

EXOTHERMAL METAMORPHOSIS OF COAL PRECURSORS

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The genesis of high rank coals, those containing more than 86 percent fixed carbon, has been a matter of conjecture since coal classification schemes were invented. The classical model for the transition of cellulose, lignin and other plant materials into coals of various ranks is described by Wilson and Wells (1);

"The chemical changes taking place in transition from wood to peat and progressively through the successive ranks of coal to anthracite are suggested...Such changes, which may have taken hundreds of thousands or millions of years, are believed to have converted peat to lignite and progressively through successively higher ranks of coal, to anthracite."

Pressure is used to help account for the difference in rank. Wilson and Wells state further "In deeply buried coals pressures of 1500 atm may have been reached.

The advanced state of transformation typified by Pennsylvania anthracite is probably due to the enormous pressures to which the deposits were subjected when the Appalachian Mountains were formed."

X-ray diffraction of high rank coals demonstrates a distinct peak corresponding to (002) graphite lattice spacing. This peak is weak or absent in lower rank coals. (2) The polymerization of carbonaceous material to graphite requires temperatures in the range 600° to 800°C, well above the 200°C maximum temperatures to which some coals have presumably been exposed.

The possibility that coalification could be rapid is suggested by a discovery made by Petzoldt (3) in 1882;

Upon unearthing a wooden pile which had been rammed into the ground, he found it to have been metamorphosed to a coal like substance. From the center, it exhibited a continuum of material from black through dark brown, and light at the surface. This he analyzed and found to resemble anthracite in the center portion, and the outer part resembling brown coal.

Teichmuller and Teichmuller (4) after studying systematically the geological factors related to the coals of western Europe concluded "according to our observations in different coal-bearing foredeeps the effect of pressure on rank increase is purely physical. The chemical reactions are caused by temperature increase, and according to the experimental observations, pressure actually retards them." They cite many examples of conflicting data where an increase in age does not correspond to higher rank. Their general conclusion respecting time is: "time has relatively small influence on the coalification process." and, "The effect of time upon coalification depends on the temperature to which the coal has been exposed during burial. If this temperature is low, the time factor is hardly important. With higher temperatures, however, the length of heating

has a marked effect."

Research in our laboratory has been concerned with the determination of the pressure coefficient and the temperature coefficient of the conversion of cellulose type materials to coal. This research and that of Pan (5) demonstrated that high pressure decreases the rate of conversion of cellulose into coal-like materials and of low rank coals into coals of higher rank. The temperature coefficient of formation of coal-like materials is positive and high. But perhaps of greater importance is the serendipitous discovery that cellulose type materials confined at high pressures when heated slowly to temperatures in the range 200^o to 240^oC decompose exothermally, raising the temperature of the material to the graphite forming range, i.e., above 600^oC.

APPARATUS AND EXPERIMENTAL PROCEDURE

High Pressure

This high pressure work was carried out in a hexahedral, 200 ton press, designed by H. T. Hall. The rams of the press have an 8" diameter piston, which at 8000 psi hydraulic pressure, exert a force of 400,000 lbs. or 200 tons. The anvils used were the 15/16" anvils. Pressure calibrations for this anvil set were made using the bismuth I-II and II-III transitions and the change of resistance of bismuth with pressure.

Differential Thermal Analysis

A description of the Differential Thermal Analysis (DTA) system will be published in a second paper. All DTA samples were pelletized as 1/4", right-circular sections. This was accomplished by melting the sample, in the case of the glucose, xylose, and inositol, and pressing the melt into 1/4" diameter teflon tubes (all done under a vacuum). The cellulose powder and wood samples were pelletized at approximately 5 kb in a 1/4" diameter piston and cylinder die system, which was equipped with "o-ring" seals, above and below the sample, to facilitate the evacuation of the sample material.

Thus pelletized, the sample was assembled in the pyrophyllite-cube-furnace-DTA system, with thermocouples. The cube assembly was evacuated in a closed vessel for one hour. The vessel was then pressurized to 100 psi with pure N₂ gas and maintained for a minimum of one hour at this pressure. Thereafter the sample was placed immediately in the press to minimize the diffusion of air into the cube and into contact with the sample.

All DTA samples were enclosed in a teflon capsule to insulate the sample from any possible mineral or catalytic effect.

Temperature Recording

Differential, and actual temperature traces were made simultaneously on a Honeywell Electronik 194, dual-pen recorder.

Constant Temperature Pyrolysis

One sample was pyrolyzed at constant temperature (after reaching reaction temperature). The equipment used was a Fisher system with both thermogravimetric analysis as well as DTA accessories (but not equipped to be used simultaneously). The Fisher Model 360 temperature programmer was used as the temperature controller and a Cahn Electrobalance monitored the weight (and weight change).

