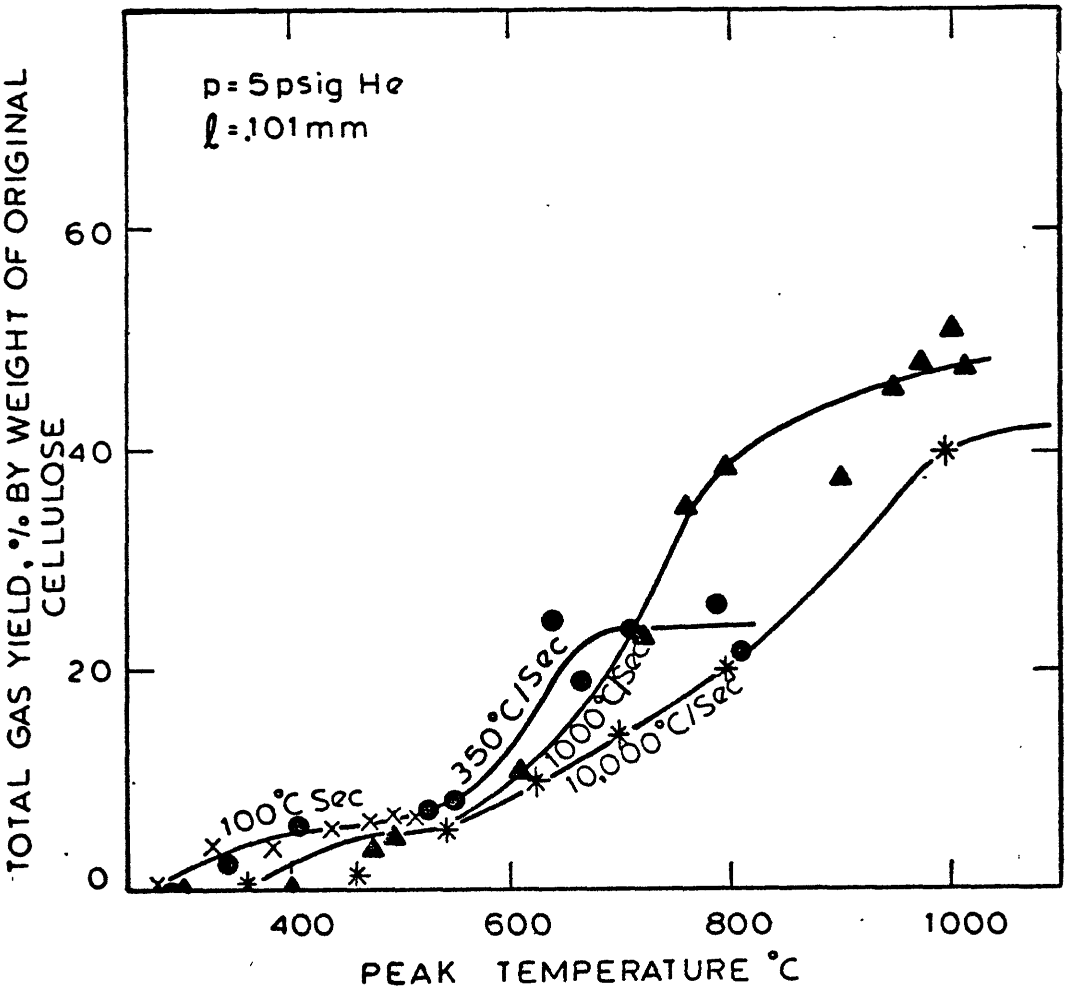


Figure IV.3-3. Effect of Heating Rate on Yields of Total Gases at 5 psig He pressure.

that tar cracking, especially at temperatures above 650 deg C, contributes most of the tar yield. The reason for the decline in gas yield with a further increase in heating rate to 10,000 deg C/sec will be discussed later in this section.

Product yields at different heating rates are shown in Figures IV.3-4 through IV.3-14. Results for water are shown in Figure IV.3-6. This indicates that different heating rates may affect the rate of production of water as a result of initial sample decomposition, but doesn't have a significant effect on the maximum yield. This could be because in these conditions water is a product of cellulose decomposition to tar rather than the product of tar cracking to lower molecular weight compounds, although the latter cannot be ruled out. The maximum yield of carbon dioxide (Figure IV.3-4) is also relatively unaffected by heating rate, although it decreases slightly with heating rates above and below 1000 deg C/sec. This is another indication of the pathways by which carbon dioxide is produced, one of which is through the initial decomposition of cellulose. The maximum yield of aldehydes, ketones, and alcohols increases as heating rate increases (Figures IV.3-10 through IV.3-12), but the effect is slight. Yields of hydrocarbons and carbon monoxide for different heating rates are shown in Figures IV.3-4, IV.3-7. through IV.3-9. These results show a maximum with a heating rate at approximately 1000 deg C/sec. This is another indication that these products come from tar cracking. while 1000 deg C/sec is the heating rate, in this apparatus, in which more tar cracks in

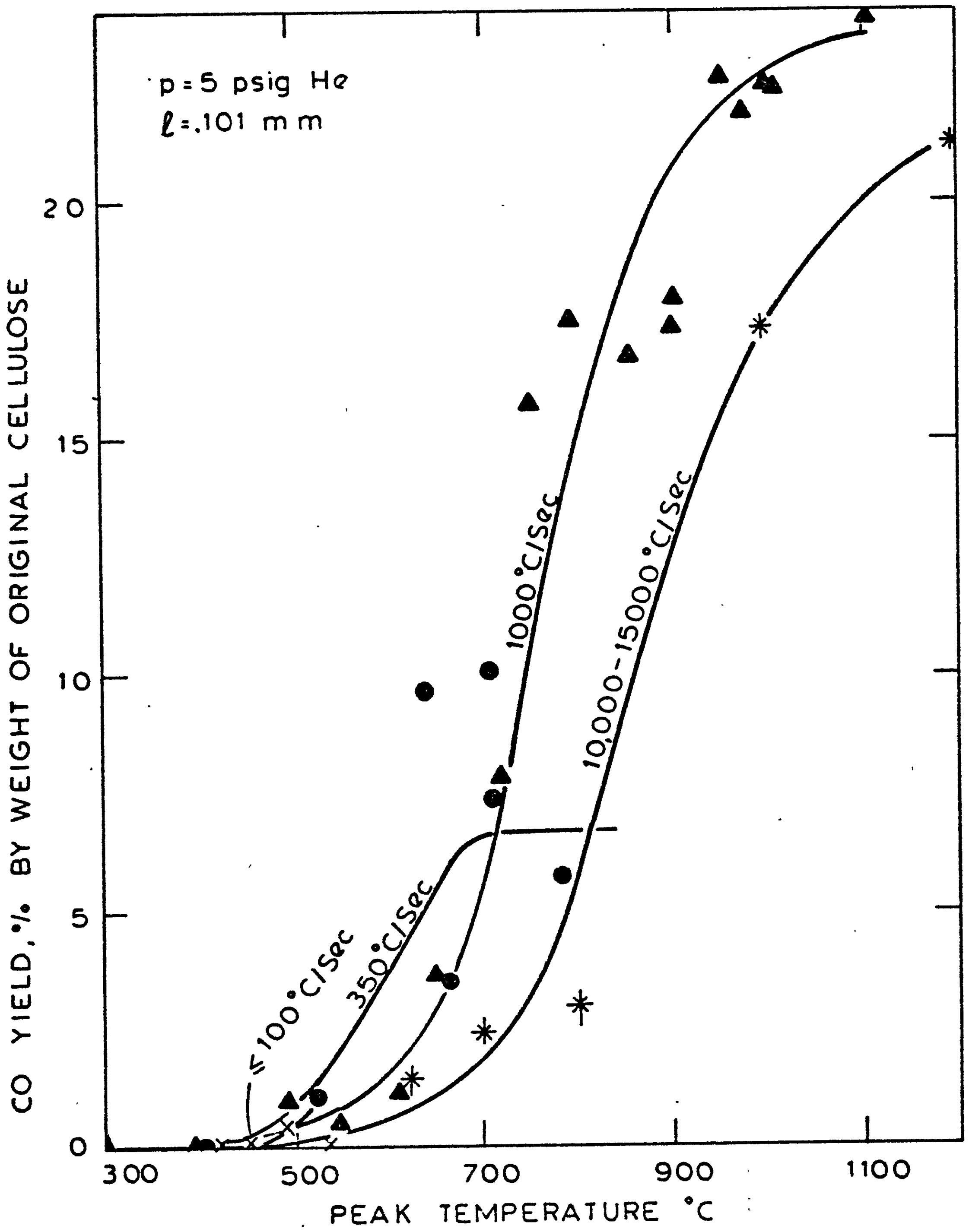


Figure IV.3-4. Effect of Heating Rate on Yields of CO at 5 psig He Pressure.

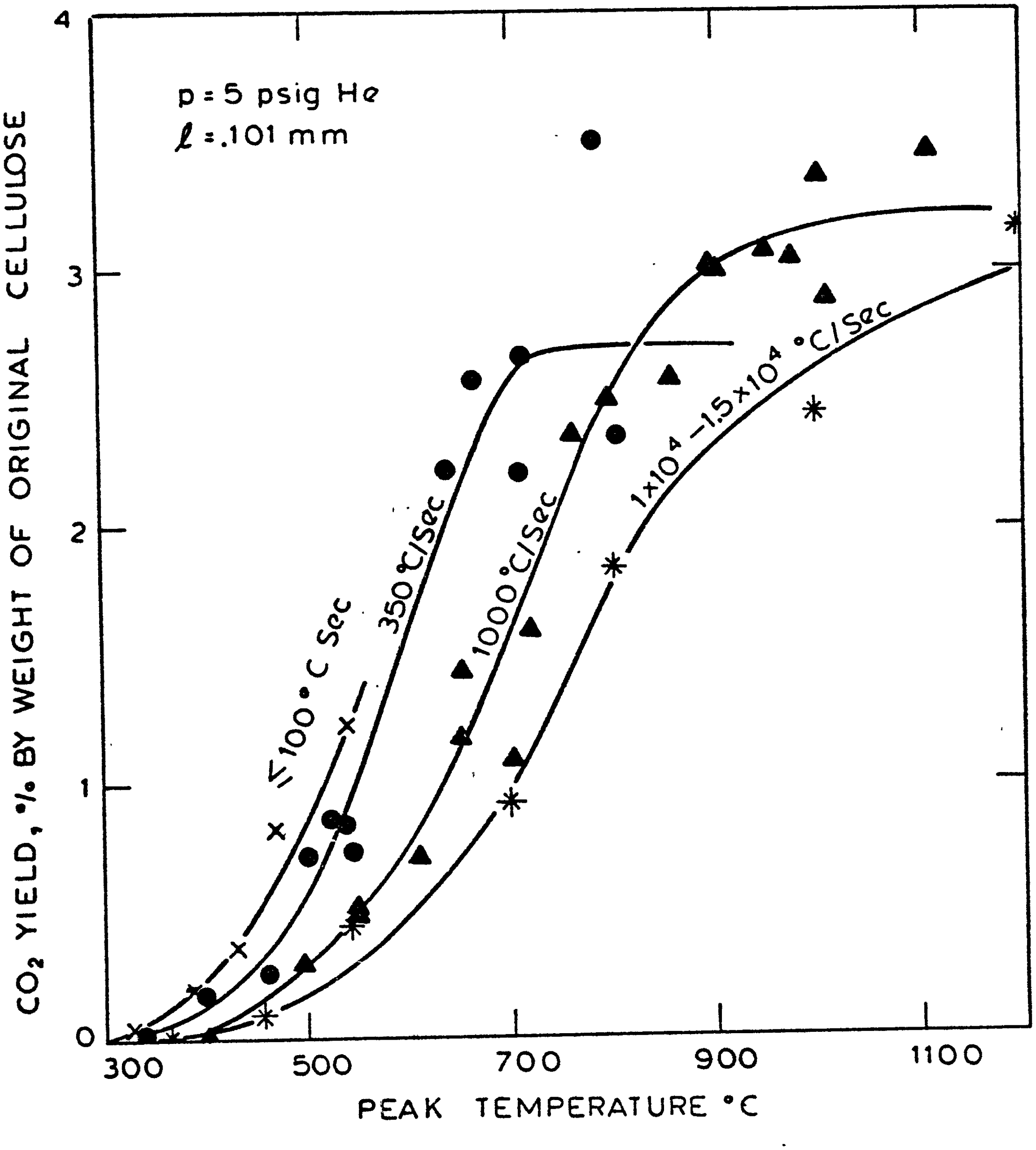


Figure IV.3-5. Effect of Heating Rate on Yields of CO2 at 5 psig He Pressure.

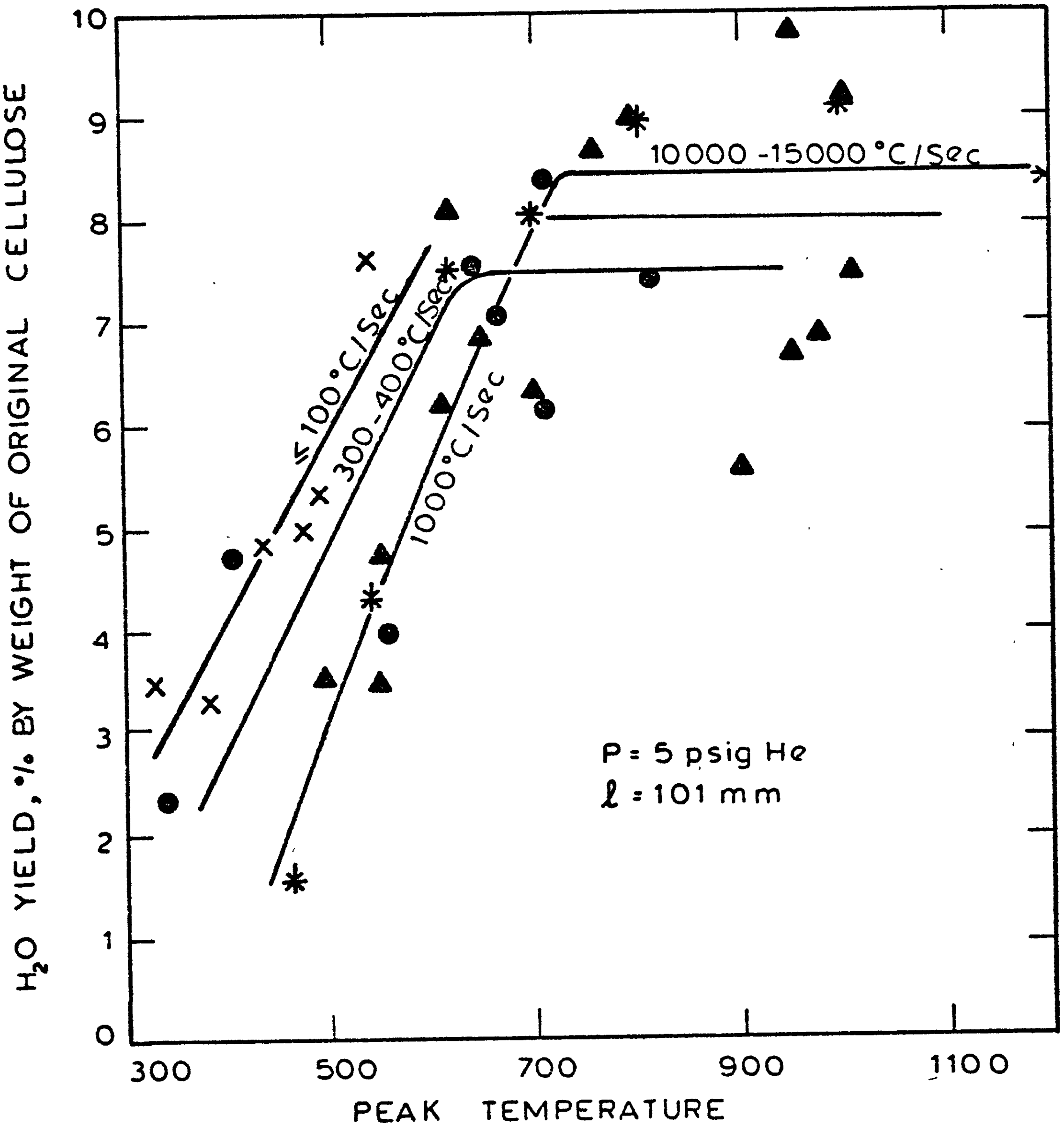


Figure IV.3-6. Effect of Heating Rate on Yields of H20 at 5 psig He Pressure.

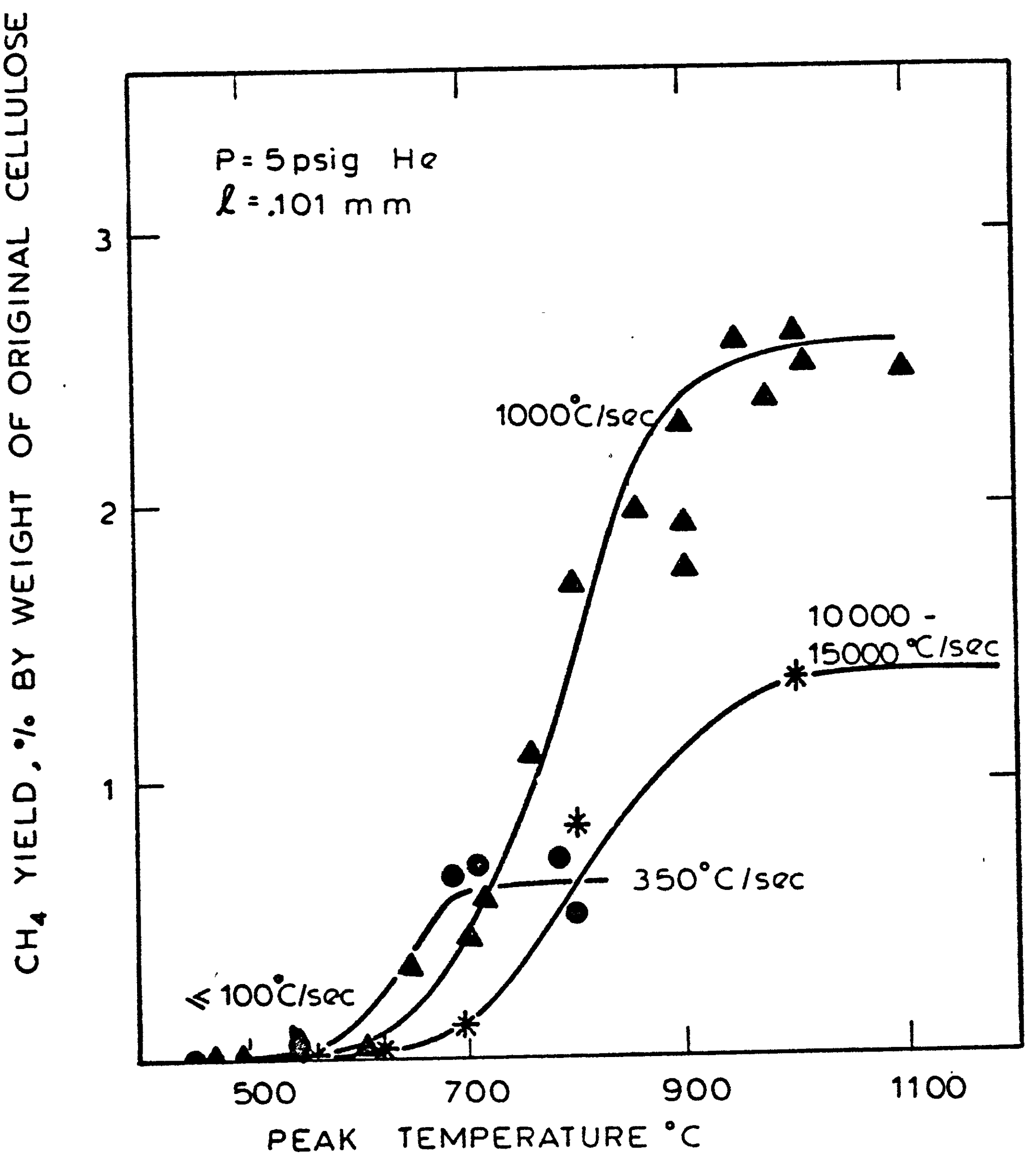


Figure IV.3-7. Effect of Heating Rate on Yields of CH_4 at 5 psig He Pressure.

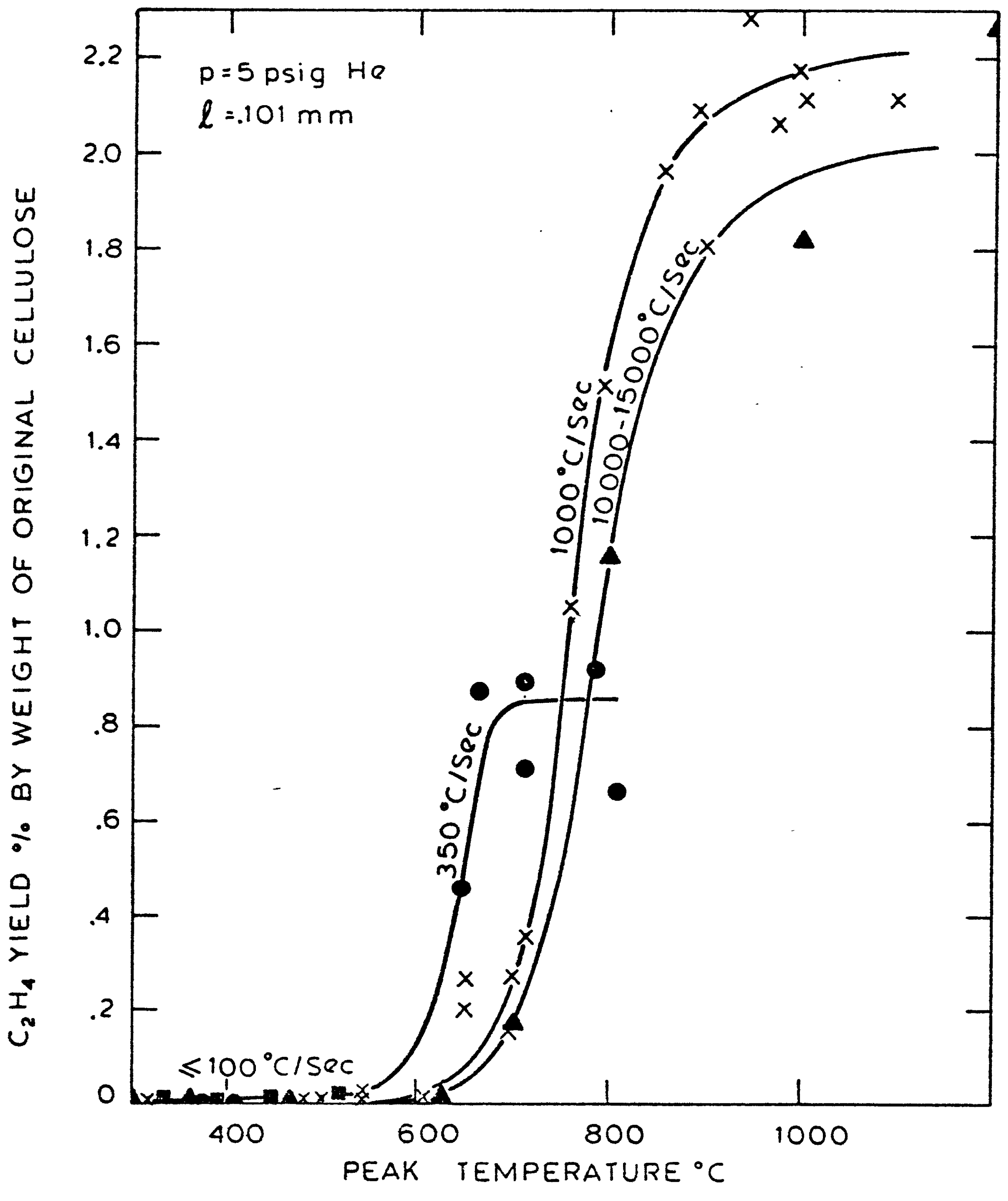


Figure IV.3-8. Effect of Heating Rate on Yields of C2H4 at 5 psig He Pressure.

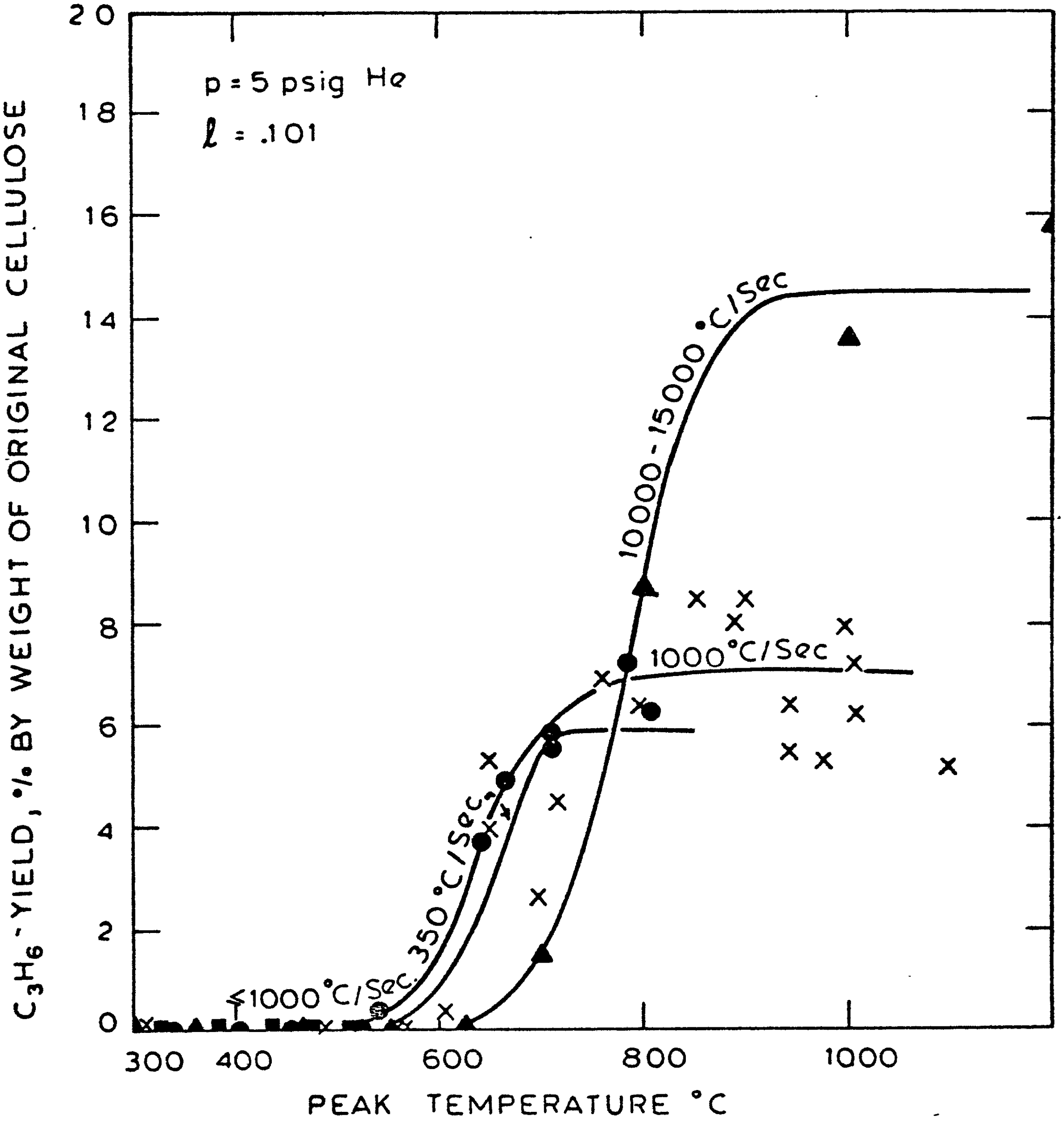


Figure IV.3-9. Effect of Heating Rate on Yields of C3H6 at 5 psig He Pressure.

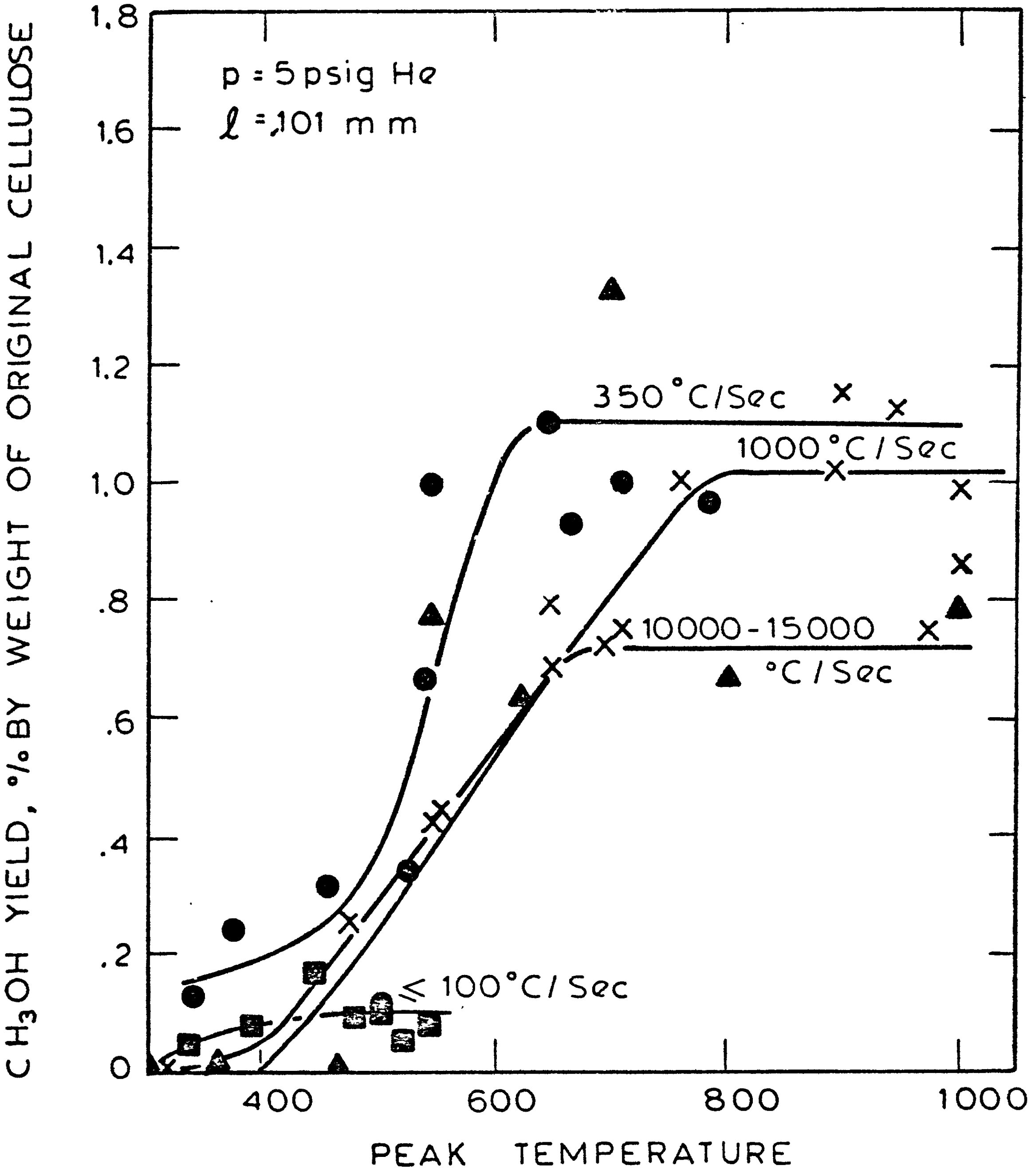


Figure IV.3-10. Effect of Heating Rate on Yields of Methanol at 5 psig He Pressure.

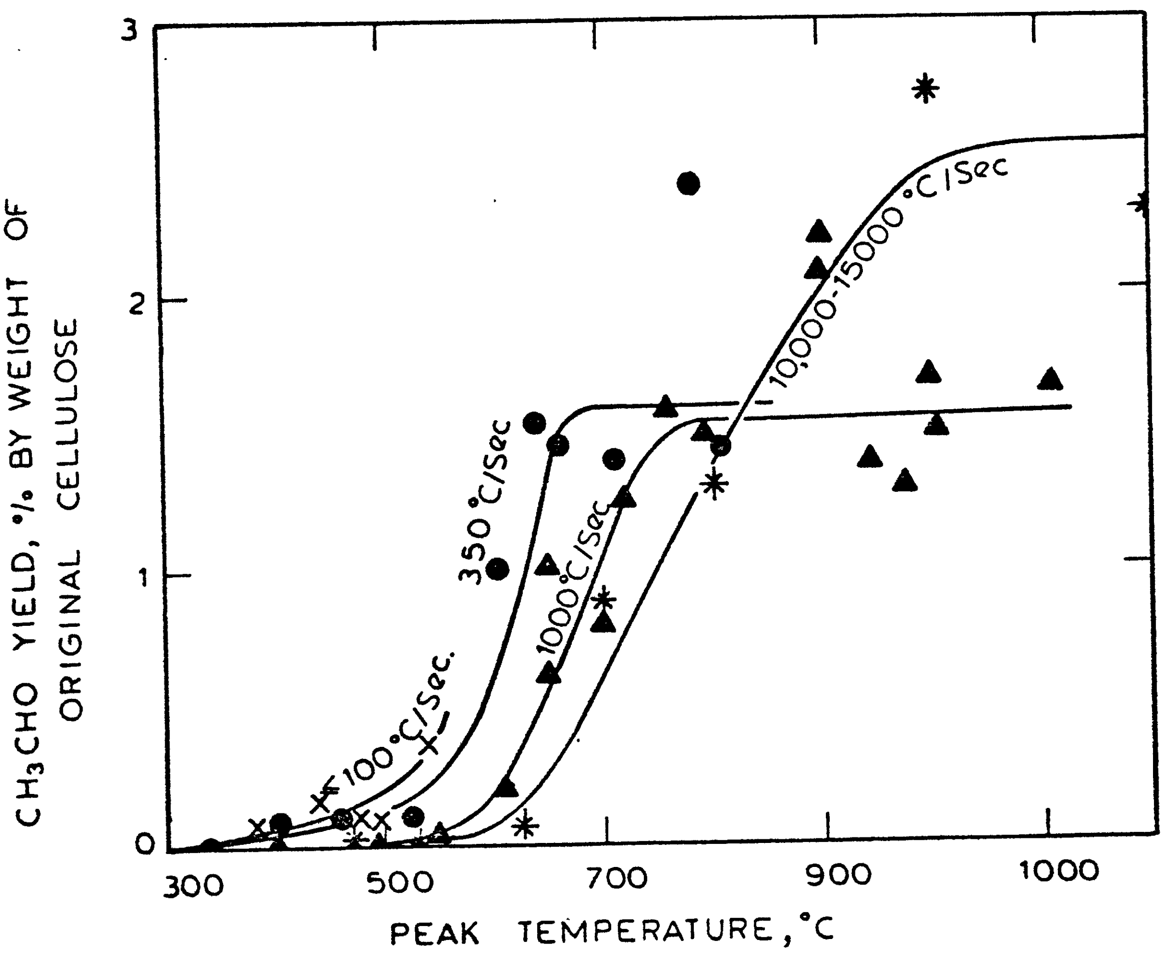


Figure IV.3-11. Effect of Heating Rate on Yields of Acetaldehyde at 5 psig He Pressure.

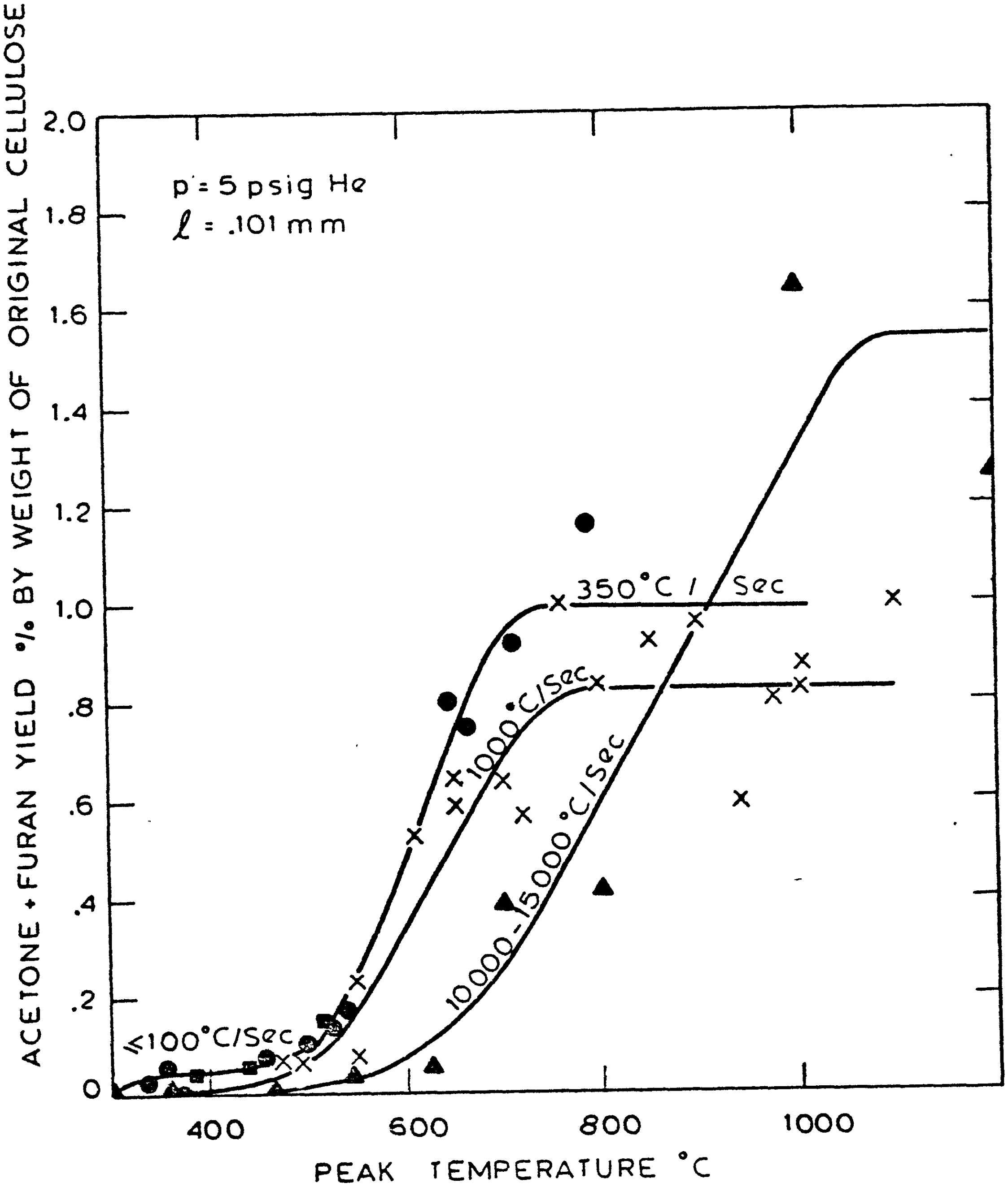


Figure IV.3-12. Effect of Heating Rate on Yields of Acetone+ Furan at 5 psig He Pressure.

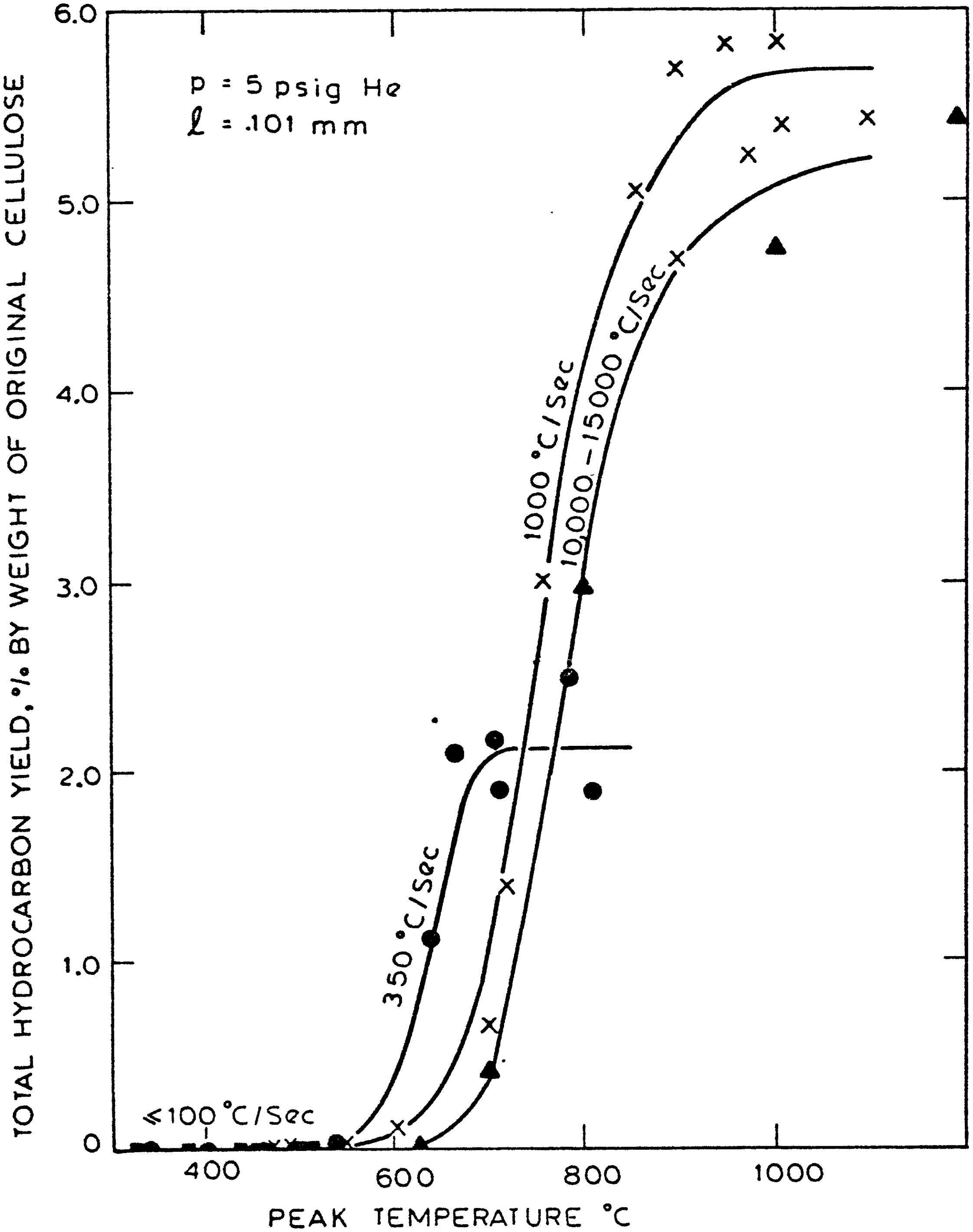


Figure IV.3-13. Effect of Heating Rate on Yields of Total Hydrocarbon Gases at 5 psig He Pressure.

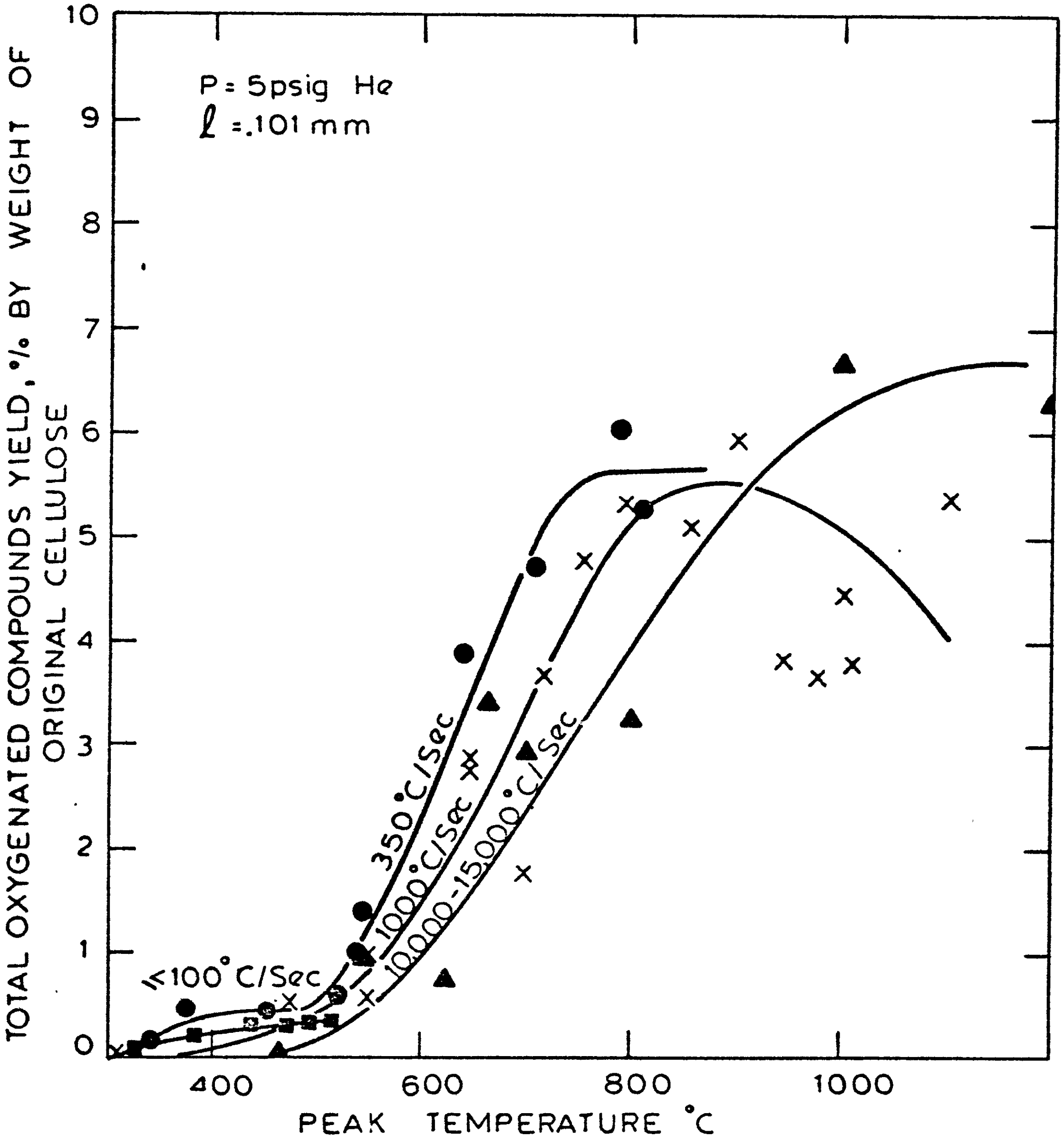


Figure IV.3-14. Effect of Heating Rate on Yields of Total Oxygenated Volatiles at 5 psig He Pressure.

runs with zero holding time, it is reasonable to see a maximum for the gases at 1000 deg C/sec.

