

THE UNIVERSITY OF MICHIGAN
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PRELIMINARY STUDIES ON EFFECTS
OF GAMMA RADIATION ON THE CARBONIZATION OF COAL

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Dr. J. J. Martin reviewed the experimental data and aided in interpreting the results.

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ABSTRACT

Powdered coal was subjected to radiation at room temperature to determine gas evolution and changes in physical properties from radiation alone.

Next, coal samples were submitted to the carbonization process at 450°, 600°, and 750°C both with and without radiation.

The results of this series of experiments indicate that the volume of gas released under a 750°C heat cycle is much reduced when the heat cycle is combined with radiation. At 600°C this effect of reduced gas evolution with radiation is not conclusive.

By analyzing gas composition by means of Orsat and gas chromatography methods, it was found that the ratio H_2/CH_4 always decreases when the carbonization process is performed under radiation.

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CHAPTER I

INTRODUCTION

Although in recent years the use of radiation has become familiar in many different fields, it seems that in the particular area of coal chemistry, fundamental research remains to be performed in studying radiation effects. This is the first of a series of exploratory experiments at the University of Michigan to investigate the effects of radiation on carbonaceous materials.

This investigation consisted of three separate steps. The first was purely exploratory, consisting of the irradiation of powdered coal in an open container at room temperature to see whether any measurable change occurred in the solid material. A physical effect was observed, leading to the first analytical part of the present study. This first analytical run was performed with the sample in a sealed tube, to determine quantitatively the physical changes occurring and to obtain an analysis of liberated gases under irradiation of coal at room temperature.

The second analytical phase, with which the greater part of this report is concerned, dealt with the effects of radiation on the carbonization process.

Carbonization of coal has been a well-known process for many years. However, the chemistry involved in the process is rather complex due mainly to the composition of coal itself. The existence of several varieties of coal makes the problem even more difficult.

The addition of radiation to the carbonization process can be expected to have:

1. A physical effect, with modification of coal and coke structures and a change in the mechanical properties of the solid product.
2. A chemical effect, causing the occurrence of certain reactions in addition to those normally observed.

It can be expected that both physical and chemical properties of the products will be affected.

The principles of the Gray-King coal testing method⁽¹⁾ were used, making necessary modifications which will be described later. The carbonization chamber was designed in such a way that it could be placed inside the 2-inch I.D. cylinder-shaped cobalt source. This arrangement of the source gives a radiation intensity of 850,000 R/hr.

The released gases were collected as in the Gray-King method and were then analysed. Analyses were made of the percent of H_2 , CO_2 , CO , O_2 , CH_4 , C_2H_6 and higher HC^S produced in radiation and non-radiation runs. Complete tabulation of these results are shown in Table II and Table III.

No attempt has been made to correlate our results with expected theoretical results due to the complex chemistry involved in coal carbonization.

The mechanisms which explain the effect of radiation in this case could be established only after many experimental sets of data and, of course, a better understanding of the chemical reactions that take place.

CHAPTER II

HISTORY OF PROCESS AND PURPOSE

The process known as carbonization of coal or coking was originated in England in 1700 and its historical importance is very often overlooked.

It was actually this process which later made possible the tremendous industrial development which depended upon vast quantities of steel for heavy machinery and volume production of consumers products.

Further improvements in the original process resulted in modern installations producing a great variety of chemicals in addition to gas and coke (solid residue of the carbonization).

Coal carbonization products are not a major energy source in the United States, due to plentiful supplies of petroleum and natural gas. However, in those countries which do not have oil, coal and its derivatives remain the principal natural fuel.

According to the temperature involved in the process, carbonization has been subdivided in three types:

1. High-temperature carb. (1500-2000°F) 800-1100°C
2. Mid-temperature carb. (1200-1300°F) 650-750°C
3. Low-temperature carb. (about 1000°F) ~ 550°C

Each temperature range results in a different product distribution.

In these experiments we are concerned with low-temperature and mid-temperature carbonization, since the object of this work is to obtain a preliminary insight into the subject.