The above specified Honeywell recorder was used to record the electrobalance output.

Temperature Programmer

An Assembly Products "Temptendor" model 732, calibrated for an Iron-Constantan thermocouple, was used as a temperature programmer. This was accomplished by attaching a variable-gear train to drive the controller potentiometer at a predetermined rate. The potentiometer was connected to a digital readout dial calibrated in degrees C. and readable to approximately $\pm 0.2^{\circ}\text{C}$. Temperature agreement between the control thermocouple and any other thermocouple at the same temperature was usually within one (1) degree C. As shown in figure 1, the programmer operated a servo-system which automatically adjusted a variable transformer for the correct power requirement to satisfy a balanced bridge condition in the temperature controller.

An additional feature of the power system was a stepdown transformer to accommodate the low resistance furnace elements. This system was rated for a continuous output to $\frac{1}{2}$ kw. It was subsequently equipped with a water-cooling coil which allowed a continuous output of approximately 1.2 kw.

X-ray Analysis

A General Electric XRD-5 diffractometer was used to obtain X-ray diffraction patterns on the sample residue. The radiation was Cu K α (Ni filtered). Samples were ground in an agate mortar from two to three minutes, mixed to a slurry with ethyl alcohol and spread in a thin film on the glass sample slide.

C, H, O, Analyses

Ultimate analyses were performed by the Utah Engineering Experiment Station on an F & M 180 C H N analyzer to obtain the percentage of carbon and hydrogen. The oxygen analysis was performed with a Coleman Oxygen Analyzer. Accuracy is estimated to be within $\pm 5\%$ for all samples.

Infra-Red Analysis

Infra-Red analyses were performed on a Model 521, Perkin-Elmer dual-beam recording spectrophotometer. KBr absorption windows were prepared, using approximately 200 mg of mixture (1:200, sample to KBr ratio). These were ground together with an agate mortar and pestle. Nujol mixes were prepared by grinding the sample in nujol with the agate mortar and pestle. The spectra of the nujol mixtures were not very satisfactory, presumably because the samples were not ground fine enough to observe the differences in absorption spectra.

Mass Spectrometry

Mass spectra were obtained from the gas samples desorbed from the product residue plus that collected directly from the blow-out of sample #134. These were analyzed on a CEC 21-620 mass spectrometer. This unit has a resolution limit of 300, and an accuracy on the order of 5 to 10%.

Pyrolysis Materials

Chemicals and materials used in these experiments were as follows:

1. Absorbent cotton (used for X-ray diffraction only).
2. Chromatographic grade cellulose pulp, Schleicher and

Schuell #2200.

3. Anhydrous glucose
4. Xylose, Eastman Organic Chemicals #542
5. i Inositol (meso), Nutritional Biochemical Corp. #1338
6. Yellow pine wood

RESULTS AND DISCUSSION

Anomalous High Pressure Effects

Low Pressure DTA

Typical of the Differential Thermal Analysis (DTA) of a cellulose in a vacuum, is an endothermal trace corresponding to thermal degradation. Figure 2 by Akita and Kase (6), compares the DTA of cellulose in air, in N_2 , and in a vacuum. Here it is noted that in the presence of O_2 , the effect of combustion of the pyrolyzate causes an exothermal peak immediately succeeding the endothermal degradation.

The atmosphere of N_2 can be observed to inhibit the extent of the endotherm probably due to the retarded transfer of the product from the reaction zone.

Exothermal Reaction

Figures 3,4, and 5 are modified high pressure DTA traces or plots of ΔT vs. the program or reference temperature for the various samples studied. The original traces were ΔT vs. time. The heating rate was a constant, for each DTA trace, and since reaction temperature was the parameter of greater interest than time, the abscissa was converted to temperature. One further change was made to facilitate the comparison of curves, the baseline was set at $\Delta T = 0$ so that (except for differences in thermal conductivity of sample and reference) the peak height essentially represents the temperature difference between samples and reference.

The high pressure DTA of cellulose demonstrates the occurrence of an anomalous exothermal reaction, quite unlike the typical vacuum DTA of pure cellulose, as illustrated in figure 2. Figure 3 shows several exothermal reactions of cellulose at pressures of 7, 16, 23, and 28 kb. Precautions were taken to exclude oxygen from the sample, however, no difference was noted between sample 121, which was prepared in an atmosphere of oxygen, and those which were excluded from oxygen. The amount of oxygen which would remain entrapped after pressurization, in contact with the sample, is reasonably very low and insufficient to effect any sustained, observable oxidation. Lipska and Parker (7) have shown that at one atmosphere of N_2 plus O_2 , oxygen content below 0.5% had no effect on the pyrolysis.