IV.4. Effect of Pressure

In order to study the effect of pressure on cellulose decomposition, tar production and cracking, and product yields, several experiments were performed at vacuum, 5psig He, and 1000psig He. The experiments at vacuum were performed for heating rates of 350 deg C/sec and 1000 deg C/sec, while the experiments at 1000 psig He were done at 1000 deg C/sec. These experiments also shed some light on the question of whether products come from the direct decomposition of cellulose, or through the cracking of some intermediates, here referred to as tar. What increasing or decreasing the pressure actually does is decrease or increase the rate of evaporation, or mass transfer, of products from the reaction zone. The results obtained in these experiments are shown in Figures IV.4.1-1, through IV.4.1-7 and IV.4.2-1 through IV.4.2-17.

A decrease in pressure to vacuum (0.10mmHg), at 350 deg C/sec, has no effect on the total decomposition of cellulose (Figure IV.4.1-1). This causes an increase in tar yield at higher temperatures (Figure IV.4.1-2), while a proportional decrease occurs in the total gas yield (Figure IV.4.1-3). This shows that, at this heating rate, the predominant effect is on the secondary reactions of the tar. By decreasing the pressure, the tar can more easily escape the reaction zone through

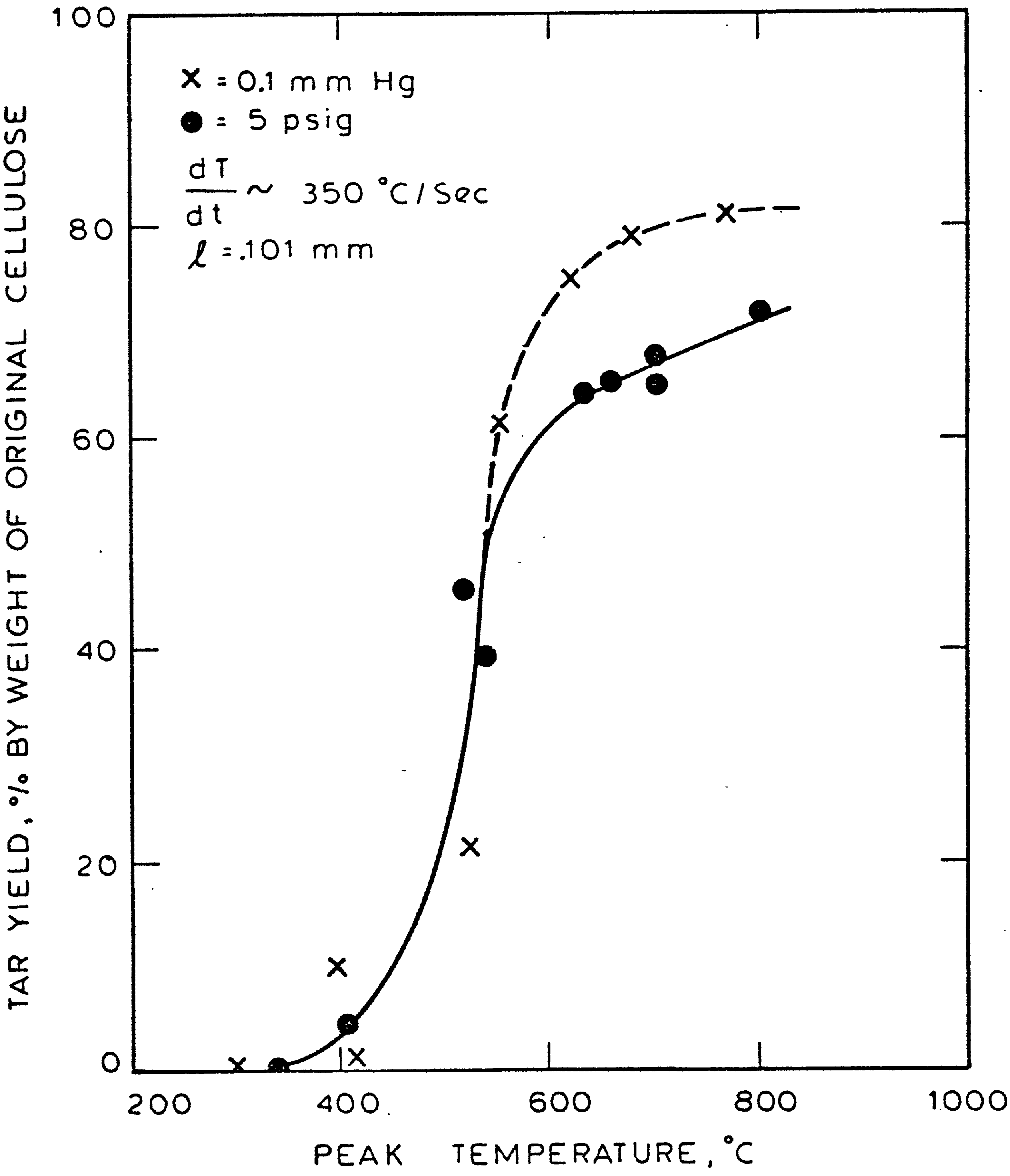


Figure IV.4.1-1.Effect of Pressure on Yields of Tar at 350°C/S Heating Rate.

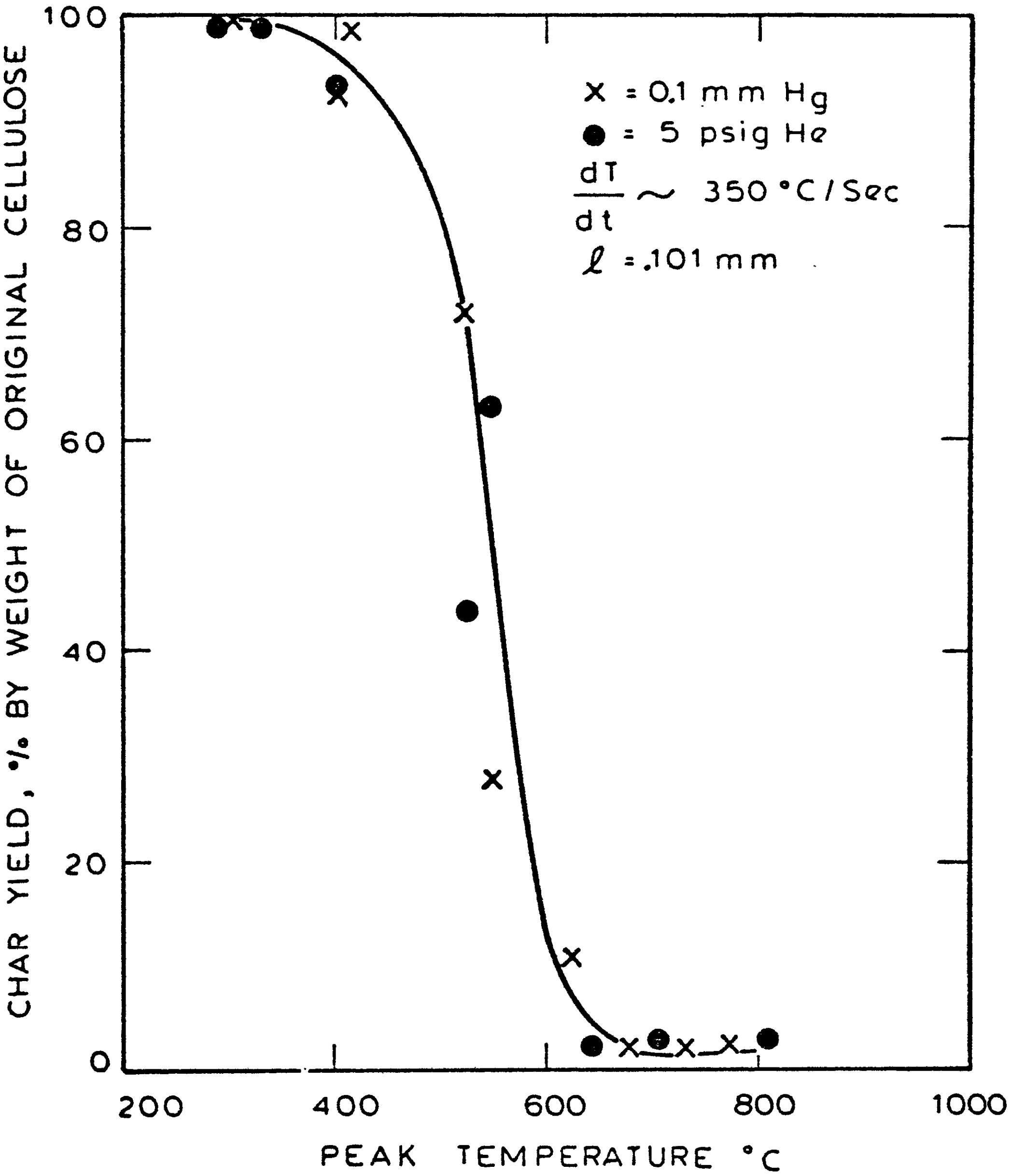


Figure IV.4.1-2. Effect of Pressure on Yields of Char at 350°C/S Heating Rate.

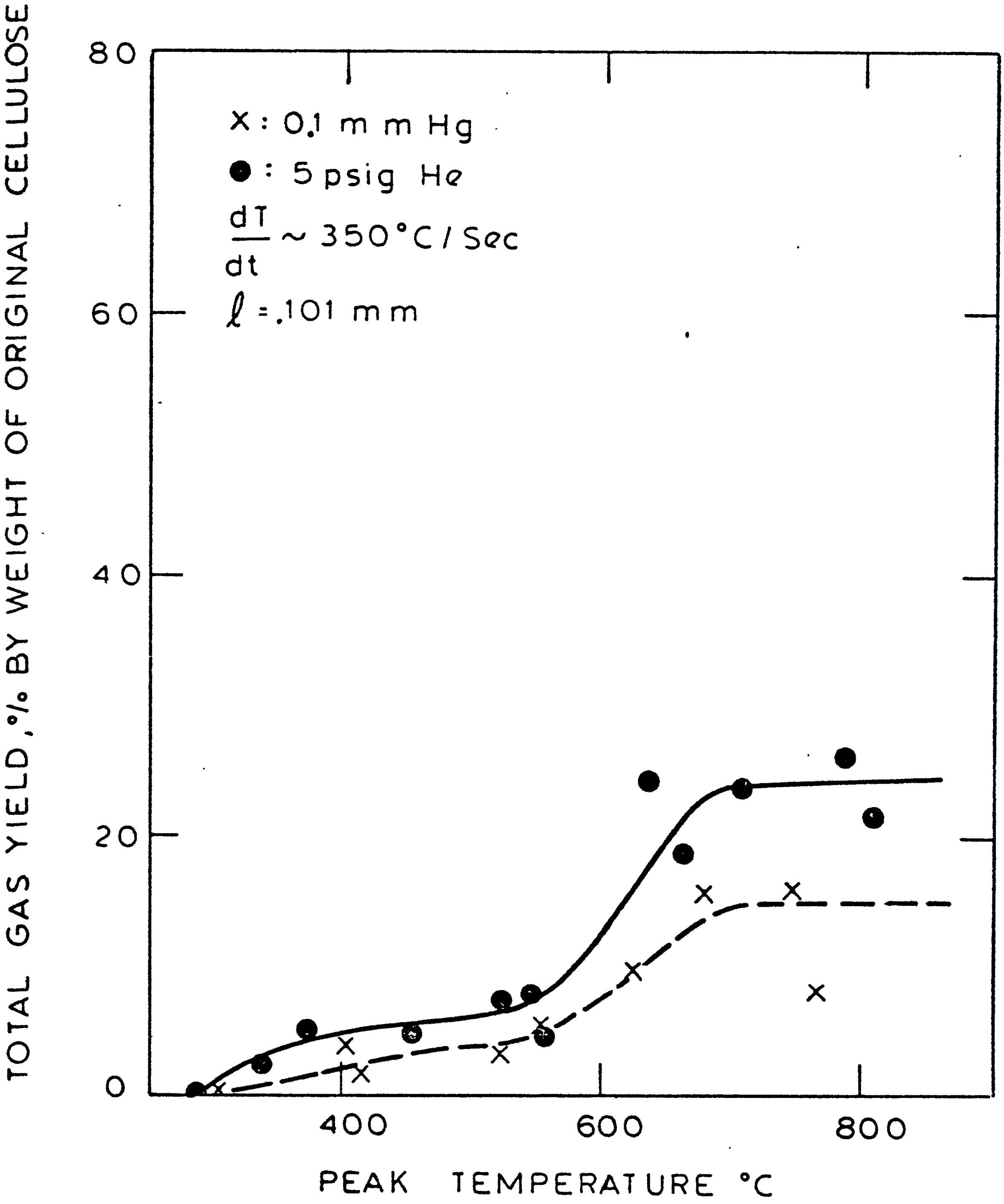


Figure IV.4.1-3. Effect of Pressure on Yields of Total Gases at 350°C/S Heating Rate.

evaporation, and avoid secondary reactions.

The effect of vacuum is not significant on water yield (Figure IV.4.1-5) and less significant for carbon dioxide yield (Figure IV.4.1-5). It has a very important effect, however, on the yields of the other products. This indicates that the rest of the products come mostly from the secondary reactions of tar. Oxygenated products increase more or less linearly with temperature at vacuum, but attain smaller asymptote yields than at 5psig He (Figures IV.4.1-6 and IV.4.1-7). Yields of hydrocarbons and carbon monoxide, are also lower in vacuum than at 5psig He (Figures IV.4.1-4 and IV.4.1-5).

Experiments at 1000 deg C/sec for 0.1 mmHg, and 5psig He follow the same trends as the results for 350 deg C/sec. Figure IV.4.2-2 shows that as pressure decreases from 5psig He, the tar yield at high temperature increases, while increasing pressure to 1000psig He, decreases tar yield. Char yield is higher at 1000psig He than at 5psig He. This is because more of the tar, which is produced, participates in coke formation reactions. At the same time, decreasing the pressure from 5psig to vacuum causes an increase in char yield at high temperature (Figure IV.4.2-1).

Since, at vacuum, tar decomposition is diminished, the gas yield drops sharply. At high pressure, where more tar cracking occurs, the total gas yield is higher (Figure IV.4.2-3). Results at vacuum show that, at higher temperatures (between 900

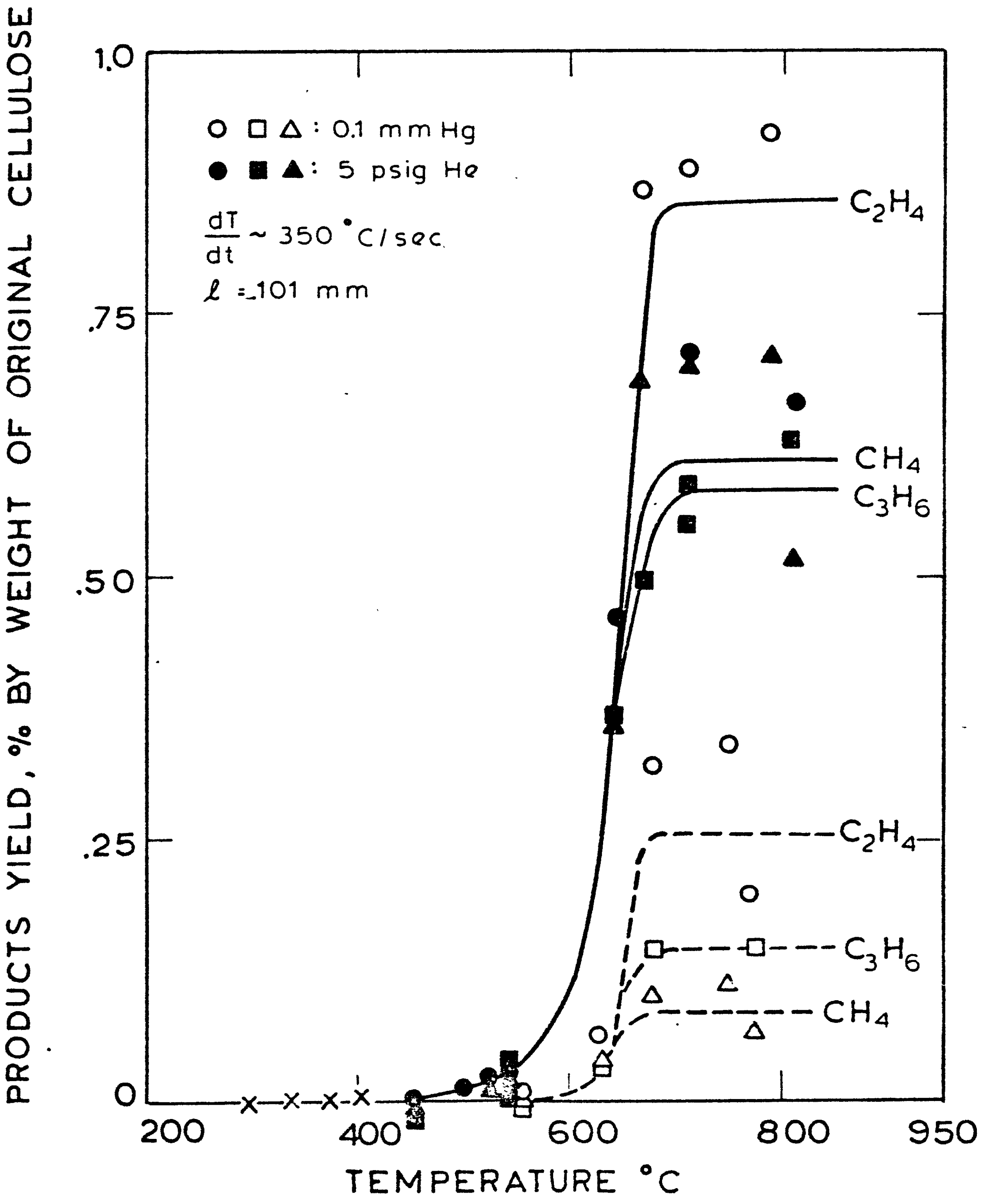


Figure IV.4.1-4. Effect of Pressure on Yields of CH_4, C_2H_4, and C_3H_6 at 350°C/S Heating Rate and Zero Holding Time.

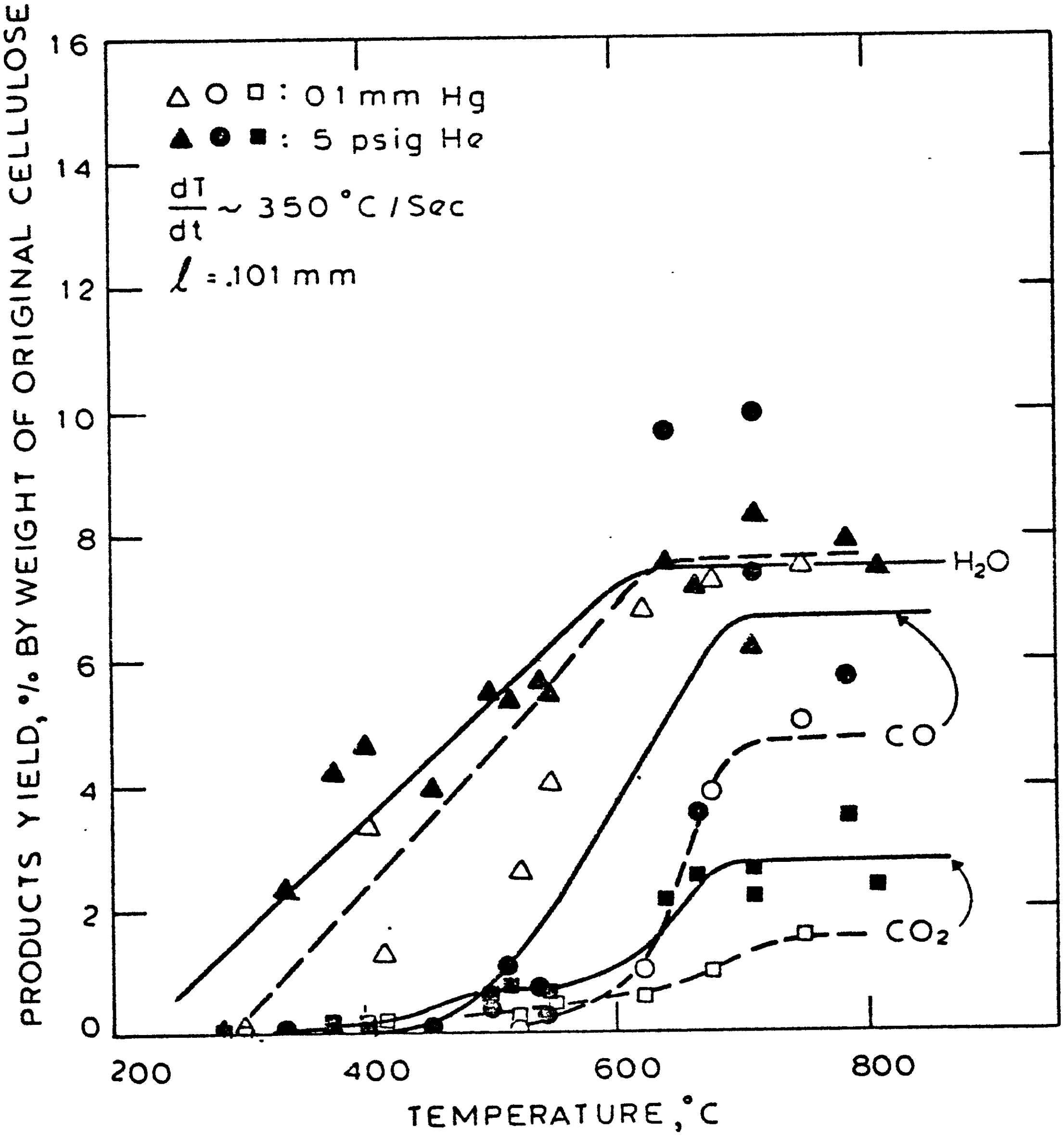


Figure IV.4.1-5. Effect of Pressure on Yields of CO, CO2, and H2O at 350°C/S Heating Rate and Zero Holding Time.

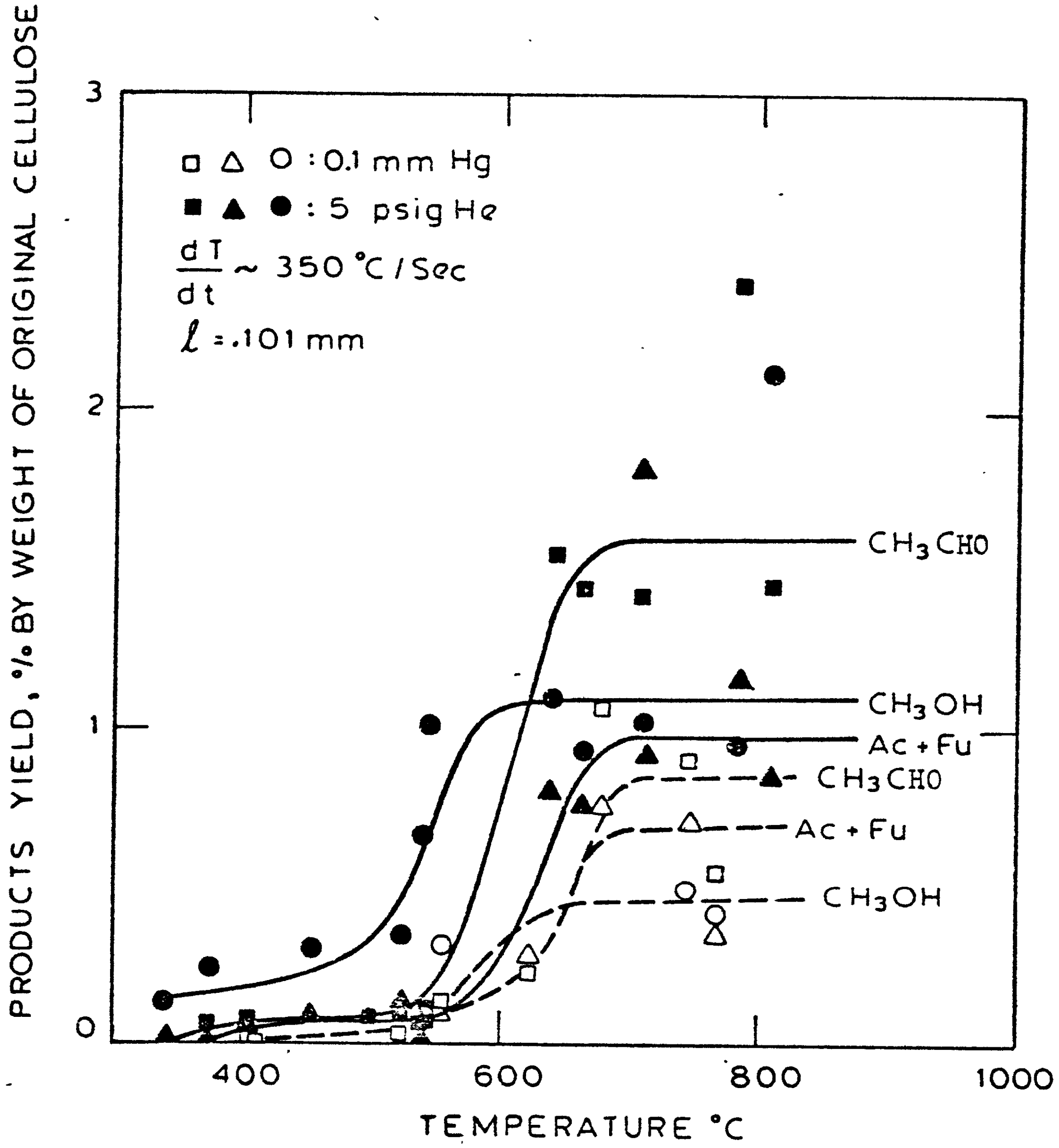


Figure IV.4.1-6. Effect of Pressure on Yields of Methanol, Acetaldehyde, and Acetone/Furan Mixture at 350°C/S Heating Rate and Zero Holding Time.

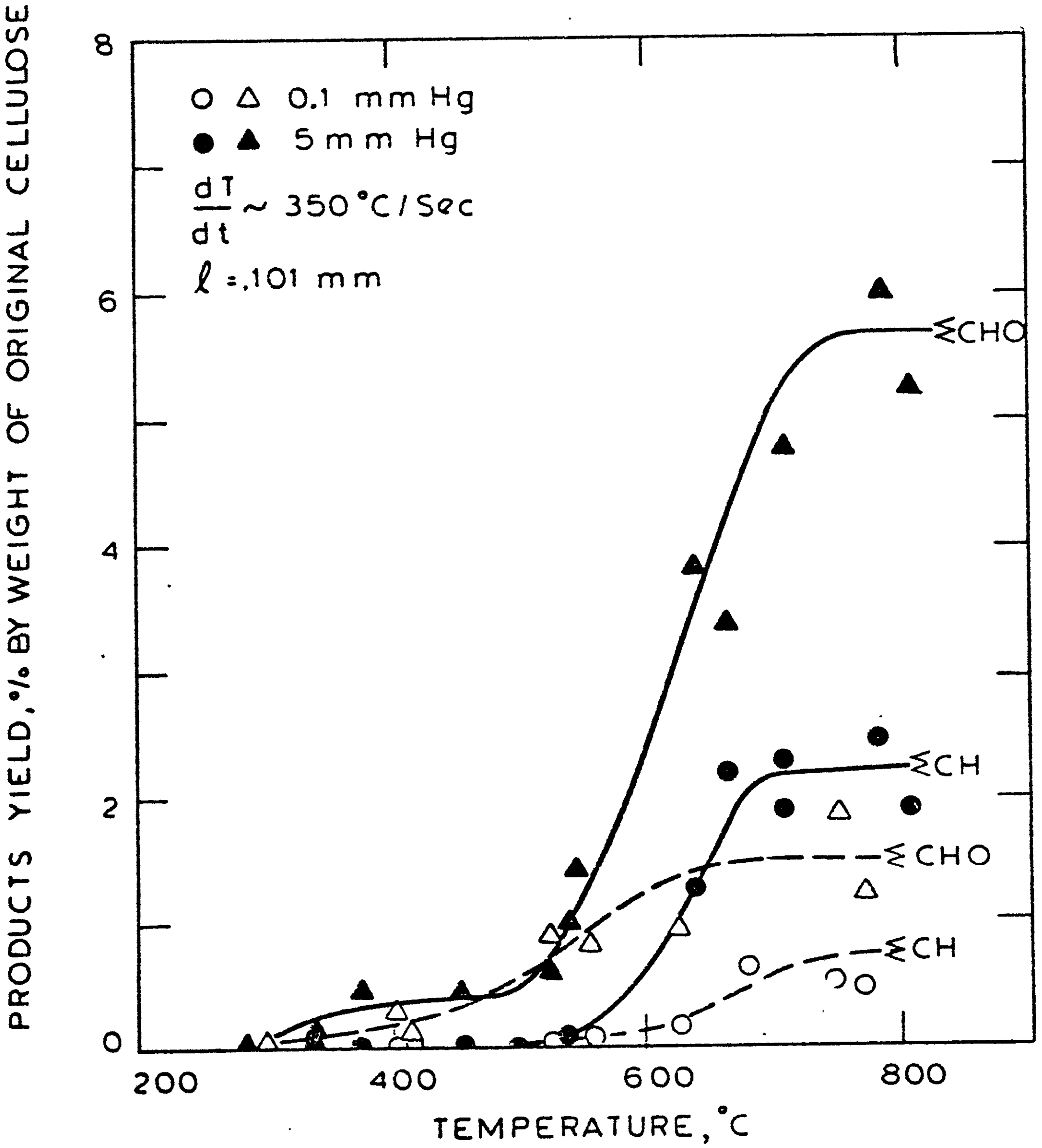


Figure IV.4.1-7. Effect of Pressure on Yields of Total Hydrocarbon Gases and Oxygenated Volatiles at 350°C/S Heating Rate and Zero Second Holding Time.

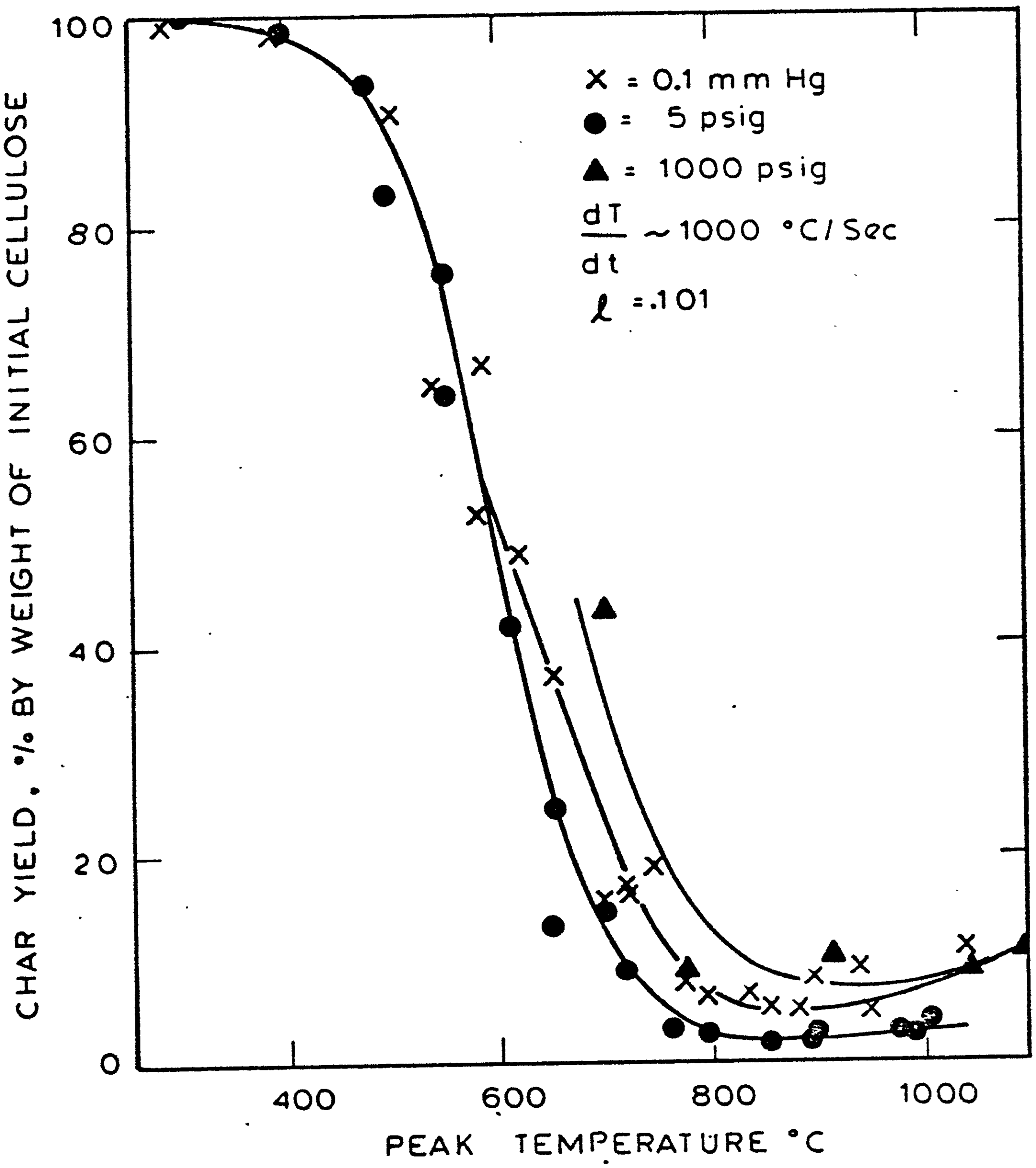


Figure IV.4.2-1. Effect of Pressure on Yields of Char at 1000°C/S Heating Rate.

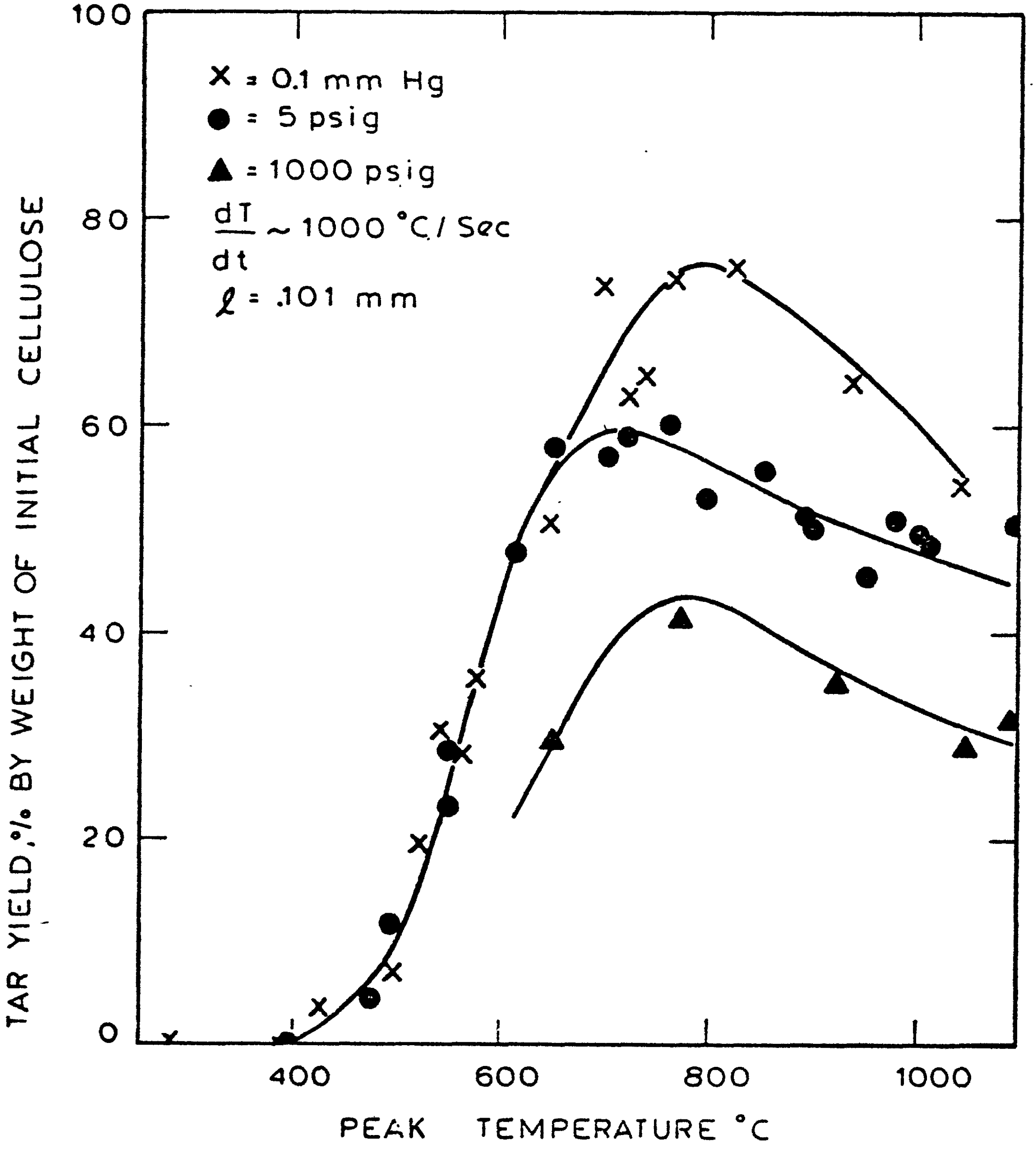


Figure IV.4.2-2. Effect of Pressure on Yields of Tar at 1000°C/S Heating Rate.

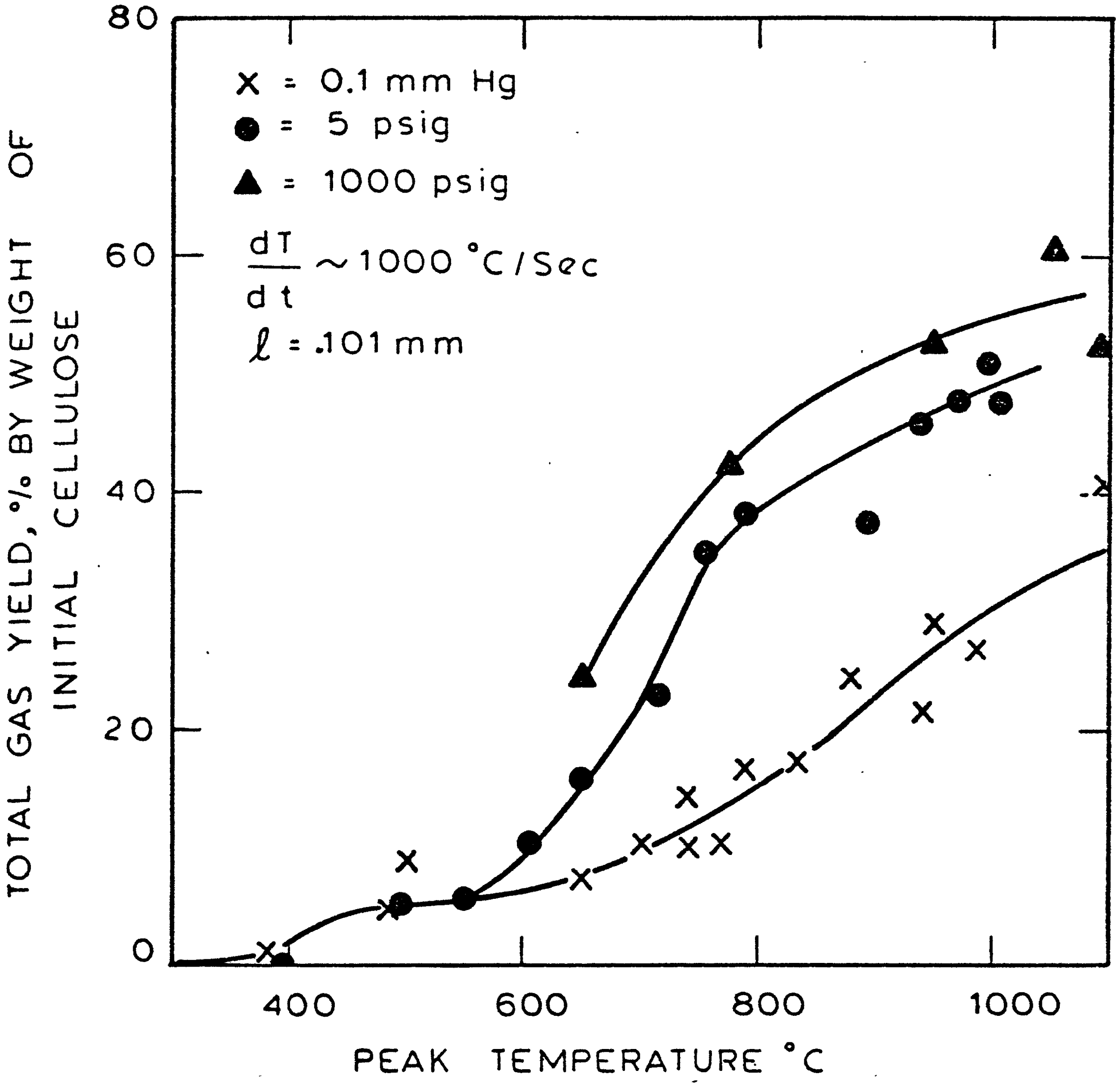


Figure IV.4.2-3. Effect of Pressure on Yields of Total Gases at 1000°C/S Heating Rate.

and 1000 deg C), where tar cracking becomes more important, even at zero holding time, the slope of the total gas yield curve increases.