Current literature reports only a few studies in the effects of radiation on coal degradation. The results are gas desorption and changes in some mechanical properties. (2), (3), (4)

This work reports specific radiation effects in the process of coal carbonization itself, the effort being confined to analyzing chemical changes only.

CHAPTER III

IRRADIATION OF COAL AT ROOM TEMPERATURE*

A ten-gram sample of coal was sealed in a glass tube $\frac{3}{4}$ " diameter and 2" long, evacuated to 0.2 microns. A vapor pressure equilibrium of 50 microns developed, at room temperature.

This sample was subjected to a radiation dosage of approximately 100 megarep by exposure to 8.6×10^5 R/hr for 120 hours. A control sample was not irradiated.

Gas Analysis

Calculation from the initial and final pressures in the glass container and the free volume above the coal, indicated that approximately 1.5 cc of gas was evolved. Analysis by mass spectrometer showed the gas to have the following composition.

<u>Components</u>	<u>Mole Per Cent (Water Free Basis)</u>
Carbon dioxide	1.2
Air	1.0
Ethane	0.1
Nitrogen and/or Carbon monoxide	2.9 (a)
Methane	1.9
Hydrogen	93. \pm 0.5

(a) ca. 2.3% Nitrogen and ca. 0.6% carbon monoxide.

Coal Analysis

Proximate analyses, swelling indices and Gieseler Plastometer test data for both the irradiated and unirradiated coal are given below.

* Analyses supplied by Koppers Company in private communication Sept. 1957.

Proximate Analyses and Free-Swelling Indices

	<u>Blank Coal</u>	<u>Irradiated Coal</u>
% Volatile Matter	30.3	29.8
% Fixed Carbon	64.0	64.4
% Ash	5.7	5.8
Free-swelling index	8-1/2	8-1/2

Gieseler Test Data

	<u>Blank Coal</u>	<u>Irradiated Coal</u>
Softening Temp. - °C	310	320
Max. Fluidity Temp. - °C	342	342
Solidification Temp. - °C	481	488
Max. Fluidity - Div. Per Min.	3150	3150

The Gieseler Plastometer test record furnished by The Koppers Company is reproduced as Figure 1.