As a consequence, the observed exotherm cannot be attributed to oxidation. The intimate confinement of reactants and activation states, however, could produce a different mechanism with different products and therefore a different thermal effect.

"Positive" and "Negative" Effects of Pressure

It can be observed from figure 3 that at 29 kb, a slightly higher temperature is required to effect the reaction than at 7 kb. Thus, the high-pressure reaction is slightly more temperature resistant.

This pressure effect might be considered as a negative effect, as it inhibits certain reactions. On the other hand, the intimate product confinement could be thought of as a positive effect, since it favors reactions which otherwise might occur infrequently or not at all.

An important effect, which might be categorized as a positive pressure effect, can also be noted by comparing figure 2 (the data of Akita and Kase) with our thermograms of the same heating rate in figure 4. The initiation temperature of the cellulose exotherm at high pressure is lower than that which occurs during vacuum pyrolysis. The low-pressure reaction begins at approximately 290°C. However, at 7 kb it occurs considerably lower, near 227°C (three-sample average of #122, 123, and 141, see Table I).

Fast vs. Slow Reaction

At least two types of reactions are observed during DTA under a confining pressure. These can be described as slow (figure 3) and fast reaction (figure 4 except #99). Note that the cellulose peak of the fast reaction is more than 400°C above the reference ($\Delta T=0$) while the slow reaction peaks of cellulose are between 2° to 3°C high. This different effect is obtained simply by varying the heating rate.

It is natural to expect that a fast heating rate would effect a higher peak, but an increase from ½°/min. to 5°/min. could not be supposed to account for a ΔT increase from 2° to 400°C. Heating rates on the order of ½ to 1° per minute will unpredictably be the fast or slow reaction type. Note that at ½°/min., sample 101 was a fast reaction (see Table I). The range of unpredictability should be a function of the temperature-control accuracy during the programmed heating. The unexpected high peak of sample 101 went off scale and so it is not plotted, but this does show that the faster and higher-temperature reaction causes a more complete and more exothermal reaction. Table I shows that the peak area of sample 101 is >5 units while the peak area of other samples heated at the same rate was approximately 2 units.

The reason for this difference may be as follows. The slow reaction corresponds to a delicate condition of programmed heating which must be slow enough to allow for the removal of the heat of reaction. If the heat of reaction cannot transfer from the reaction zone as rapidly as it is generated, the temperature climbs, accelerating the exothermal reaction, and runs out of control to completion. The sample size is important here and a larger sample would produce a higher temperature and require a slower heating rate to maintain the control of the slower reaction.

A major problem encountered in the rapid heating rates is the retention of the gases generated by the reaction. Excessive volatility in the sample cube leads to violent rupture of the cube and explosive loss of product.

Sample rupture and the escape of product gases was never a problem at the lower heating rate with the slower reactions.

I-R Analysis of Residue

Figure 6 shows the IR absorption spectra of the various sample residues, illustrating the effects of variation in pressure, heating rate, and type of molecular structure.

Samples 95 and 121, pyrolyzed at $\frac{1}{2}^{\circ}$ /minute and at 28 and 7 kb, respectively, produced almost identical spectra, indicating very little difference in the product residue due to this pressure difference.

Cellulose-sample 123, with the heating rate of 5° /minute (which produced the very rapid reaction and high temperature) showed a very different absorption. The 1700 cm^{-1} band, (generally thought to be due to C=O) is very much reduced. The 2860 to 2950 cm^{-1} bands, attributed to naphthenic-CH, CH_2 , and CH_3 groups is so completely reduced that it would almost appear that CH groups are essentially all that are left (near the 2920 peak). Aromatic absorption in the bands 750, 820, and 860 cm^{-1} show up very well.

Sample 149, (yellow pine wood) compared with #123, shows the same or slightly more absorption in the 750 to 860 bands, slightly more absorption in the 1590 band (also attributed to aromatic structure and perhaps C=O groups), much less at 1700; and about the same or less absorption in the 2920 area. All of this seems very natural in spite of the fact that #123 reached a higher temperature (670°C vs. 513°C) since the aromatic content of wood is high to begin with.

For the most part, the difference between #142, glucose, and #146, xylose, can be explained on the basis of the difference in the peak temperatures (440°C for #146, vs. 322°C for #142).

The inositol was not completely reacted and gave adsorption spectra very similar to pure inositol and for that reason is not included here. (For a very excellent discussion on IR band assignments see reference 8.)