The results from individual species are another indication that the gases are products of the secondary reactions of tar, rather than the direct decomposition of cellulose. Except for the oxygenated products such as acetaldehyde, methanol, acetone, and furan, which go through a maximum, most of the products increase with pressure. The behavior of oxygenated products show that they are not only products of tar decomposition, but function as intermediates for hydrogen, hydrocarbon gases, carbon monoxide, and carbon dioxide production. A decrease in the yield of ethylene with increasing pressure from 5psig He to 1000psig He could be attributed to either cracking of the ethylene, or through the increasing dominance of another mechanism which becomes more important at high pressures, in which ethylene is not produced. Another possibility is that the smaller volume of the high pressure apparatus (one tenth the volume of the low pressure apparatus) could have an effect on the ethylene yield, perhaps by changing the rates of free convection, and hence, of mass transfer of primary products near the screen. The effect of the apparatus on pyrolysis has been reported in an extensive review by Anthony and Howard (99). The present data also shows a decrease in the carbon monoxide yield with increasing pressure from 5psig He to 1000 psig He. This could again be partially attributed to reactor size, and partially because of some

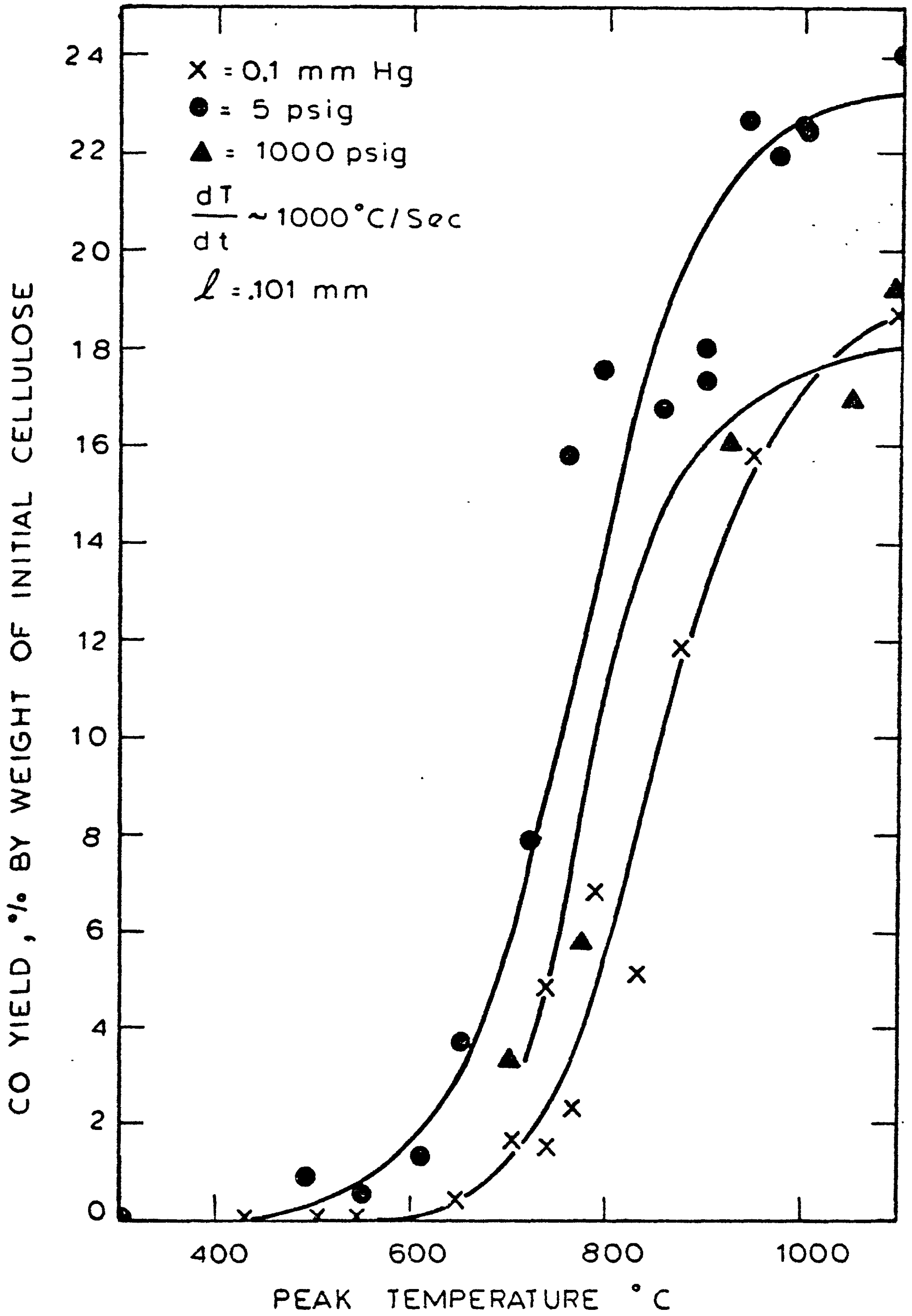


Figure IV.4.2-4. Effect of Pressure on Yields of CO at 1000°C/S Heating Rate.

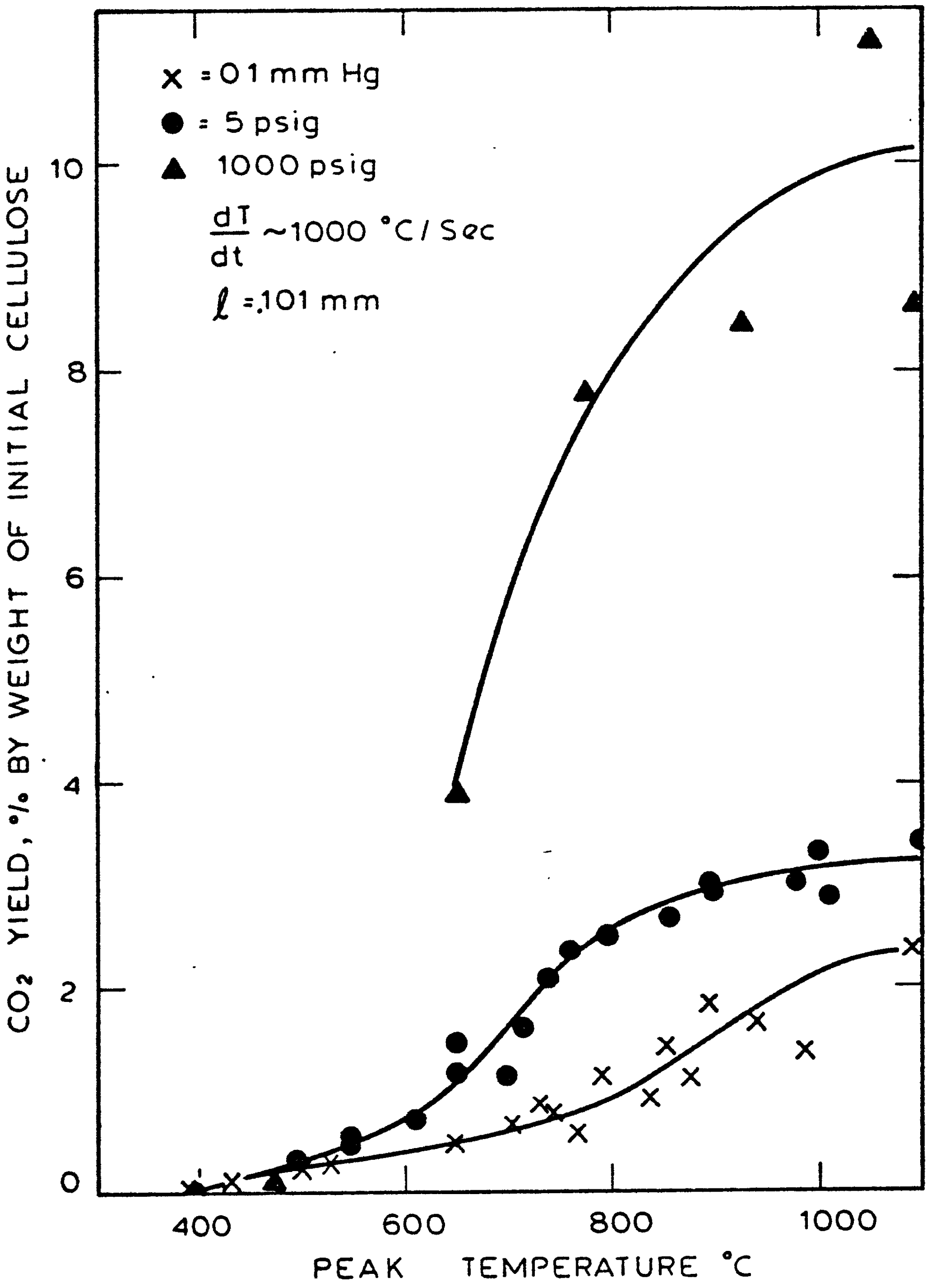


Figure IV.4.2-5. Effect of Pressure on Yields of CO2 at 1000°C/S Heating Rate.

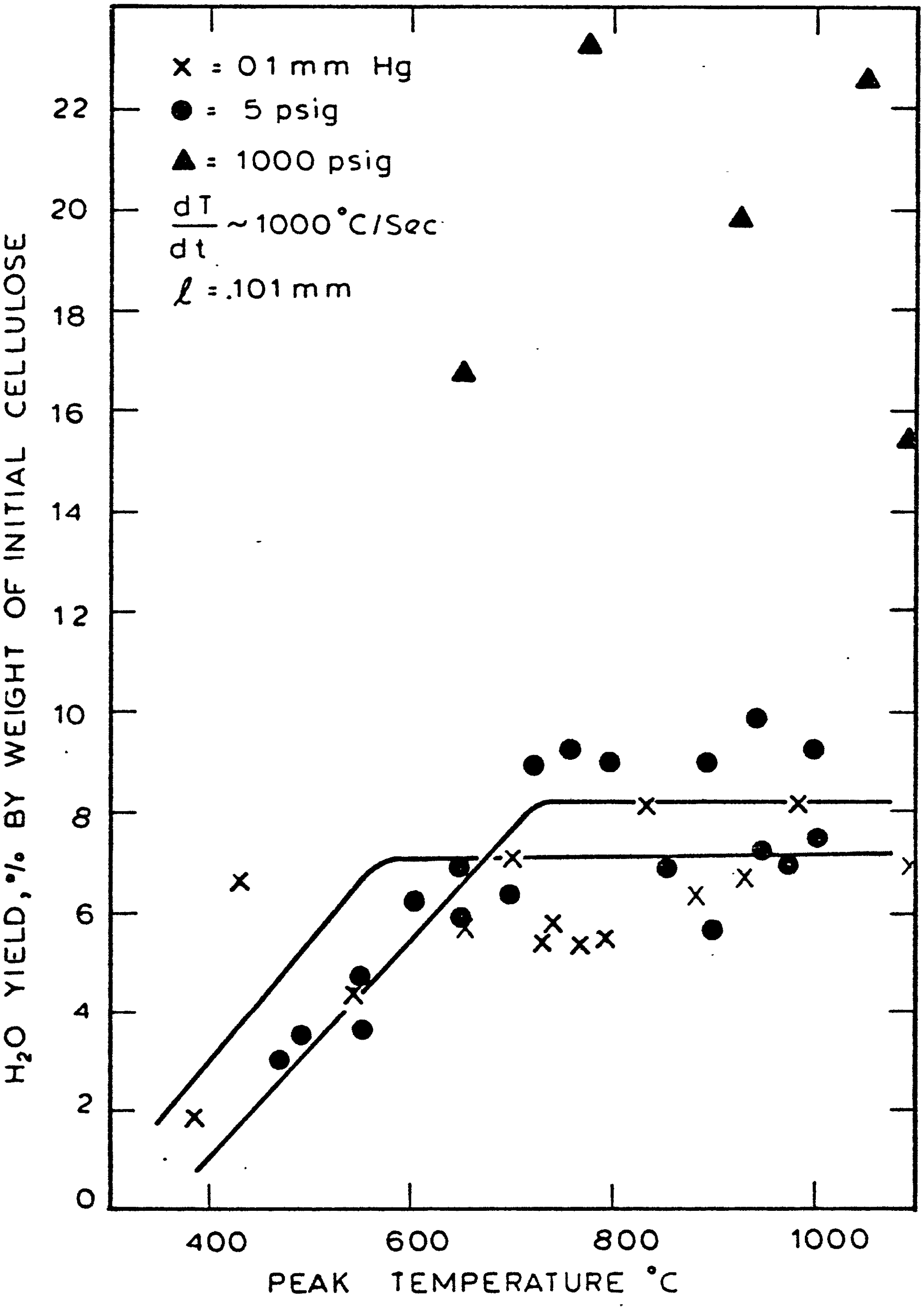


Figure IV.4.2-6. Effect of Pressure on Yields of H20 at 1000°C/S Heating Rate.

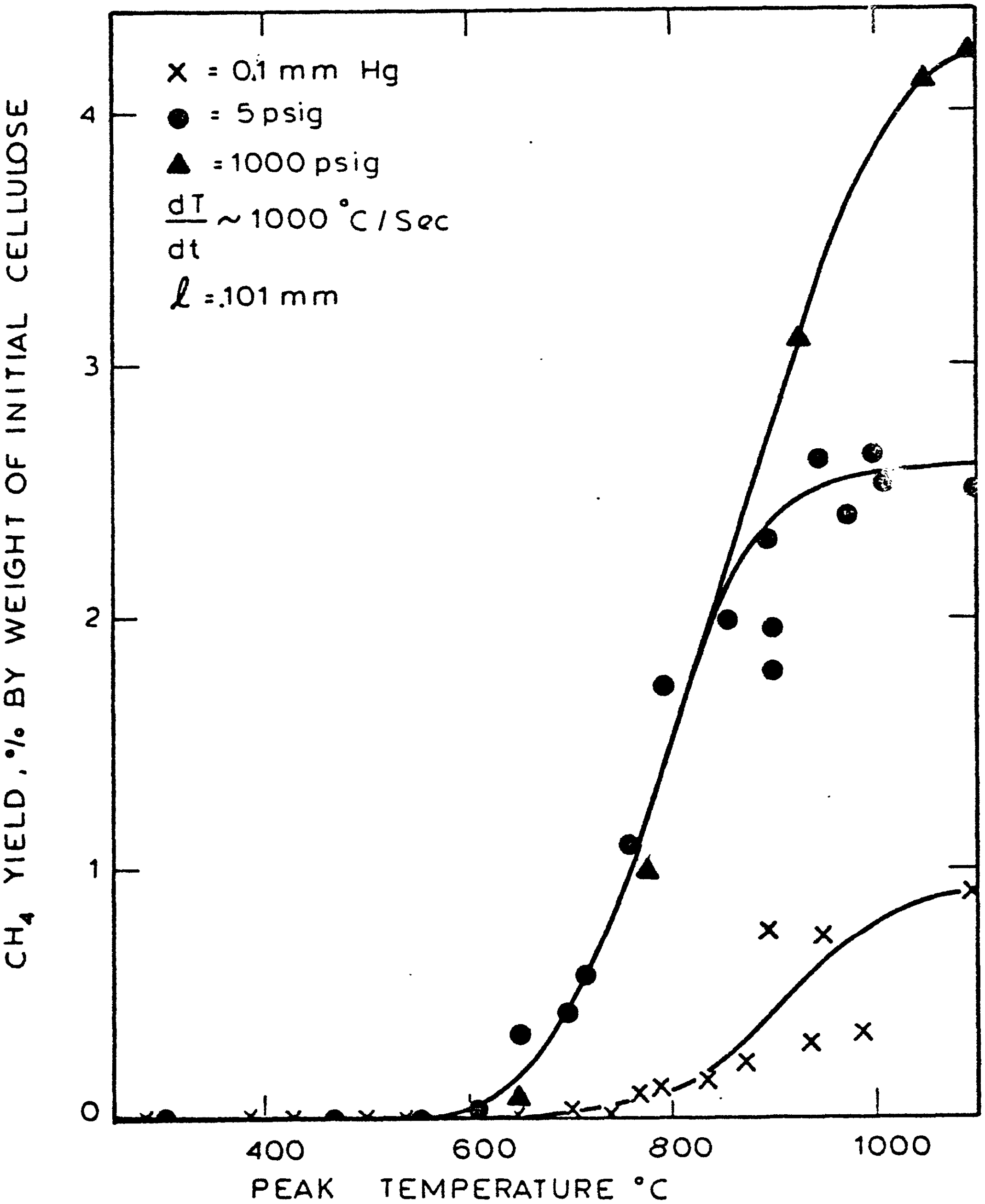


Figure IV.4.2-7. Effect of Pressure on Yields of CH_4 at 1000°C/S Heating Rate.

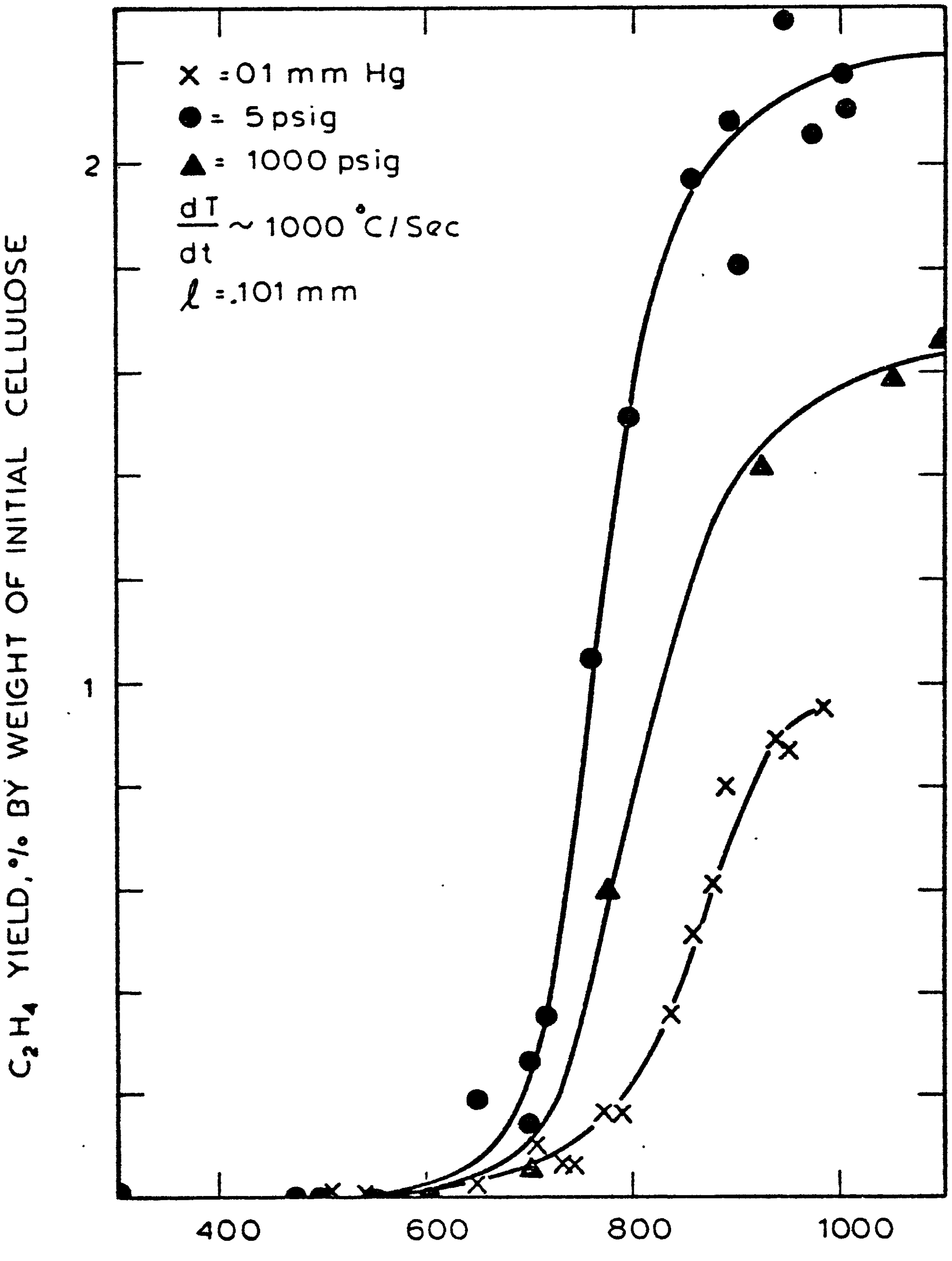


Figure IV.4.2-8. Effect of Pressure on Yields of C2H4 at 1000°C/S Heating R^A^te.

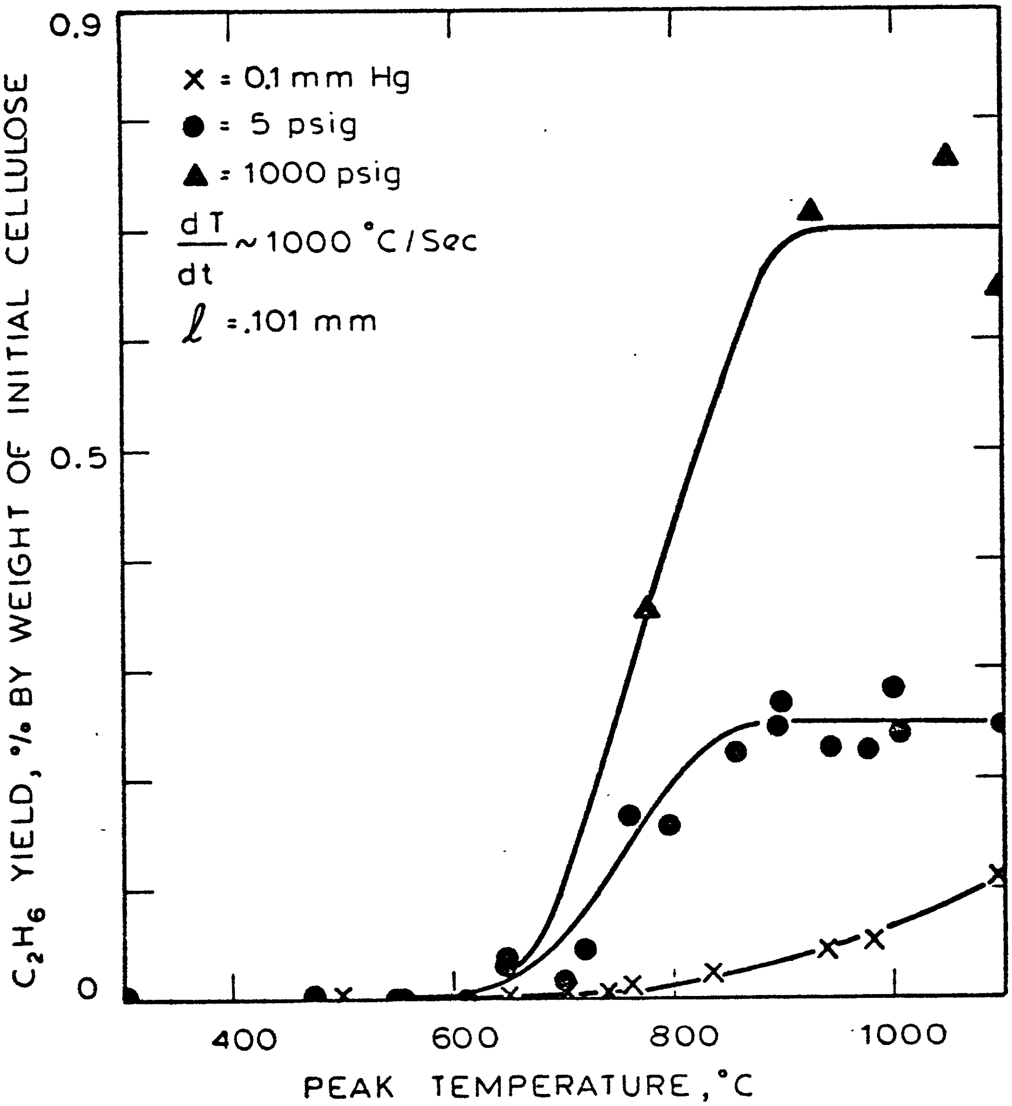


Figure IV.4.2-9. Effect of Pressure on Yields of C2H6 at 1000°C/S Heating Rate.

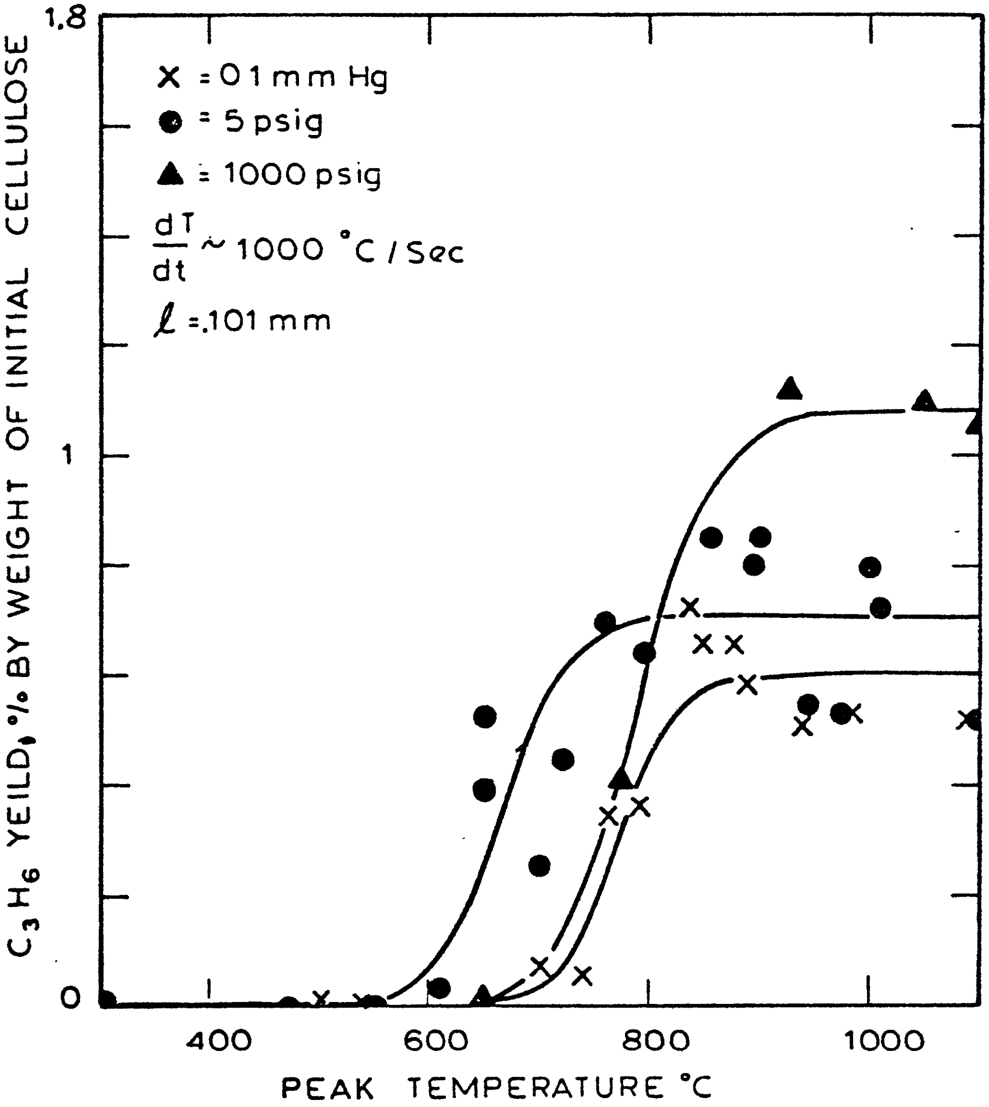


Figure IV.4.2-10. Effect of Pressure on Yields of C3H6 at 1000°C/S Heating Rate.

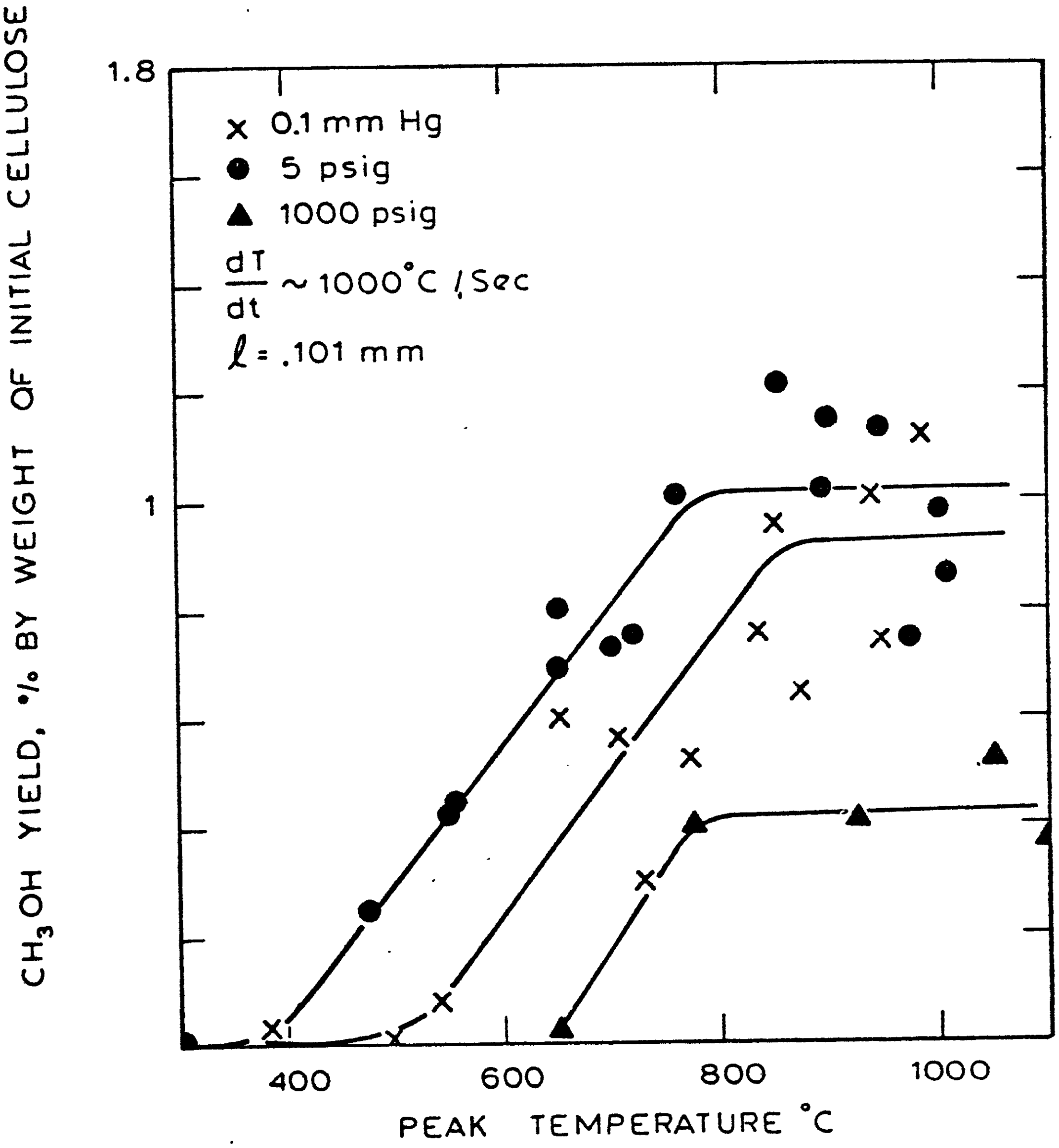


Figure IV.4.2-11. Effect of Pressure on Yields of Methanol at 1000°C/S Heating Rate.

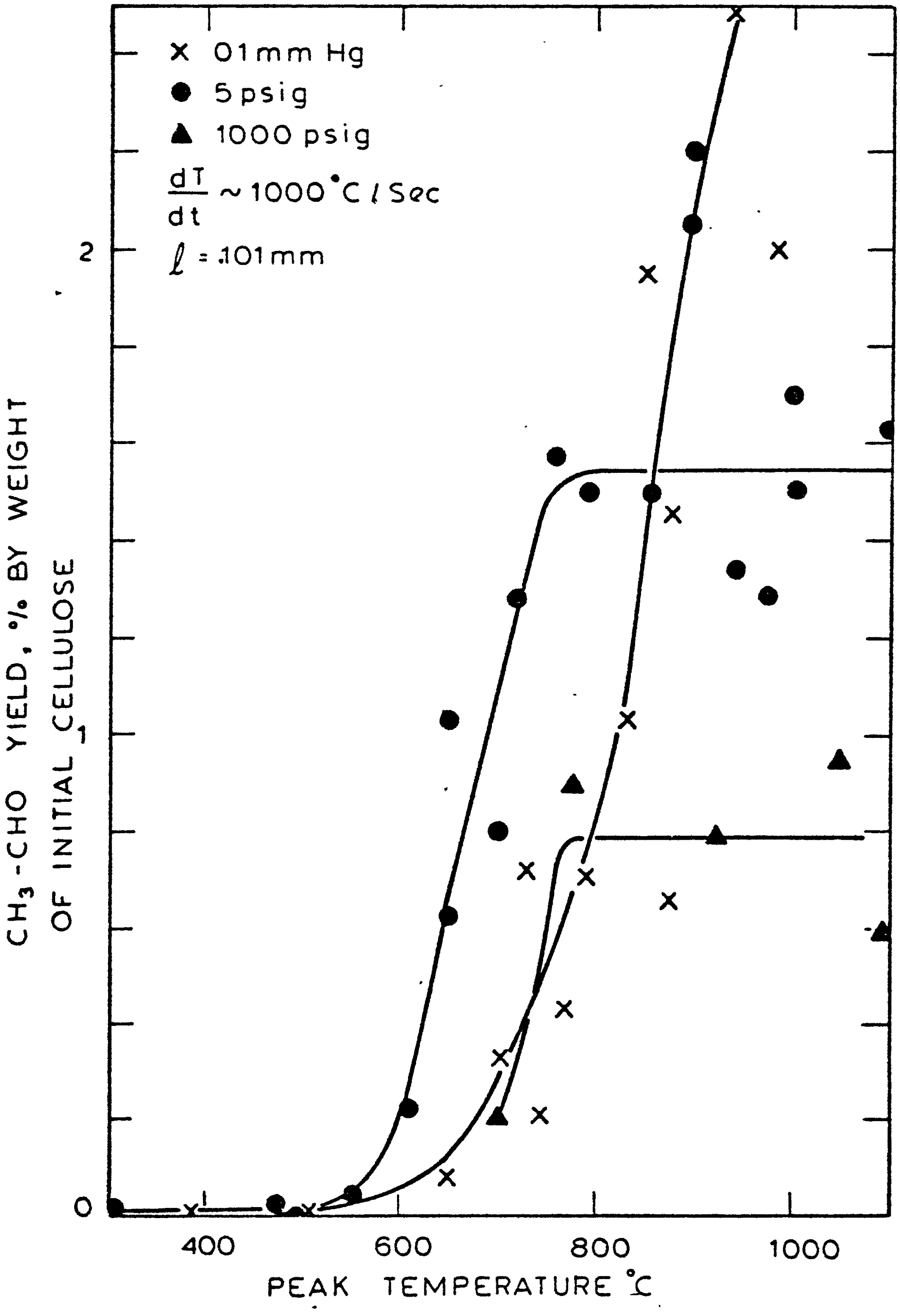


Figure IV.4.2-12. Effect of Pressure on Yields of Acetaldehyde at 1000°C/S Heating Rate.

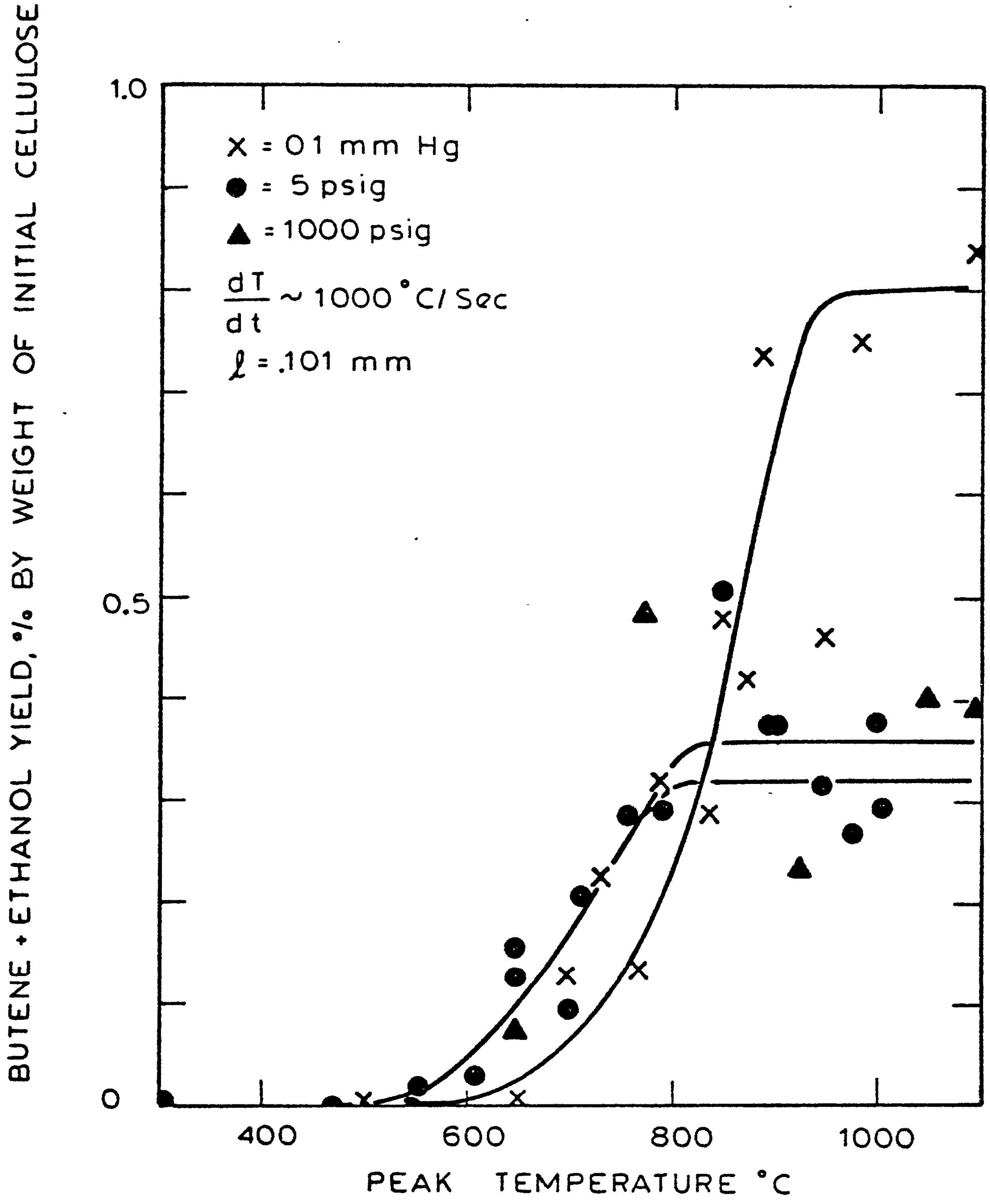


Figure IV.4.2-13. Effect of Pressure on Yields of Butene + Ethanol at 1000°C/S Heating Rate.

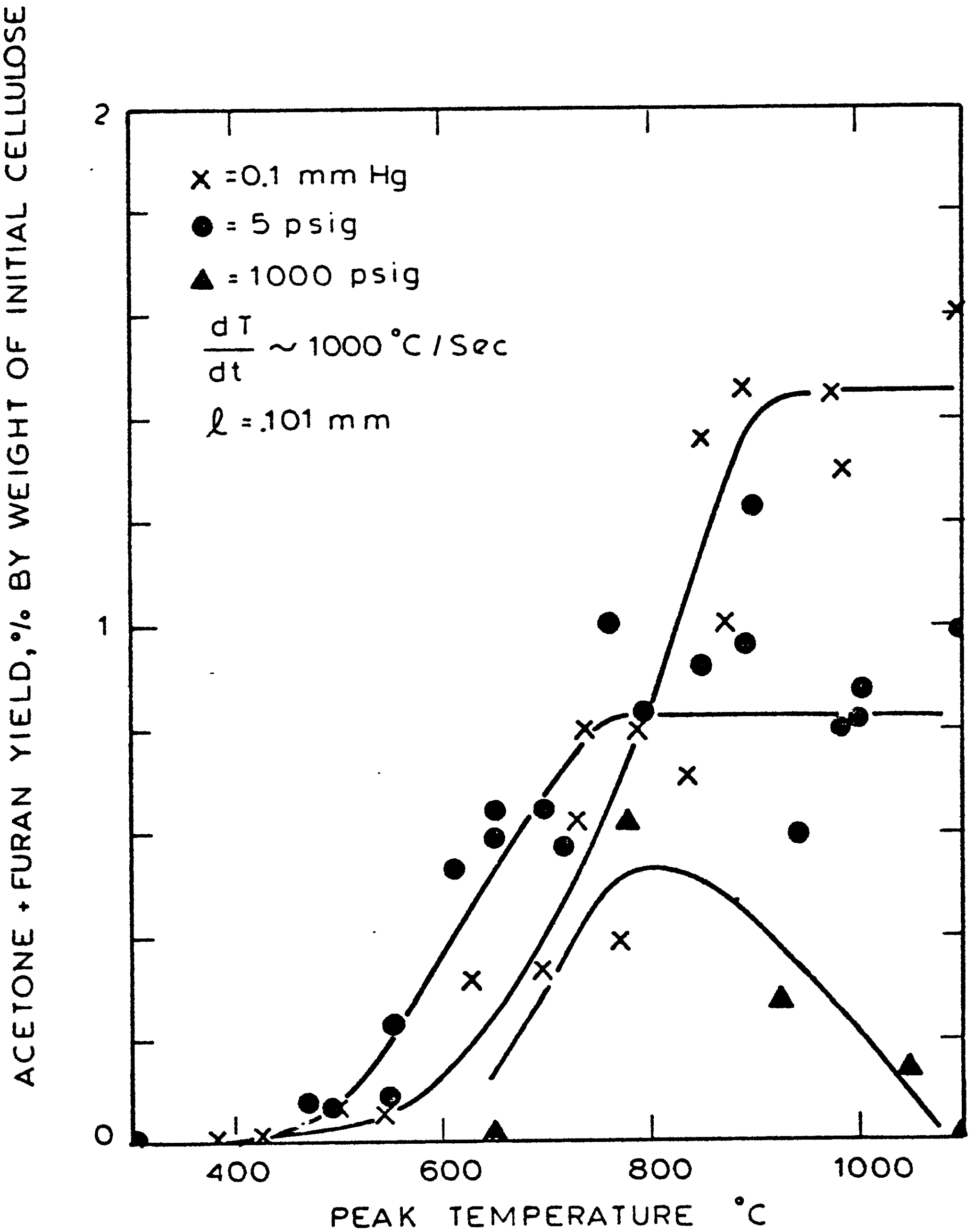


Figure IV.4.2-14. Effect of Pressure on Yields of Acetone + Furan at 1000°C/S Heating Rate.

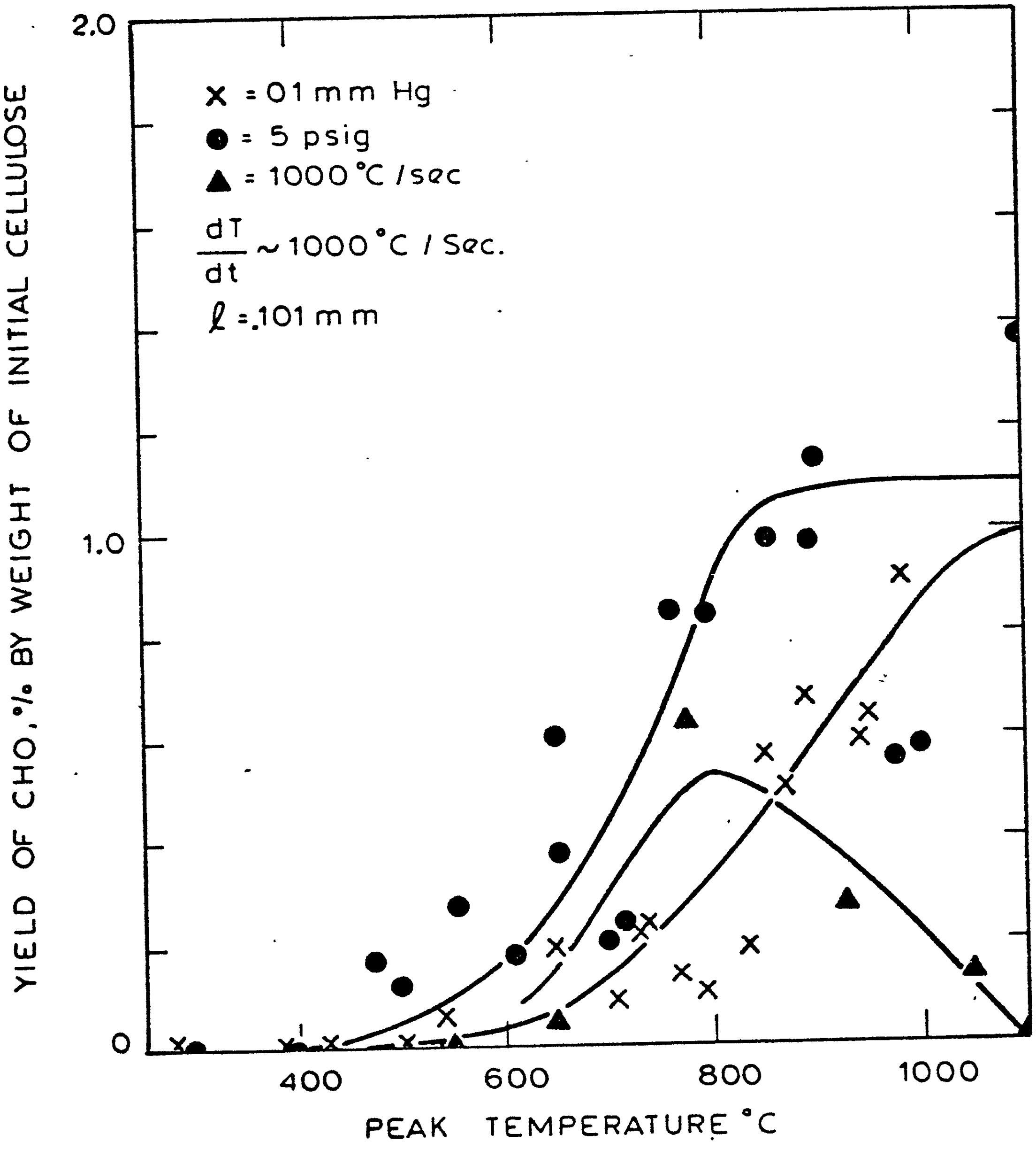


Figure IV.4.2-15. Effect of Pressure on Yields of CHO (Mainly Acetic Acid) at 1000°C/S Heating Rate.