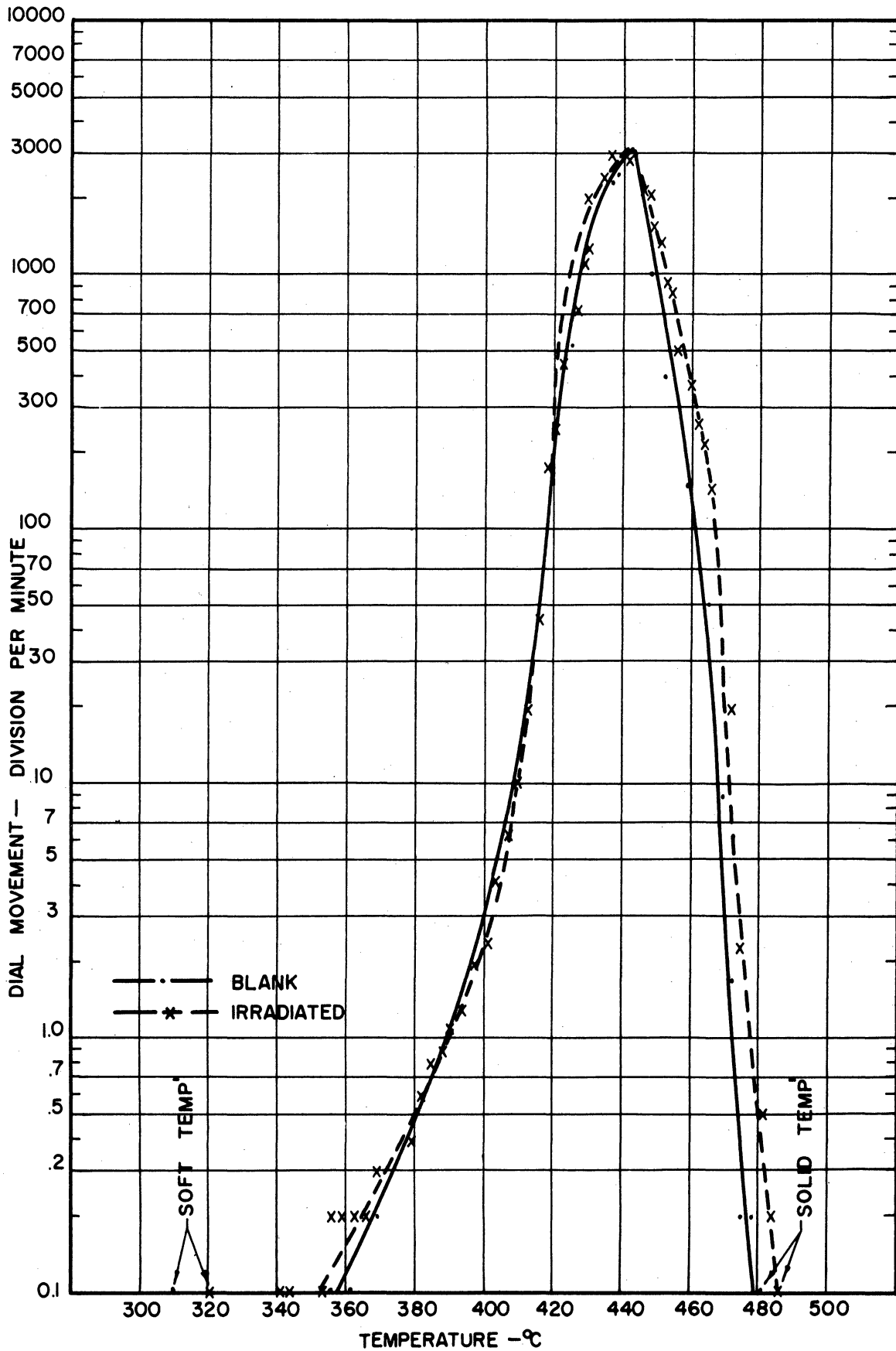


Figure 1. Gieseler Plastometer Test. Effect of Irradiation with Co-60

CHAPTER IV

EQUIPMENT FOR CARBONIZATION

The standard technique for high-temperature carbonization assay, known as the Gray-King method, proved to be suitable for the purposes of this work. The apparatus used in the set-up is represented diagrammatically in Figure 2, and scale drawings of certain parts are shown in Figure 3, 4, and 5.

The tube (D) which is 2.8 cms. in diameter by 15 cms. long is charged with glass beads drenched with dilute sulfuric acid to absorb ammonia. The U-tube (C) acts as a condenser; it may be cooled externally and has an extension with a capacity of at least 5 ml. for the reception of the liquid products (tars).

The gas holder (E), which is filled with a mixture of equal volumes of glycerin and water, is connected to a glass reservoir (G) by means of rubber or tygon tubing. This reservoir (G), which permits keeping the gas in (E) at atmospheric pressure, is suspended by a cord passing over a pulley and counterbalanced by a glass vessel (J) floating on the liquid in (K). This liquid comes from the gas holder (E) after it has been replaced by the released gas.

The carbonization chamber (A), Figure 4, was designed instead of the conventional silica tube that is placed horizontally in the Gray-King method. In our case a vertical chamber was required being made of stainless steel tubing (Carpenter 220) with the following dimensions:

O.D. 1.25 inches
Thickness 0.12 inches
Length 14.5 inches

The heating system consists of a resistance wire (Chromel-A, 16 gauge), which was wound alternately with asbestos cord. One asbestos layer was placed between the surface of the tube and the heating element and another was used to cover the element. Finally the whole assembly was wrapped with aluminum foil to reduce the heat losses to a minimum. The outer diameter was designed to fit the inner diameter of the Co⁶⁰ source, 2 in.