X-ray Diffraction

Ergun (2) has shown a correlation of vitrinite coal rank with the general peak form particularly in the $2\theta = 20^{\circ}$ to 27° range (i.e., $s-(2\sin\theta)/\lambda$ range of approximately .23 to .33). He states, "With decrease in rank the most pronounced band becomes broader, and its position is shifted to lower 2θ values ... peak position could serve as a simple but reliable index of coal rank." (Lower s values corresponds with lower 2θ value.)

Figure 7 is a comparison of the X-ray diffraction patterns of several different samples which were investigated. They are: 1) metamorphosed samples of cellulose (124, 105, 148, 132, 58); 2) metamorphosed anhydrous glucose (142); 3) metamorphosed xylose (146); 4) samples of high volatile bituminous (HVB), low volatile bituminous (LVB), and graphite (all reproduced from reference 5); and 5) ball-milled and natural cotton.

These curves have been arranged in order of decreasing 2θ value, from top to bottom (i.e., high rank at the top). This arrangement also turns out to be a function of the heating rate. Samples which were heated rapidly and which reached a high temperature are high on the chart. Sample #123 heated to 670°C at the exotherm peak; #149, to 513°C ; #105 (slow heating rate) heated to approximately 225°C at the exotherm peak.

Cellulose sample #58 is the highest on the scale of synthetic coals. This sample was heated very rapidly, without the use of DTA and at 28 kb pressure. It was heated to 225°C in 3 minutes and

continued at a rough rate of 10°/minute, to 300°C (manual temperature control). That this sample (#58) exhibits a distinct (002) graphite peak of 26.5° 2θ, (probably the most pronounced graphite peak of all those compared here, except pure graphite) is thought to be very significant. The coal sample which was heated to 850°C at 30 kb for 30 minutes does not approach the graphite peak as well. This would appear to show that the heat generated during the exothermal metamorphosis is a more effective graphitization heat than externally applied heat on a previously coalified sample.

High Oxygen Content in Press Samples

One important effect on high pressure, which would be considerably different in coalification of large vegetal accumulations is this: the confining pressure acts to retain a very high percentage of oxygen. One probable reason for this, in the fast reactions, is that the small, ¼-gram samples cool very rapidly after attaining peak temperature. Not only would a larger sample be likely to reach higher temperatures but it would also remain heated for longer periods allowing for diffusion of volatiles away from the reaction zone, perhaps to condense in a cooler locality. After attaining maximum temperature, slow cooling would probably encourage growth of the more stable molecular structure and the elimination of oxygen.

Stability From Inter-Ring and Intra-Ring Effects

It is obvious that the 1,4-glycosidic linkage helps in the stabilization of cellulose. This can be seen by a comparison of the thermogram of anhydrous glucose with that of cellulose (see figures 4 and 5). The initiation temperature is approximately 141°C for glucose. This is more than 80°C below that observed for cellulose at the same heating rate of 5°/min.

By comparing the exotherm of anhydrous glucose (#142) with that of xylose (#146), the effect of the pendant -CH₂OH group becomes apparent. Pendant groups have been observed to detract from the thermal stability of a molecule. The xylose reaction began approximately 45°C (i.e., 186°C) above the glucose reaction temperature.

The -CH₂OH is likely the site of the reaction initiation. Xylose reacted slower than cellulose (at the same heating rate) until it reached approximately 215 to 220°C whereupon it converted very rapidly to the fast reaction similar to the cellulose (and at a temperature nearly as high as with cellulose). This seems to imply that the 1,4-glycosidic linkage (and perhaps other stabilizing factors) inhibits the decomposition of the cellulose chain until the temperature is sufficiently high to open the ring.

Without the C-O-C bond nor the pendant -CH₂OH, inositol is seen to be remarkably more stable than either anhydrous glucose or xylose. Note that even at the high initiation temperature of 270°C the sample did not overheat and run out of control. The uniformity of the inositol ring is a strong stabilizing effect. It appears that inositol began a very rapid exotherm but was suddenly checked perhaps by an endothermal reaction (or a series of endothermal reactions) such as dehydration.

Analysis of Low-Pressure-Pyrolyzate Gases

Sample #124 (see figure 8) was pyrolyzed at 300°C to analyze

the evolved gases of the early stages of pyrolysis of cellulose. This was carried out with the TBA equipment but at constant temperature (after about eight minutes required to reach 300°C). The pyrolyzate was collected in four bottles during the periods of 0 to 5, 5 to 10, 10 to 20, and 20 to 165 minutes. Mass spectrometric analysis of the gas is included in the same figure. Here it can be observed that: 1) almost pure H₂O is evolved initially (below 260°C). 2) The very low initial fraction of CO₂ gradually increases. 3) Short-chain hydrocarbons were observed, but only in the initial moments of the 300°C period. 4) The initial irregularity of the rate of weight-loss curve, is probably due to the time required for the sample and container to come to reaction temperature. The effect of an immediate 300°C reaction temperature could correspond to the extrapolated, dashed line.