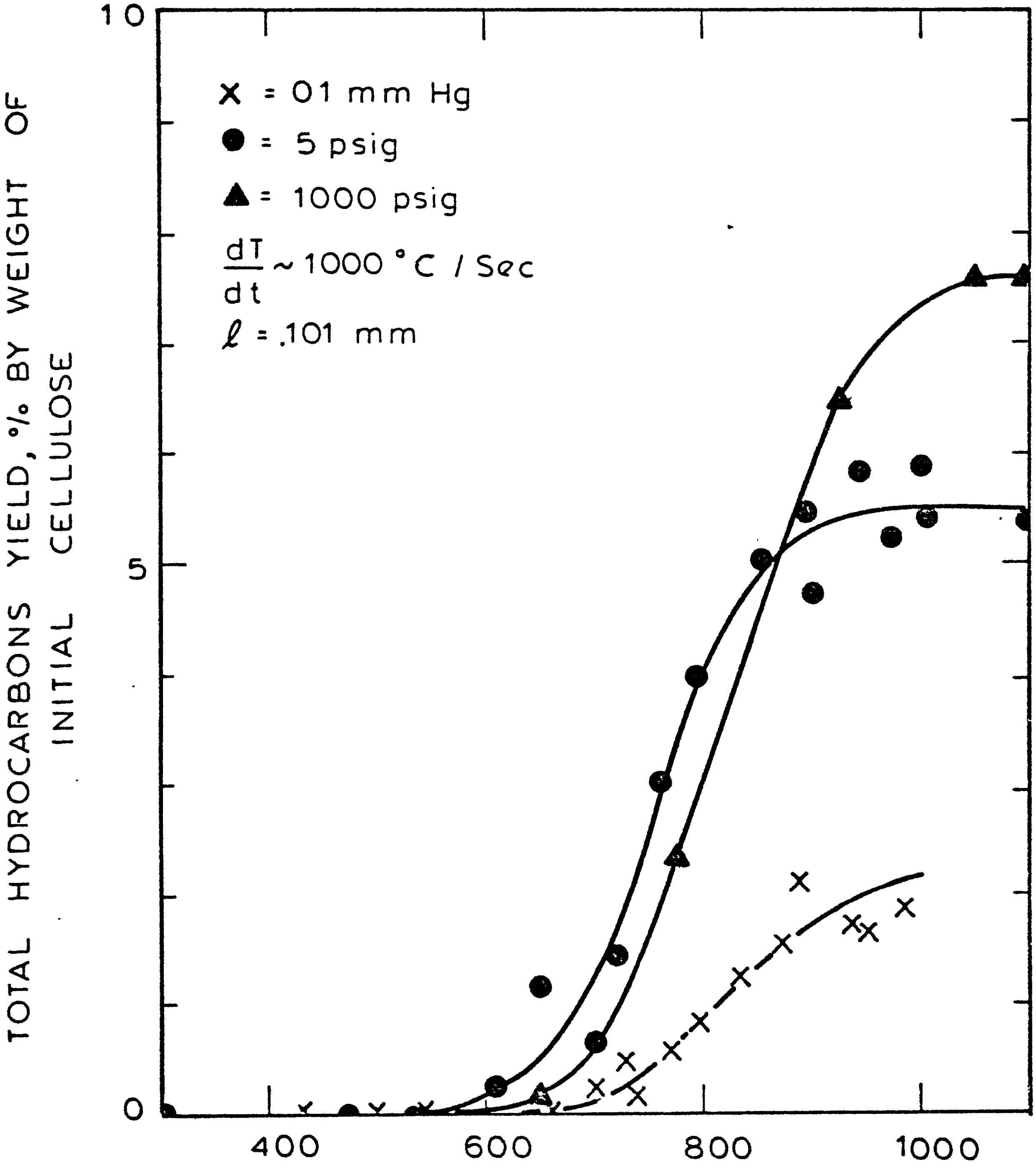


Figure IV.4.2-16. Effect of Pressure on Yields of Total Hydrocarbon Gases at 1000°C/S Heating Rate.

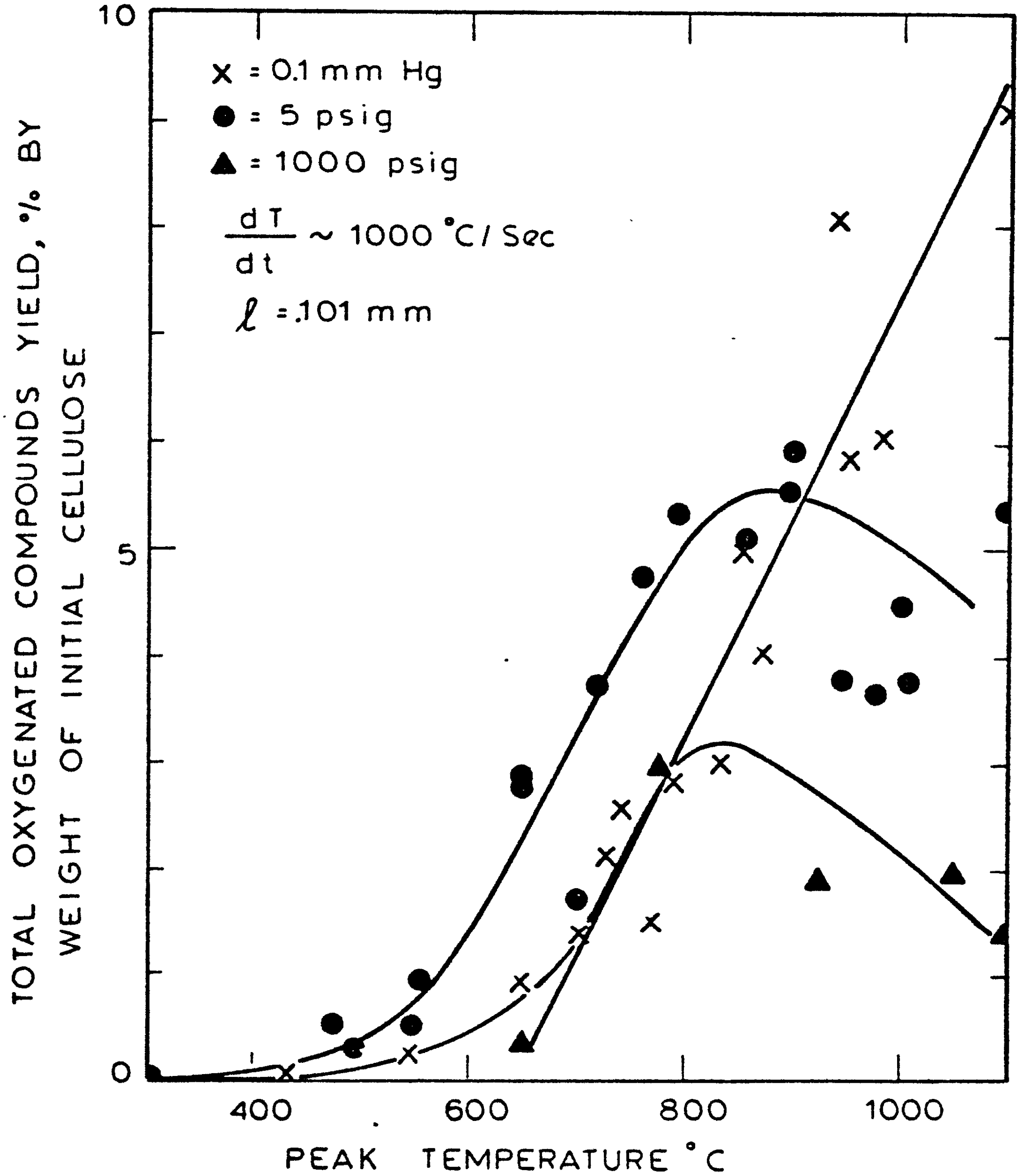


Figure IV.4.2-17. Effect of Pressure on Yields of Total Oxygnated Volatiles at 1000°C/S Heating Rate.

reactions such as:

$$C + 2H2O \underset{2}{\overset{1}{\rightleftarrows}} 2H2 + CO2$$

$$C + H2O \rightleftarrows CO + H2$$

$$C + CO2 \rightleftarrows 2CO$$

It is clear that as pressure increases in a chemical reaction, the laws of equilibrium force the reaction to go to the left to diminish the effect of pressure from the equation:

$$k_{eq.} = \frac{k_1}{k_2} \alpha \frac{1}{P_{total}}$$

Which states that as pressures increase, the reaction goes to the left.

IV.5. The Effect of Sample Size

To determine how valid the assumption of an isothermal temperature gradient across the cellulose sample is, a series of experiments were carried out changing sample thickness and changing sample quantity. These experiments also provided data to determine the importance of intra and extra sample secondary cracking of the tar.

IV.5.1 Sample Thickness

In order to see whether the sample is isothermal under the conditions under study, filter paper #895, Black Ribson S&S, with a thickness of 0.0193cm, and filter paper #589 S&S, with a thickness of 0.040cm was used (in all other runs in this study, the sample thickness is 0.0101cm). A comparison of results from paper #895 (0.0193cm thick) and paper #507 (0.0101cm thick) are presented in Figures IV.5.1-1 through IV.5.1-4. It is obvious from these graphs that doubling the thickness of the sample has no significant effect on the total cellulose decomposition or total yields of tar and volatiles. Apparently, there is no effect on the residence time of the tar within the reaction zone, otherwise, there would be observable differences in the tar and volatile yields.

Increasing the sample thickness to four times by using filter paper #584 (0.040cm thick), has some effect on the results obtained. These results are shown in Figures IV.5.1-1. through IV.5.1-4, and show a 10% to 15% loss in tar yield and a proportional increase in total gas yield. Since the residence time of the tar has increased, more of it is cracked to lower molecular weight species such as carbon monoxide, carbon dioxide, methane, ethylene, water, etc. Although the differences in the yields of individual gases is not very significant, these changes indicate that for a thickness of 0.040cm, the cellulose sample is not isothermal through the cross section. The assumption that the 0.0101cm thick sample is isothermal during the reaction, however, is valid. This result is consistent with the theoretical sample thickness calculated to be isothermal (App. III).

The effect of increasing the residence time of the tar inside the reaction zone was shown in another set of experiments. Samples of paper #507 folded over for double and quadruple

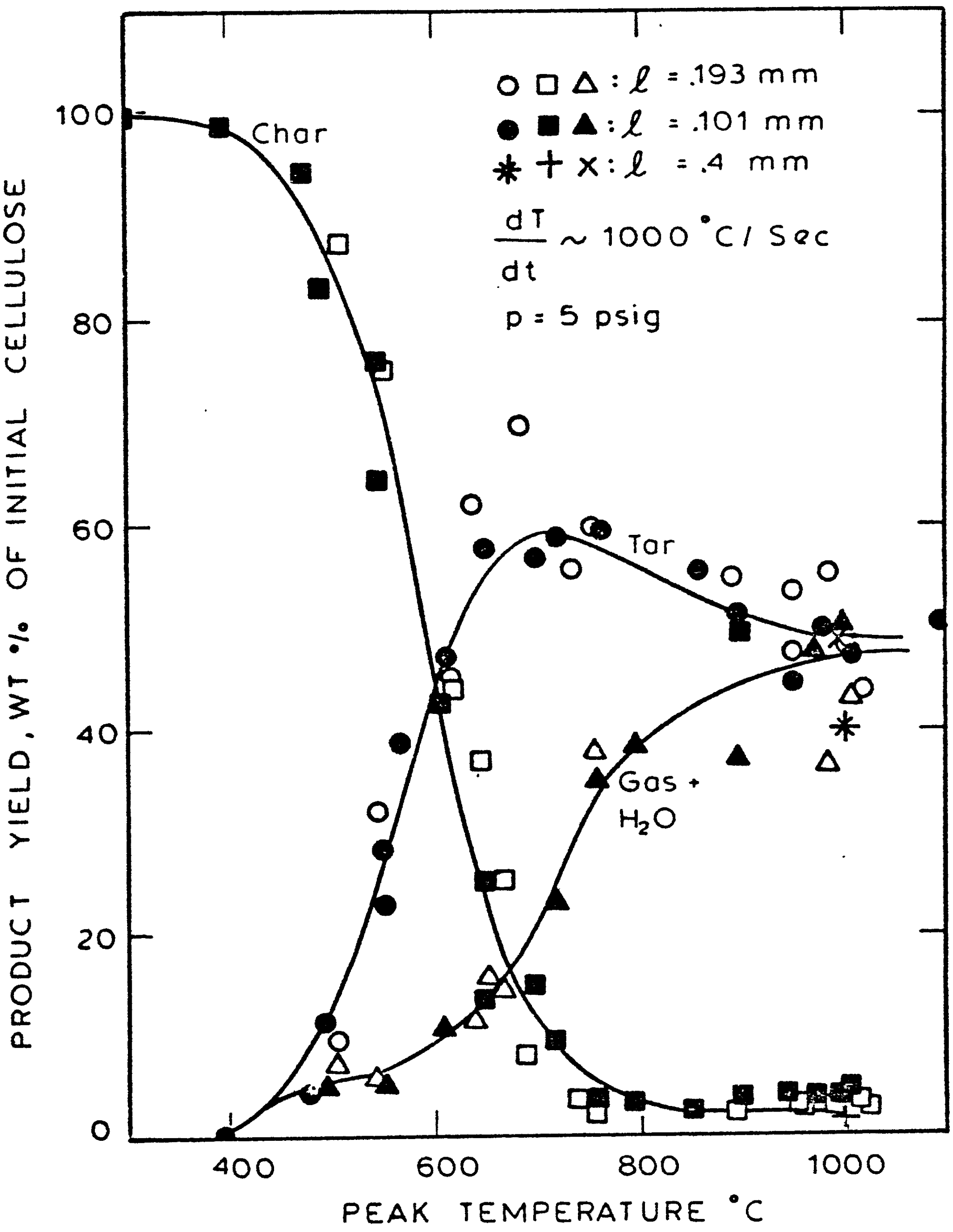


Figure IV.5.1-1. Effect of Sample Thickness on Yields of Char, Tar, and Total Gases at 5 psig He Pressure.

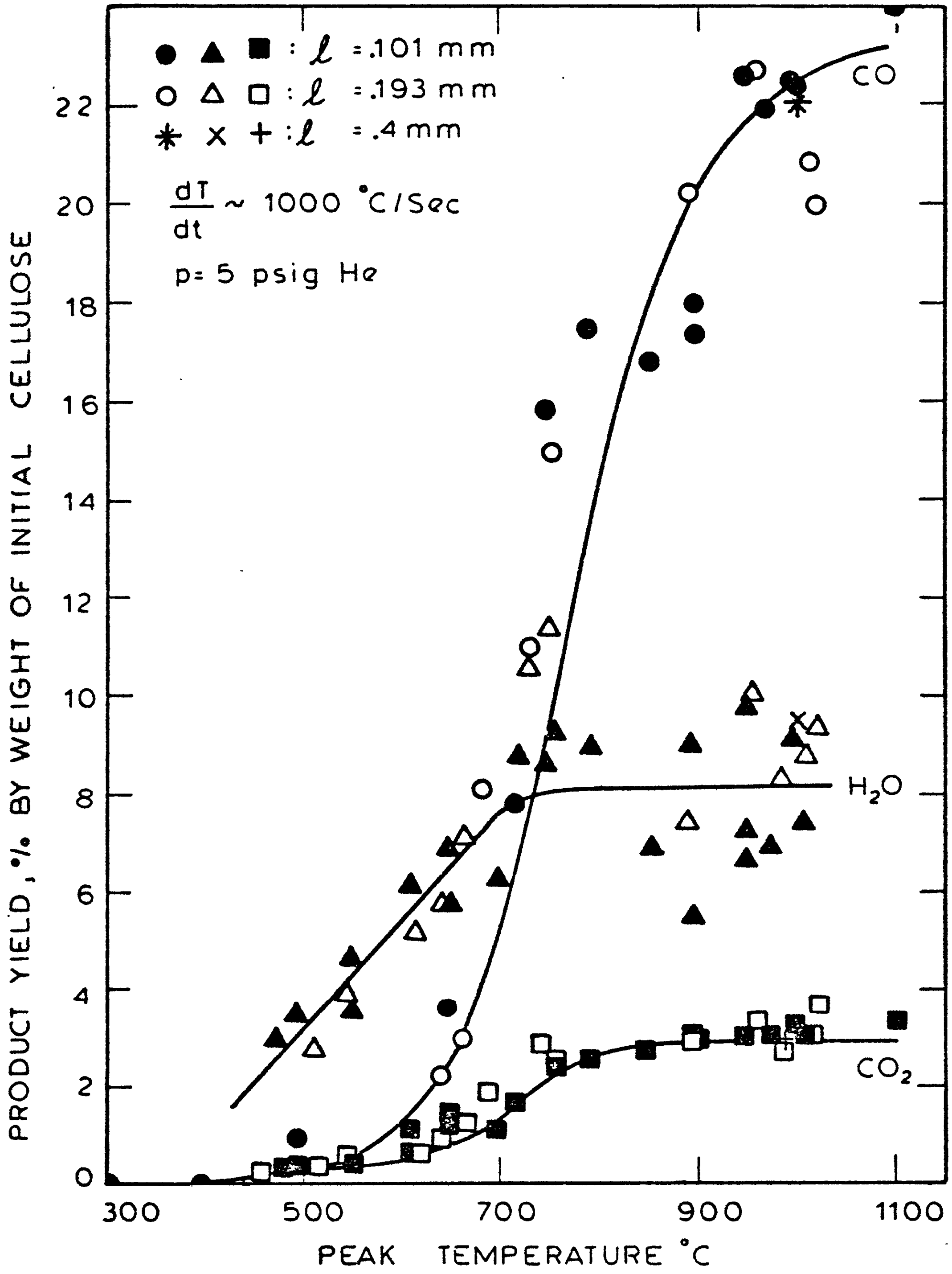


Figure IV.5.1-2. Effect of Sample Thickness on Yields of CO, CO2, and H20 at 5 psig He Pressure.

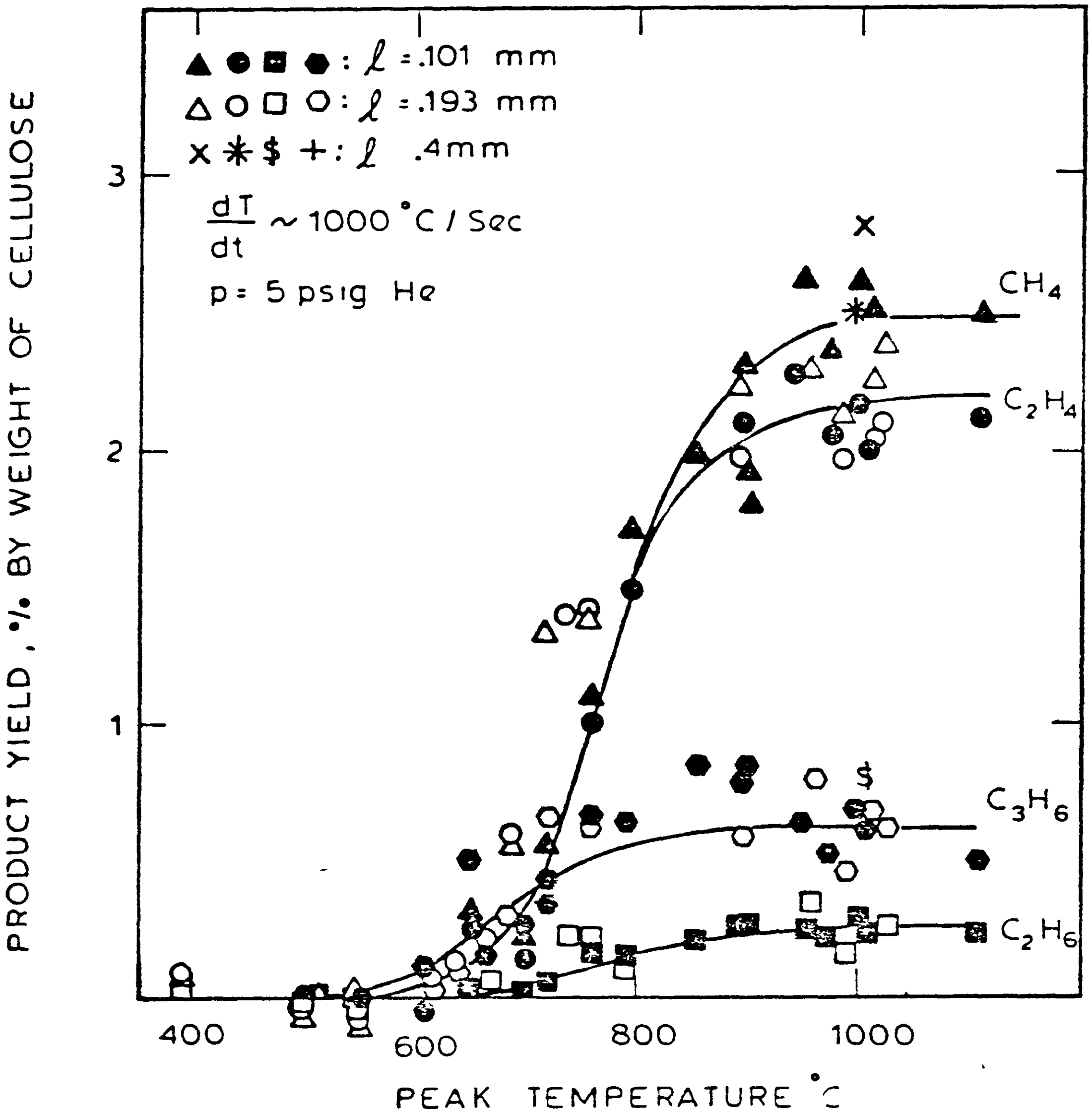


Figure IV.5.1-3. Effect of Sample Thickness on Yields of CH4,C2H4, C2H6, and C3H6 at 5 psig He Pressure.

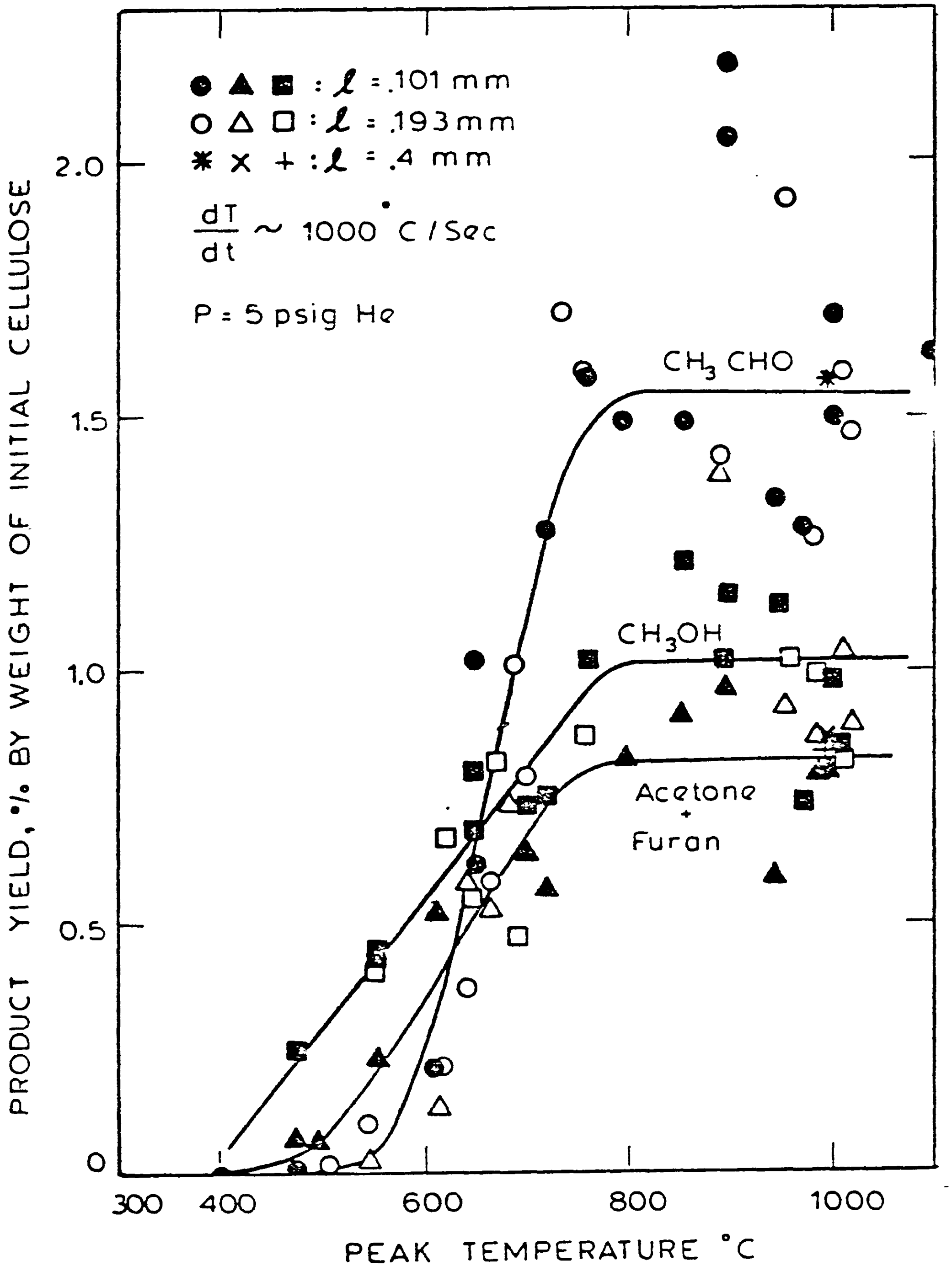


Figure IV.5.1-4. Effect of Sample Thickness on Yields of Methanol , Acetaldehyde , and Acetone + Furan at 5 psig HE pressure.

thickness were pyrolyzed. Since there was a layer of gas between the folds of paper, it cannot be said that the sample thickness doubled or quadrupled. In each experiment, the samples were heated to a peak temperature and held there from 2 to 10 seconds to get a maximum conversion of the samples.

Some of the results of these runs, which are shown in Table IV.5.1-1, indicate that increasing the holding time of the tar, by folding the sample, has a strong effect on the products. These effects are especially evident on those species which are believed to be the final ones in the reaction pathway such as methane, carbon monoxide, ethylene, carbon dioxide, and hydrogen. The yield of char increases with the number of folds in the cellulose, while tar yield decreases. Some oxygenated compounds, which are believed to be an intermediate between tar and hydrocarbon gases, decrease or remain unchanged. The yields of methane, carbon monoxide, carbon dioxide, ethylene, ethane, propylene, and hydrogen, however, increase with a greater number of folds.

IV.5.2. The Effect of Sample Quantity

By changing the sample quantity, different amounts of volatiles, such as tar and gases, are produced. To determine how important outside screen cracking is, experiments with samples of about 25, 50, 100, and 150 mg were performed. The results from these experiments, which are shown in Table IV.5.2-1, show that there is no significant change in relative yield and composition

Table IV.5.1-1. Effect of Tar residence time on products yield

No. of layers of Sample Products	1	2	4
CH_4	2.01	2.37	3.60
C_2H_4	1.8	2.23	3.36
C_2H_6	.22	.26	.40
C_3H_6	.76	.70	1.20
H_2	1.22	1.41	2.27
CH_3OH	1.09	1.05	.98
CH_3-CHO	2.13	1.38	1.63
Butene and Ethanol	.38	.40	.49
Acetone and Furan	1.11	.57	.63
CHO (Mainly CH_3COOH)	1.05	.56	.76
CO	17.69	-	32.61
CO_2	3.05	3.21	4.95
H_2O	7.31	6.78	7.18
Tar	50.29	47.59	34.66
Char	3.41	4.4	8.61
Balance	93.12	-	103.33

1) peak temperature, about 900°C

2) holding time, 0 - 5 sec

3) 5 psig He pressure

Table IV.5.2-1. Effect of Sample Quantity on Products Yield

Mass of Cellulose being used (mg) / Products	25	50	100	150
CH_4	2.86	2.96	2.46	2.38
C_2H_4	1.99	2.45	2.04	2.13
C_2H_6	.21	.26	.24	.25
C_3H_6	.59	.66	.57	.48
H_2	N.M.	N.M.	1.25	N.M.
CH_3OH	.97	.83	.8	.68
CH_3CHO	1.46	1.82	1.39	1.37
Butene and Ethanol	.39	.39	.29	.34
Acetone and Furan	.97	1.16	.83	.79
CHO (Mainly CH_3COOH)	.68	.99	.41	1.05
CO	20.75	-	22.21	-
CO_2	4.4	3.69	2.98	3.21
H_2O	8.81	-	7.20	-
Tar	50.73	45.49	49.68	50.38
Char	6.13	6.11	3.97	3.73
Balance	100.91	-	96.32	-

1) Each date point is average of 2-3 experiments.

2) Experiments are all performed at 1000°C/sec, 5 psig He, zero holding time, and 1000°C peak temperature.

of products with changes in sample quantity. The slight differences observed could be because as the sample size is decreased, the relative perimeter is increased. Therefore, it can be concluded that secondary cracking, which is caused by free convection flow (in this apparatus, at: 5psig He and 1000 deg C/sec), is negligible. This is consistent with the other results obtained in this study.

IV.6. Elemental Balance

Elemental balances were calculated for experiments where the yield of volatile products, and where elemental analysis of tar and char were available. For the purposes of estimation, butane + ethanol, acetone + furan, and CHO fractions were assumed to be ethanol, acetone, and acetic acid, respectively. The elemental compositions of tar and char are taken from figures IV.6.1. and IV.6.2. The typical results for four runs, three to a peak temperature, and one with a 30 second holding time, are presented in Table IV.6.1., along with the total mass balances. The mass balances of the total mass, hydrogen, carbon, and oxygen are excellent. In these calculations, the total amount of nitrogen, sulfur, and ash are assumed to be virtually zero. The results validate this assumption.

IV.7. Possible Mechanism for the Formation of Products

IV.7.1. Tar

Tar is the major product of cellulose pyrolysis, under all

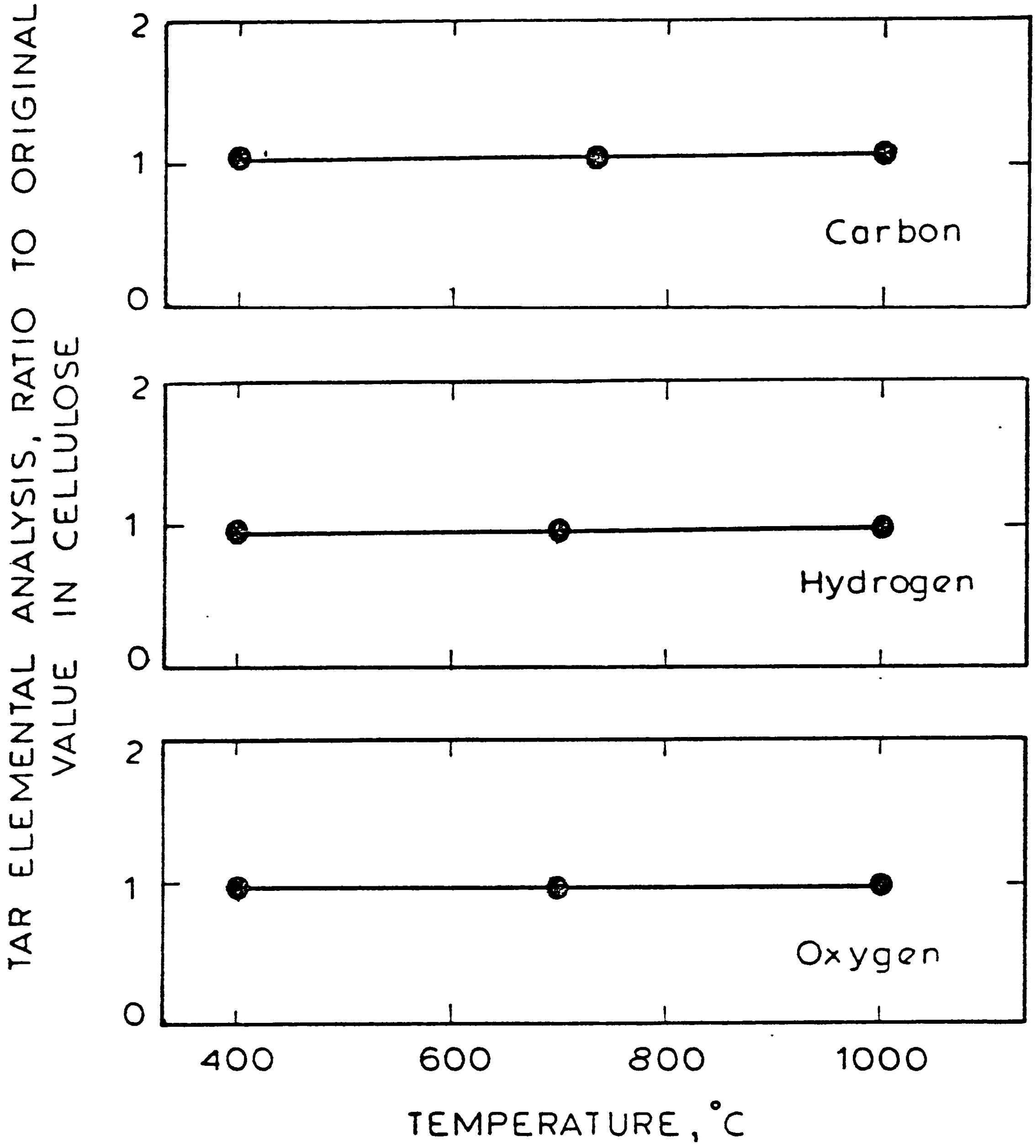


Figure IV.6-1. Effect of Temperature on Elemental Composition of Tar at 1000°C/S Heating Rate, 5 psig He Pressure, 0.1 mm Sample Thickness, and 0-30 Sec Holding Time.

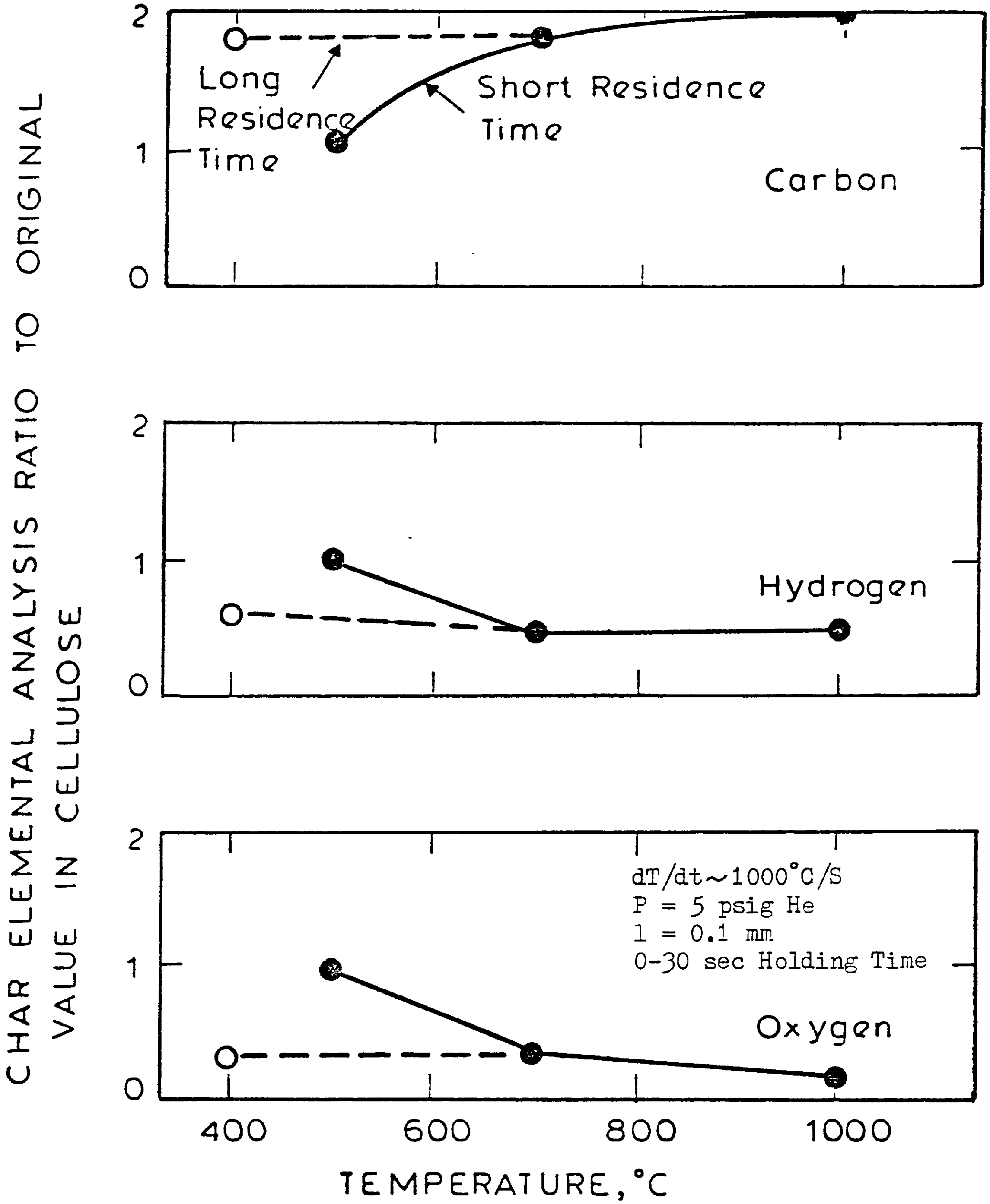


Figure IV.6-2. Effect of Temperature and Holding Time on Elemental Composition of Char .

Table IV.6-1. Carbon, Hydrogen, Oxygen and Total Mass Balance for Cellulose Pyrolysis

Products	Peak Temperature 500°C				Holding Temperature[1] 400°C				Peak Temperature 750°C				Peak Temperature 1000°C			
	Total	C	H	O	Total	C	H	O	Total	C	H	O	Total	C	H	O
CO	.99	.42	-	.57	.25	.11	-	.14	15.82	6.78	-	9.04	22.57	9.67	-	12.9
CO_2	.3	.08	-	.22	1.45	.40	-	1.05	2.38	.65	-	1.73	3.36	.92	-	2.44
H_2O	3.55	-	.39	3.16	6.49	0.	.72	5.77	8.72	-	.97	7.75	9.22	-	1.03	8.19
CH_4	0.	0.	0.	-	0.	0.	0.	-	1.11	.83	.28	-	2.62	1.96	.66	-
C_2H_4	0.	0.	0.	-	0.	0.	0.	-	1.05	0.9	.15	-	2.18	1.87	.31	-
C_2H_6	0.0	0.	0.	-	0.	0.	0.	-	.17	.14	.03	-	.28	.22	.06	-
C_3H_6	0.	0.	0.	-	0.	-	0.	-	.70	.6	.1	-	.80	.69	.11	-
H_2	0.	-	0.	-	0.	0.	0.	-	.36	-	.86	-	1.18	-	1.18	-
CH_3OH	.25	.09	.02	.14	.21	.08	.03	.1	1.03	.39	.13	.51	.98	.37	.12	.49
CH_3CHO	.01	.01	.0	0.	.05	.03	0.	.02	1.58	.86	.14	.58	1.7	.93	.15	.62
C_4+ Ethanol	.00	0.	0.0	0.	0.	0.	0.	0.	.29	.15	.04	.10	.38	.2	.05	.13
AC + FU	0.07	.04	.01	.02	.16	.1	.02	.04	1.00	.62	.10	.28	.82	.51	.08	.23
$CHO(CH_3COOH)$	.12	.05	.01	.06	.0	0.	0.	0.	.85	.34	.06	.45	.58	.23	.04	.31
Tar	16.37	7.5	.97	7.9	83.35	38.28	4.95	40.32	59.92	27.77	3.63	28.63	49.12	22.89	2.98	23.23
Char	83.63	38.13	5.34	40.16	6.17	4.94	.24	.99	3.32	2.65	.1	.57	3.91	3.46	.13	.32
Total	105.25	46.32	6.74	52.23	98.36	43.96	5.96	48.43	98.8	42.68	6.59	49.53	99.86	43.92	6.9	48.88
Closure	105%	105%	108%	105%	98%	100%	96%	97%	99%	97%	106%	99%	100%	100%	111%	98%

(1) Holding Time = 30s

of the conditions used in this study, although its precise yield depends on the condition of pyrolysis. From the results presented in this study, it can be seen that the yield of tar changes from about 40% to 85% when the cellulose is completely pyrolyzed. The maximum yield of tar is obtained at conditions of low heating rate, low pressure, low temperature, and high holding time. These conditions promote a higher evaporation rate of the tar from the reaction zone and favor a slower rate of tar destruction by secondary cracking reactions. The minimum yield of tar is obtained at conditions of high pressure, high temperature, high heating rate, and greater sample thickness. At these conditions, either the rate of evaporation of tar is slower because of higher pressure, or there is a longer residence time of tar in the reaction zone. These results indicate that realization of the maximum yield of tar under these conditions requires careful selection and optimization of reaction conditions. For example, if large amounts of tar are kept in the reaction zone for protracted periods by using a high sample temperature, increasing the pressure, or otherwise increasing the volatiles residence time, most of the tar is converted to lower molecular weight compounds through secondary reactions.

The following evidence shows that tar is undoubtedly a primary product of cellulose decomposition:

1) When cellulose is pyrolyzed at low heating rates, and a maximum weight loss of 94% is obtained, the tar yield is 85%. The remaining volatile products are gases, mainly water and

carbon dioxide, and a fraction of a percent (0.85) of oxygenated volatiles.

2) Experiments at vacuum show that when no other products are produced in significant yield, tar is in high yield. At high heating rates (1000 deg C/sec) and low temperature with high holding time (500 deg C, 30 sec), tar yield is about 80%, while total gases other than water and carbon dioxide are 1.18%.

3) Results of 1000 deg C/sec heating rate, low temperature (about 400 deg C), and high holding time (30 sec) at 5psig He, show a tar yield of about 83%, and a total gas yield of about 8%, of which only 7.3% is water and carbon dioxide.

Therefore it is obvious that there is no precursor to the tar other than cellulose.

It is important to have a knowledge of the identity of the tar, since, in some cases, it accounts for 85% of the cellulose decomposition. It is widely reported in literature that the major portion of tar is levoglucosan. Identification of the major components of tar will either discredit or confirm this theory. Furthermore, an understanding of the composition of tar is necessary to provide a realistic mechanicsm for the pyrolysis of cellulose and production of products, and provide a more realistic kinetic model. Although attempts to identify the components of the tar fraction were not successful in this study, the following results were obtained:

1) The elemental analysis of tar obtained from runs conducted at

three different temperatures (400, 700, and 1000 deg C), showed no changes in the composition of carbon, oxygen, and hydrogen. These results, which are shown in Figure IV.6.1., gives an empirical formula of CH1.5700.78, which remains constant throughout the temperature range. This indicates that at least part of the tar, if not the entire fraction, is some kind of monomer of the cellulose initially used.

2) A qualitative analysis of tar, on a 2ft x 1/8in carbowax 20m column, shows that some part of the tar is not thermally stable, even at temperatures as low as 150 deg C. Some of these products pyrolyze in the column and give a peak on the TCD detector without showing on the FID detector, along with the other peaks which have a FID response. Finally some kind of char remains behind in the column.

3) A study on the composition of the tar is currently being conducted in this laboratory (95). In this study, a protocol involving acid / base separation, followed by elution chromotagraphy of the neutral fraction was employed to fractionate the raw tar into seven components that ideally would be comprised of a relatively small number of chemical functionalities. The results are presented in table IV.7.1-1. As these results show, the combined acids and bases fraction (mainly acids), appears at a constant yield of 2 to 3%, regardless of the temperature of the run. The fraction of aromatics and hydrocarbons appears to increase with temperature from about 2% at 460 deg C to about 8% at 1000 deg C, although

Table V.7.1—1. Fractions from Cellulose Tars (expressed as wt.% of Tar Sample)

Run No.	Temp. °C	Acids and Bases %	Parrafins and Aromatics %	Transitionals %	Oxygenates %	Methanol Extractables %	Mass Balance %
17	425	2.37	2.32	7.05	57.66	17.47	84.53
28	475	1.38	2.00	5.15	55.12	34.5	98.15
25	510	1.26	1.74	3.39	50.13	23.53	80.05
24	695	2.38	3.89	2.13	61.02	16.56	85.98
22	732	3.74	4.00	1.53	60.20	19.65	89.15
23	875	2.29	4.18	1.93	56.41	25.95	90.76
21	1020	2.68	8.14	0.0	54.85	13.57	79.24

the investigator reported some uncertainty as to the accuracy of this fraction. The major fraction of the tar is the oxygenated fraction which includes all ketones, aldehydes, esters, and alcohols. This fraction gives a maximum between the temperatures of 400 deg C and 1000 deg C. This behavior is consistent with the behavior of total tar yield, and the behavior of reactive oxygenated compounds like acetaldehyde, acetone, furan, etc. About 20 to 30% of the tar is very polar and of high molecular weight, so it doesn't elute from the separation column. Therefore it can be concluded that tar is, by and large, made up of polar, oxygenated products.

4) When the tar is left in contact with oxygen or light, it turns from its normal color of yellow to brown. This is a further indication of the existence of some unstable products. The chemical mechanism responsible for the color change is not known and neither radical reactions nor precyclic reactions are being ruled out at this time.

5) The pyrolysis of the tar obtained from cellulose pyrolysis provided some very interesting results. A sample of tar from pyrolysis of cellulose at about 700 deg C, zero holding time, 1000 deg C/sec heating rate, and 5 psig He pressure, was dissolved in solvent. A prefired and preweighed screen was then immersed in the resulting solution and the solvent was allowed to evaporate to achieve good contact of the tar with the screen. The tar on the screen was then pyrolyzed in the same manner as the cellulose. The results of these experiments are tabulated in

Table IV.7.1 2. These results show that tar pyrolysis gives the same products as cellulose pyrolysis. The same results were reported by Shafizedeh (16) and Glassner and Pierce (40). These finding provide further indication that tar is an important intermediate in the thermal degradation of cellulose.

With the information obtained on tar decomposition in this study and from previous works, it is clear that tar has an important role in the pyrolysis of cellulose to volatiles.

Since it is obvious that different kinds of compounds with similar molecular weight, some of which are unstable, exist in tar, certain conclusions about the possible mechanisms of tar formation cannot be reached. Alpha, D-Glucose, Beta, D-Glucose, levoglucosan, and levoglucosanone all have about the same molecular weight, but have different thermal behavior. Even a thorough knowledge of the composition of the tar would not necessarily give a complete mechanism for the decomposition of cellulose to tar. Nonetheless, some conclusions can be drawn from the evidence of this study. It can be seen that at lower temperatures, rearrangement and unzipping mechanisms are more possible, but at high temperatures, where all of the cellulose is suddenly converted to tar, radical mechanisms predominate. In both cases, however, it should be kept in mind that a small portion of the tar might be glucose, which is a thermally unstable product. Therefore, some portion of the cellulose must be converted to tar in a pathway in which glucose is obtained (section II.5).

Table V.7.1-2. Comparison of Results from Cellulose Pyrolysis and Tar Pyrolysis*

Products	Low Temperature (600°C)		High Temperature (900 - 1000°C)	
	Tar[1]	Cellulose	Tar	Cellulose
CH_4	.25	.17	.78	2.46
C_2H_4	.29	.16	.76	2.04
C_2H_6	.06	.03	.13	.24
C_3H_6	-	.17	-	.57
H_2	-	0.0	-	1.25
CH_3OH	1.3	.22	3.33	.8
CH_3CHO	1.13	.65	.55	1.39
Butene and Ethanol	.23	.06	.26	.29
Acetone and Furan	.47	.58	.40	.83
CHO	.2	.21	.34	.41
CO	3.48	7.27	6.77	22.21
CO_2	3.19	1.86	3.66	2.98
H_2O	23.44	5.94	12.35	7.2
Tar	32.25	76.13	32.36	49.68
Char	30.36	2.91	32.77	3.97
Material Balance	94.65	96.36	94.48	96.35

[1] Yield is weight percent of initial tar pyrolyzed

*Experiments performed at 1000°C/sec, 5 psig He, for a holding time of 0-10 seconds.

IV.7.2. Char

As the results indicate, at most, 97 to 98% of the cellulose can be converted to volatiles, the remainder appears as char. The char yield changes with temperature, pressure, and heating rate. This is an indication that char formation occurs through several different pathways. The supporting evidence obtained in this study is:

1) The elemental analysis of the char shows no significant change in the empirical formula of the char with respect to temperature. The ratio remains unchanged, regardless of temperature (Figure IV.6-2).

2) Experiments at low temperature, with a long enough holding time to get maximum weight loss, yields a residue which is completely separated from the screen, has a similar shape to the original sample (except smaller), and is black (rich in carbon). A run at low temperature and zero holding time gives similar results, but the residue is brown and more fragile. Indeed, at lower peak temperatures, the char residue has an empirical formula of $(CH_{1.68}O_{0.79})$, which is similar to cellulose $(CH_{1.7}O_{0.85})$, since at these temperatures, cellulose hasn't been completely pyrolyzed yet.

3) In runs performed at vacuum and low heating rate (350 deg C/sec), and at vacuum and high heating rates (1000 deg C/sec), also at low temperatures, the char produced can be separated from the screen. However, at high temperatures part of the char is

separable from the screen, but most of it appears as coke on the screen.

4) At high temperatures, and atmospheric or high pressures (1000psig He), the residue also has a similar shape to the original cellulose, but is not separate from the screen, rather it is embedded in the screen. At these conditions, almost all of the sample is initially converted to volatiles, some of these volatiles, mainly tar, repolymerize and leave coke residues as they pass through the screen. This residue is only found on the layers of the screen which touched the sample.

5) There is another kind of char which comes from the secondary cracking of volatiles, in addition to the other two kinds of char. This char forms either when the volatiles pass through the screen for the first time and undergo cracking, or by circulation through the reaction zone by free convection flow.

6) An experiment done at 1300 deg C and zero holding time yielded no char at all.

7) Some char was obtained by pyrolyzing cellulose at low temperature and high holding time. This char was then further pyrolyzed, and yielded the results shown in Table IV.7.2-1. The important result from this experiment was that char contained some hydrogen and oxygen which could be pyrolyzed one step further to yield methane and some higher hydrocarbons.

In summary char results from cellulose pyrolysis by three

Table IV.7.2-1. Comparison of Results from Cellulose Pyrolysis and Pyrolysis of Char Obtained from Cellulose Pyrolysis at Low Temperature*

Products	Char(1)	Cellulose
CH_4	2.11	2.46
C_2H_4	.47	2.04
C_2H_6	.23	.24
C_3	-	-
C_4^+	1.17	-
CO	9.0	22.21
CO_2	4.05	2.98
H_2O	24.67	7.2
Tar	2.10	49.68
Char	72.18	3.97

(1)yield is weight percent of initial char pyrolyzed.

*Experiment performed at 1000°C/sec, 5 psig He, 10 sec holding time, at about 1000°C mechanisms: 1) Carbonizations reactions (dehydration) at low temperature, low heating rate, and/or vacuum, 2) Tar repolymerization and/or cross linking reactions at higher temperatures and/or pressure, and 3) Secondary cracking of volatiles, when they come in contact with the reaction zone (the hot screen and immediately surrounding gas). Nonetheless, at certain conditions, one or two reactions could dominate. For example, at high temperature and pressure, repolymerization, cross linking, and cracking reactions occur simultaneously.

IV.7.3. Water

Water is among the first products of the pyrolysis process, making its first appearance immediately after cellulose pyrolysis starts. The origin of this water has not yet been clearly determined, but a review of the results obtained in this study may shed some light on this question.

1) At vacuum and 5psig He, the yield of water reaches a maximum of about 7%, most of which appears even before the pyrolysis if cellulose is completed (Figure IV.1-2). In fact the water yield exhibits an asymptote when the other products are still present in only small yield.

2) At low peak temperatures, an increase in holding time has an effect on the yield of water, but as soon as the cellulose decomposes to tar, char, and gases, this effect is no longer observed. At this temperature, the total yield of hydrocarbons and oxygenated volatiles is about 0.5%, while the yield of water

is between 5.5% and 6.5%.

3) At high peak temperature, holding time has no effect on the yield of water.

4) In an experiment conducted at very low peak temperature (320 deg C) with a heating rate of 50 deg C/sec and 0.1mm Hg pressure, out of a total weight loss of 5.6%, the yield of water was 4.04%. The remaining material (residue) was brown in color and very fragile. These results are tabulated in Table IV.7.3-1.

5) An experiment was conducted with two steps. In the first step, the sample was heated to about 320 deg C and held there for 90 seconds at 5 psig He. In the second step the sample residue was heated to a peak temperature of 1000 deg C. The weight loss from the first step was about 35%, and a 5.5% yield of water was obtained. In the second step, where the remaining material was pyrolyzed, the yield of water was about 10% (results shown in Table IV.7.3-2).

6) In the high pressure runs, the water yield was quite high, between two and three times the yield at vacuum and 5psig He (Figure IV.4.2-6).

7) Pyrolysis of the tar obtained from cellulose pyrolysis yielded a high quantity of water regardless of the condition used (high or low peak temperature).

Therefore, from this evidence, it can be concluded that, at vacuum, 5psig He, and lower heating rates, most of the water

Table IV.7.3-1. Pyrolysis Products of Cellulose at Low Temperature*

Products	Yield(%)
H_2O	4.04
CO_2	.29
CO	.005
CH_3OH	.18
CH_3CHO	.08
Acetone and Furan	.02
CHO	.01
Char	94.4

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*Experiment performed at ≤ 50°C/sec, 0.1 mm Hg, 60 sec holding time for a temperature of 300 - 320°C.

Table IV.7.3-2. Pyrolysis Products of Cellulose in Two Step Process*

Products	Step 1	Step 2	Total
CH_4	0.	1.51	1.51
C_2H_4	0.	1.60	1.6
C_2H_6	0.	.17	.17
C_3H_6	0.	.77	.77
HCHO	.49	.80	1.29
CH_3OH	1.03	1.15	1.25
C_4 and Ethanol	0.	.23	.23
Acetone and Furan	.03	.67	.70
CHO	.05	.13	.18
CO	.28	21.76	22.04
CO_2	.63	2.60	3.23
H_2O	5.07	9.30	14.37
Tar	-	-	53.65
Char	-	-	4.75
Balance			100.1

*In first step, sample pyrolyzed at ≤ 50°C/s, .1 mm Hg, 300-320°C for 90 sec. Then gases collected and analyzed. In second step, remaining material from first step pyrolyzed at 1000°C/sec, 5 psig, for a peak temperature of 983°C.

comes from primary reactions rather than through the decomposition of tar to lower molecular weight compounds. At 1000psig He, however, most of the water comes from secondary reactions. At the pressures normally studied in this work (vacuum and 5psig He), most of the water comes from primary reactions. The results indicate, however, that if the temperature is kept low, water yield is quite high, even though no significant tar production occurs. This shows that it could come from the dehydration of cellulose. At higher temperatures, however, where the tar decomposition reaction appears rapid, and also appears to be the dominant reaction, the water comes mostly from the decomposition reaction. Thus, when the conditions are favorable for the secondary cracking of tar, most of the water is obtained as a by product of these reactions. Nevertheless, the two step run shows that even though some of the water is eliminated through dehydration and depolymerization reactions, in the first step, a high yield of water can be obtained in the second step.

IV.7.4. Carbon Dioxide

Results obtained on the yield of carbon dioxide can be summarized as follows:

1) Carbon dioxide makes up the major portion of the total gas yield after water, at low temperature when the maximum weight loss is achieved. At these conditions, however, the total yield of carbon dioxide is about 1.5%, which is about 50% of the

maximum carbon dioxide yield possible at ordinary pressure.

2) At vacuum and low temperature, it has the highest yield among the gases, after water.

3) At heating rates of about 100 deg C/sec, it is one of the major components of the products. This is also true at heating rates of about 350 deg C/sec, at low peak temperature.

4) As the number of layers of sample increases, so does the yield of carbon dioxide.

5) In an experiment with a total weight loss of 5.6%, 0.23% of that was carbon dioxide (Table IV.7.3-1). In the two step run, its yield behavior was like water.

6) At high pressures (1000psig He), its yield increases two or threefold because of secondary reactions.

7) At high temperatures and 5psig He, the yield of carbon dioxide exhibits an asymptote of about 3%. This asymptote doesn't change with holding time.

8) At low pressure (0.1mmHg) and high holding temperature, where the secondary reactions of tar and oxygenated volatiles, like aldehydes, become important, the yield of carbon dioxide starts to increase with holding time. In other words, as the secondary reactions are extended, the carbon dioxide yield increases.

Therefore, it can be concluded that carbon dioxide is produced through primary and secondary reactions. At low peak temperatures, low heating rate, and low pressure, where secondary reactions are not important, it comes from reactions like cellulose carbonization reactions or cellulose decomposition reactions to tar. At high temperatures and high pressures, where secondary cracking reactions become more important, most of the carbon dioxide is yielded from these reactions, through mechanisms presented in section III.5.

IV.7.5. Carbon Monoxide

The results of the carbon monoxide yields for different conditions are:

1) Carbon monoxide is a high temperature product, and it is a major component of the gas fraction at high temperatures. It is the second major component in volatile cellulose pyrolysis products at high temperatures, after tar.

2) Carbon monoxide yield at low peak temperatures is very small (0.25%), even with a high holding time, while carbon dioxide has a higher yield of 1.5%.

3) As the heating rate and pressure decreases, the yield of carbon monoxide decreases. In other words, as secondary cracking of tars and volatiles decreases, carbon monoxide yield decreases.

4) At conditions which favor secondary cracking, such as high peak temperature, the carbon monoxide yield is high.

5) The results from the high pressure runs (1000 deg C) don't

show an increase in carbon monoxide yield.

Therefore, carbon monoxide is a product of secondary reactions and is produced in higher yield at conditions which favor secondary reactions. On possible mechanism by which carbon monoxide might be produced is through the pyrolysis of aldehydes, ketones, and esters:

$$CH_3\ CHO \longrightarrow 1/2\ C_2H_6 + H_2 + CO$$

$$\longrightarrow CH_4 + CO$$

$$CH_3\ COCH_3 \longrightarrow CO +$$

$$HCHO \longrightarrow CO + H_2$$

:

:

When there is a great deal of circulation of the gases through the screen, by high free convection flow, the following reactions are also feasible:

$$C + H_2O \longrightarrow CO + H_2$$

$$C + CO_2 \longrightarrow 2CO$$

Carbon monoxide, however, could be produced in very small yield through a carbonization mechanism if there is any reaction of that kind. Since the existence of such a reaction for the conditions used in this study is very doubtful, it can be concluded that carbon monoxide comes mainly from the decomposition of very reactive oxygenated materials.

IV.7.6. Hydrocarbon Gases (methane, ethylene, ethane, propylene, etc)

Data on the hydrocarbons yield indicate that:

1) Increasing the peak temperature causes an increase in the hydrocarbon yield.

2) Increasing the heating rate increases the yields of hydrocarbon gases. At very high heating rates, between 10,000 and 15,000 deg C/sec, however, the yields of hydrocarbon gases decreases because the residence time of the tar in the reaction zone decreases.

3) Increasing the pressure gives a higher yield of hydrocarbon gases. This is because the volatiles are forced to leave the reaction zone at a slower rate, and undergo more secondary cracking. An exception to this rule is ethylene. Its yield increases with pressure from vacuum to 5psig He, then decreases when the pressure increases to 1000 psig He.

4) Experiments with different layers of sample gave an increase in the hydrocarbon and hydrogen yields.

5) When the tar appears in high yield, the yield of hydrocarbons and hydrogen is low.

6) When compounds like aldehydes and ketones undergo further reaction (a maximum is an indication of the threshold for these compounds), hydrocarbon yields increase.

7) Methane, ethylene, ethane,propylene, and hydrogen could be

identified positively and quantitatively. Propane and butane are found in very small quantities. C4 appears with ethanol, and propane, which is found only in trace amounts, compared to the yields of ethylene and ethane, appears very close to methanol.

8) The high hydrocarbons, with more than five carbons, haven't been identified in the gas chromatography. In the tar portion, however, a fraction has been identified as aromatics and hydrocarbons. There are, of course, uncertainties about this portion being completely pure in hydrocarbons and aromatics.

Therefore, it could be concluded that hydrocarbons and hydrogen are products of secondary reactions. They appear in higher yield when cracking of the tar and oxygenated compounds occurs with increasing temperature, or increasing pressure. High peak temperature, however, is not necessarily a prerequisite for the production of these compounds. This is because the tar from cellulose pyrolysis is not thermally stable and could decompose between 250 and 300 deg C. The important factor in the production of hydrocarbons is the residence time, as it was in carbon monoxide production. This is because, as the residence time is increased, the tar and its products are kept longer in the reaction zone, and a higher yield of hydrocarbon products are obtained, such as the high yields obtained by the Shafizedeh group (16, 23, 45). Increasing the temperature also increases the reaction rates, especially for reactions with large activation energies such as those involving radical mechanisms, which are believed to be responsible for the production of some of the present products. Since char was found to have some hydrogen, pyrolysis at high temperature and pressure, with a long holding time could yield some higher hydrocarbons or aromatics through secondary reactions and pyrolysis, but there is no strong evidence to support this hypothesis.

No aromatics like benzene or toluene were found in the gas analysis. The results of different fractions of tar (Table IV.7.1-1), however, show that some material was observed in the region where aromatics are normally found. From these data, it can also be seen that the yields of this material increase with peak temperature. It is, however, difficult to envision a mechanism for converting a structure like cellulose to that of an aromatic compound.

IV.7.7. Oxygenated Compounds (alcohols, aldehydes, and ketones)

The oxygenated compounds which have been positively and quantitatively identified are methanol, acetaldehyde, ethanol, which appears with C4, and acetone, which appears with furan, acrolein, and propion-aldehyde. Formaldehyde, formic acid, glyoxal, and acetic acid, were identified qualitatively.

1) The oxygenated volatiles appear right after the decomposition starts, and their yield increases with further cellulose pyrolysis.

2) As the temperature increases, the yield of oxygenates increases, but at higher pressures, the yield goes through a

maximum. This is more obvious for acetaldehyde and acetone than for others.

3) At vacuum, the yield increases with temperature, and doesn't go through a maximum.

4) In experiments with holding time, the maximum is more clearly defined, especially for the curves of acetaldehye and total oxygenated materials. The effects of vacuum and holding time are shown in Figure IV.2-11., IV.2-19, and IV.2-23.

5) Decreasing the heating rate from 1000 deg C/sec doesn't have a significant effect on the yield of the oxygenated compounds. Increasing the heating rate from 1000 deg C/sec, however, does increase the yields of oxygenates.

The mechanism of oxygenated compound formation is through the tar decomposition. If the secondary cracking reactions of tar decreases, the yield of total oxygenates decreases, and vice-versa. These reactive compounds behave as intermediates for hydrocarbon, hydrogen, and carbon monoxide production. A direct reaction mechanism from cellulose to at least some of these compounds cannot be ruled out, however. Different compounds exist in the tar portion, and one of the less stable ones could yield some aldehydes and alcohols, etc. with further reaction.

Formaldehyde, formic acid, glyoxal, and acetic acid are the products which can be identified qualitatively but not quantitatively. On the chromatograph, formaldehyde and formic acid appear with water most of the time, or in the tailing peak of water. Therefore, the quantitative results are not correct. Some of the results available for formaldehyde, however, are tabulated in Table IV.7.7-1. Glyoxal is not usually detected by the hot wire (thermal conductivity) detector, acetic acid appears under what is labelled as CHO. CHO contains some other compounds, such as methyl furan, and so forth, which have not been identified.

IV.8 Modeling

IV.8.1 Kinetic Modeling

The development of a kinetic model to account for the large quantity of data collected in this study is very important. Several different approaches have been used to describe the pyrolysis behavior of cellulose.

One straight forward and generally applicable method is the single, first order reaction model for total pyrolysis (total weight loss). Thus, for the reaction:

$$\text{Cellulose} \xrightarrow{k} \text{products}$$

$$dV/dt = K(V^* - V)$$

$$K = K_o\, e(-E/RT)$$

$$V/V^* = 1 - \exp[-\int_o^t K_o \exp(-E/RT)dt]$$

Since the time temperature history and the final yield of each experiment are known, it is possible to get a best fit for the kinetic parameter. The computer program used for the

Table IV.7.7-1. Formaldehyde yield (% by weight)

P = 5 psig He					P = .1 mm Hg	
Zero Holding Time		2-10 sec holding Time			Zero Holding Time	
Temp(C°)	Yield	Temp(C°)	H.T.	Yield	Temp(C°)	Yield
495	.30	426	5	.61	503	.44
550	.46	403	10	1.32	631	.96
610	1.03	610	2	.99	731	1.21
700	1.20	610	10	.765	789	1.25
718	1.26	760	2	1.49	853	1.39
759	1.54	787	5	1.54	877	1.52
795	1.48	887	2	.78	896	.99
900	1.14	892	5	1.11	949	1.28
947	2.78	950	2	1.16		
977	2.55	935	2	1.16		
1000	1.28	994	2	.94		
1008	1.14	1051	10	.97		

modeling is listed in Appendix V. It is important to note which experiments were used to give the data points to obtain the best fit. The conversion of cellulose to volatiles is almost complete between 800 and 900 deg C, at a heating rate of 1000 deg C/sec. Therefore, only those experiments which have a peak temperature of 900 deg C or less, with a heating rate of 1000 deg C/sec, are taken into account. The best fitting kinetic parameters for total weight loss were obtained and summarized in Table IV.8-1 , for different run conditions.

Experimental data are tabulated along with the predictions of the model in Figure IV.8-1. It can be seen that the results are in good agreement. The ease and accuracy with which the first order reaction model fits the data leads to some important conclusions. A comparison of the kinetic parameters obtained in this study with those obtained in previous investigations (Table III.4-2, Figure III.4-1), show that there is considerable agreement between the results for ordinary pressure and heating rate. The kinetic results derived from a single reaction model using data obtained at one set of conditions can predict the rate of pyrolysis for a variety of other conditions (Figure IV.8-2). This indicates that the basic reactions involved, in the initial pyrolysis of cellulose, are similar. The exception is for very low peak temperatures of about 250 deg C, which the main reaction is the charring of cellulose.

Although the single reaction model provides a good fit to the experimental data, a model of many independent parallel

Table IV.8-1. Kinetic Parameters for Cellulose Pyrolysis by a Single First-Order Model[1]

Temperature Range	Heating Rate(°C/sec)	Pressure (atm)	E(kcal/gmole)	$\log_{10} k_o$	V*(%)
400-900	1,000	1.34	31.79	8.30	94.08
300-800	350	1.34	33.21	9.475	95.31
250-540	100	"	33.39	9.567	96.17
400-850	10,000	"	16.37	4.12	99.47
400-900	1000	1.31×10^{-4}	31.25	7.93	86.09
300-750	250	"	32.94	9.135	95.26

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[1] It shoud be noted that first-order reaction models can be only used for those components which at least at a given pressure their yields don't go through a maximum such as weight loss, CO2,and CO but not tar.

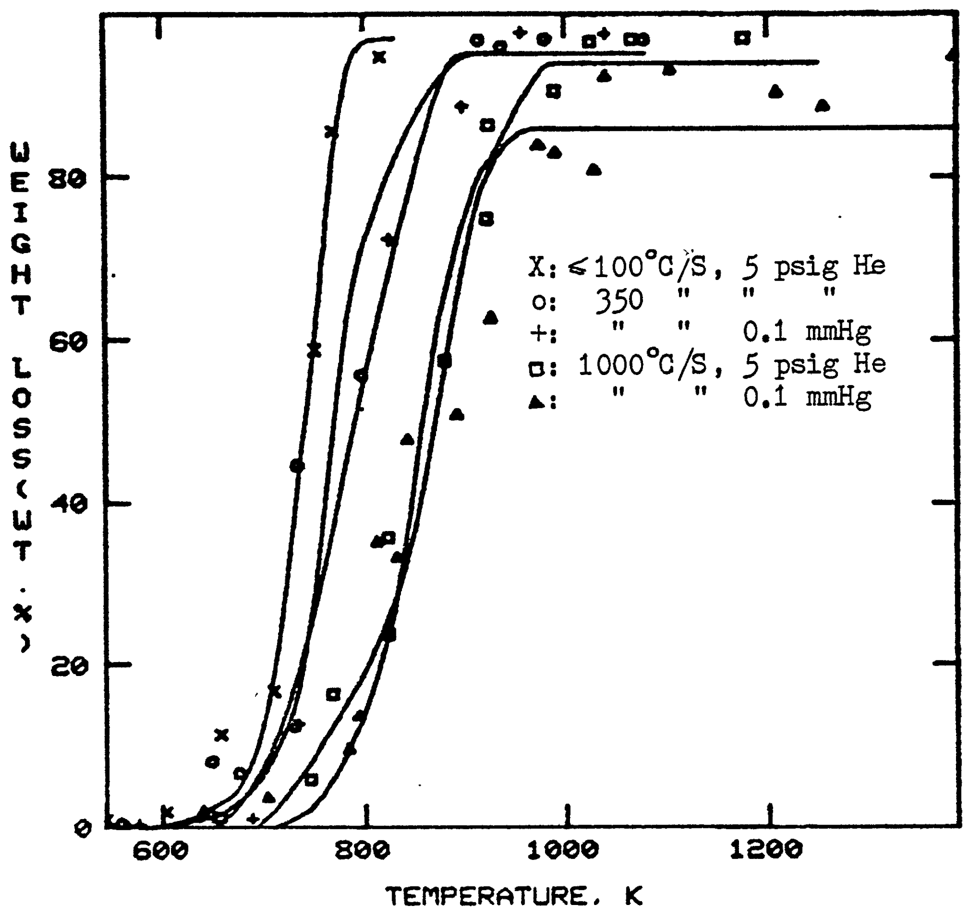


Figure IV.8-1. Comparison of Calculated and Experimental Weight Loss of Cellulose at Various Condition.

Prameters for each set of conditions are those in Table IV.8-1.

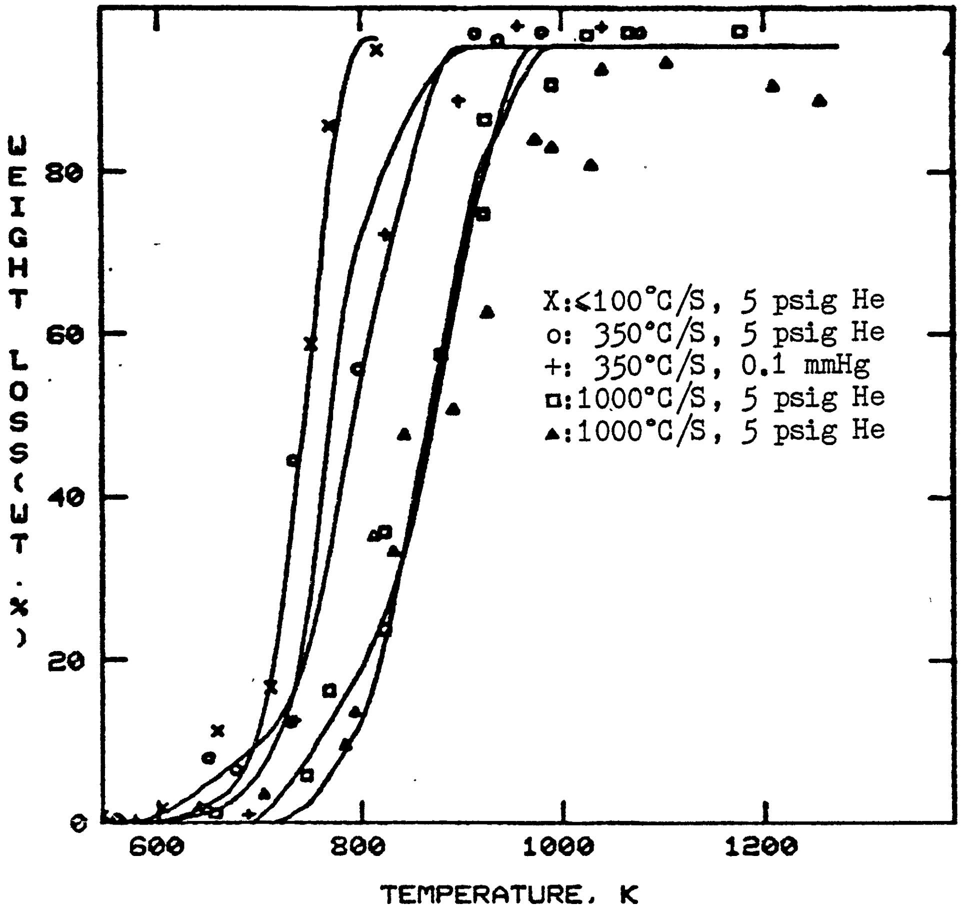


Figure IV.8-2. Comparison of Calculated and Experimental Weight Loss of Cellulose When One Set of Kinetic Parameters are used for Various Conditions (E=33.21 Kcal/gmole; $\log_{10}k_0$=9.475; V*=95.31 wt.%).

reactions might be more realistic, since cellulose pyrolysis is obviously not a simple, single step reaction. In the multiple parallel reaction model, a distribution of activation energies with identical frequency factors are assumed for the reactions. Therefore, the kinetic parameters have more freedom than in a simple, single reaction model. In order to fit all the reactions which occur in different temperature ranges, the activation energy and frequency factor are forced to be low in the single reaction model. This is to fit the overall temperature dependence that actually results from the occurrence of different reactions in different temperature intervals. The experimental data, along with the predicted yields from the single reaction model and the multiple reaction model, are compared in Figure IV.8-3. Although the two curves in Figure IV.8-3 are very similar and the kinetic parameters very close, a large number of independent reactions seems to be the more reasonable model.

The predicted kinetic parameters, for the conditions of 5psig He, and 1000 deg C/sec heating rate, for a model of many independent, parallel, first order reactions are:

$E = 40.30$ kcal/gmole

$\sigma = 3.25$ kcal/gmole

$\log Ko = 10.44\ \mathrm{sec}^{-1}$

$V^* = 95.73$ wt.%

The rate of formation of each volatile species can also be modelled. The results on individual products show that, most of

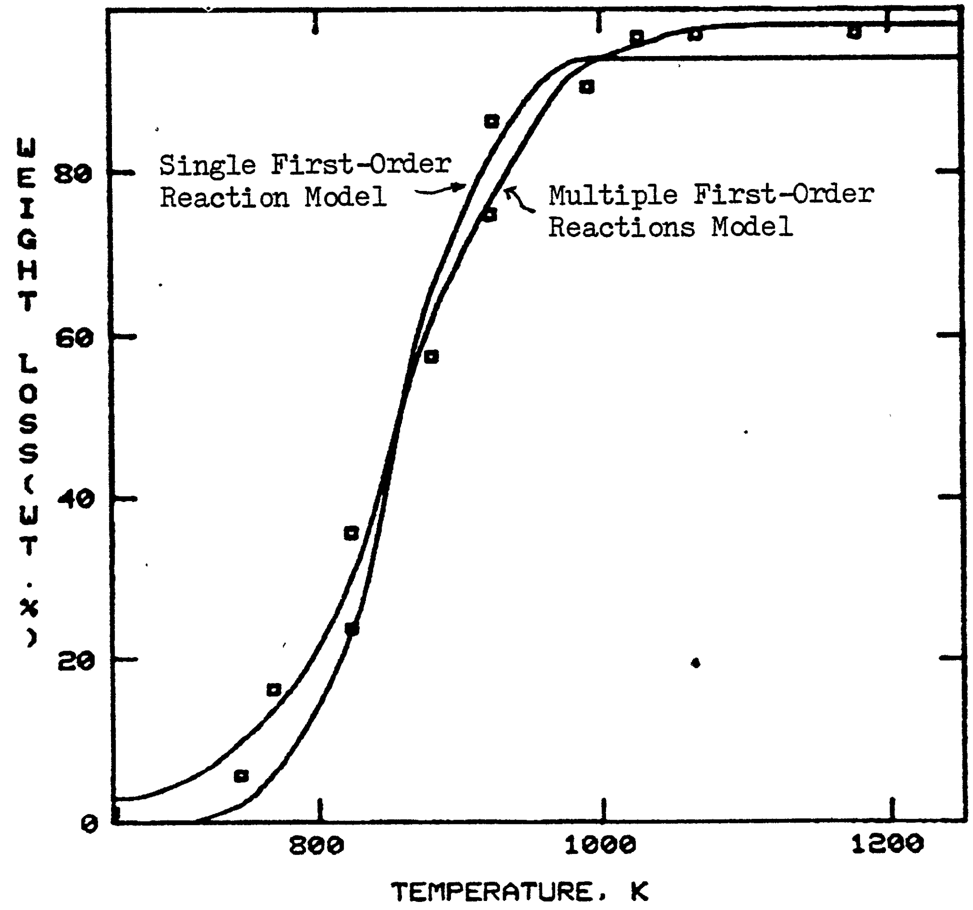


Figure IV.8-3. Comparison of Measured Cellulose Weight Loss with Calculated Values from Single First-Order Reaction Model and Multiple First-Order Reactions Model.

the products are well fitted by a single step process, suggesting that one reaction may dominate the production of these products. The kinetic parameters for the volatile formation reactions, however, were obtained by applying a single reaction model to the yields obtained at different conditions. A summary of these parameters is given in Table IV.8-2.

The ability of the single, first order reaction model to predict the volatile product yields, under a variety of conditions, is quite good. The kinetic parameters for some of the components are lower than for organic decomposition. However, these parameters should be considered only as useful tools for correlating the experimental data for the ranges of operating conditions under which they were measured. They do not reflect the detailed chemistry of cellulose decomposition to specific volatile products (13).

Table IV.8.2, Kinetic Parameters for Individual Products in Cellulose Pyrolysis

Reaction Conditions	E(kcal/gmole)	log k_1 (sec^{-1})	V*(%)
	CH_4		
1,000 °C/sec, 5 psig	60.04	13.00	2.41
1,000 °C/sec, Vacuum	52.60	10.08	.86
350, 5 psig	57.77	13.98	.614
350, Vacuum	55.83	13.65	.085
10,000 °C/sec, 5 psig	60.99	14.4	1.395
	C_2H_4		
1,000, 5 psig	49.82	10.82	2.07
1,000, Vacuum	52.56	10.59	.905
350, 5 psig	27.99	6.58	.99
350, Vacuum	64.06	15.53	.26
10,000, 5 psig	40.32	9.603	2.03
	C_2H_6		
1,000, 5	41.55	9.056	.255
1,000, Vacuum	68.98	13.95	.05
10,000, 5	59.06	14.06	.22
	C_3H_6		
1,000, 5	60.67	14.93	.67
1,000, Vacuum	74.09	15.81	.60
350, 5	54.20	13.11	.575
10,000, 5	41.65	9.94	1.46
	H_2		
1,000 °C/sec, 5 psig	27.29	6.169	1.156
	CH_3OH		
1,000, 5	49.35	13.42	.920
1,000, Vacuum	22.86	4.979	.83
350, 5	39.00	11.77	.90
350, Vacuum	67.89	19.31	.72
10,000, 5	21.14	6.917	.115

(con't)

Table IV.8-2. Kinetic Parameters for Individual Products in Cellulose Pyrolysis (continued)

Reaction Conditions	E(kcal/gmole)	log k_1(sec^{-1})	V*(%)
	CH_3CHO		
1,000 °C/sec, 5 psig	55.1	13.56	1.54
1,000 °C/sec, Vacuum	31.84	6.087	4.11
350 °C/sec, 5 psig	40.48	10.35	1.47
350, Vacuum	56.02	13.8	.57
10,000, 5 psig	55.06	12.96	2.52
	BUTENE and ETHANOL		
1,000, 5	42.54	9.9	.32
1,000, Vacuum	44.76	9.002	.80
350, 5	59.98	12.99	.52
350, Vacuum	26.08	6.661	.38
10,000, 5	39.48	9.649	.64
	ACETONE and FURAN		
1,000, 5	43.04	11.07	.81
1,000, Vacuum	40.27	8.341	1.46
350, 5	57.12	14.94	.84
10,000, 5	44.37	10.18	1.44
	CHO (Mainly CH_3COOH)		
1,000, 5	58.18	12.8	1.19
1,000, Vacuum	32.99	6.596	.82
350, 5	42.00	9.398	.38
10,000, 5	31.45	7.543	.71
	H_2O		
1,000, 5	24.62	6.714	8.04
1,000, Vacuum	8.189	1.915	7.17
350, 5	8.932	2.401	7.31
350, Vacuum	16.27	4.224	7.31
10,000, 5	21.74	6.258	8.45
$\leq$ 100, 5	6.675	1.315	8.78

(con't)

Table IV.8-2. Kinetic Parameters for Individual Products in Cellulose Pyrolysis (continued)

Reaction Conditions	E(kcal/gmole)	log k_1(sec^{-1})	V*(%)
	CO		
1,000 °C/sec, 5 psig	52.74	11.75	21.64
1,000 °C/sec, Vacuum	45.02	8.922	17.94
350°C, 5 psig	58.72	15.19	7.15
350°C, Vacuum	40.69	9.994	2.83
10,000, 5 psig	58.92	12.61	22.44
	CO_2		
1,000 °C/sec, 5 psig	23.42	5.392	3.08
1,000 °C/sec, Vacuum	26.64	5.34	2.04
350 °C/sec, 5 psig	27.42	7.262	2.39
350 °C/sec, Vacuum	13.12	2,766	1.34
10,000 °C/sec, 5 psig	18.13	4.327	3.02
≤ 100 °C/sec, 15 psig	14.39	3.618	1.39

IV.8.2 Secondary Reactions and Mass Transport Limitation

Neither a single first-order reaction nor multiple first-order reactions model fully explains the observed influence of total reactor pressure on the yield of volatiles from cellulose pyrolysis. Consequently the cellulose pyrolysis data could only be correlated at a single pressure using the previously described models. The results and discussion in the previous sections strongly suggest that: (1) most of the lighter volatiles from cellulose pyrolysis are produced via secondary reactions of an intermediate product consisting of a large number of high molecular weight compounds and globally defined as tar; (2) total reactor pressure strongly affects these secondary reactions and; (3) at vacuum, holding time and temperature also effect these reactions. Therefore, to extend the applicability of the model, the influence of pressure on the coupling of mass-transfer and chemical reaction effects must be considered.

In the first step of the reaction, cellulose is converted mainly to tar with some water, carbon dioxide, and a small amount of organics. The tar in turn, partially cracks to give lower molecular weight volatiles. The remainder of the tar leaves the reaction zone, and it is this remainder which is experimentally measured as the yield of tar. The escape of the tars from the reaction zone, however, is not simply a mass transfer process, but involves a simultaneous chemical reaction as well. This is evident, as the composition of tar changes with temperature (Table IV.7.1-1).

In order to explain this pyrolysis behavior of cellulose in the present captive sample apparatus, the following picture is postulated, a model for the combination of chemical reactions and physical transport processes occurring in this equipment. The reactions which take place can be divided in three parts; primary reactions (conversion of cellulose to tar, box 1 in Figure IV.8-4), secondary reactions, part of which occur inside a hot reaction zone (Zone II) defined as the region enclosed by the screen (box 2, Figure IV.8-4) and part of which occur outside of Zone II in a region between the screen and an imaginary surface beyond which the temperature is too low for secondary reactions (Zone III, and Box 3 in Figure IV.8-4). Figure IV.8-4 graphically explains the significance of each zone at different conditions. At atmospheric and higher pressure, where the density of the ambient gas in the reactor is high, and free convection is strong upon heating the screen, volatiles are both cooled and swept away by convective flow of the cold ambient reactor gas as soon as they exit Zone II. Under these conditions, therefore, the amount of cracking occurring outside of Zone II is not important, but that which occurs within Zone II accounts for most of the secondary reactions (Figure IV.8-4b). At vacuum because the rate of evaporation from Zone II is very fast, due to the inverse pressure dependence of the evaporative diffusion coefficient, cracking within Zone II is not important. But as indicated earlier (Section IV.2) cracking in Zone III becomes important. This is because at 0.1 mm Hg pressure, free convection is expected to make contribute little to volatiles transport in Zone III because of the low gas density. Further, it is obvious that the cracking which occurs in Zone III increases as holding time increases (Figure IV.8-4c). This is probably because the gas in this zone moving slowly by weak free convection, has more and more time to be heated by molecular conduction,

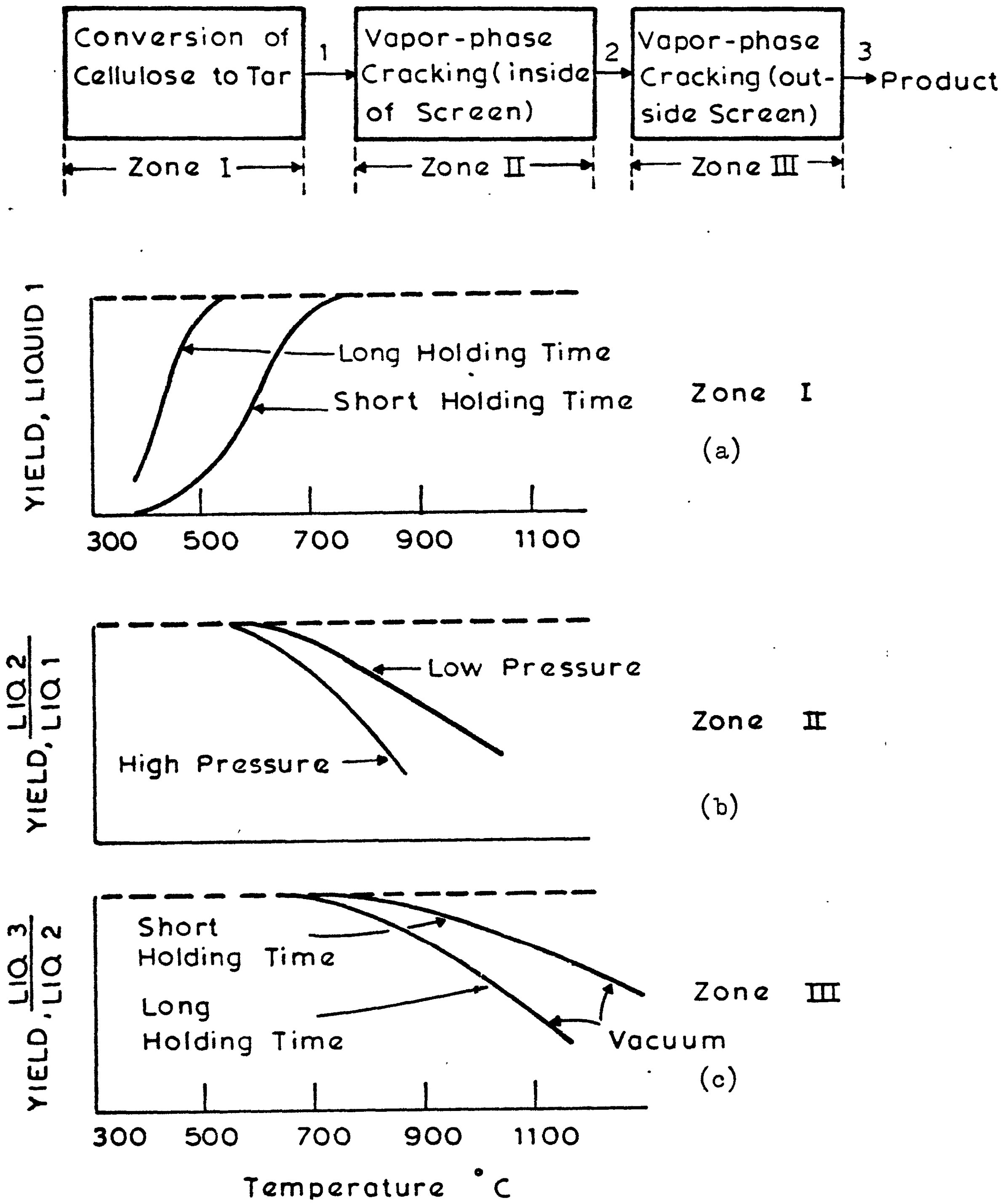
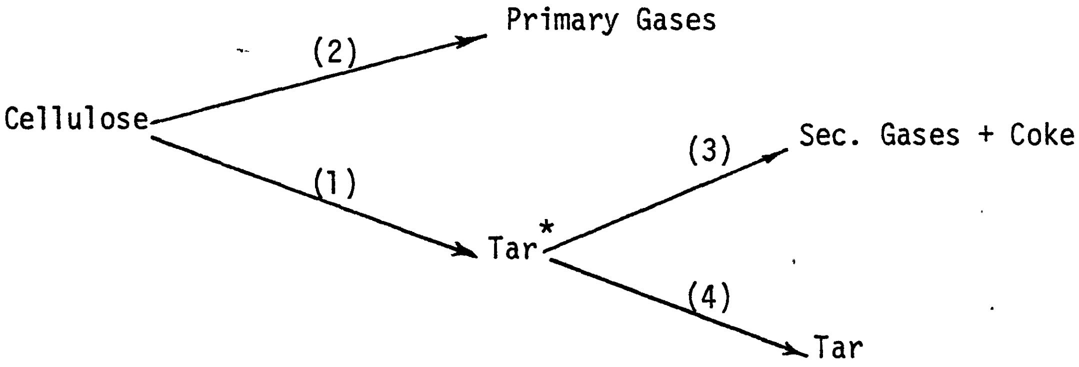


Figure IV.8-4. Graphical Presentation of Secondary Reactions with Mass Transport Limitation Model.

as holding time increases. This means that Zone III becomes larger and hotter as holding time increases.

In order to put this picture on a more quantitative basis, an approximate model is developed below for the simultaneous mass-transfer and secondary reactions of tar. The kinetic scheme for such a model is as follows:

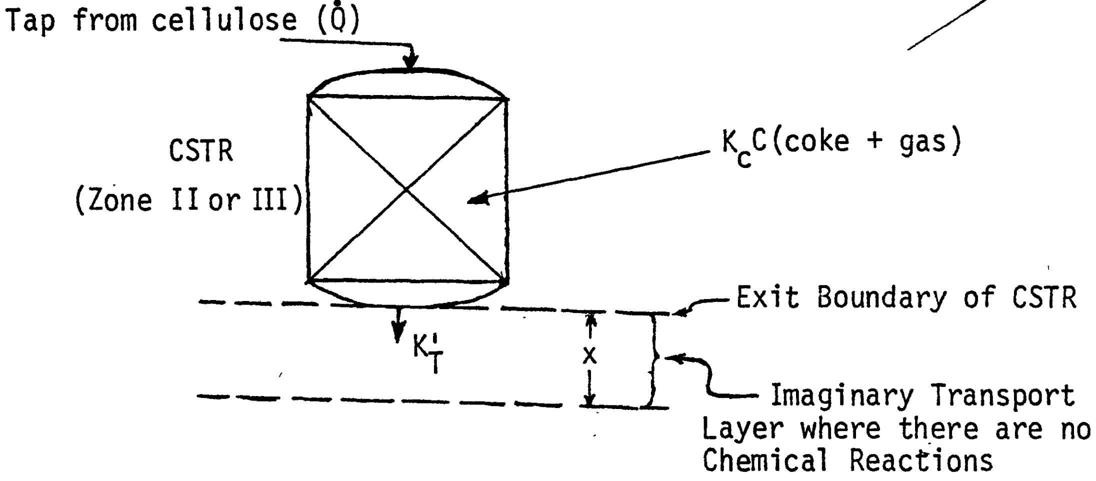


The following assumptions are made:

- In reaction zone, tar generation (Step 1) is first-order in concentration of tar yet to be evolved from the cellulose.
- Tar cracking is first-order in the concentration of tar in reaction zone, where the cracking occurs (Zone II or Zone III in the present model).
- Observation from experiments performed indicate that the rate of evolution of volatiles is very fast. Therefore, it is assumed that there is no limitation on tar evaporation from liquid to vapor and cracking reactions in liquid phase are not significant, but vapor-phase cracking is considered to be important.
- The rate of mass-transfer of tar across the boundary of a given reaction zone (Zone II or III) is proportional to the concentration of tar in reaction zone. This mass transfer can occur by either convective or diffusion flow.
- Concentration of tar in the ambient reactor gas is negligible.