Small amounts of CO are thought to have been present but were unobservable due to the masking effect of the contaminating air (M/e = 28, due to N₂). Experiments by Madorsky (9,10) show that there is about one-third as much CO as CO₂ during pyrolysis at temperatures between 280 to 400°C.

Rapid, Mature Stabilization

The case of the sudden, out of control, high-temperature reaction, and the resulting high temperatures (exceeding 670°C in the non-blow-out sample 123) could allow a very complete reorientation of the molecular structure. The hot reactive mass of many short chain segments would favor elimination of oxygen, particularly where it occurs as a pendant hydroxyl group. Benzene ring structurization which would probably form infrequently at low temperature would be favored. Note that figure 6, showing the IR spectra of sample 123, has accordingly the most prominent absorption in the 750, 820, and 860 cm⁻¹ region, which have been attributed to benzoid aromatic structure (7). At very high temperatures for example during coalification of a clean concentration of vegetal material, the graphite structure should be favored. Here again this effect can be noted: Figure 7, showing the X-ray diffraction for various samples, illustrates how samples 58, 123, and 149 (sample of wood which autogeneously heated above 520°C) most nearly approach the high-rank coal patterns and diffraction of the (002) graphite peak at 26.5° 2θ.

Factors Responsible for Maximum Temperature

Among the factors determining the maximum temperature attainable by a coalifying exotherm, are mass, concentration of reactive groups in the deposit, and initiation temperature. A very small sample (e.g., ¼ gram, such as those used in this work) would probably lose heat very rapidly and not attain the maximum temperature. Reduced concentration of reactive groups, perhaps due to the rapid decay of cellulose from woody materials, would tend to diminish the maximum temperature, as would dilution with mineral matter. Thus, highly concentrated vegetal material might convert to anthracite or graphite, whereas, decayed material with significant mineral contamination, upon attaining initiation temperature might heat spontaneously and be converted to one of the intermediate ranks of coal. Low rank coals with considerable mineral content and/or those which were heated very slowly, say, due to gradual sinking and accumulation of overburden may have had an analogous metamorphosis of the slow, annealing or controlled-temperature cellulose pyrolysis, without heating significantly above ambient

conditions. Some upranking may thus occur from high ground temperatures.

Possible Factors Influencing the Initiation Temperature

Factors which might account for elevating the temperature to reaction initiation could be combustion of overlying vegetation, earth-movement friction, magmatic heat sources, and perhaps natural ground temperatures. If the ground temperature increased very slowly it might tend to yield low-rank coals without the coal experiencing a significant autogenous heating.

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Table I. DTA DATA AND RESIDUE ANALYSIS

sample no.	material	pressure (kp)	sample wt. (mg.)	heat rate °C/min.	blowout	Initial Reaction Temp. (°C)	ΔT peak (°C)	Maximum Temp. (°C)	peak area (μV-min)	wt. % CHO	wt. % H	wt. % N	Residue of total
90	cellulose	3	281	9	yes	233	high	high	-	73.6	3.5	22.8	42.7
94	"	28	269	10	no	210	high	high	-	87.5	3.1	9.5	64.3
95	"	28	230	k	no	215	2.8	300	1.3	72.6	4.3	23.1	56.5
96	"	23	284	k	no	200	2.9	237	2.3	67.3	4.0	28.7	77.8
99	"	7	299	k	no	188	2.7	237	-	67	4	29.6	77.0
100	"	23	305	k	no	-	-	300	-	71.6	2.7	25.7	65.9
101	"	16	300	k	no	210	>15	300	>5	72.6	2.7	24.7	-
105	"	16	271	k	no	207	1.1	308	2.20	74	4.0	23	51.3
120	"	7	307	k	no	192	1.85	300	2.22	61	3.4	25	53.2
121	"	7	295	k	no	198	1.2	276	2.20	-	-	-	52.2
122	"	7	285	5	yes	223	high	high	-	85.4	4.0	10.6	8.87
123	"	7	299	5	no	231	415	>454	-	-	-	-	40.5
141	"	7	300	5	yes	227	216	>454	2.4	incomplete reaction	-	-	54.4
129	inositol	7	285	5	no	287	9.7	350	1.2	incomplete reaction	-	-	-
135	"	7	292	5	no	270	-	-	-	-	-	-	-
142	glucose	7	263	5	no	141	10.1	322	6.1	79	5.8	15	26
146	xylose	7	233	5	no	175	185	440	-	82	4.8	13	37.5
149	wood	7	276	5	no	242	250	513	-	92	4.1	4	37.0
134	cellulose	5	290	-	-	-	-	-	-	-	-	-	-