While mass transfer and chemical reactions probably occur simultaneously, to simplify the model for a better physical understanding of the problem, it can be assumed that each zone can be divided into two regions. In the first region which is next to the sample matrix secondary reactions occur at a Constant Concentration. This region can be compared with well mixed reactor (CSTR) in which chemical reactions occur at constant concentration. In this region mass-transfer is not important. In the remaining region of the zone chemical reactions are assumed to be unimportant, but mass-transfer process takes place. Thus a mass balance on the vapor-phase for tar over the two regions with a further assumption of pseudo-steady state conditions gives:

$$\text{Input} = \text{output} + \text{Loss (or Gain) Due to Reaction} + \cancelto{0}{\text{Accumulation}}$$



$$\dot{Q} = dV_T/dt + K_C C \qquad \text{(for CSTR)}$$

$$\frac{dV_T}{dt} = K'_T \frac{C}{x} = K_T C \qquad \text{for Mass-Transfer B.L.}$$

or:

$$\dot{Q} = K_T C + K_C C \qquad \text{(IV.8.2.1)}$$

where $\dot{Q}$ is the rate of generation of tar $\left(\frac{\text{gr} \cdot \text{sec}^{-1}}{\text{gr initial cellulose}}\right)$,

K_T is overall Mass-Transfer Coefficient or the proportionality for convective flow (sec^{-1}),

K_c is Rate Constant of secondary reaction (sec^{-1}), C is tar concentration in reaction zone, and V_T is the net yield of tar which is measured experimentally.

Since, from Equation (IV.8.2.1), $\dot{Q} = C(K_c + K_T)$

Therefore:

$$\frac{\frac{dV_T}{dt}}{\dot{Q}} = \frac{K_T C}{C(K_c + K_T)}$$

$$\frac{dV_T}{dt} = \frac{\dot{Q}}{1 + \frac{K_c}{K_T}} \qquad \text{(IV.8.2.2)}$$

Integration of Equation IV.8.2.2 for a period of time τ gives:

$$V_T = \int_0^{\tau} \frac{\dot{Q}}{1 + \frac{K_c}{K_T}} dt \qquad \text{(IV.8.2.3)}$$

The kinetic parameters for the generation of tar can be obtained by assuming that the secondary reactions of tar are negligible at temperatures below 650°C (Fig. IV.8-5). This is a valid assumption, since in this temperature interval, the tar yield at 5 psig He is equal to the yield of tar under vacuum, for which the secondary reactions are undoubtedly of abbreviated importance. The following kinetic information was found for rate of generation of tar by a best fit analysis of the 5 psig He data over the temperature range to 650°C using runs with no holding time.

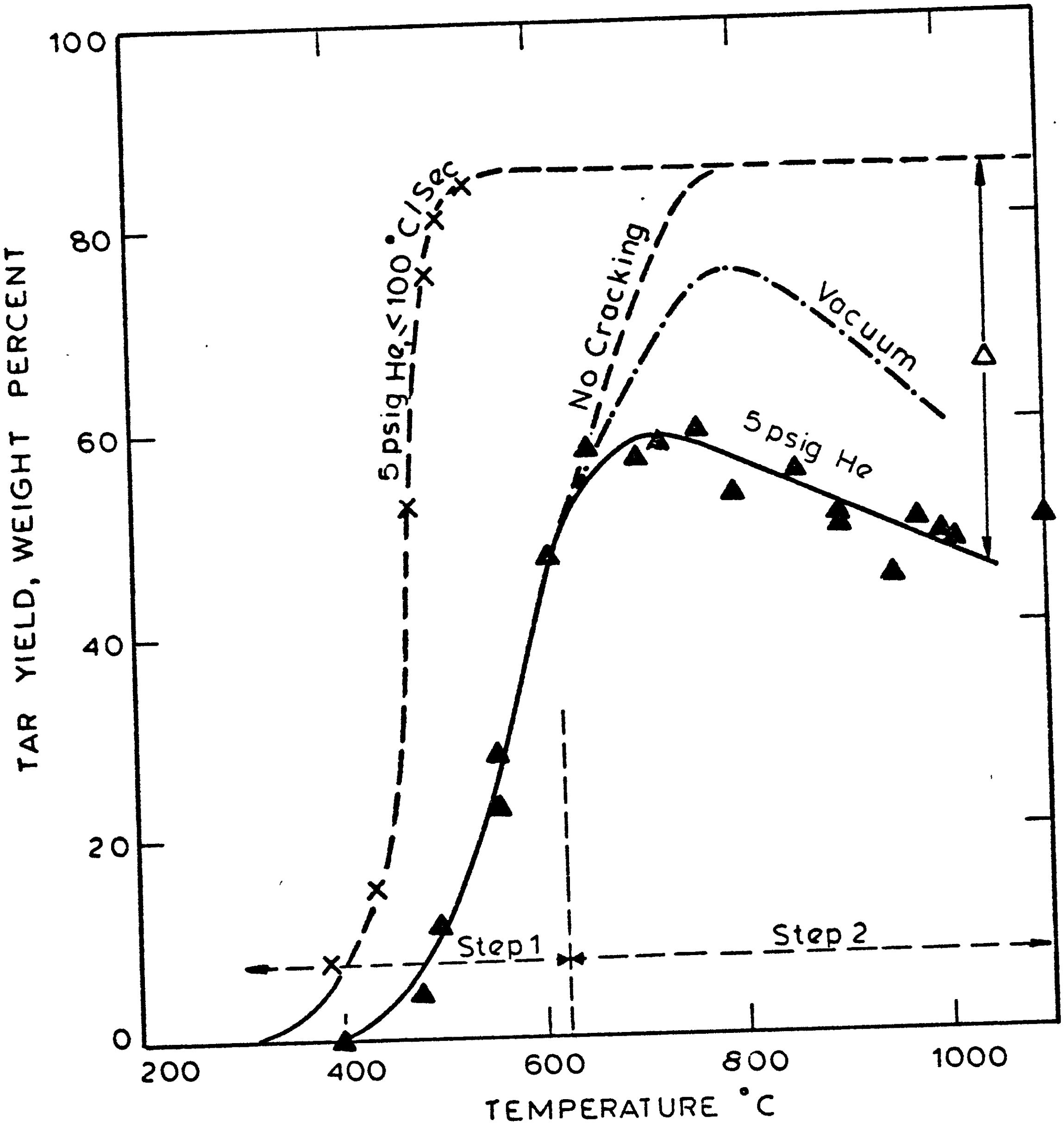


Figure IV.8-5. Effect of Temperature on Yields of Tar.

$E_1 = 18.57$ kcal/gmole

$\mathrm{lag}_{10} k_{01} = 4.886\ \mathrm{sec}^{-1}$

$V^* = 85.00$ wt.%

The rate constant for secondary reactions was assumed to have the Arrhenius form:

$$K_c = K_{0c} \exp(-E_c/RT) \qquad \text{(IV.8.2.4)}$$

The overall mass-transfer coefficient is assumed to be a function of temperature and pressure, and to have the form

$$K_T = (\alpha\,\mathrm{sec}^{-1})(T/273°\mathrm{K})^{\rho}\left(\frac{1.34\mathrm{atm}}{P}\right)^{\partial} \qquad \text{(IV.8.2.5)}$$

Substituting Equations IV.8.2.4 and IV.8.2.5 in Equation IV.8.2.3, the best fitted parameters from integration of Equation IV.8.2.3 over the experimental time-temperature histories for 5 psig He (0,2 and 5 sec holding time) and 1000 psig He (0 holding time) and 1000°C/sec runs are:

$E_c = 62.69$ Kcal/gmole

$\log_{10} K_{0c} = 14.17\ \mathrm{sec}^{-1}$ Case I

$K_T=(0.52)(T/273)^{0.76}\left(\frac{1.34}{P}\right)^{.69}$

where this mass-transfer coefficient corresponds to the mass-transfer limitation at the boundary of Zone II. Data from vacuum runs (0 and 2 sec holding time) were separately subjected to a best fit analysis and gave the following results.

$E_c = 55.98$ Kcal/gmole

$\log K_{0c} = 12.21\ \mathrm{sec}^{-1}$ Case II

$K_T = (0.64)(T/273)^{0.77}$

where this mass-transfer coefficient refers to limitations on the transfer of volatiles under vacuum at the outer boundary of Zone III. However, when a best fit analysis was made using the data from the three different pressures 0.1 mm Hg, 5 psig, and 1000 psig He the following parameters are found:

$$E_c = 58.58 \text{ Kcal/gmole}$$

$$\log_{10}K_{0c} = 13.5 \text{ sec}^{-1} \qquad \text{Case III}$$

$$K_T = 0.07(T/273)^{1.13}\left(\frac{1.34}{P}\right)^{0.11}$$

Experimental results along with calculated yields for Cases I and II are shown in Figures IV.8-6,7 respectively. The complete comparison of the results is tabulated in Appendix VI.

In order to demonstrate the significance of the values obtained for the mass-transfer coefficient, different limiting cases of mass transfer were examined. If diffusion was the most important process for mass transfer, the rate of mass-transfer would obey the following porportionality:

$$\frac{dV_T}{dt} \propto \frac{D}{L} C$$

where D is the Diffusion Coefficient (cm/sec), L is the boundary layer thickness for mass transfer (cm), and C is concentration (gr/cm^3).

Comparing this expression with Equation IV.8.2.5. gives $K_T \propto D/L$. Since $D/L \propto T^{1.5}/M^{1.5}p$ and in this study it was assumed that molecular weight is not function of temperature and pressure, then; $K_T \propto T^{1.5}p^{-1}$.

This means that if mass-transfer process is purely controlled by diffusion the exponents of temperature and pressure in mass-transfer coefficient should be about 1.5 and -1.0 respectively. But if convective flow influences the mass transfer

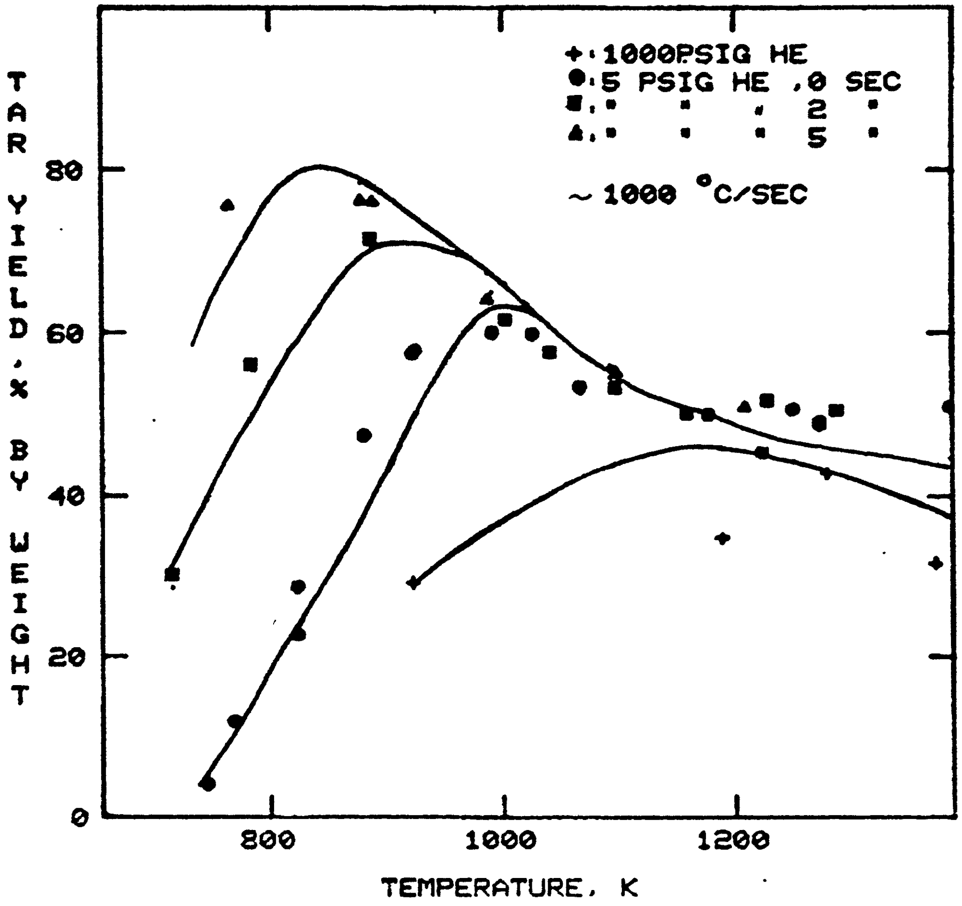


Figure IV.8-6. Comparison of Calculated and Measured Yields of Tar, using Secondary Reactions Model for 5 psig and 1000 psig He Pressure.

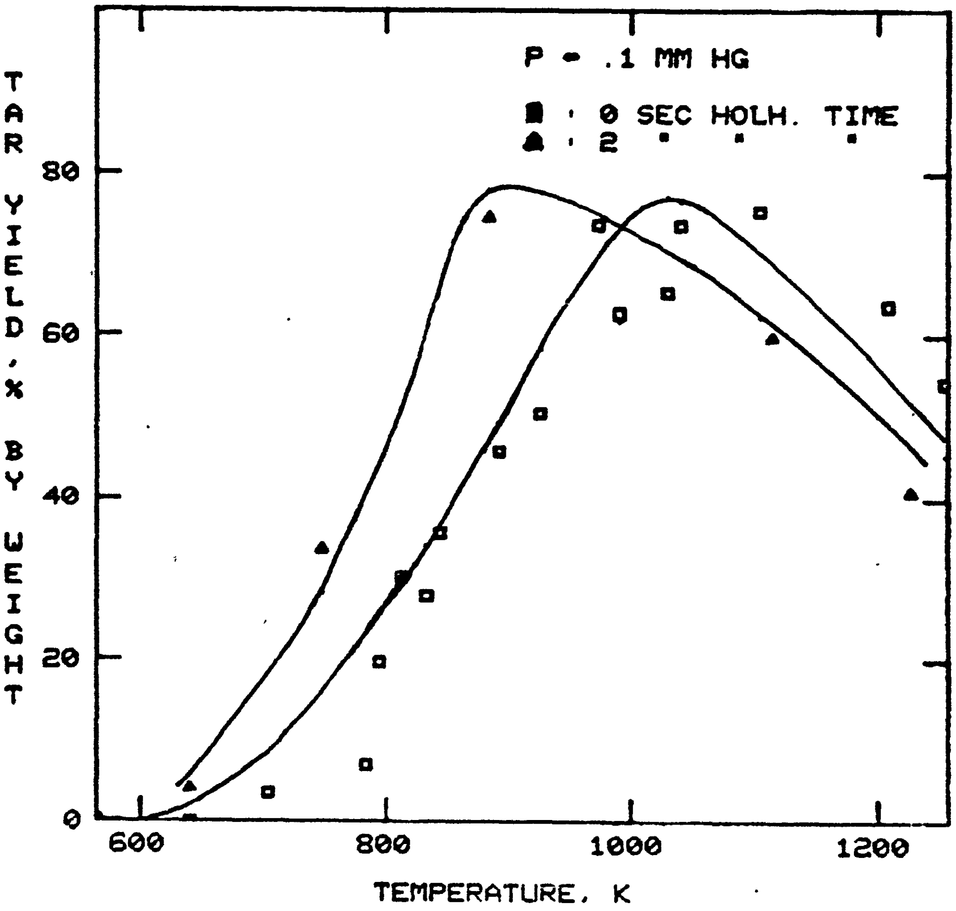


Figure IV.8-7. Comparison of Calculated and Measured Yields of Tar , using Secondary Reaction Model for 0.1 mm of Hg Pressure.

process, which in this study it does, the proportionality of mass-transfer coefficient to temperature and pressure changes. For example, with a free convection flow around a horizontal flat plate, the mass-transfer coefficient becomes (100):

$$\frac{K \cdot L}{D} \propto (Gr\ S_c)^{1/4}$$

or

$$K \propto \frac{D}{L}(Gr\ S_c)^{1/4}$$

where Gr is Grashof number, and S_c is Schmit number.

Since

$$Gr \propto \bar{\rho}\ \Delta p$$

$$S_c \propto \frac{\mu}{\rho D}$$

$$\rho = \frac{MP}{R_T}$$

$$D \propto \frac{T^{1.5}}{P}$$

therefore:

$$G_r\ S_c \propto \frac{P^2}{T^{0.5}}$$

or

$$K \propto \frac{T^{1.1}}{P^{.5}}$$

This rough calculation shows that as convective flow increases the exponents for T and P terms decrease. Therefore, in this study which convective flow is also important, it is not surprising that the observed temperature and pressure dependences of the experimentally derived mass-transfer coefficients depart from those expected for a mass-transfer process which is controlled only by molecular diffusion.

The above modeling is still a global model. However, given the absence of data on the tar molecular weight, tar vapor-pressure, and the fluid mechanics of the system which in this study play an important role in the transportation of products from reaction zone, this model correlates all the data produced in this study very well. Especially when, results for cracking process are comparable with those expected for organic decomposition (78,84).

Another approach to obtain kinetic results for tar cracking reaction is as follows. Above about 650°C for a 100°C/sec heating rate and 5 psig He experiments, the secondary reactions of tar become more important. This is evident from the change in slope of the tar yield curve (Figure IV.8-5). The results from the runs at conditions where the secondary reactions of tar are insignificant, show no change in the slope of tar yield curve until the maximum yield of tar is achieved (Figure IV.8-5). Therefore, the quantity of tar which is converted to gases and coke through secondary reactions, is the difference between the experimental tar yield curve (solid line in Figure IV.8-5) and a theoretical tar yield curve (dashed line corresponding to the predicted tar yield in the hypothetical case of no secondary reactions). The kinetic parameters for the best fit for 5 psig He runs when heating rate is 1000°C/sec are:

$$
\begin{aligned}
E_c &= 48.39 \text{ k cal/g mole} \\
\log_{10} k_{0c} &= 10.77 \text{ sec}^{-1} \\
V^* &= 35.27 \text{ wt.\%}
\end{aligned}
$$

In order to get some kinetic information for primary gas production step, the following method is used. As it is shown by the curve

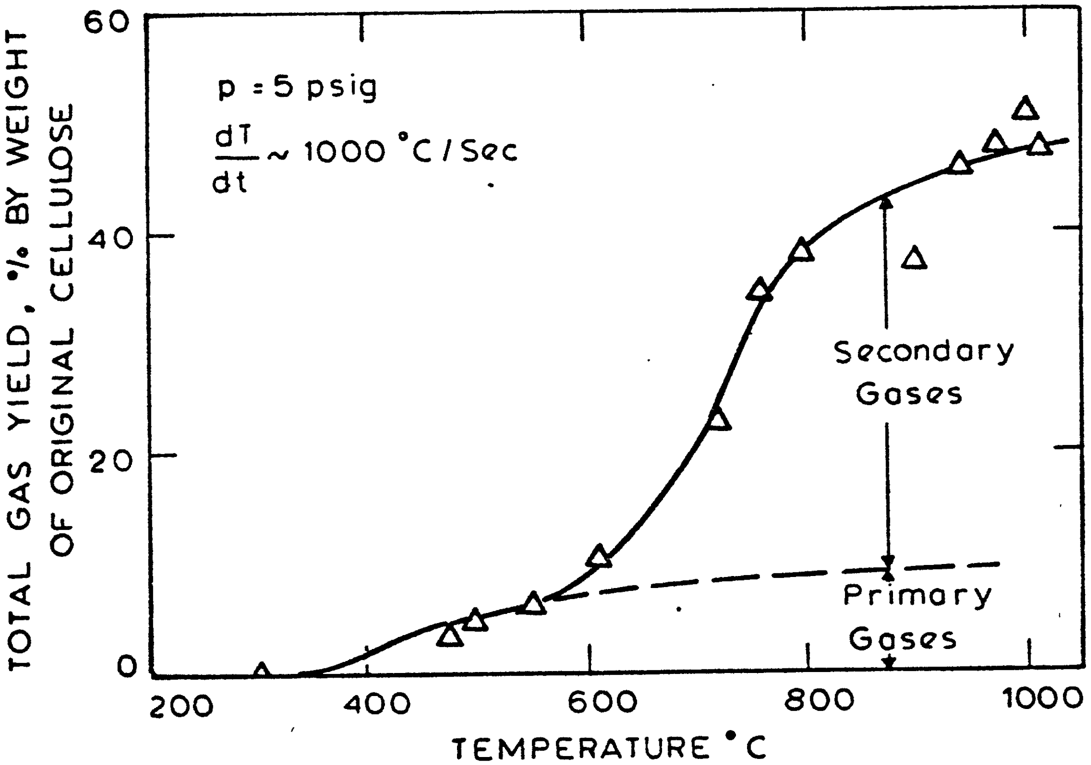


Figure IV.8-8. Effect of Temperature on Yields of Primary and Secondary Gases from Cellulose Pyrolysis.

of total gas yield, the gases are produced through a two-step process (Figure IV 8-8). In the first step which is important at low temperature, the gases come from primary reaction. At higher temperatures (>650°C) the secondary reactions of tar become more important, and the second step becomes dominant. Therefore, the kinetic parameters of the first step are a measure of primary gas production kinetics, and the kinetic parameters of the second step are for the secondary reactions of tar.

	Primary Gases	Secondary Gases
E(kcal/gmole)	31.84	46.17
$\log_{10} K_0 (\text{sec}^{-1})$	9.13	10.38
V^*(ωt.%)	8.11	34.17

As the results for tar secondary reactions show, there is striking agreement between the parameters calculated by these independent methods. However, because in the first approach mass-transport limitation as well as secondary reactions were considered, its results are more realistic than the later approach.

VI. CONCLUSION AND RECOMMENDATIONS

The following are the major conclusions of this study:

1) This apparatus provides excellent results at all temperatures (350-1100°C), holding times (0-30 sec) for heating rates ranging from about 100°C/sec to 10,000 °C/sec at atmospheric pressure and also under vacuum except at temperatures above 850°C. The results could be interpreted and used for industrial work. However, at vacuum and high temperature (850°C) with or without holding time, because of occurrence of some undesirable cracking on the screen the results required more detailed interpretation to eliminate apparatus effects and permit their application to other systems. Vapor phase reactions cannot be conveniently studied with this apparatus.

2) Reaction conditions affect the cellulose pyrolysis as follows:

a) pyrolysis temperature ranging from 350°C to 1100°C is the most important factor on cellulose decomposition and products yield and composition.

b) Heating Rate ranging from $\leq$ 100°C/sec to 10,000°C/sec is not as effective as temperature. But because it embodies collaborative effects of temperature and residence time, its effects on product yields and compositions can be interpreted in terms of their influence on these two reaction conditions.

c) Pressure ranging from 1.13×10^{-4} atm to 69 atm has a great effect on tar decomposition and therefore on products yield and composition.

d) Holding time ranging from 0 sec to 30 sec has a modest effect on yields of non tar volatiles at atmospheric pressure at all temperatures studied and under vacuum at low temperatures (<850°C). However, it exerts a strong effect on tar yield and total weight loss at low temperature for atmospheric pressure and under vacuum. It is also an important factor on products yield and composition under vacuum at high temperatures (>850°C).

e) Sample thicknesses up to 200μm have very little effect on product yield. Thicknesses over this result in decreased tar production accompanied by a proportional increase in gas yield.

3) Results obtained in this study on cellulose pyrolysis indicate that:

a) Almost 97-98% of cellulose by weight for the conditions indicated below can be converted to volatiles. i) holding time range from 0 sec at about 800°C to about 5-10 sec at about 500-700°C for a heating rate of 1000°C/sec at atmospheric pressure. ii) holding time of 5-10 sec at about 700°C for a heating rate of 1000°C/sec and under vacuum. iii) zero holding time at about 700-800°C for a heating rate of 350°C at atmospheric pressure or under vacuum.

b) For the well dispersed samples, tar is the major product of cellulose pyrolysis. Its yield varied from 85% by weight of cellulose at low heating rate and low temperature, or high heating rate, low temperature and high holding time (30 sec) for atmospheric pressure or under vacuum, to 35% at high temperature, high pressure (69 atm). It was found that undoubtfully it is one of the primary products of cellulose pyrolysis and also an intermediate for production of lower molecular weight compounds and gases.

c) Char was found in almost all experiments. It is produced by these three mechanisms; i) carbonization reactions of cellulose at low temperature, low/high heating rates, under atmospheric pressure or vacuum, 2) Tar repolymerization, and/or cross-linking reaction on or within the decomposing sample at high heating rate (1000°C/sec) and high temperature at atmospheric pressure or higher, and 3) secondary cracking of volatiles when they contact the screen, or encounter the hot gas surrounding the sample.

d) Chemical water is (i.e. not moisture) produced mainly during the primary decomposition of cellulose to tar. However, at conditions where tar cracking is important (high pressure, or tar pyrolysis) it can also be produced from secondary reactions.

e) Depending on reaction conditions Carbon-dioxide is produced either through primary reactions (low temperatures, low/high heating rate, under vacuum or atmospheric pressure) or secondary cracking (high temperature, high heating rate at high pressures or under vacuum and longer holding times).

f) Carbon-monoxide is a product of both primary pyrolysis of the cellulose and of secondary reactions of the volatiles. It is produced in higher yield at conditions which favor secondary reactions, such as high temperature at atmospheric pressure. One possible mechanism for co-production might be through pyrolysis of aldehydes, ketones and ester like structures in the tar (84).

g) Hydrocarbon gases and hydrogen are produced by secondary reactions. They appear in higher yield when cracking of tar and oxygenated products is increased either by increasing temperature or pressure. Their yields are very small at low temperatures (400-600°C) low heating rate (350°C/sec) under vacuum or atmospheric pressure.

h) Oxygenated compounds such as methanol, acetone/furan, acetaldehyde, etc. appear in almost all experiments. Their yields however are smaller at conditions which tar cracking is minimum. Suggesting that secondary reactions are important pathways for their production. However, production of at least some of these compounds by direct conversion of cellulose cannot be ruled out.

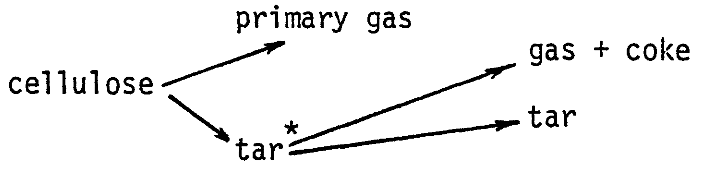
j) Modes quantities of H_2 (~1ωt.%), cH_4, c2H_4,c_2H_6(~0.2-2.5 t % each) and light oxygenated liquids such as acetaldrhyole, methanol, acetone/ furan mixture (~.8-1.5 ωt%) are formed primarily over the temperature range 600-800 for 1000 ec/sec heating rate, 5 psig He pressure, and short sample holding time. At all holding times, pressure, heating rates for temperature above 750°C, CO dominated the product gases, and attained a yield above 23% at 1000°C.

4) Kinetic Modeling provides the following conclusions.

a) The overall pyrolysis can be fitted to a single first-order model as well as a multiple first-order reaction model very well. The single reaction parameters derived from data obtained under one set of conditions give good predictions of the rate of pyrolysis for a variety of other conditions.

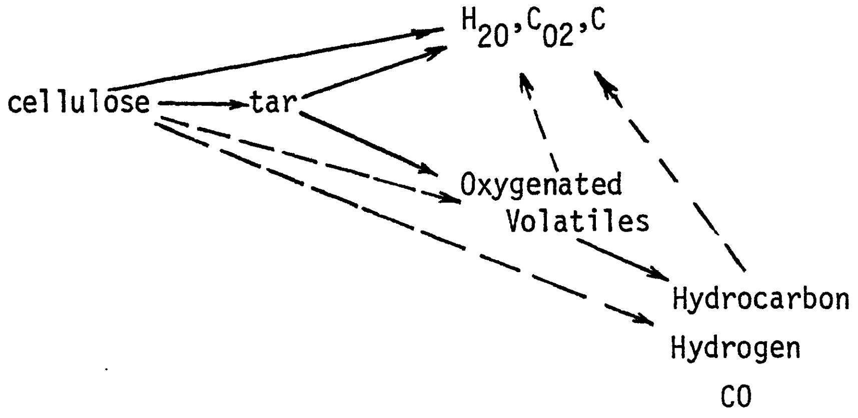
b) Yields of individual species can also be well-modelled through a single-first-order reaction model.

c) A more sophisticated model proposed to describe the present data is:



in which secondary reactions along with mass transport limitation were considered.

Therefore, based on previous discussions and conclusions the following scheme can be proposed for cellulose pyrolysis.



5) One final conclusion is that these results are generally consistent with previous studies.

Recommendations for Future Work

The followings are the recommendation of this study:

1) Pyrolysis of lignin, hemicellulose, wood, hydrocarbon rich plants, especially since this captive sample apparatus can provide a great deal of data relatively inexpensively.

2) Study the effect of inorganic salt and solid additives such as CaO on the pyrolysis behavior of cellulose.

3) More work needs to be done for detailed analysis of light liquids and tar.

4) As it was mentioned earlier the effect of the reaction conditions on the vapor reactions cannot be studied by this apparatus. Therefore, some work needs to be done, using for example, a fluidized bed, packed bed reactor, or entrained flow reactor.

5) With the great deal of data which are available on pyrolysis of refined treatments of coupling between chemical kinetics and physical transport should be investigated.

VI. Appendices

Appendix I. Analysis of Oxygenated Compounds

Effort has been made in this study to identify the products both quantitatively and qualitatively. The focus here is on oxygenated products (compounds with carbon, hydrogen, and oxygen atoms in the molecule).

A review of literature indicated that a Tenax-GC porous polymer packing material, based on 2,6-diphenyl-p-phenylene-oxide, was a good choice as a column packing. This packing could separate very volatile materials such as acetaldehyde and methanol in a low temperature range (between 50 and 240 deg C), and also could be used in a high temperature range (between 200 and 350 deg C) to separate high molecular weight compounds. Unlike many other columns, such as Poropak QS, it can be used at high temperatures.

A mixture of known compounds, a model mixture, was used to determine the best operating conditions for the optimum separation. This mixture was composed of compounds generally found in cellulose pyrolysis. For this mixture, of which the highest molecular weight compounds were furfural and furfural alcohol, increasing the length of the column had no effect on the separation, it only lengthened the retention time and increased the tailing of the water. It was determined that a column 2 feet x 1/8 inch, programmed from 50 deg C with 0 seconds holding, to 240 deg C with a heating rate of 16 deg C/min, and a helium flow rate of 30 ml/min, gave the best results. A typical chromatogram is presented in Figure App.I.1., and the retention times and response factors of the compounds eluted from the column are presented in Table App.I.1. The response factors are calculated with methanol as the reference compound (response factor equals one).

Since this column is very polar, water tails very badly in this column, since it is also very polar. This is especially evident when there is a high yield of water. Therefore, one problem was the separation of water before the other products were trapped. Different materials to absorb the water prior to the first, -77 deg C, trap were used, but not only didn't they absorb all the water, but absorbed some of the other compounds as well, which was another problem in itself. A glass wool trap in an ice bath or ice salt bath was used, but once again did not absorb all the water. The flow rate for purging the gaseous products, however, was very low. It is believed that, under the present circumstances, the partial pressure of many of the products are too low for them to condense even at these reduced temperatures, where normally, not only water, but also methanol, ethanol, acetone, etc., would be expected to exist primarily as a liquid.

The escape of oxygenated volatile compounds such as methanol, acetaldehyde, and acetone from the first trap, which was usually operated at -77 deg C, was another problem in addition to the difficulty of separating water from the oxygenated materials. This is another indication of the reason

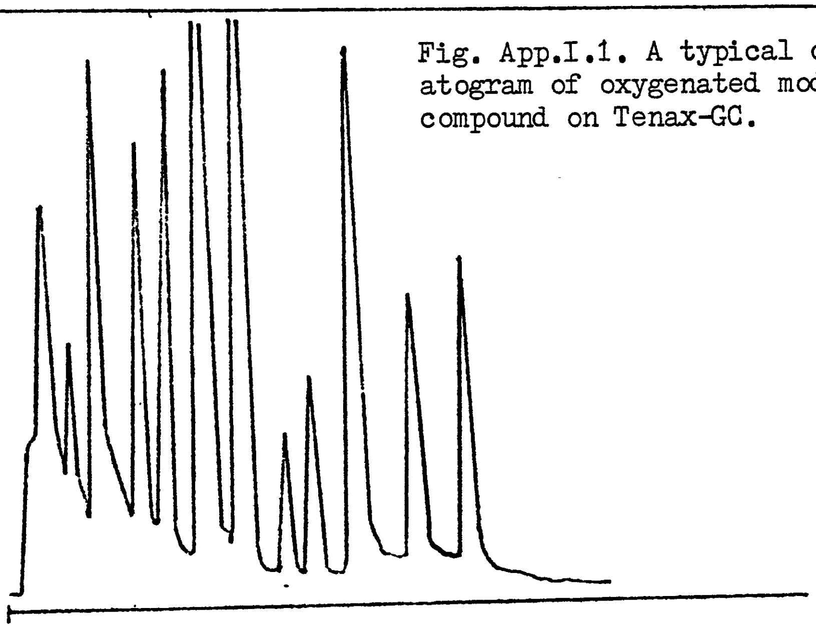


Fig. App.I.1. A typical chromatogram of oxygenated model compound on Tenax-GC.

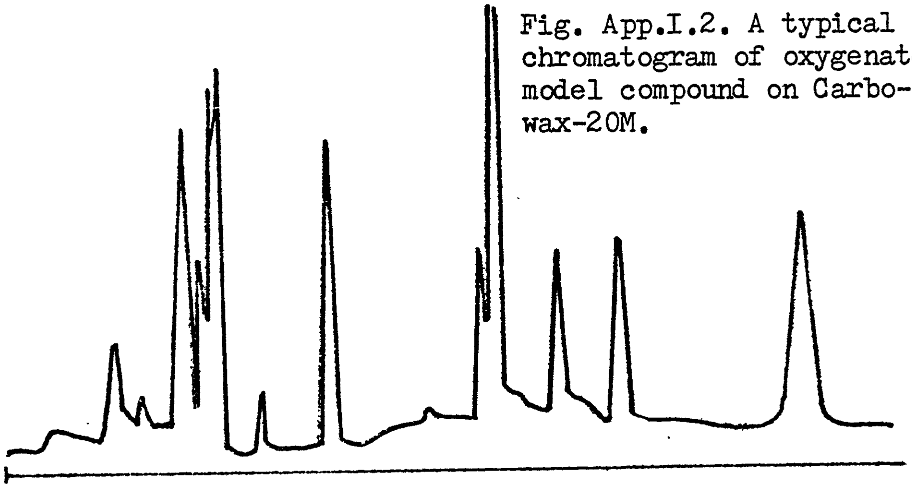


Fig. App.I.2. A typical chromatogram of oxygenated model compound on Carbowax-20M.

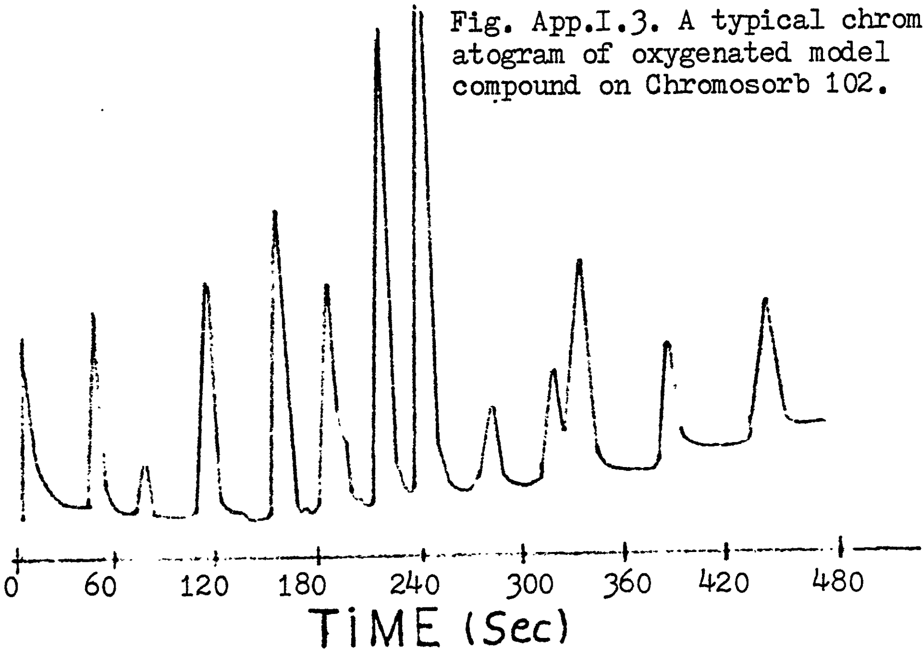


Fig. App.I.3. A typical chromatogram of oxygenated model compound on Chromosorb 102.

Table - APPENDIX I.1 Retention Time and Response Factor on a 2' x 1/8" Tenax Column

Component	Retention Time (sec)	Response Factor
Water	50	.743
Methanol	65	1.000
Acetaldehyde	96	1.23
Ethanol	126	1.06
Arolein	180	1.41
Furan		1.29
Propionaldehyde		1.62
Acetone		0.95
Acetic Acid	230	1.1
2-Butanone	260	1.345
2-Butenal	295	1.386
Acetol	307	1.87
2-Methylfuran	255	1.326
2,3-Butanedione	260	1.579
Acetoin	350	1.103
Furfural	425	1.72
Furfural alc.		
Toluen	390	1.456
Phenol	600	-
Glyoxal	500(?)	-

why water couldn't be absorbed by a trap at 0 deg C. In a series of runs, results were obtained (Table APP.I.2.) which showed the amount of each compound escaping the first trap (dry-ice and alcohol at -77 deg C). This was another indication that this was not the optimum method of product collection, since the separation of individual hydrocarbon compounds, which are absorbed in the lipophilic trap, and of individual high boiling, high molecular weight oxygenated compounds, is not believed to be possible on a single chromatographic column. For the separation of gases like carbon monoxide, methane, ethylene, etc., a lower temperature and longer column must be used. These conditions are not suitable for the separation of high molecular weight compounds. Also, a column which is suitable for less polar compounds such as fixed gases, is not necessarily suitable for very polar compounds such as aldehydes and alcohols.

The biggest problem was the mixture of oxygenated products itself, which is composed of alcohols, acids, ketones, esters, etc. A column which can separate all these compounds is not listed in the literature and has not been found in this study. Of course, if some of the gas fraction gets separated prior to the gas analysis, and a mixture of different fractions is available, single columns could be used to separate specific classes of compounds such as aldehydes, acids etc. Some work on fractionating the heavier molecular weight tar produced in this work into various compound classes was carried out by another investigator (95).

Table - APPENDIX I.2 Absorptivity of Traps for Products

Component	Trap I(-77°C)	Trap II(-196°C)
Water	60-80[a]	20-40
Methanol	43	57
Acetone	13	87
Ethanol	40	60
Acetaldehyde	20	80

[a] percent by weight

It is clear from the results from the Tenax-GC column that some products, like acetone, furan, acrolein, and proprionaldehyde, have the same retention time. Therefore they cannot be distinguished in this experiment. Other columns were employed with similar results. This showed that the only way to solve this problem would be to separate the fractions before using gas chromatography. A column of Poropak Q showed that, once again, acetone, furan, acrolein, and proprionaldehyde appear at the same retention time. Two other columns, carbowax 20M and Chromosorb 102, were used and typical results of these are shown in Figures App.I.2. and App.I.3. These results show that, for the mixture used in the Tenax GC column, which has a relatively low boiling point (the boiling point of furfural, the highest boiling compound, is 170 deg C), Chromosorb 102 gives better overall results, and as a bonus, gives less tailing for water.

The conclusions of this study are:

1) A mixture of high molecular weight and low molecular weight compounds can't be effectively separated in a single column. In other words, different mixtures require different conditions to give the best results. For example, low molecular weight and low boiling compounds require longer columns with very low starting temperatures, while high molecular weight, high boiling compounds need short columns and higher temperatures.

2) Water is a troublesome compound in the Gas Chromatograph, and should be separated somehow before injecting

the material into the column.

3) A mixture of aldehydes, acids, esters, alcohols, and ketones can't be separated in a single column, unless they are fractionated before injection. Of course, in special cases, a mixture of some of each fraction can be separated on a single column.

Appendix II. Response Factors for the Thermal Conductivity Detector on the 3920B Gas Chromatograph

The following response factors were determined by direct calibration on the model 3920B Chromatograph, on a 12 foot x 1/4 inch, Poropak QS column, with a detector temperature of 250 deg C and other operator conditions as specified in Section III.

Carbon Dioxide	1.00	(Reference Compound)
Carbon Monoxide	0.702	
Methane	0.562	
Ethylene	0.706	
Ethane	0.722	
Propylene	0.810	
Methanol	0.753	
Acetaldehyde	0.753	
Butane and Ethanol	0.869	
Acetone	0.827	
Furan	1.133	
Acrolein	1.20	
Acetic Acid	1.07	
Glyoxal	1.33	
Formaldehyde	0.695	
Water	0.695	

The response factor is used to calculate the number of milligrams of a compound i in a sample given by the formula:

$$m_{gi} = \left(\frac{A_i R_i}{A_{CO_2}}\right)(mg_{CO_2})$$

Where: A_{CO_2} = the area of the chromatographic peak produced by component i

A_{CO_2} = the area of a carbon dioxide calibration peak

R_i = the response factor for component i

mg CO_2 = the number of milligrams of carbon dioxide in the calibration sample

In order to obtain the response factor for each component the following steps were taken:

1) Inject different amounts of component i into the gas chromatograph.

2) Plot the area of each chromatographic peak of component i versus the amount of component i in milligrams.

3) Calculate the average area for a known amount of carbon dioxide, which is A_1.

4) Take the slope of the curve of Area of component i vs. an amount of component i in mg. The slope = S. This yields the formula:

$$R_i = \frac{A_1}{mg_{CO2}} \cdot \frac{1}{S_i}$$

Appendix III. Calculation of Centerline Temperature of Sample

In order to determine the temperature profile inside the sample, it was assumed that the sample is an infinite slab. Therefore, heat transfer is only one dimensional and occurs by conduction. Thus, the non-steady state differential equation for heat transfer is:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial x^2} = \alpha \frac{\partial^2 T}{\partial x^2}$$

Any advanced heat transfer text can be referred to for a detailed derivation of this equation. General solutions for certain shapes are readily available. For example, the solution of the above differential equation for an infinite slab of known thickness, heating or cooling from both sides at a surface temperature of Ts, such as the sample used in this study, is:

$$\frac{T_s - \bar{T}_b}{T_s - T_a} = \frac{8}{\pi^2} \left(e^{-a_1 N_{F\circ}} + \frac{1}{a} e^{-9\, a_1 N_{F\circ}} + \frac{1}{25} e^{-25 a_1 N_{F\circ}} + \ldots \right)$$

Where:

T_s = Constant average temperature at the surface of the slab.

T_a = Initial temperature of the slab.

T_b = Average temperature of the slab at time t_T

$N_{F\circ}$ = Fourier number, defined as $\alpha t_T / s^2$

α = thermal diffusivity

t_T = time of heating or cooling

S = One half of slab thickness, in this study, one fourth.

$a_1 = (\pi/2)^2$

A graphical solution of this equation is shown in Figure App.III.1.(96).

The following equations are used to calculate the physical and thermal properties of cellulose (19).

D = 1.58 gr/cc

$K_{30} = (0.9769 + 0.1348\ D + 2.633\ D^2) \times 10^4$ cal/cm - sec -°c deg C

$K_t = K_o \times (T_o + 273) / (T + 273)$

$Cp = 0.29 + 0.64 \times 10^{-3}\ T$

where T is the temperature of the sample in deg C

Therefore:

α = 5.25 x 10-4 cm2/sec @ 300 deg C

α = 1.22 x 10-4 cm2/sec @ 1000 deg C

For a sample of cellulose with 1 = 0.0101cm thickness:

t_T = 0.011 sec @ 300 deg C

t_T = 0.028 sec @ 1000 deg C

Which are quite small for the assumption of constant temperature

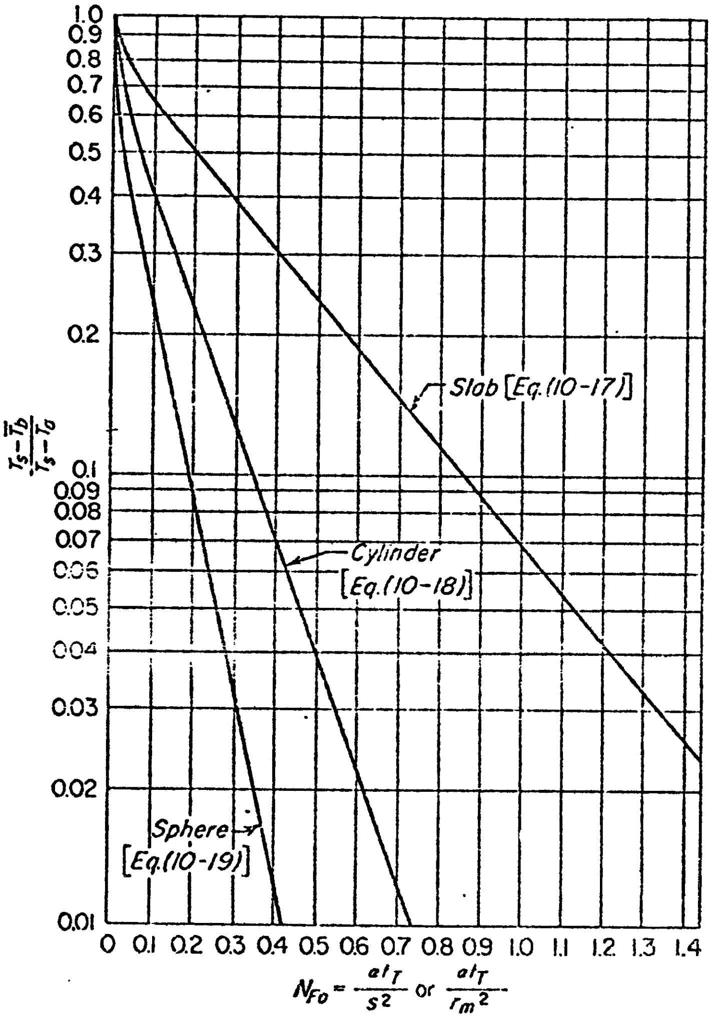


Figure App.III.1. Average temperature during unsteady-state heating or cooling of a large slab, an infinity iong cylinder, or a sphere (96).

gradient in the pyrolysis process.

Appendix IV

Experimental Results

The original data for this thesis are in the possession of Professor Jack B. Howard of the Chemical Engineering Department, M.I.T.

Runs with Zero Holding Time at
5 psig He Pressure and 1000°C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH_4	CO_2	C_2H_4	C_2H_6	H_2O	C_3H_6	CH_3OH	CH_3CHO	C_4.+ C_2H_5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
202A	1112	-	23.99	2.51	3.46	2.11	0.25	-	0.52	0.44	1.63	0.68	0.99	1.37	50.89	4.63	93.48
63TA	977	-	21.92	2.40	3.06	2.06	0.22	6.94	0.52	0.74	1.29	0.27	0.80	0.57	50.62	3.57	95.04
64TA	1000	-	22.56	2.62	3.36	2.18	0.28	9.22	0.80	0.98	1.7	0.38	0.82	0.56	49.12	3.91	98.53
65TA	1008	-	22.46	2.53	2.89	2.01	0.24	7.45	0.62	0.86	1.50	0.30	0.87	-	48.75	4.38	95.09
66TA	947	-	22.7	2.64	3.08	2.28	0.27	9.86	0.64	1.13	1.34	0.32	0.59	-	45.37	3.83	95.09
107A	950	-	-	-	-	-	-	6.70	-	-	-	-	-	-	50.00	3.66	-
67TA	900	-	17.38	1.95	-	-	-	-	-	-	-	-	-	-	49.64	3.29	-
106A	900	-	18.00	1.78	2.48	1.81	0.27	5.62	0.85	1.16	2.06	0.38	1.24	1.13	50.00	2.94	90.21
68TA	795	-	17.57	1.73	2.53	1.51	0.16	9.01	0.64	1.86	1.50	0.29	0.84	0.84	53.34	3.08	94.90
69TA	759	-	15.82	1.10	2.38	1.05	0.17	8.72	0.69	1.03	1.58	0.29	1.00	0.85	59.92	3.32	97.03
74TA	718	-	7.92	0.57	1.60	0.35	0.04	8.91	0.44	0.75	1.30	0.21	0.58	0.24	60.09	9.35	92.25
116A	650	-	3.71	0.32	1.46	0.27	0.04	6.87	0.52	0.69	1.03	0.13	0.64	0.37	57.92	13.51	87.49
70TA	700	-	-	0.22	1.11	0.15	0.01	6.34	0.25	0.74	0.80	0.09	0.64	0.20	57.11	14.95	-
71TA	610	-	1.14	0.03	0.72	0.01	0.0	6.21	0.10	-	0.21	0.03	0.53	0.18	47.42	42.46	99.06
73TA	550	-	-	0.0	0.53	0.0	0.0	4.75	0.0	0.42	0.04	0.0	0.09	0.0	28.77	64.30	98.92
207A	551	-	0.54	0.01	0.49	0.02	0.01	3.56	0.0	0.45	0.04	0.02	0.23	0.28	22.84	76.19	104.68
72TA	495	-	0.99	0.0	0.30	0.0	0.0	3.55	0.0	-	0.01	0.0	0.07	0.12	12.14	83.63	100.51
95TA	393	-	-	-	-	-	-	-	-	-	-	-	-	-	-	98.72	98.72
173A	473	-	-	0.0	0.31	0.0	0.0	2.98	0.0	0.25	0.02	0.0	0.07	0.18	4.20	94.10	102.12
174A	650	-	-	-	1.17	0.20	0.03	5.88	0.39	0.80	0.64	0.16	0.59	0.60	57.46	25.08	92.99
190A	854	-	15.81	1.99	2.70	1.98	0.21	6.92	0.86	1.22	1.51	0.51	0.91	1.00	56.39	3.71	96.72
191A	895	-	-	2.31	3.12	2.10	0.24	8.99	0.80	1.02	2.21	0.38	0.98	0.98	51.22	3.99	-

Runs with Holding Time at 5 psig He pressure and 1000°C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH_4	CO_2	C_2H_4	C_2H_6	H_2O	C_3H_6	CH_3OH	CH_3CHO	C_4.+ C_2H_5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
94TA	426	5	-	0.0	0.63	0.0	0.0	4.07	0.0	0.09	0.01	0.0	0.08	0.0	30.24	65.24	100.34
96TA	403	10	-	0.01	0.90	0.0	0.0	6.49	0.0	0.11	0.08	0.0	0.06	0.0	45.20	44.81	97.65
93TA	415	30	0.25	0.01	1.45	0.01	0.0	5.41	0.0	0.21	0.05	0.0	0.16	0.0	83.55	6.16	97.27
89TA	510	2	4.65	0.1	0.89	0.20	0.0	5.72	0.0	0.42	0.08	0.0	0.16	0.0	56.09	33.24	101.28
91TA	495	5	-	0.2	1.39	0.1	0.0	6.80	0.1	0.15	0.19	0.02	0.04	0.06	75.68	4.44	-
90TA	510	10	-	0.05	1.53	0.04	0.01	6.38	0.01	0.28	0.22	0.01	0.26	0.09	75.32	4.19	-
92TA	510	30	-	0.05	1.58	0.04	0.01	5.38	0.02	0.29	0.25	0.01	0.29	0.11	78.35	3.75	-
83TA	610	2	5.70	0.03	1.15	0.05	0.01	5.31	0.16	0.99	0.42	0.02	0.48	0.07	71.69	10.73	96.70
87TA	605	5	7.04	0.15	1.55	0.18	0.03	5.62	0.31	0.82	0.69	0.06	0.59	0.17	76.33	3.12	96.57
85TA	600	10	6.48	0.19	2.50	0.13	0.02	6.10	0.17	0.22	0.45	0.04	0.38	0.13	76.24	3.17	96.23
86TA	595	30	8.28	0.17	1.54	0.17	0.03	6.13	-	-	0.80	0.07	0.78	0.33	75.81	2.44	96.56
80TA	705	2	12.93	1.42	2.66	0.77	0.12	5.46	0.70	0.79	2.03	0.30	1.14	0.41	61.90	2.74	93.34
81TA	710	5	11.57	0.70	2.88	0.84	0.11	5.37	0.56	1.00	1.99	0.79	1.49	1.71	64.16	2.59	95.75
82TA	715	10	13.26	0.81	2.91	0.76	0.11	5.13	0.47	0.59	1.24	0.19	0.73	0.48	65.24	2.75	94.67
115A	738	30	11.27	0.70	2.55	0.58	0.08	5.19	0.70	0.69	1.52	0.23	0.84	0.38	61.67	2.74	90.15
78TA	760	2	16.08	-	-	-	-	6.44	0.99	1.64	2.40	0.52	1.52	1.46	57.62	2.86	-
79TA	782	5	-	2.07	2.88	1.43	0.22	5.97	0.74	0.71	2.14	0.34	1.37	0.84	55.14	2.85	-
99TA	795	2	20.69	2.05	2.81	1.64	0.24	6.51	0.82	0.76	1.88	0.35	0.94	1.63	53.33	3.11	96.87
100A	790	5	23.34	1.20	2.32	1.22	0.18	6.39	0.58	0.67	1.42	0.24	0.81	0.37	55.35	2.77	96.77
114A	823	30	27.45	2.15	2.78	1.37	0.18	5.54	0.79	1.00	1.78	0.33	1.15	0.57	51.71	4.63	101.43
101A	887	2	21.08	1.89	2.77	1.65	0.21	5.88	0.71	0.70	1.60	0.30	0.93	0.48	50.18	3.41	91.18
102A	892	5	21.50	2.60	2.77	1.64	0.15	5.88	0.61	0.70	1.25	0.33	0.68	0.99	51.31	3.89	94.36
118A	907	5	-	2.30	3.05	2.00	0.27	4.72	0.82	0.75	1.81	0.35	0.98	0.77	42.83	3.72	-
112A	911	10	-	2.29	3.42	1.37	0.17	4.54	0.42	0.33	1.50	0.30	0.95	0.56	44.28	6.6	-
97TA	950	2	27.85	2.19	3.01	1.84	0.21	5.60	0.49	0.50	1.08	0.26	0.64	0.26	51.70	3.80	99.42
98TA	935	5	-	2.23	2.86	1.85	0.24	4.40	0.73	1.03	1.52	0.27	0.71	0.38	50.82	4.70	-
104A	1008	2	23.41	2.67	4.13	2.06	0.24	7.71	0.80	0.78	1.31	0.50	0.83	0.54	50.40	3.45	98.81
105A	1006	5	-	2.04	2.39	1.72	0.18	4.99	0.55	0.55	1.16	0.26	0.64	0.25	51.46	2.77	-
110A	1051	10	25.64	2.02	2.39	1.61	0.18	4.70	0.27	0.27	0.87	0.19	0.59	0.25	53.89	4.67	97.53
109A	1032	10	-	2.64	2.80	1.45	0.14	4.51	0.57	0.67	1.33	0.26	0.71	0.59	45.15	5.17	-
108A	1021	30	30.62	2.36	3.36	1.97	0.26	4.86	0.32	0.28	0.78	0.25	0.44	0.43	50.85	7.22	103.98
204A	N.M.	30	-	3.31	3.97	1.88	0.21	-	0.46	0.67	1.26	0.34	0.77	0.38	46.12	7.08	-
133A	981	30	-	2.63	3.79	1.46	0.14	-	0.32	0.47	0.86	0.35	0.32	0.86	47.42	6.96	-

Runs with no Holding Time at 0.1 mm HG Pressure and 1000°C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH_4	CO_2	C_2H_4	C_2H_6	H_2O	C_3H_6	CH_3OH	CH_3CHO	C4.+ C_2H_5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
V1	281	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0	99.2	99.2
V2	383	-	0.0	0.0	0.05	0.0	0.0	1.80	0.0	0.03	0.0	0.0	0.01	0.01	0.0	97.95	99.85
V3	501	-	0.0	0.0	0.23	0.0	0.0	8.80	0.0	0.0	0.0	0.0	0.06	-	6.94	90.49	106.55
V4	429	-	0.0	-	0.08	-	-	6.52	-	-	-	-	0.0	-	3.35	96.36	106.51
V5	1112	-	18.69	0.92	2.42	-	0.12	7.07	0.52	1.86	4.09	0.84	1.62	0.63	44.07	5.19	90.26
V19	483	-	0.0	0.0	0.36	0.0	0.0	4.31	0.0	0.07	0.03	-	0.05	0.06	30.39	64.82	100.09
V18	650	-	0.49	0.0	0.47	0.01	0.0	5.74	0.0	0.60	0.07	0.0	0.06	0.19	50.64	37.32	95.59
181	740	-	1.53	0.0	0.74	0.06	0.0	5.72	0.05	1.36	0.21	0.0	0.80	0.24	65.29	19.06	94.7
177	721	-	-	-	-	-	-	-	-	-	-	-	-	-	62.76	16.86	-
V20	7.0	-	1.61	0.02	0.64	0.10	0.01	7.02	0.07	0.56	0.33	0.07	0.32	0.08	73.37	15.99	100.57
171	562	-	-	-	-	-	-	-	-	-	-	-	-	-	28.08	66.61	-
V21	769	-	2.33	0.09	0.54	0.16	0.01	5.33	0.34	0.53	0.43	0.13	0.39	0.13	73.85	7.52	91.79
V22	833	-	5.09	0.15	0.90	0.35	0.02	8.06	0.72	0.76	1.03	0.29	0.71	0.19	75.55	6.7	100.17
V23	940	-		0.29	1.65	0.89	0.04	7.02	0.51	1.01	2.67	1.49	2.3	0.59	63.69	9.61	94.65
V24	983	-	9.66	0.33	1.36	0.95	0.05	8.15	0.53	1.12	1.99	0.75	1.31	0.90	54.2	11.24	92.54
V28	524	-	-	-	-	-	-	-	-	-	-	-	-	-	19.80	84.4	-
V27	583	-	-	-	-	-	-	-	-	-	-	-	-	-	35.71	52.33	-
V26	621	-	-	-	-	-	-	-	-	-	-	-	-	-	45.98	49.1	-
119A	949	-	15.86	0.74	1.09	0.37	0.01	4.89	0.55	0.73	2.59	0.46	1.44	0.64	-	4.91	-
122A	896	-	-	0.76	1.88	0.80	0.02	5.53	0.58	0.40	2.21	0.74	1.46	0.70	-	8.40	-
125A	853	-	-	-	1.43	0.53	0.01	5.57	0.66	0.95	1.96	0.48	1.32	0.56	-	5.49	-
120A	877	-	10.89	0.22	1.14	0.61	0.04	6.61	0.66	0.65	1.45	0.43	1.08	0.50	-	5.30	-
124A	789	-	6.99	0.10	1.13	0.32	0.02	5.45	0.36	0.38	0.71	0.32	0.81	0.10	-	6.64	-
121A	731	-	4.90	0.01	0.86	0.12	0.00	5.36	0.31	0.29	0.74	0.22	0.62	0.23	-	9.03	-

Runs with Holding Time at 0.1 mm Hg Pressure and 1000°C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH4	CO2	C2H4	C2H6	H2O	C3H6	CH3OH	CH3CHO	C4.+ C2H5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
176	545	2	0.0	0.0	0.35	0.02	0.0	3.73	-	-	0.14	0.07	-	0.24	49.25	12.89	
V10	378	2	0.0	0.0	0.10	0.0	0.0	0.38	0.0	0.06	0.04	0.0	0.0	0.04	4.02	94.76	101.4
V11	475	2	0.01	0.0	0.46	0.0	0.0	5.48	-	0.81	0.06	0.0	0.04	0.06	33.82	52.92	93.67
V14	591	2	1.19	0.02	0.63	0.65	0.0	5.91	0.05	0.75	0.55	0.26	0.23	0.15	74.63	9.09	93.5
V12	843	2	10.39	0.23	1.96	0.68	0.04	6.13	0.34	1.59	2.58	1.49	2.62	1.31	59.8	8.35	97.51
V13	955	2	15.83	0.44	2.64	2.14	0.10	6.43	1.43	1.89	4.02	1.89	2.94	1.78	40.89	11.01	93.43
V17	955	1	15.51	1.07	2.58	2.43	0.13	7.19	1.43	1.31	4.56	1.76	2.98	3.32	45.08	7.61	96.95
V16	1034	5	18.	1.35	3.18	2.65	0.13	8.35	1.57	1.33	3.24	1.54	1.71	0.56	40.03	9.8	93.47
V7	420	30	0.0	0.0	0.94	0.0	0.0	7.51	0.0	0.19	0.07	0.0	0.08	0.04	77.02	4.06	89.91
V6	545	30	0.33	0.01	1.18	0.01	0.01	10.01	0.0	0.55	0.10	0.0	0.09	0.07	78.65	2.4	93.42
V15	721	30	3.13	0.13	1.63	0.18	0.03	6.70	0.12	0.85	1.79	0.90	1.16	0.61	68.01	2.7	87.97
V8	786	30	7.82	0.51	1.89	0.88	0.07	8.51	0.52	1.94	2.70	0.51	1.37	-	70.30	5.34	102.35
V9	955	30	20.79	2.38	5.47	2.45	0.08	6.20	1.45	1.24	1.28	1.36	0.57	0.34	36.27	15.42	95.79

Runs at High Pressure (1000 psig He) at 1000°C/Sec Heating rate with no Holding Time

Run #	Temp. (°C)	Holding Time(S.)	CO	CH4	CO2	C2H4	C2H6	H2O	C3H6	CH3OH	CH3CHO	C4.+ C2H5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
HP2	1097	-	19.14	4.21	8.63	1.65	0.64	15.28	1.05	0.36	0.58	0.38	0.05	0.0	31.63	10.34	93.94
HP3	925	-	16.01	3.20	8.41	1.41	0.71	19.68	1.11	0.40	0.78	0.23	0.27	0.17	34.83	10.08	96.29
HP4	650	-	3.21	0.06	3.86	0.05	0.0	16.65	0.0	0.01	0.18	0.07	0.03	0.0	29.27	40.31	93.29
HP5	775	-	5.66	0.98	7.76	0.59	0.35	23.18	0.40	0.39	0.89	0.48	0.62	0.52	40.83	8.76	91.41
HP6	1050	-	16.85	4.10	11.16	1.58	0.76	22.46	1.09	0.59	0.93	0.40	0.13	0.0	28.36	8.97	97.3

Runs with no Holding Time at 5 psig He Pressure and 350 C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH4	CO2	C2H4	C2H6	H2O	C3H6	CH3OH	CH3CHO	C4.+ C2H5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
TB5	286.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	99.48	99.48
TB2	338.	-	0.0	0.0	0.03	0.0	0.0	2.35	0.0	0.13	0.0	0.0	0.03	0.0	0.10	98.27	100.72
TB1	403.	-	0.0	0.0	0.18	0.0	0.0	4.71	0.0	-	0.09	0.02	0.06	0.0	4.45	93.38	102.88
TB6	500.	-	0.40	0.01	0.60	0.01	0.0	5.45	0.0	0.11	0.10	0.0	0.10	0.03	40.60	55.36	102.78
TB13	457.	-	0.01	0.0	0.25	0.0	0.0	3.99	0.0	0.32	0.07	0.0	0.08	0.0	8.32	87.52	100.55
TB14	540.	-	0.74	0.02	0.74	0.03	0.0	5.7	0.04	0.67	0.06	0.07	0.18	0.05	46.88	37.58	92.76
TB15	525	-	1.09	0.01	0.77	0.02	0.0	5.36	0.01	0.34	0.10	0.01	0.14	0.01	45.51	44.2	97.56
TB3	545	-	0.28	0.01	0.63	0.01	0.0	5.49	0.0	1.19	0.12	0.0	0.09	0.02	34.49	62.91	105.3
TB7	665	-	3.51	0.69	2.57	0.87	0.15	7.16	0.49	0.93	1.45	0.25	0.76	0.04	64.98	3.95	81.81
TB12	642	-	9.73	0.36	2.16	0.46	0.07	7.54	0.37	1.11	1.55	0.43	0.80	0.64	64.01	3.18	91.81
TB4	709	-	10.05	0.7	2.66	0.89	0.14	6.11	0.59	1.02	-	1.61	2.01	2.16	65.08	2.99	96.73
TB9	709	-	7.41	0.55	2.21	0.71	0.10	8.36	0.55	1.07	1.42	0.94	0.92	0.39	68.1	3.03	95.81
TB8	807	-	5.22	0.52	2.35	0.66	0.10	7.46	0.63	2.11	1.45	0.53	0.85	0.35	72.1	3.09	96.91
TB21	376	-	0.0	0.0	0.20	0.0	0.0	4.22	0.0	0.24	0.08	0.08	0.0	0.12	4.84	92.01	101.78
TB23	787	-	5.74	0.72	3.51	0.92	0.14	7.93	0.73	0.94	2.41	1.22	1.16	0.28	76.68	3.51	105.89

Runs with no Holding Time at 0.1 mm Hg Pressure and 1000°C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH4	CO2	C2H4	C2H6	H2O	C3H6	CH3OH	CH3CHO	C4.+ C2H5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
TB22	304	-	-	-	-	-	-	-	-	-	-	-	-	-	-	99.66	99.66
TB18	416	-	0.0	0.0	0.05	0.0	0.0	1.22	0.0	0.03	0.0	0.0	0.02	0.02	0.98	98.89	101.22
TB17	403	-	0.0	0.0	0.22	0.0	0.0	3.26	0.0	0.09	0.06	0.0	0.05	0.03	9.79	87.4	100.91
TB16	526	-	0.0	0.0	0.22	0.0	0.0	2.57	0.0	0.08	0.05	0.0	0.02	0.01	21.39	71.63	95.97
TB11	553	-	0.29	0.0	0.42	0.01	0.0	3.97	0.0	0.32	0.14	0.09	0.11	0.12	61.86	27.62	95.00
TB10	626	-	1.01	0.03	0.54	0.06	0.01	6.74	0.03	0.27	0.25	0.03	0.29	0.04	74.65	11.12	95.07
TB20	679	-	3.82	0.10	0.95	0.32	0.02	7.20	0.14	0.88	1.09	0.29	0.80	0.15	79.39	2.15	97.31
TB19	769	-	1.10	0.07	0.48	0.20	0.01	4.01	0.14	0.41	0.57	0.08	0.38	0.05	81.09	2.34	91.55
180	942	-	-	0.27	1.36	0.30	-	5.85	0.37	0.53	1.24	0.20	1.36	0.05	75.22	3.11	-
TB24	751	-	4.99	0.11	1.54	0.34	0.02	7.45	-	0.50	0.91	0.17	0.72	0.04	74.78	2.76	94.33

Runs with no Holding Time at 5 psig He pressure and 10000-15000°C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH_4	CO_2	C_2H_4	C_2H_6	H_2O	C_3H_6	CH_3OH	CH_3CHO	C4.+ C_2H_5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
TC1		-	0.0	0.0	0.0	0.0	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	-	98.2	98.2
TC2		-	0.0	0.0	0.0	0.0	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	-	97.53	97.53
TC4		-	1.53	0.0	0.43	0.01	0.0	7.45	0.0	0.63	0.08	0.0	0.05	0.0	33.07	72.51	115.85
TC3		-	2.46	0.10	0.90	0.16	0.02	8.06	0.14	1.32	0.86	0.28	0.38	0.14	48.23	38.6	101.56
TC9		-	0.0	0.0	0.1	0.0	0.0	1.54	0.0	0.0	0.0	0.0	0.0	0.0	-	97.73	99.37
TC8		-	0.0	0.0	0.27	0.0	0.0	4.39	0.0	0.77	0.09	0.0	0.3	0.05	7.94	89.55	103.11
TC7		-	3.0	0.84	1.84	1.15	0.14	8.94	0.86	0.67	1.31	0.46	0.41	0.41	56.82	15.85	92.68
TC5		-	17.3	1.38	2.46	1.81	0.23	9.15	1.35	0.87	2.74	0.69	1.64	0.83	48.73	2.51	91.59
TC6		-	21.23	1.41	3.19	2.25	0.21	8.38	1.57	1.59	2.29	0.60	1.24	0.58	46.89	3.5	94.91

Runs with no Holding Time at 5 psig He Pressure and ≤100°C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH_4	CO_2	C_2H_4	C_2H_6	H_2O	C_3H_6	CH_3OH	CH_3CHO	C4.+ C_2H_5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
TD1	280	-															
TD2	331	-	0.0	0.0	0.04	0.0	0.0	3.48	0.0	0.03	0.0	0.0	0.05	0.0	0.13	98.0	101.72
TD3	385	-	0.0	0.0	0.21	0.0	0.0	3.31	0.0	0.07	0.05	0.0	0.03	0.48	7.44	88.69	99.85
TD4	438	-	0.0	0.0	0.35	0.0	0.0	4.86	0.0	0.16	0.07	0.0	0.05	0.04	15.57	83.25	104.36
TD6	475	-	-	0.0	0.82	0.0	0.0	4.98	0.0	0.08	0.10	0.0	0.07	0.04	52.96	41.16	100.22
TD5	497	-	0.43	0.0	0.72	0.01	0.0	5.33	0.0	0.09	0.09	0.0	0.08	0.03	75.03	14.17	95.99
TD7	538	-	3.95	0.01	1.23	0.02	0.0	7.61	0.0	0.71	0.36	0.12	0.23	0.12	83.98	5.03	102.19
TD8	514	-	0.46	0.01	1.08	0.01	0.0	4.64	0.0	0.04	0.15	0.0	0.14	0.01	80.99	14.19	101.72

Runs with Different Sample Thickness at 5 psig Pressure and 1000°C/Sec Heating Rate

Run #	Temp. (°C)	Holding Time(S.)	CO	CH4	CO2	C2H4	C2H6	H2O	C3H6	CH3OH	CH3CHO	C4.+ C2H5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
l=0.0193 cm	1020	-	20.00	2.39	5.60	2.10	0.24	9.29	0.61	-	1.47	0.31	0.89	0.43	43.85	2.43	89.59
	987	-	17.41	2.12	2.67	1.87	0.19	8.26	0.44	0.98	1.26	0.23	0.86	0.27	55.56	2.23	94.02
	1010	-	20.96	2.23	2.94	2.04	0.24	8.75	0.66	0.81	1.59	0.68	1.31	1.18	47.61	2.70	93.35
	955	-	22.68	2.28	3.26	2.26	0.31	10.01	0.78	1.01	1.93	0.33	0.92	0.68	-	2.49	-
	891	-	20.27	2.21	2.94	2.11	-	7.36	0.48	-	1.42	0.50	1.38	1.22	55.14	1.52	-
	755	-	14.47	1.36	2.44	1.39	0.21	11.14	0.64	-	1.60	0.47	-	0.58	59.75	1.42	98.64
	733	-	11.09	1.31	2.79	1.39	0.21	10.48	0.65	0.86	1.71	0.36	-	1.06	55.55	2.91	-
	685	-	8.13	0.53	1.78	0.60	0.08	-	0.40	0.46	1.18	0.19	0.73	0.35	69.8	7.35	-
	667	-	3.04	0.16	1.05	0.20	0.02	7.08	0.16	0.81	0.58	0.08	0.53	0.26	61.93	24.74	100.73
	640	-	2.16	0.08	0.94	0.12	0.01	5.72	0.09	0.54	0.37	0.01	0.57	0.40	56.64	31.23	99.119
	613	-	-	0.03	0.51	0.07	0.0	5.11	0.02	0.66	0.20	0.0	0.12	0.15	45.4	43.54	-
	547	-	0.53	0.01	0.47	0.02	0.0	3.76	0.0	0.14	0.10	0.0	0.01	0.11	31.86	75.16	112.17
	509	-	2.18	0.0	0.25	0.0	0.0	2.64	0.0	-	0.01	0.0	-	0.07	9.58	86.70	103.04
l=0.04 cm	943	-	18.01	2.84	3.11	2.54	0.29	9.23	0.83	0.60	1.72	0.39	1.72	0.93	-	3.53	-
	1050	-	26.15	3.18	3.64	2.69	0.29	10.53	0.67	1.17	1.52	0.32	1.01	1.42	36.46	4.64	93.45
	1000	-	-	2.39	3.00	2.55	-	7.48	-	-	-	-	-	-	39.63	3.44	-
	1021	-	-	-	3.46	2.38	0.24	10.38	0.92	0.71	1.51	0.30	0.71	0.51	41.39	4.08	-

EFFECT OF SAMPLE THICKNESS BY FOLDING IT OVER

Run #	Temp. (°C)	Holding Time(S.)	CO	CH_4	CO_2	C_2H_4	C_2H_6	H_2O	C_3H_6	CH_3OH	CH_3CHO	C_4.+ C_2H_5OH	Acetone+ Furan	C.H.O.	Tar	Char	Material Balance
63	977 (1)*	0	21.97	2.40	3.06	2.06	0.22	6.94	0.52	0.74	1.29	0.27	0.80	0.57	50.62	3.57	95.04
65	1008 (1)	0	22.46	2.53	2.89	2.01	0.24	7.45	0.62	0.86	1.50	0.30	0.87	0.24	48.75	4.38	98.53
151	967 (2)	0	-	2.43	3.16	1.30	0.13	5.89	0.73	0.75	1.30	0.26	-	0.53	52.74	5.86	-
158	108 (4)	0	17.21	3.73	5.86	2.21	0.22	3.08	1.05	-	1.70	0.22	0.44	-	28.33	45.63	109.68
170	968 (4)	5	44.71	5.32	4.95	2.15	0.14	9.30	0.84	1.44	0.85	0.33	0.92	0.90	25.74	11.20	108.79
106	900 (1)	0	18.00	1.78	2.98	1.81	0.27	5.62	0.85	1.16	2.06	0.38	1.24	1.13	50.00	2.94	92.21
153	923 (2)	0	26.86	2.75	3.87	2.1	0.22	-	-	0.99	1.58	0.39	1.08	0.77	48.52	10.17	99.31
169	908 (2)	2	-	2.37	3.22	2.23	0.26	6.78	0.67	1.05	1.38	0.40	0.57	0.56	47.59	4.39	-
157	873 (4)	0	6.68	0.52	2.20	0.96	0.11	-	0.51	-	0.52	0.16	0.29	0.13	24.07	63.05	99.2
168	903 (4)	5	32.61	3.60	4.95	3.36	0.40	7.18	1.20	0.98	1.63	0.49	0.63	0.76	34.66	8.61	101.36

*- Numbers inside of prantices are number of layers.

RUN CONDITIONS: P= 5 psig He
dT/dt=1000°C/Sec

1 = 0.101 mm.

HYDROGEN DETERMINATION

Run #	Heating Rate (°C/Sec)	Temperature (C)	Holding Time(S)	Pressure (Atm.)	Thickness (M.M.)	H2 (Wt.%)
HR1	1000	1009	0	1.34	0.101	1.34
HR9	"	1024	"	"	"	1.02
HR8	"	928	"	"	"	1.38
HR2	"	861	"	"	"	1.02
HR7	"	842	"	"	"	0.85
HR4	"	769	"	"	"	0.86
HR6	"	720	"	"	"	0.74
HR10	"	656	"	"	"	0.23
HR5	"	631	"	"	"	0.11
HR12	"	955	5	"	"	1.12
HR13	"	950	30	"	"	1.68
HR14	"	843	5	"	"	1.02
HR15	"	867	30	"	"	1.23
HR17	"	769	5	"	"	0.64
HR16	"	781	30	"	"	0.74
HR21	"	901	0	"	0.101(2)*	1.50
HR22	"	970	5	"	0.101(4)	2.65
HR24	"	882	2	"	0.101(2)	1.41
HR25	"	900	10	"	0.101(4)	2.27
HR18	"	950	0	0.000131	0.101	0.86
HR19	"	855	"	"	"	0.45
HR20	"	741	"	"	"	0.09
HR23	100	600	60	1.34	"	0.00
HR30	350	886	5	"	"	0.22
HR29	400	1005	0	"	"	1.64
HR27	1000	889	0	"	0.193	0.87
HR28	"	907	"	"	0.40	0.97

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*- Number inside prantice is number of layers.

Appendix V

Computer Programs used in this Study

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C     PROGRAM CLFIT                                                     CEL00010
C                                                                       CEL00020
C     MARK W. ZACHARIAS(96)- SEPTEMBER 18, 1978                         CEL00030
C                                                                       CEL00040
C          CLFIT, CFIN, CFOUT, AND INTEG COMPRISE A SET OF MODULAR,     CEL00050
C     VERSATILE, AND WELL DOCUMENTED PROGRAM TO PERFORMS A 'BEST FIT'   CEL00060
C     ANALYSIS ON COAL PYROLYSIS DATA.  THE SYSTEM IS DESIGNED TO BE    CEL00070
C     APPLICABLE FOR A WIDE VARIETY OF PYROLYSIS MODELS, WITH A MINIMUM CEL00080
C     EFFORT EXPENDED BY THE USER.                                      CEL00090
C          CLFIT IS THE MAIN CALLING PROGRAM WHICH DECLARES ARRAYS AND  CEL00100
C     LABELED COMMONS, AND CALLS THE FOLLOWING SYSTEM SUBPROGRAMS:      CEL00110
C                                                                       CEL00120
C          CFIN - READS INPUT DATA                                      CEL00130
C          CFOUT - PRINTS RESULTS                                       CEL00140
C          INTEG - INTEGRATES THE PYROLYSIS MODEL OVER THE INPUT TIME-  CEL00150
C                       TEMPERATURE HISTORY                             CEL00160
C                                                                       CEL00170
C     EACH OF THE ROUTINES LISTED ABOVE IS DESCRIBED IN MORE DETAIL IN  CEL00180
C     THE COMMENTS OF THEIR RESPECTIVE SOURCE CODE.                     CEL00190
C          IN ADDITION TO THESE SYSTEM SUBPROGRAMS, TWO ADDITIONAL      CEL00200
C     ROUTINES ARE REQUIRED IN ORDER TO USE CLFIT:                      CEL00210
C                                                                       CEL00220
C          ZXSSQ - THIS IS A SUBROUTINE INCLUDED IN THE IMSL SUBROUTINE CEL00230
C                  PACKAGE, WHICH IS AVAILABLE TO IPC USERS.  THE       CEL00240
C                  ROUTINE FINDS THE MINIMUM VALUE OF THE SUM OF        CEL00250
C                  THE SQUARES OF TWO OR MORE FUNCTIONS OF SEVERAL      CEL00260
C                  VARIABLES.  FOR MORE INFORMATION, SEE MIT-IPS        CEL00270
C                  DOCUMENT AP-9, REVISION 3 (FEB. 1, 1978).            CEL00280
C                                                                       CEL00290
C          MODEL - THIS IS A USER PROVIDED SUBROUTINE WHICH EVALUATES   CEL00300
C                  THE PYROLYSIS MODEL BEING USED.  THE CALLING         CEL00310
C                  SEQUENCE FOR MODEL IS:                               CEL00320
C                                                                       CEL00330
C                 CALL MODEL(PARM,NPAM,TEMP,DELTT,J,RATE,VSTAR)         CEL00340
C                                                                       CEL00350
C                  A DESCRIPTION OF EACH OF THE VARIABLES IN THE        CEL00360
C                  ARGUMENT LIST IS AS FOLLOWS:                         CEL00370
C                                                                       CEL00380
C       VARIABLES  I/O   TYPE  DIMENSION       DESCRIPTION              CEL00390
C         PARM      I    REAL     NPAM     VECTOR OF PARAMETERS         CEL00400
C                                               BEING VARIED            CEL00410
C         NPAM      I   INTEGER    -       DIMENSION OF PARM            CEL00420
C         TEMP      I    REAL      -       TEMPERATURE AT WHICH THE     CEL00430
C                                               MODEL IS BEING          CEL00440
C                                               EVALUATED               CEL00450
C         DELTT     I    REAL              TIME INTERVAL LENGTH         CEL00460
C         J         I   INTEGER    -       TIME-TEMP POINT NUMBER       CEL00470
C                                          (DELTT AND J ARE NEEDEDCEL00480
C                                               FOR MORE COMPLICATED    CEL00490
C                                               MODELS)                 CEL00500
C         RATE      O    REAL      -       RATE AT WHICH COMPONENT INCEL00510
C                                               CONSIDERATION IS BEING  CEL00520
C                                               EVOLVED FROM THE COAL   CEL00530
C                                               PARTICLE                CEL00540
C         VSTAR     O    REAL      -       YIELD OF COMPONENT AFTER     CEL00550
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C                                            AN INFINITE AMOUNT OF  CEL00560
C                                            TIME                   CEL00570
C                                                                   CEL00580
C                         IN ADDITION TO THE INPUTS IN THE ARGUMENT CEL00590
C                         LIST, MODEL SHOULD ACCESS LABELED COMMON  CEL00600
C                         'CONST', WHICH CONTAINS ANY INPUT CONSTANTS CEL00610
C                         WHICH ARE NEEDED BY THE MODEL.            CEL00620
C                                                                   CEL00630
C          IN MOST CASES, THE PYROLYSIS MODEL WILL BE TOO COMPLICATED TOCEL00640
C      USE THE STANDARD FORM OF 'INTEG.'  IN THIS CASE, THE USER SHOULD CEL00650
C      WRITE HIS OWN VERSION OF 'INTEG' WHICH COMBINES THE DUTIES OF  CEL00660
C      'MODEL' AND 'INTEG' DESCRIBED ABOVE.  THE CALLING SEQUENCE FOR CEL00670
C      INTEG IS AS FOLLOWS:                                           CEL00680
C                     CALL INTEG(PARM,NRUNS,NPAM,ERROR)               CEL00690
C                                                                     CEL00700
C      THE VARIABLES INT THE ARGUMENT LIST ARE DEFINED BELOW.  IN ALL CEL00710
C      CASES, INTEG SHOULD ACCESS LABELED COMMONS 'TMTMP' AND 'CONST,' CEL00720
C      WHICH CONTAIN, AMOUNG OTHER THINGS, TIME-TEMPERATURE HISTORIES CEL00730
C      AND CONSTANTS REQUIRED BY THE PYROLYSIS MODEL.                 CEL00740
C                                                                     CEL00750
C      NOMENCLATURE FOR THIS PROGRAM IS AS FOLLOWS:                   CEL00760
C                                                                     CEL00770
C         VARIABLES  I/O   TYPE   DIMENSION      DESCRIPTION          CEL00780
C          CALVL      -    REAL     NRUNS    VECTOR OF CALCULATED     CEL00790
C                                                WEIGHT LOSSES        CEL00800
C          CONST      -    REAL      10      VECTOR OF CONSTANTS      CEL00810
C                                                REQUIRED BY 'MODEL'  CEL00820
C          DELTA      -    REAL       -      ABSOLUTE GRADIENT CONV.  CEL00830
C                                                TOLERANCE FOR ZXSSQ  CEL00840
C          EPS        -    REAL       -      RELATEIVE SUM-OF-SQUARES CEL00850
C                                                CONVERGENCE TOLERANCE CEL00860
C                                                FOR ZXSSQ            CEL00870
C          ERROR      -    REAL     NRUNS    VECTOR OF DIFFERENCES    CEL00880
C                                                BETWEEN THE ELEMENTS OFCEL00890
C                                                CALVL AND EXPVL      CEL00900
C          IOPT       -   INTEGER     -      OPTION PARAMETER PASSED  CEL00910
C                                                TO ZXSSQ             CEL00920
C          IER        -   INTEGER     -      ZXSSQ ERROR PARAMETER:   CEL00930
C                                                0 = NO ERROR         CEL00940
C                                                129 OR 132 = SINGULAR CEL00950
C                                                   JACOBIAN MATRIX   CEL00960
C                                                131 = CONVERGENCE    CEL00970
C                                                   MAY HAVE OCCURED. CEL00980
C                                                   SEE ZXSSQ FOR     CEL00990
C                                                   FURTHER INFO.     CEL01000
C                                                133 = MAXIMUM NUMBER OFCEL01010
C                                                   ITERATIONS NEEDED CEL01020
C          INFER      -   INTEGER     -      CONVERGENCE FLAG FROM    CEL01030
C                                                ZXSSQ                CEL01040
C          MAXFN      -   INTEGER     -      MAXIMUM NUMBER OF CALLS TOCEL01050
C                                                INTEG                CEL01060
C          MAXIT      -   INTEGER     -      MAXIMUM NUMBER OF        CEL01070
C                                                ITERATIONS           CEL01080
C          MXNTM      -   INTEGER     -      MAXIMUM NUMBER OF TIME-  CEL01090
C                                                TEMP POINTS FOR AN   CEL01100
C
```

```
C                                             EXPERIMENTAL RUN        CEL01110
C     MXTDF      -   INTEGER     -      DEFAULT VALUE FOR MAXIT       CEL01120
C     NAMDL      -    CHAR.      6      MODEL NAME                    CEL01130
C     NAMRN      -    CHAR.    NRUNS    RUN NUMBER                    CEL01140
C     NMCMP      -    CHAR.      2      COMPONENT NAME                CEL01150
C     NPAM       -   INTEGER     -      NUMBER OF PARAMETERS BEINGCEL01160
C                                          VARIED (MAXIMUM 10)        CEL01170
C     NRUNS      -   INTEGER     -      NUMBER OF EXPERIMENTAL        CEL01180
C                                          RUNS (MAXIMUM 10)          CEL01190
C     NSIG       -   INTEGER     -      NUMBER OF SIGNIFICANT         CEL01200
C                                          DIGITS AGREEMENT           CEL01210
C                                          NECESSARY BETWEEN          CEL01220
C                                          SUCCESSIVE PARAMETER       CEL01230
C                                          VALUES FOR CONVERGENCE     CEL01240
C     NSGDF      -   INTEGER     -      DEFAULT VALUE FOR NSIG        CEL01250
C     PARM       -   INTEGER   NPAM     VECTOR OF PARAMETERS          CEL01260
C                                          BEING VARIED               CEL01270
C     PZX        -    REAL       4      OPTIONAL VECTOR PASSED TO     CEL01280
C                                          ZXSSQ                      CEL01290
C     RUNVL      -    REAL     NRUNS    VECTOR OF INPUT VALUES        CEL01300
C                                          WHICH VARY FOR EACH        CEL01310
C                                          RUN.                       CEL01320
C     SSQ        -    REAL       -      SUM OF THE SQUARES OF THE     CEL01330
C                                          ELEMENTS IN ERROR          CEL01340
C     TEMP       -    REAL  NRUNS,MXNTM ARRAY OF TEMPERATURES         CEL01350
C     TIME       -    REAL  NRUNS,MXNTM ARRAY OF TIME INTERVALS       CEL01360
C     VSTAR      -    REAL       -      YIELD OF THE COMPONENT IN     CEL01370
C                                          CONSIDERATION AFTER AN     CEL01380
C                                          INFINITE AMOUNT OF TIMECEL01390
C     WORK       -    REAL      160     WORK AREA FOR ZXSSQ           CEL01400
C     XJAC       -    REAL     60,10    JACOBIAN MATRIX OUTPUT        CEL01410
C                                          FROM ZXSSQ                 CEL01420
C     XJTJ       -    REAL       -      WORK AREA FOR ZXSSQ           CEL01430
C                                                                     CEL01440
C          THE MAXIMUM NUMBER OF EXPERIMENTAL RUNS IS 60, AND THE     CEL01450
C     MAXIMUM NUMBER OF TIME-TEMPERATURE POINTS PER RUN IS 20.  ALSO, CEL01460
C     THERE SHOULD BE NO MORE THAN 10 VARIABLE PARAMETERS, OR 10 INPUT CEL01470
C     CONSTANTS REQUIRED FOR THE PYROLYSIS MODEL.                     CEL01480
C          THE DEFAULT VALUE FOR THE NUMBER OF TIME-TEMPERATURE POINTS CEL01490
C     IS 15.  DEFAULTS FOR EPS, NSIG, AND MAXIT ARE 0.0005, 3, AND    CEL01500
C     20 RESPECTIVELY.  IF A VALUE OF ZERO IS DESIRED FOR EPS, ONE    CEL01510
C     SHOULD USE A VERY SMALL NUMBER RATHER THAN ZERO, SINCE ZERO     CEL01520
C     INDICATES THAT THE DEFAULT VALUE IS TO BE USED.                 CEL01530
C                                                                     CEL01540
      EXTERNAL        INTEG                                           CEL01550
      DIMENSION       PARM(10)   , PZX(4)     , ERROR(60)  , XJAC(600) , CEL01560
     1                XJTJ(55)   , WORK(225)                          CEL01570
      COMMON /TMTMP/  TIME(60,20), TEMP(60,20),EXPVL(60)   , CALVL(60) , CEL01580
     1                                        , NUM(60)    , VSTAR    CEL01590
      COMMON /NAME /  NMCMP(2)   , NAMRN(60)  , NAMDL(6)              CEL01600
      COMMON /CONST/  CONST(10)  , RUNVL(60)                          CEL01610
      DATA            DELTA, EPSDF, IOPT , NSGDF, MXTDF/              CEL01620
     1                0.0  , .0005, 1    , 3    , 20   /              CEL01630
C                                                                     CEL01640
C     READ INPUT                                                      CEL01650
```