Not DTA (blow-out gas collected for analysis: 50% H₂O, 20% CO₂, 2% acetone, 2% H₂ + CO % undetermined)

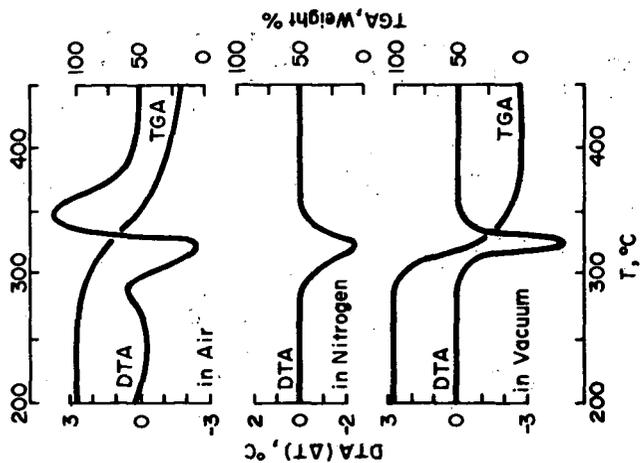


Fig. 2. DTA AND TGA CURVES OF CELLULOSE IN AIR, N₂, AND IN VACUO. ● = 50C/MIN (6)

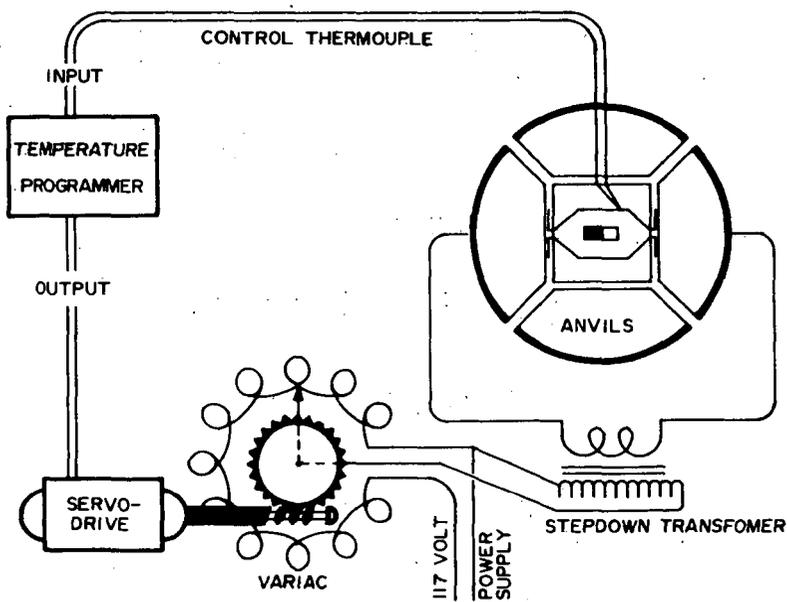


Fig. 1. TEMPERATURE PROGRAMMER AND POWER SYSTEM

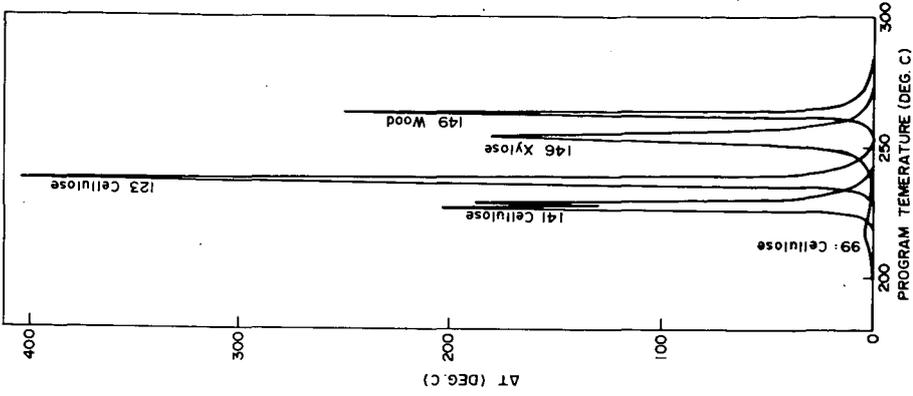


Fig. 4. DTA THERMOGRAMS AT 7 KB, HEATING RATE $6^{\circ}/\text{MIN}$.