```
C
      CALL CFIN(PARM,NRUNS,NPAM,NSIG,EPS,MAXIT)
      IXJAC = NRUNS
C
C        CALCULATE TIME INTERVALS FOR NUMERICAL INTEGRATION
C
      DO 10 I=1,NRUNS
           NPNT = NUM(I)* 3
           DO 20 K=2,NPNT
                J = NPNT-K+2
                TIMEN(I,J)=TIMEN(I,J)-TIMEN(I,J-1)
 20        CONTINUE
 10   CONTINUE
C
C        SET DEFAULT VALUES
C
      IF(EPS.EQ.0) EPS = EPSDF
      IF(NSIG.EQ.0) NSIG = NSGDF
      IF(MAXIT.EQ.0) MAXIT = MXTDF
      MAXFN = (NPAM+2)*MAXIT
C
C       EXECUTE LEAST SQUARES FIT
C
      CALL ZXSSQ(INTEG,NRUNS,NPAM,NSIG,EPS,DELTA,MAXFN,IOPT,PZX,PARM,
     1        SSQ,ERROR,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
C
C        PRINT OUTPUT
C
      CALL CFOUT(PARM,NRUNS,NPAM,SSQ)
      STOP
      END
```

```
      SUBROUTINE CFIN (PARM, NRUNS, NPAM, NSIG, EPS, MAXIT)
C
C         CFIN READS ALL INPUT DATA.  THE FORMAT FOR THE INPUT DATA
C     SHOULD BE SELF-EXPLANATORY FROM THE CODE, HOWEVER, FORMS
C     ILLUSTRATING THE PROPER INPUT FORMAT FOR CLFIT ARE AVAILABLE
C     FROM PROF. J. B. HOWARD.  ALL DATA INPUT IS PERFORMED IN THIS
C     SEPARATE ROUTINE SO THAT THE USER CAN EASILY MAKE CHANGES IN THE
C     INPUT FORMAT IF NECESSARY.
C
C        THE INPUT VARIABLES ARE AS FOLLOWS:
C
C        VARIABLES   I/O   TYPE   DIMENSION      DESCRIPTION
C         CONST       -    REAL      10      VECTOR OF CONSTANTS
C                                               REQUIRED BY 'MODEL'
C         EPS         -    REAL      -       SUM-OF-SQUARES CONV.
C                                               TOLERANCE FOR ZXSSQ
C         EXPVL       O    REAL     NRUNS    VECTOR OF EXPERIMENTAL
C                                               WEIGHT LOSSES
C         MAXIT       O   INTEGER    -       MAXIMUM NUMBER OF
C                                               ITERATIONS
C         MXNTM       -   INTEGER    -       MAXIMUM NUMBER OF TIME-
C                                               TEMP POINTS FOR AN
C                                               EXPERIMENTAL RUN .
C         NAMDL       -    CHAR.     6       MODEL NAME
C         NAMRN       -    CHAR.    NRUNS    RUN NUMBER
C         NMCMP       -    CHAR.     2       COMPONENT NAME
C         NIN         -   INTEGER    -       INPUT FILE NUMBER
C         NPAM        O   INTEGER    -       NUMBER OF PARAMETERS BEING
C                                               VARIED (MAXIMUM 10)
C         NRUNS       O   INTEGER    -       NUMBER OF EXPERIMENTAL
C                                               RUNS (MAXIMUM 60)
C         NSIG        O   INTEGER    -       NUMBER OF SIGNIFICANT
C                                               DIGITS AGREEMENT
C                                               NECESSARY BETWEEN
C                                               SUCCESSIVE PARAMETER
C                                               VALUES FOR CONVERGENCE
C         PARM        O   INTEGER   NPAM     VECTOR OF PARAMETERS
C                                               BEING VARIED
C         RUNVL       -    REAL     NRUNS    VECTOR OF INPUT VALUES
C                                               WHICH VARY FOR EACH
C                                               RUN
C         TEMP        O    REAL  NRUNS,MXNTM  ARRAY OF TEMPERATURES
C         TIME        O    REAL  NRUNS,MXNTM  ARRAY OF TIME INTERVALS
C
C          THE MAXIMUM NUMBER OF EXPERIMENTAL RUNS IS 60, AND THE
C     MAXIMUM NUMBER OF TIME-TEMPERATURE POINTS PER RUN IS 20.  ALSO,
C     THERE SHOULD BE NO MORE THAN 10 VARIABLE PARAMETERS, OR 10 INPUT
C     CONSTANTS REQUIRED FOR THE PYROLYSIS MODEL.
C          THE DEFAULT VALUE FOR THE NUMBER OF TIME-TEMPERATURE POINTS
C     IS 15.  DEFAULTS FOR EPS, NSIG, AND MAXIT ARE 0.0005, 3, AND 20,
C     RESPECTIVELY.  IF A VALUE OF ZERO IS DESIRED FOR EPS, ONE SHOULD
C     USE A VERY SMALL NUMBER RATHER THAN ZERO, SINCE ZERO INDICATES
C     THAT THE DEFAULT VALUE IS TO BE USED.
C
      DIMENSION      PARM(10)
```

```
      COMMON /MORK/ RUSH(47,20)
      COMMON /TMTMP/  TIME(60,20), TEMP(60,20),EXPVL(60)  , CALVL(60)  ,
     1                                        ,NUM(60)    , VSTAR
      COMMON /NAME / NMCMP(2)   , NAMRN(60)  , NAMDL(6)
      COMMON /CONST/ CONST(10)  , RUNVL(60)
      DATA           NIN  , N   / 5   , 3   /
C
C        READ THE MODEL TITLE AND THE COMPONENT NAME
C
      READ(NIN,100)(NAMDL(I),I=1,6)
      READ(NIN,100)(NMCMP(I),I=1,2)
C
C        READ THE VALUES OF CONSTANTS REQUIDED BY 'MODEL'
C
      READ(NIN,110)(CONST(I),I=1,10)
C
C        READ THE NUMBER OF VARIABLE PARAMETERS AND THE NUMBER OF
C           EXPERIMENTAL RUNS
C
      READ(NIN,120)NPAM,NRUNS
C
C        FOR EACH RUN, READ THE EXPERIMENTAL VOLATILE YIELD, THE RUN
C           NUMBER, AND THE NUMBER OF TEMPERATURE READINGS GIVEN
C
      DO 10 I=1,NRUNS
           READ(NIN,130)EXPVL(I),NAMRN(I),NUM(I),RUNVL(I)
C
C        SET THE DEFAULT VALUE FOR THE NUMBER OF TEMPERATURE POINTS, IF
C           NECESSARY
C
           IF(NUM(I).EQ.0) NUM(I) = 15
 10   CONTINUE
C
C        READ THE TIME-TEMPERATURE HISTORIES
C
      DO 30 I=1,NRUNS
           L = NUM(I)
           READ(NIN,140)(TIME(I,J),TEMP(I,J),J=1,L)
C
C        CONVERT TEMPERATURES TO DEGREES ABSOLUTE
C
           DO 20 J=1,L
      RUSH(I,J) = TIME(I,J)
                TEMP(I,J) = TEMP(I,J)+273.15
 20   CONTINUE
C
 30   CONTINUE
C
C        READ THE VARIABLE PARAMETER ESTIMATES
C
      READ(NIN,110)(PARM(I),I=1,NPAM)
C
C        READ THE ERROR ESTIMATE AND CONVERGENCE PARAMETERS
C
      READ(NIN,150)NSIG,EPS,MAXIT
```

```
      RETURN                                                            CFI01110
C                                                                       CFI01120
C        FORMAT STATEMENTS                                              CFI01130
C                                                                       CFI01140
 100  FORMAT(6A4)                                                       CFI01150
 110  FORMAT(5E11.3)                                                    CFI01160
 120  FORMAT(2I3)                                                       CFI01170
 130  FORMAT(F5.4,13X,A4,8X,I2,8X,E10.3)                                CFI01180
 140  FORMAT(8(F4.2,F5.0))                                              CFI01190
 150  FORMAT(8X,I2,E10.3,5X,I5)                                         CFI01200
      END                                                               CFI01210
```

```
      SUBROUTINE CFOUT (PARM, NRUNS, NPAM, SSQ)
C
C        CFOUT HANDLES ALL OUTPUT FROM THE CLFIT SYSTEM.  IN ADDITION
C     TO PRINTING HEADINGS AND RESULTS, CFOUT ALSO CALCULATES THE FINAL
C     NORMALIZED ROOT-MEAN-SQUARE ERROR.  VARIABLES PRINTED IN THE
C     OUTPUT ARE AS FOLLOWS:
C
      DIMENSION       PARM(NPAM) , PEAKT(60)
      COMMON /TMTMP/  TIME(60,20), TEMP(60,20),EXPVL(60)  , CALVL(60)  ,
     1                                         NUM(60)    , VSTAR
      COMMON /NAME / NMCMP(2)   , NAMRN(60)  , NAMDL(6)
      COMMON /CONST/ CONST(10)
      EQUIVALENCE    (EACT1,CONST(1)),(AK01,CONST(1)),(FSTAR,CONST(3))
      DATA           NOUT       / 6          /
C
C        PRINT HEADING AND ASSUMED CONSTANT VALUES
C
      WRITE(NOUT,100)(NAMDL(I),I=1,6)
      WRITE(NOUT,110)(NMCMP(I),I=1,2)
      WRITE(NOUT,120)(CONST(I),I=1,10)
C
C        PRINT THE FINAL PARAMETER VALUES
C
      WRITE(NOUT,130)
      DO 10 I=1,NPAM
         WRITE(NOUT,140)I,PARM(I)
 10   CONTINUE
C
C        CALCULATE THE PEAK TEMPERATURE FOR EACH RUN
C
      WRITE(NOUT,150)
      DO 30 I=1,NRUNS
         PEAKT(I) = TEMP(I,1)
         NPNT = NUM(I)
         DO 20 J=2,NPNT
            IF(PEAKT(I).LT.TEMP(I,J)) PEAKT(I) = TEMP(I,J)
 20      CONTINUE
C
C        PRINT THE CALCULATED AND EXPERIMENTAL RESULTS
C
         WRITE(NOUT,160)NAMRN(I),PEAKT(I),CALVL(I),EXPVL(I)
 30   CONTINUE
C
C        CALCULATE NORMALIZED ROOT-MEAN-SQUARE ERROR
C
      RMSN = (SSQ/FSTAR**2)/NRUNS
      RMSN = SQRT(RMSN)
C
C        PRINT ERRORS
C
      WRITE(NOUT,170)SSQ,RMSN
      RETURN
C
C        FORMAT STATEMENTS
C
```

```
 100  FORMAT(1H1,15X,'****RESULTS OF COAL PYROLYSIS BEST-FIT ANALYSIS***
     1*'///1X,'MODEL NAME: ',6A4)
 110  FORMAT(/1X,'COMPONENT EVOLVED: ',2A4)
 120  FORMAT(//1X,'ASSUMED CONSTANT VALUES: '/8X,5E12.4/8X,5E12.4)
 130  FORMAT(///1X,'FINAL PARAMETER VALUES:')
 140  FORMAT(1X,'PARAMETER NO. ',I2,':',E11.4)
 150  FORMAT(///32X,'**RESULTS OF FIT**',//6X,'RUN NO.    PEAK TEMP. ('K
     1)    CALCULATED YIELD    EXPERIMENTAL YIELD')
 160  FORMAT(7X,A4,11X,F5.0,14X,F6.4,15X,F6.4)
 170  FORMAT(///1X,'SUM OF THE SQUARED ERRORS:',E12.4/1X,'NORMALIZED ROO
     1T-MEAN-SQUARE ERROR:',E12.4)
      END
```

```
      SUBROUTINE INTG(TSPNT,FUNC,N,AREA)
C
C         INTG INTEGRATES A FUNCTION USING SIMPSON'S RULE.  ALL
C            FUNCTION EVALUATIONS ARE PASSED TO INTG AS A VECTOR
C            'FUNC'.  THE NUMBER OF FUNCTION EVALUATIONS MUST BE ODD,
C            AND PAIRS OF INDEPENDENT VARIABLE INTERVALS MUST BE EQUAL.
C
C        NOMENCLATURE:
C
C        VARIABLE    I/O   TYPE   DIMENSION       DESCRIPTION
C         AREA        O    REAL       -       VALUE OF THE INTEGRAL
C         FUNC        I    REAL       N       VECTOR OF FUNCTION
C                                                EVALUATIONS
C         N           I   INTEGER     -       NUMBER OF FUNCTION
C                                                EVALUATIONS
C         TSPNT       I    REAL       N       VECTOR OF INDEPENDENT
C                                                VARIABLE POINTS AT
C                                                WHICH THE FUNCTION
C                                                IS EVALUATED
C
      DIMENSION TSPNT(N), FUNC(N)
      AREA = 0.0
      IFNL = N-1
      DO 10 I=2,IFNL,2
           ALOC = FUNC(I-1)+4.0*FUNC(I)+FUNC(I+1)
           ALOC = ALOC*(ABS(TSPNT(I)-TSPNT(I-1)))
           AREA = AREA+ALOC
   10 CONTINUE
      AREA = AREA/3.0
      IF(N.EQ.1) AREA = FUNC(1)
      RETURN
      END
```

```
      SUBROUTINE SETG (PARM, DIST, TSTMW, N)
C
C        THIS ROUTINE INITIALIZES A GAUSSIAN DISTRIBUTION OF
C           ACTIVATION ENERGIES
C
C     NOMENCLATURE:
C
C        VARIABLE     I/O    TYPE    DIMENSION        DESCRIPTION
C         AVE          I     REAL        -       AVERAGE ACTIVATION ENERGY
C         DIST         O     REAL        7       VECTOR OF DISTRIBUTION
C                                                   VALUES
C         N            O    INTEGER      -       DIMENSION OF DIST
C         SIGMA        I     REAL        -       ACTIVATION ENERGY STANDARD
C                                                   DEVIATION
C         TSTMW        O     REAL        -       VECTOR OF POINTS AT WHICH
C                                                   THE DISTRIBUTION IS
C                                                   EVALUATED
C
      DIMENSION PARM(2), DIST(7), TSTMW(7)
C
C        INITIALIZE GAUSSIAN DISTRIBUTION
C
      GAUSS(X) = (0.39834/SIGMA)*EXP(-((X-AVE)/SIGMA)**2/2.0)
C
C        INITIALIZE PARAMETERS
C
      N = 7
      AVE = PARM(1)
      SIGMA = PARM(2)
      EACT = AVE - 3.*SIGMA
C
C        CALCULATE DISTRIBUTION VALUES OVER SIX STANDARD DEVIATIONS
C
      DO 10 I=1,N
           TSTMW(I) = EACT
           DIST(I) = GAUSS(EACT)
           EACT = EACT+SIGMA
   10 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE INTEG (PARM, NRUNS, NPAM, ERROR)                       INT00010
C                                                                       INT00020
C     SINGLE FIRST ORDER REACTION MODEL                                 INT00030
C                                                                       INT00040
C          THIS VERSION OF INTEG FITS THE SINGLE FIRST ORDER REACTION   INT00050
C             MODEL TO EXPERIMENTAL DATA.                               INT00060
C                                                                       INT00070
C         NOMENCLATURE:                                                 INT00080
C                                                                       INT00090
C         VARIABLES   I/O   TYPE   DIMENSION     DESCRIPTION            INT00100
C           AKOX       -    REAL       -      FREQUENCY FACTOR          INT00110
C           AKNEW      -    REAL       -      RATE CONSTANT, END OF     INT00120
C                                                A TIME INTERVAL        INT00130
C           AKOLD      -    REAL       -      RATE CONSTANT, BEGINNING  INT00140
C                                                OF A TIME INTERVAL     INT00150
C           CALVL      -    REAL     NRUNS    VECTOR OF CALCULATED      INT00160
C                                                YIELDS                 INT00170
C           DELTH      -    REAL       -      DELTT/2                   INT00180
C           DELTT      -    REAL   NRUNS,NUM  ARRAY OF TIME INTERVAL    INT00190
C                                                LENGTHS                INT00200
C           EACTX      -    REAL       -      ACTIVATION ENRGY          INT00210
C           ERROR      O    REAL     NRUNS    VECTOR OF ERRORS          INT00220
C                                                BETWEEN CALCULATED     INT00230
C                                                VALUES AND             INT00240
C                                                EXPERIMENTAL VALUES.   INT00250
C           EXPVL      -    REAL     NRUNS    VECTOR OF EXPERIMENTAL    INT00260
C                                                YIELDS                 INT00270
C           NPAM       I   INTEGER     -      NUMBER OF VARIABLE        INT00280
C                                                PARAMETERS (=3)        INT00290
C           NRUNS      I   INTEGER     -      NUMBER OF EXPERIMENTAL    INT00300
C                                                RUNS                   INT00310
C           NUM        -   INTEGER   NRUNS    VECTOR CONTAINING THE     INT00320
C                                                NUMBER OF TIME-TEMP    INT00330
C                                                POINTS IN A RUN        INT00340
C           PARM       I    REAL      NPAM    VECTOR OF VARIABLE PARMS.INT00350
C           TEMP       -    REAL   NRUNS,NUM  ARRAY OF TEMPERATURES     INT00360
C           VSTAR      -    REAL       -      ULTIMATE VOLATILE YIELD   INT00370
C                                                                       INT00380
      COMMON /TMTMP/ DELTT(60,20)    , TEMP(60,20)     , EXPVL(60)     ,INT00390
     1               CALVL(60)       , NUM(60)         , VSTAR          INT00400
      DIMENSION      PARM(3) , ERROR(10)                                INT00410
      DATA           R     / 1.987  /                                   INT00420
C                                                                       INT00430
C          INITIALIZE THE ARRHENIUS EXPRESSION                          INT00440
C                                                                       INT00450
      AK(T,AKO,EACT) = AKO*EXP(-EACT/(R*T))                             INT00460
C                                                                       INT00470
C          INITIALIZE PARAMETERS                                        INT00480
C                                                                       INT00490
      EACTX = PARM(1)                                                   INT00500
      AKOX = 10.0**PARM(2)                                              INT00510
      VSTAR = PARM(3)                                                   INT00520
C                                                                       INT00530
C          CALCULATE YIELDS FOR EACH EXPERIMENTAL RUN                   INT00540
C                                                                       INT00550
```

```
      DO 100 I=1,NRUNS                                                  INT00560
         SUMKX = 0.0                                                    INT00570
         AKOLD = AK(TEMP(I,1),AKOX,EACTX)                               INT00580
         NPNT = NUM(I)                                                  INT00590
C                                                                       INT00600
C        INTEGRATE REACTION RATE OVER ENTIRE TIME-TEMPERATURE HISTORY   INT00610
C                                                                       INT00620
         DO 30 J=2,NPNT                                                 INT00630
            DELTH = DELTT(I,J)/2.0                                      INT00640
            AKNEW = AK(TEMP(I,J),AKOX,EACTX)                            INT00650
            SUMKX = SUMKX+(AKNEW+AKOLD)*DELTH                           INT00660
            AKOLD = AKNEW                                               INT00670
 30      CONTINUE                                                       INT00680
         CALVL(I) = VSTAR*(1.0-EXP(AMAX1(-SUMKX,-150.0)))               INT00690
C                                                                       INT00700
C        CALCULATE MODEL ERROR                                          INT00710
C                                                                       INT00720
         ERROR(I) = CALVL(I)-EXPVL(I)                                   INT00730
 100  CONTINUE                                                          INT00740
      RETURN                                                            INT00750
      END                                                               INT00760
```

```
      SUBROUTINE INTEG (PARM, NRUNS, NPAM, ERROR)
C
C     MULTIPLE REACTION MODEL
C
C        THIS VERSION OF INTEG FITS THE MULTIPLE REACTION MODEL (I.E.,
C           A CONTINUOUS DISTRIBUTION OF ACTIVATION ENERGIES) TO
C           EXPERIMENTAL DATA
C
C        NOMENCLATURE:
C
C        VARIABLES   I/O   TYPE    DIMENSION       DESCRIPTION
C          AKNEW      -    REAL        -       RATE CONSTANT, END OF
C                                                 TIME INTERVAL
C          AKOLD      -    REAL        -       RATE CONSTANT, BEGINNING
C                                                 OF TIME INTERVAL
C          CONST      -    REAL       10       VECTOR OF CONSTANTS
C          DELTT      -    REAL    NRUNS,NUM   ARRAY OF TIME INTERVAL
C                                                 LENGTHS
C          DISTE      -    REAL        7       VECTOR OF PROBABILITY
C                                                 DISTRIBUTION VALUES
C                                                 FOR ACTIVATION
C                                                 ENERGIES
C          CALVL      -    REAL      NRUNS     VECTOR OF CALCULATED
C                                                 YIELDS
C          ERROR      O    REAL      NRUNS     VECTOR OF DIFFERENCES
C                                                 BETWEEN CALCULATED
C                                                 AND EXPERIMENTAL
C                                                 YIELDS
C          EXPVL      -    REAL      NRUNS     VECTOR OF EXPERIMENTAL
C                                                 YIELDS
C          NPAM       I   INTEGER      -       NUMBER OF VARIABLE
C                                                 PARAMETERS
C          NPNT       -   INTEGER      -       NUMBER OF TIME-TEMP
C                                                 POINTS
C          NRUNS      I   INTEGER      -       NUMBER OF EXPERIMENTAL
C                                                 RUNS
C          NUM        -   INTEGER    NRUNS     VECTOR CONTAINING THE
C                                                 NUMBER OF TIME-TEMP
C                                                 POINTS FOR EACH RUN
C          PARM       I    REAL        4       VECTOR OF VARIABLE
C                                                 PARAMETERS
C          SUMK       -    REAL        7       VECTOR CONTAINING
C                                                 NUMERICAL INTEGRATION
C                                                 SUMS
C          TEMP       -    REAL    NRUNS,NUM   ARRAY OF TEMPERATURES
C          TSTEA      -    REAL        7       VECTOR OF ACTIVATION
C                                                 ENERGIES
C          VSTAR      -    REAL        -       ULTIMATE VOLATILE YIELD
C
       COMMON /TMTMP/ DELTT(60,20)     , TEMP(60,20)      , EXPVL(60)      ,
     1                CALVL(60)        , NUM(60)          , VSTAR
       DIMENSION      PARM(NPAM)       , ERROR(NRUNS)     , TSTEA(7),
     1                DISTE(7)         , SUMK(7)
       DATA           R                /  1.987           /
C
```

```
C          INITIALIZE ARRHENIUS EXPRESSION
C
      AK(T,EACT) = AKO*EXP(-EACT/(R*T))
C
C          INITIALIZE PARAMETERS
C
      AKO = 10.0**PARM(3)
      VSTAR = PARM(4)
      SIGMA = PARM(2)
C
C          INITIALIZE DISTRIBUTION OF ACTIVATION ENERGIES
C
      CALL SETG(PARM,DISTE,TSTEA,N7)
C
C          CALCULATE THE VOLATILE YIELD FOR EACH EXPERIMENTAL RUN
C
      DO 50 I=1,NRUNS
           NPNT = NUM(I)
C
C          INTEGERATE THE YIELDS OVER THE RANGE OF ACTIVATION ENERGIES
C
           DO 30 J=1,7
                SUMK(J) = 0.0
                AKOLD = AK(TEMP(I,1),TSTEA(J))
C
C          INTEGRATE THE RATE EXPRESSION OVER THE COMPLETE TIME-
C             TEMPERATURE HISTORY
C
                DO 10 K=2,NPNT
                     AKNEW = AK(TEMP(I,K),TSTEA(J))
                     SUMK(J) = SUMK(J)+(AKNEW+AKOLD)*DELTT(I,K)/2.0
                     AKOLD = AKNEW
   10           CONTINUE
                SUMK(J) = DISTE(J)*EXP(AMAX1(-30.0,-SUMK(J)))
   30      CONTINUE
           CALL INTG(TSTEA,SUMK,N7,CALVL(I))
C
C          CALCULATE THE YIELD FOR EACH RUN, AND THE CORRESPONDING
C             ERROR
C
           CALVL(I) = 0.025+VSTAR*(1.0-CALVL(I))
           ERROR(I) = EXPVL(I)-CALVL(I)
C          CALVL(I) = VSTAR*(1.0-.025*CALVL(I)/SIGMA)
C          ERROR(I) = EXPVL(I)-CALVL(I)
   50 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE INTEG (PARM, NRUNS, NPAM, ERROR)
C
C    MASS-TRANSFER WITH A SINGLE FIRST-ORDER REACTION MODEL
C
C         THIS VERSION OF INTEG FITS THE SINGLE FIRST ORDER REACTION
C            MODEL TO EXPERIMENTAL DATA.
C
C        NOMENCLATURE:
C
C        VARIABLES    I/O   TYPE   DIMENSION      DESCRIPTION
C          AKOX        -    REAL       -       FREQUENCY FACTOR
C          AKNEW       -    REAL       -       RATE CONSTANT, END OF
C                                                 A TIME INTERVAL
C          AKOLD       -    REAL       -       RATE CONSTANT, BEGINNING
C                                                 OF A TIME INTERVAL
C          AK1         -    REAL       -       RATE CONSTANT FOR TAR
C                                                 GENERATION STEP
C          AKC         -    REAL       -       RATE CONSTANT FOR TAR
C                                                 CRACKING STEP
C          AKT         -    REAL       -       OVERALL MASS-TRANSFER
C                                                 COEFFICIENT
C          CALVL       -    REAL     NRUNS     VECTOR OF CALCULATED
C                                                 YIELDS
C          DELTH       -    REAL       -       DELTT/2
C          DELTT       -    REAL   NRUNS,NUM   ARRAY OF TIME INTERVAL
C                                                 LENGTHS
C          EACTX       -    REAL       -       ACTIVATION ENRGY
C          ERROR       O    REAL     NRUNS     VECTOR OF ERRORS
C                                                 BETWEEN CALCULATED
C                                                 VALUES AND
C                                                 EXPERIMENTAL VALUES.
C          EXPVL       -    REAL     NRUNS     VECTOR OF EXPERIMENTAL
C                                                 YIELDS
C          NPAM        I   INTEGER     -       NUMBER OF VARIABLE
C                                                 PARAMETERS (=3)
C          NRUNS       I   INTEGER     -       NUMBER OF EXPERIMENTAL
C                                                 RUNS
C          NUM         -   INTEGER   NRUNS     VECTOR CONTAINING THE
C                                                 NUMBER OF TIME-TEMP
C                                                 POINTS IN A RUN
C          PARM        I    REAL      NPAM     VECTOR OF VARIABLE PARMS.
C          TEMP        -    REAL   NRUNS,NUM   ARRAY OF TEMPERATURES
C          VSTAR       -    REAL       -       ULTIMATE VOLATILE YIELD
C
      COMMON /TMTMP/ TIME (60,20)  , TEMP (60,20),EXPVL(60), CALVL(60) ,
     1                                           NUM(60)   , VSTAR
      COMMON/CONST/CONST(10)
      DIMENSION    PARM(NPAM) , ERROR(60)
      EQUIVALENCE  (EACT1,CONST(1)),(AK01,CONST(2)),(FSTAR,CONST(3))
C    1(EACTC,CONST(4)),(AKOC,CONST(5)) ,
C    2(ALFA,CONST(6)), (BETA,CONST(7))
      DATA          R , N / 1.987 , 3 /
C
C          INITIALIZE THE ARRHENIUS EXPRESSION
C
```

```
      AK(T,AKO,EACT) = AKO*EXP(-EACT/(R*T))
C
      AKT(T,ALFA,BETA,P)=ALFA*((T/273.)**BETA)*((1.34/P)**GAMA)
C     AKT(T,ALFA,BETA)=ALFA*(T/273.)**BETA
C
C        INITIALIZE PARAMETERS
C
      EACTC = PARM(1)
      AKOC = 10.0**PARM(2)
      ALFA = PARM(3)
      BETA = PARM(4)
      GAMA = PARM(5)
C
C        CALCULATE YIELDS FOR EACH EXPERIMENTAL RUN
C
      DO 100 I=1,NRUNS
           SUMJX = 0.0
           SUMKX = 0.0
           FTOTL = 0.0
           FOLD =0.0
           VOLD = 0.0
           AKOLD = AK(TEMP (I,1),AKO1,EACT1)
           NPNT = NUM(I)* N -2
C
C          P = 1.34
C        INTEGRATE REACTION RATE OVER ENTIRE TIME-TEMPERATURE HISTORY
C
           DO 30 J=2,NPNT
C                IF(I.EQ.35) P=69.
C                IF(I.EQ.39) P=0.000131
                 DELTH = DELTT(I,J)/2.
                 AKNEW = AK(TEMP (I,J),AKO1,EACT1)
                 SUMKX = SUMKX+(AKNEW+AKOLD)*DELTH
                 DIF = FSTAR*AKNEW*EXP(AMAX1(-SUMKX,-150.0))
                 AKC = AK(TEMP (I,J),AKOC,EACTC)
                 AKTR = AKT(ALFA,TEMP (I,J),BETA)
                 VNEW = DIF/(1.0+AKC/AKTR)
                 SUMJX = SUMJX+(VOLD+VNEW)*DELTH
                 VOLD = VNEW
                 FOLD = FTOTL
                 AKOLD=AKNEW
 30              CONTINUE
                 CALVL(I)= SUMJX
C
C        CALCULATE MODEL ERROR
C
            ERROR(I) = CALVL(I)-EXPVL(I)
 100  CONTINUE
      RETURN
      END
```

```
      SUBROUTINE COALS(NRUNZ,NPAM,PARAM,SSQ,ERROR)
C
C      **********************************************
C
C
C      COALS IS A MODIFIED VERSION OF CURFIT (BEVINGTON, 1969) AND
C      UTILIZES A GRADIENT SEARCH TECHNIQUE
C
C      NOMENCLATURE
C         ALPHA(K,L)     CURVATURE MATRIX
C         ARRAY(K,L)     MODIFIED CURVATURE MATRIX
C         BETA(K)        ROW MATRIX
C         BPAM(K)        NO. OF PARAMETERS
C         DELTA          INCREMENTS FOR PARAMETERS
C         DERIV(K)       DERIVATIVE OF FUNCTION WITH RESPECT TO PARAMTER
C                        K
C         LAMDA          PROPORTION OF GRADIENT SEARCH INCLUDED
C         LDUMY(K)       DUMMY VARIABLE FOR MATRIX INVERSION SUBROUTINE
C         MDUMY(K)       DUMMY VARIABLE FOR MATRIX INVERSION SUBROUTINE
C         VECTO(M)       VECTOR EQUIVALENT TO THE ARRAY MATRIX
C
C     **********************************************
      REAL LAMDA
       COMMON/INTMP/DELTT(60,20),TEMP(60,20),EXPVL(60),
     1CALVL(60),NUM(60),VSTAR
       DIMENSION PARAM(10),ERROR(60),VECTO(100),ARRAY(10,10),
     1BETA(10),ALPHA(10,10),DERIV(10),BPAM(10),LDUMY(10),MDUMY(10)
       LAMDA=.01
       SSQ1=0.
       DO 998 I=1,NRUNZ
       CALL INTEG(PARAM,I,NPAM,ERROR)
998    SSQ1=SSQ1+ERROR(I)*ERROR(I)
99    LAMDA=.1*LAMDA
C
C      EVALUATE ALPHA AND BETA MATRICES
C
       DO 34 J=1,NPAM
       BETA(J)=0.
       DO 34 K=1,J
34     ALPHA(J,K)=0.
C
C      EVALUATE DERIVATIVES OF THE FITTING FUNCTION FOR THE ITH TERM
C      WITH RESPECT TO EACH PARAMETER
C
       DO 50 I=1,NRUNZ
       DO 98 JFOO=1,NPAM
       PARA=PARAM(JFOO)
       DELTA=.01*PARA
       PARAM(JFOO)=PARA+DELTA
       CALL INTEG(PARAM,I,NPAM,ERROR)
       VAL2=CALVL(I)
       PARAM(JFOO)=PARA
       CALL INTEG(PARAM,I,NPAM,ERROR)
98     DERIV(JFOO)=(VAL2-CALVL(I))/DELTA
       DO 46 J=1,NPAM
       BETA(J)=BETA(J)+ERROR(I)*DERIV(J)
       DO 46 K=1,J
46     ALPHA(J,K)=ALPHA(J,K)+DERIV(J)*DERIV(K)
50     CONTINUE
       DO 53 J=1,NPAM
       DO 53 K=1,J
```

```
53       ALPHA(K,J)=ALPHA(J,K)
C
C        INVERT MODIFIED CURVATURE MATRIX TO FIND NEW PARAMETERS
C
71       DO 74 J=1,NPAM
         DO 73 K=1,NPAM
73       ARRAY(J,K)=ALPHA(J,K)/SQRT(ABS(ALPHA(J,J)*ALPHA(K,K)))
74       ARRAY(J,J)=ARRAY(J,J)*(1.+LAMDA)
         CALL MINV(ARRAY,NPAM,PARA,LDUMY,MDUMY)
         DO 84 J=1,NPAM
         BPAM(J)=PARAM(J)
         DO 84 K=1,NPAM
84       BPAM(J)=BPAM(J)+BETA(K)*ARRAY(J,K)/SQRT(ABS(ALPHA(J,J)*ALPHA(K,K)))
         SSQ=0.
         DO 999 I=1,NRUNZ
         CALL INTEG(BPAM,I,NPAM,ERROR)
999     SSQ=SSQ+ERROR(I)*ERROR(I)
C
C        IF ERROR INCREASES, INCREASE LAMDA AND TRY AGAIN
C
         IF(SSQ1-SSQ)95,101,101
95       LAMDA=10.*LAMDA
         GO TO 71
101      DO 105 J=1,NPAM
         IF (ABS(BPAM(J)-PARAM(J))-.005*ABS(PARAM(J)))105,105,106
105      CONTINUE
         GO TO 700
C
C        EVALUATE PARAMATERS
C
106      DO 107 J=1,NPAM
107      PARAM(J)=BPAM(J)
         SSQ1=SSQ
         GO TO 99
700      SSQ1=SSQ
         DO 707 J=1,NPAM
707      PARAM(J)=BPAM(J)
         RETURN
         END
C
```

```
      SUBROUTINE MINV(A,N,D,L,M)
      DIMENSION A(1),L(1),M(1)
      D=1.
      NK=-N
      DO 80 K=1,N
      NK=NK+N
      L(K)=K
      M(K)=K
      KK=NK+K
      BIGA=A(KK)
      DO 20 J=K,N
      IZ=N*(J-1)
      DO 20 I=K,N
      IJ=IZ+I
      IF(ABS(BIGA)-ABS(A(IJ)))15,20,20
15    BIGA=A(IJ)
      L(K)=I
      M(K)=J
20    CONTINUE
      J=L(K)
      IF(J-K)35,35,25
25    KI=K-N
      DO 30 I=1,N
      KI=KI+N
      HOLD=-A(KI)
      JI=KI-K+J
      A(KI)=A(JI)
30    A(JI)=HOLD
35    I=M(K)
      IF(I-K)45,45,38
38    JP=N*(I-1)
      DO 40 J=1,N
      JK=NK+J
      JI=JP+J
      HOLD=-A(JK)
      A(JK)=A(JI)
40    A(JI)=HOLD
45    IF(BIGA)48,46,48
46    D=0.
      RETURN
48    DO 55 I=1,N
      IF(I-K)50,55,50
50    IK=NK+I
      A(IK)=A(IK)/(-BIGA)
55    CONTINUE
      DO 65 I=1,N
      IK=NK+I
      HOLD=A(IK)
      IJ=I-N
      DO 65 J=1,N
      IJ=IJ+N
      IF(I-K)60,65,60
60    IF(J-K)62,65,62
62    KJ=IJ-I+K
      A(IJ)=HOLD*A(KJ)+A(IJ)
65    CONTINUE
      KJ=K-N
      DO 75 J=1,N
      KJ=KJ+N
      IF(J-K)70,75,70
70    A(KJ)=A(KJ)/BIGA
```

```
75      CONTINUE
        D=D*BIGA
        A(KK)=1./BIGA
80      CONTINUE
        K=N
100     K=(K-1)
        IF(K)150,150,105
105     I=L(K)
        IF(I-K)120,120,108
108     JQ=N*(K-1)
        JR=N*(I-1)
        DO 110 J=1,N
        JK=JQ+J
        HOLD=A(JK)
        JI=JR+J
        A(JK)=-A(JI)
110     A(JI)=HOLD
120     J=M(K)
        IF(J-K)100,100,125
125     KI=K-N
        DO 130 I=1,N
        KI=KI+N
        HOLD=A(KI)
        JI=KI-K+J
        A(KI)=-A(JI)
130     A(JI)=HOLD
        GO TO 100
150     RETURN
        END
```

Appendix VI

Results of Model

The data tabulated in this section is from secondary reaction with mass transport limitation model. However, all of the data (both tabulated here or not) for this thesis are in the possession of Professor Jack B. Howard.

```
FILE: CELFIT   OUTPUT   A                    CONVERSATIONAL MONITOR SYSTEM                    PAGE 001

1              ****RESULTS OF COAL PYROLYSIS BEST-FIT ANALYSIS****

 MODEL NAME: MASS-TRANSFER WITH A SINGLE FIRST-ORDER RXN MODEL

 COMPONENT EVOLVED: TAR(ATMOSPHERIC & HIGH PRESSURE)


 ASSUMED CONSTANT VALUES:
           0.1857E+05  0.4886E+05  0.8500E+00  0.0         0.0
           0.0         0.0         0.0         0.0         0.0


 FINAL PARAMETER VALUES:
 PARAMETER NO.  1: 0.6269E+05
 PARAMETER NO.  2: 0.1417E+02
 PARAMETER NO.  3: 0.5242E+00
 PARAMETER NO.  4: 0.7647E+00
 PARAMETER NO.  5: 0.6878E000


                            **RESULTS OF FIT**

      RUN NO.    PEAK TEMP. (*K)    CALCULATED YIELD    EXPERIMENTAL YIELD
       202A           1384.              0.4459              0.5089
       63TA           1250.              0.4431              0.5062
       64TA           1273.              0.4589              0.4912
       65TA           1273.              0.4599              0.4875
       104A           1287.              0.4653              0.5040
       105A           1274.              0.4760              0.5146
       66TA           1224.              0.4663              0.4536
       97TA           1228.              0.4423              0.5170
       98TA           1209.              0.4878              0.5082
       106A           1178.              0.4835              0.5000
       101A           1160.              0.5315              0.5018
       68TA           1068.              0.5720              0.5334
       99TA           1098.              0.5285              0.5333
       100A           1094.              0.5449              0.5535
       69TA           1027.              0.6244              0.5992
       78TA           1042.              0.5770              0.5762
       79TA           1099.              0.5284              0.5514
       74TA            992.              0.6509              0.6009
       116A            925.              0.4410              0.5792
       80TA           1003.              0.6626              0.6190
       81TA            988.              0.6743              0.6416
       71TA            881.              0.4037              0.4742
       73TA            824.              0.2363              0.2877
       83TA            887.              0.7618              0.7167
       87TA            879.              0.7856              0.7633
       85TA            889.              0.7897              0.7624
       207A            824.              0.2330              0.2284
       72TA            769.              0.1057              0.1214
       89TA            784.              0.4201              0.5609
```

```
FILE: CELFIT   OUTPUT   A                 CONVERSATIONAL MONITOR SYSTEM                 PAGE 002

      91TA          765.          0.5997          0.7568
      95TA          656.          0.0141          0.0
      94TA          716.          0.2871          0.3024
      173A          923.          0.5142          0.5746
      174A          746.          0.0537          0.0420
      HP.1         1279.          0.4282          0.4282
      HP.2         1371.          0.3959          0.3163
      HP.3         1190.          0.4553          0.3483
      HP.4          923.          0.2901          0.2927


  SUM OF THE SQUARED ERRORS:  0.1250E+00
  NORMALIZED ROOT-MEAN-SQUARE ERROR:  0.6748E-01
```

```
FILE: R5       OUTPUT   A                    CONVERSATIONAL MONITOR SYSTEM                         PAGE 001

1              ****RESULTS OF COAL PYROLYSIS BEST-FIT ANALYSIS****


 MODEL NAME: MASS-TRANSFER WITH A SINGLE FIRST-ORDER RXN MODEL

 COMPONENT EVOLVED: TAR(VACUUM)


 ASSUMED CONSTANT VALUES:
          0.1857E+05  0.4886E+05  0.8500E+00  0.0         0.0
          0.0         0.0         0.0         0.0         0.0


 FINAL PARAMETER VALUES:
 PARAMETER NO.  1: 0.5598E+05
 PARAMETER NO.  2: 0.1221E+02
 PARAMETER NO.  3: 0.6367E+00
 PARAMETER NO.  4: 0.7724E+00


                               **RESULTS OF FIT**

       RUN NO.    PEAK TEMP. ('K)    CALCULATED YIELD    EXPERIMENTAL YIELD
        177T           992.               0.6184              0.6276
        175T           833.               0.3426              0.2808
        V.27           844.               0.3926              0.3571
        V.26           893.               0.4950              0.4598
        V.28           794.               0.2730              0.1980
        V..1           564.               0.0027              0.0
        V..2           640.               0.0289              0.0
        V..3           784.               0.2555              0.0694
        V..4           704.               0.0789              0.0353
        V.18           927.               0.5830              0.5064
        V.19           813.               0.2343              0.3039
        V.20           975.               0.6215              0.7373
        181T          1031.               0.7724              0.6529
        V.21          1042.               0.7675              0.7385
        V.22          1106.               0.6233              0.7555
        V.23          1210.               0.4966              0.6369
        V.24          1256.               0.4536              0.5420
        V.10           640.               0.0548              0.0402
        V.11           748.               0.2854              0.3382
        V.12          1116.               0.6566              0.5980
        V.13          1228.               0.5200              0.4089
        V.14           885.               0.7816              0.7463


  SUM OF THE SQUARED ERRORS:  0.1900E+00
  NORMALIZED ROOT-MEAN-SQUARE ERROR:  0.1093E+00
```

```
FILE: CELFIT   OUTPUT   A                  CONVERSATIONAL MONITOR SYSTEM                     PAGE 001

1               ****RESULTS OF COAL PYROLYSIS BEST-FIT ANALYSIS****

 MODEL NAME: MASS-TRANSFER WITH A SINGLE FIRST-ORDER RXN MODEL

 COMPONENT EVOLVED: TAR


 ASSUMED CONSTANT VALUES:
          0.1857E+05  0.4886E+05  0.8500E+00  0.0         0.0
          0.0         0.0         0.0         0.0         0.0


 FINAL PARAMETER VALUES:
 PARAMETER NO.  1: 0.5858E+05
 PARAMETER NO.  2: 0.1350E+02
 PARAMETER NO.  3: 0.7439E-01
 PARAMETER NO.  4: 0.1135E+01
 PARAMETER NO.  5: 0.1144E000


                                 **RESULTS OF FIT**

      RUN NO.     PEAK TEMP. (*K)    CALCULATED YIELD     EXPERIMENTAL YIELD
       202A           1384.               0.4653                0.5089
       63TA           1250.               0.4603                0.5062
       64TA           1273.               0.4784                0.4912
       65TA           1273.               0.4794                0.4875
       104A           1287.               0.4869                0.5040
       105A           1274.               0.5015                0.5146
       66TA           1224.               0.4859                0.4536
       97TA           1228.               0.4606                0.5170
       98TA           1209.               0.5117                0.5082
       106A           1178.               0.5034                0.5000
       101A           1160.               0.5593                0.5018
       68TA           1068.               0.5773                0.5334
       99TA           1098.               0.5419                0.5333
       100A           1094.               0.5587                0.5535
       69TA           1027.               0.6178                0.5992
       78TA           1042.               0.5816                0.5762
       79TA           1099.               0.5453                0.5514
       74TA            992.               0.6376                0.6009
       116A            925.               0.4309                0.5792
       80TA           1003.               0.6513                0.6190
       81TA            988.               0.6614                0.6416
       71TA            881.               0.3949                0.4742
       73TA            824.               0.2328                0.2877
       83TA            887.               0.7384                0.7167
       87TA            879.               0.7621                0.7633
       85TA            889.               0.7658                0.7624
       207A            824.               0.2294                0.2284
       72TA            769.               0.1049                0.1214
       89TA            784.               0.4135                0.5609
```

```
     91TA            765.              0.5914              0.7568
     95TA            656.              0.0141              0.0
     94TA            716.              0.2854              0.3024
     173A            923.              0.5016              0.5746
     174A            746.              0.0535              0.0420
     HP.1           1279.              0.4848              0.4282
     HP.2           1371.              0.4307              0.3163
     HP.3           1190.              0.4886              0.3483
     HP.4            923.              0.2823              0.2927
     177T            992.              0.6585              0.6276
     175T            833.              0.4194              0.2808
     V.27            844.              0.4778              0.3571
     V.26            893.              0.5880              0.4598
     V.28            794.              0.3352              0.1980
     V..1            564.              0.0030              0.0
     V..2            640.              0.0342              0.0
     V..3            784.              0.3137              0.0694
     V..4            704.              0.0949              0.0353
     V.18            927.              0.6721              0.5064
     V.19            813.              0.2867              0.3039
     V.20            975.              0.6654              0.73[illegible]3
     181T           1031.              0.6158              0.6529
     V.21           1042.              0.6159              0.7385
     V.22           1106.              0.5433              0.7555
     V.23           1210.              0.4915              0.6369
     V.24           1256.              0.4767              0.5420
     V.10            640.              0.0652              0.0402
     V.11            748.              0.3506              0.3382
     V.12           1116.              0.6107              0.5980
     V.13           1228.              0.5190              0.4089
     V.14            885.              0.7175              0.7463


  SUM OF THE SQUARED ERRORS:  0.4087E+00
  NORMALIZED ROOT-MEAN-SQUARE ERROR:  0.9710E-01
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