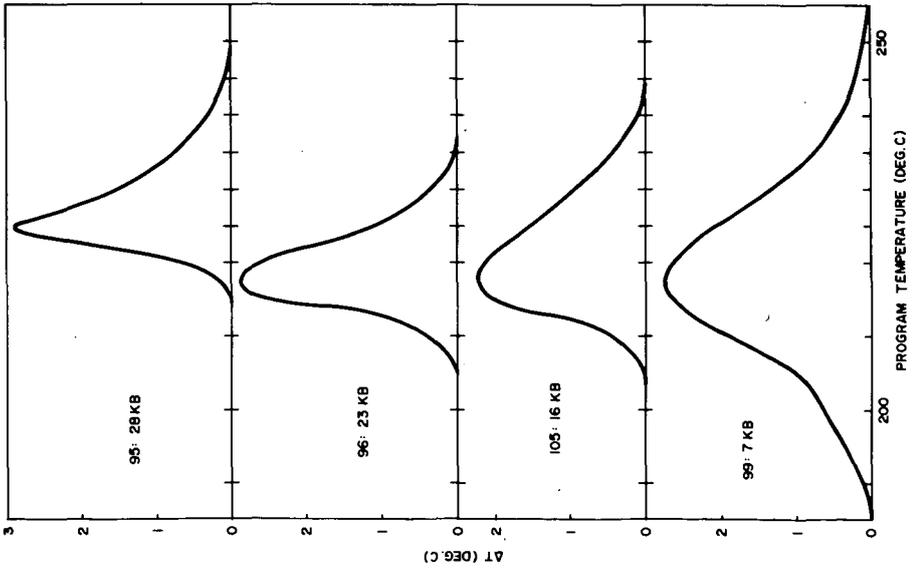


Fig. 3. CELLULOSE DTA EXOTHERMS AT VARIOUS PRESSURES HEATING RATE = $1/20^{\circ}/\text{MIN}$.

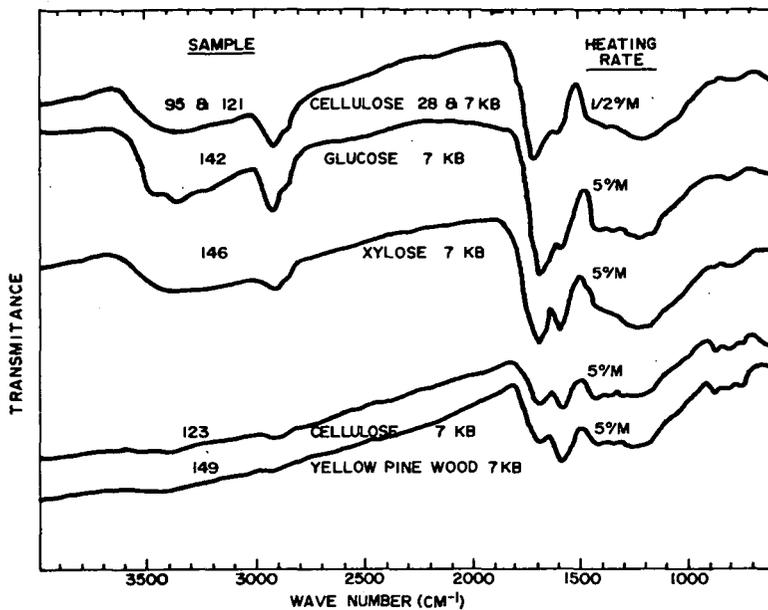


Fig. 6. I-R SPECTRA OF SAMPLE RESIDUE

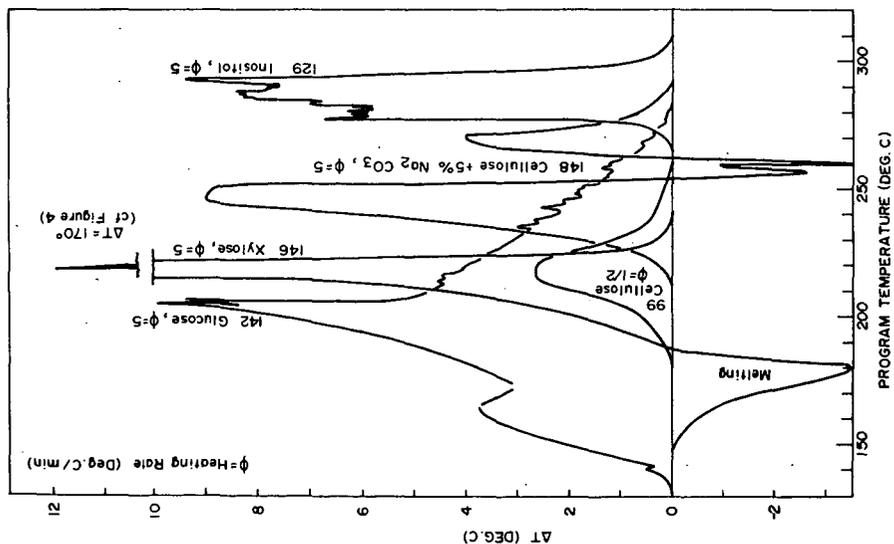
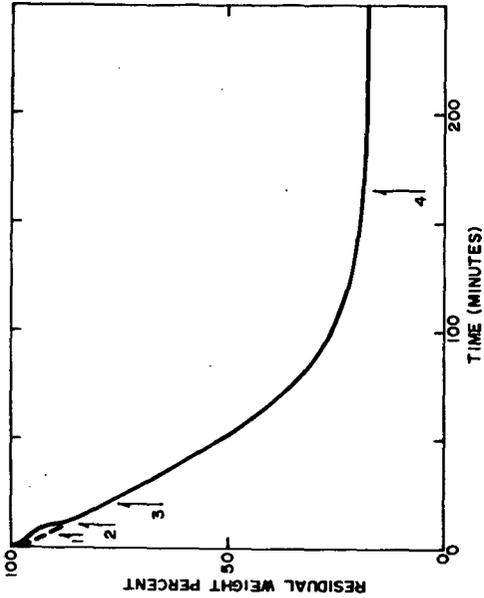


Fig. 5. DTA THERMOGRAMS AT 7 KB



INITIAL WT.: 124.0 MG.
AFTER 10 HRS.: 18.75 MG.

PYROLYZATE ANALYSIS	COLLECTION PERIOD	TEMP. (°C)
#1. 100% H ₂ O	0 - 5 MINUTES	Rm.T. - 160°
#2. 91% H ₂ O, 4% CO ₂ , 4% HC'S*	5 - 10 "	160° - 300°
#3. 82% H ₂ O, 15% CO ₂	10 - 20 "	300°
#4. 74% H ₂ O, 20% CO ₂	20 - 165 "	300°

*HC'S: PROBABLY 4% CH₄ + SMALL FRACTION ETHANE, ACETONE, AND ACETALDEHYDE.

CO PRESENCE NOT DISTINGUISHABLE DUE TO MASKING EFFECT OF H₂ (SAME W/E VALUE). PERCENTAGES ARE BASED ON VOLUME WITHOUT AIR.

Fig. 8. SAMPLE #124: VACUUM PYROLYSIS OF CELLULOSE AND ANALYSIS OF GASEOUS PRODUCTS

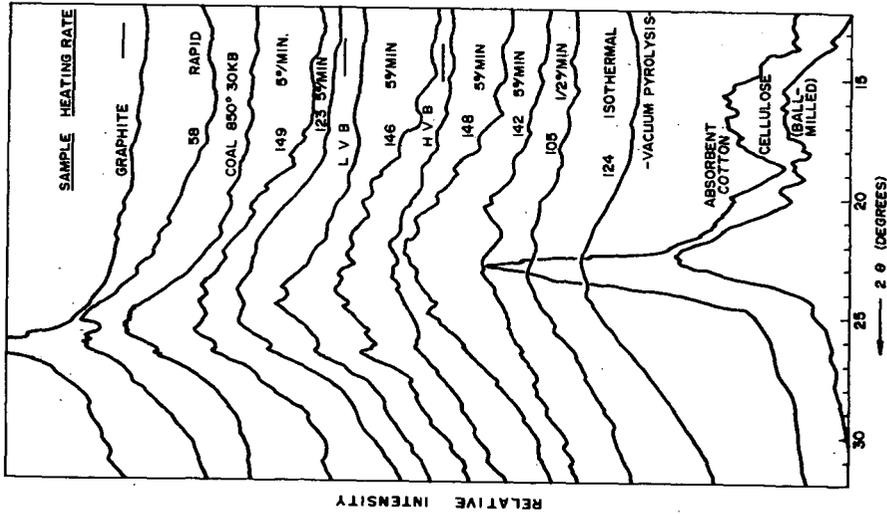


Fig. 7. A COMPARISON OF X-RAY DIFFRACTION PATTERNS