As a portion of the carbonization chamber was outside of the heated part, a solid metallic (S.S.) piece was put inside at the bottom of the chamber. The purpose of this was to raise the carbon sample to a region of uniform heat distribution.

The temperature history of the process was obtained by a metallic-coated Chromel-Alumel thermocouple. The temperature was measured right in the center of the coal sample. It is reasonable to assume that a uniform heating was attained.

Other accessories to the system include a Hg-differential manometer, which is connected to the gas holder. The rest of the connections and joints were made using glass and/or tygon tubing reinforced with copper wire to prevent gas leaks.

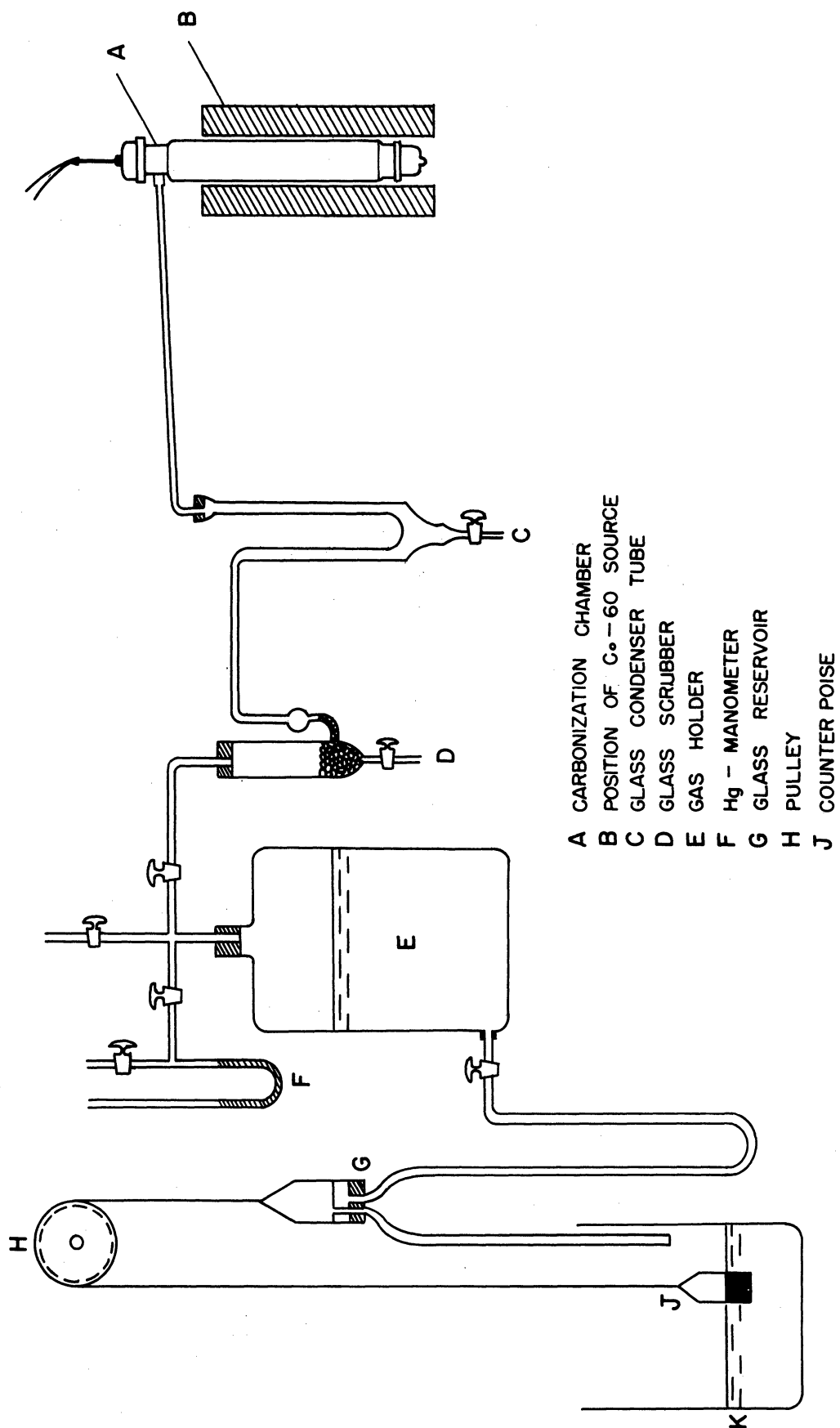


Figure 2. Apparatus Used in Coal Carbonization Experiments

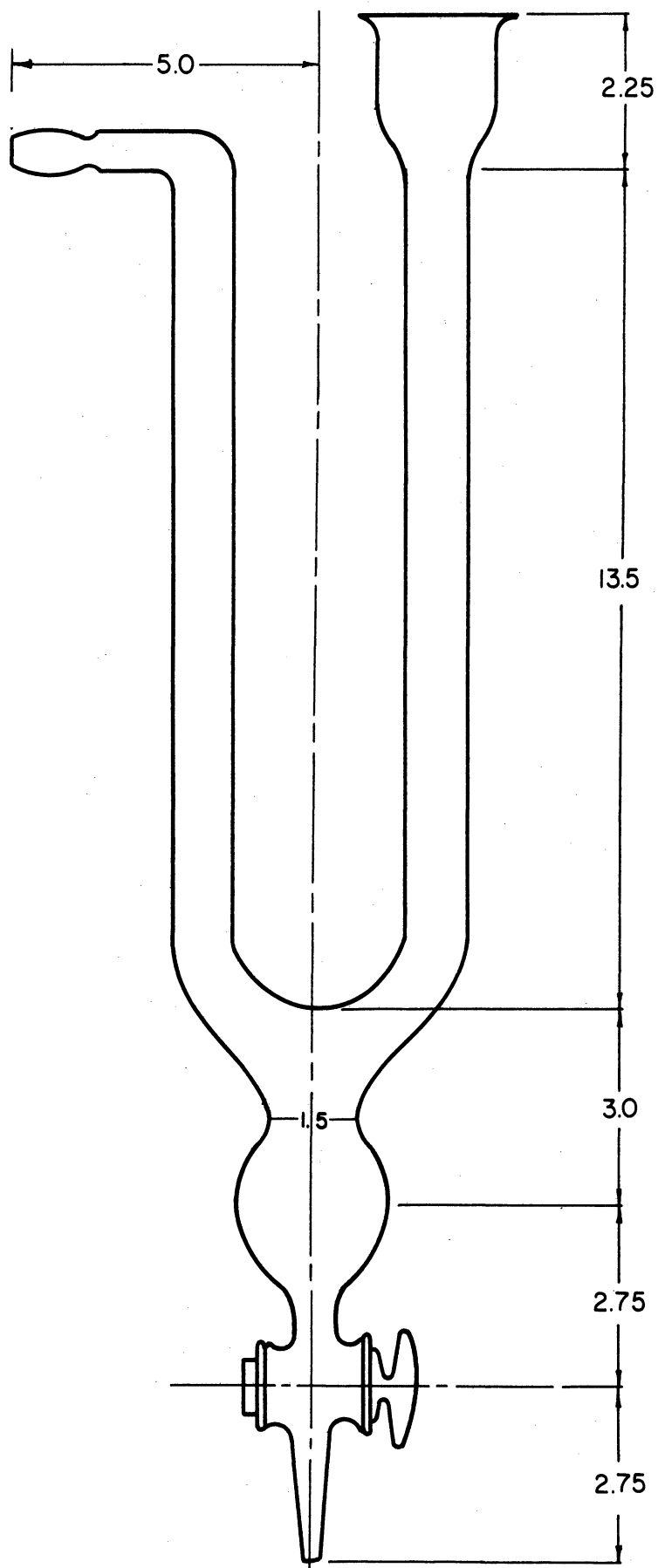
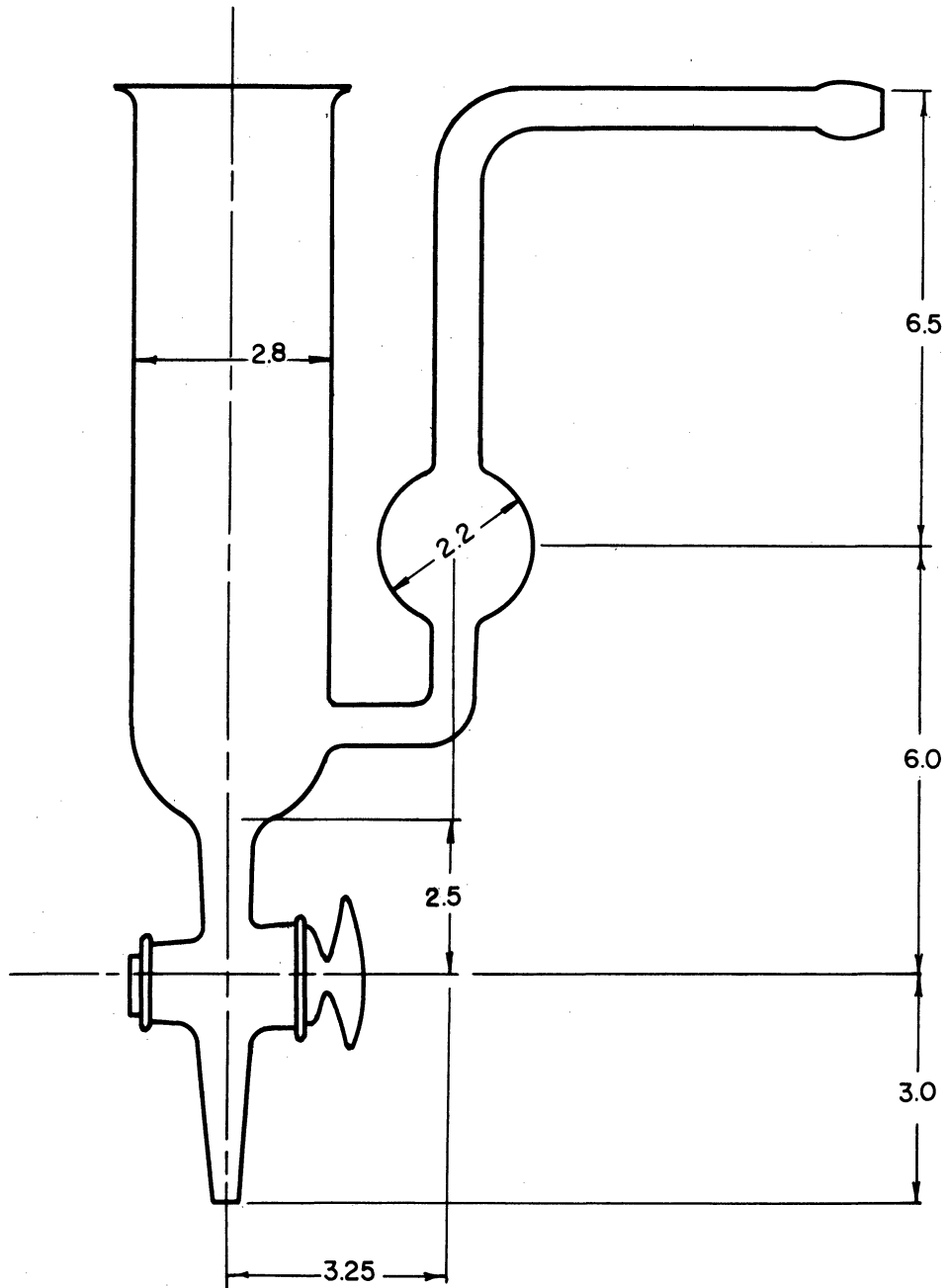


Figure 3. Glass Condenser (Dimensions in cms)



(DIMENSIONS IN CMS)

Figure 4. Glass Scrubber (Dimensions in cms)

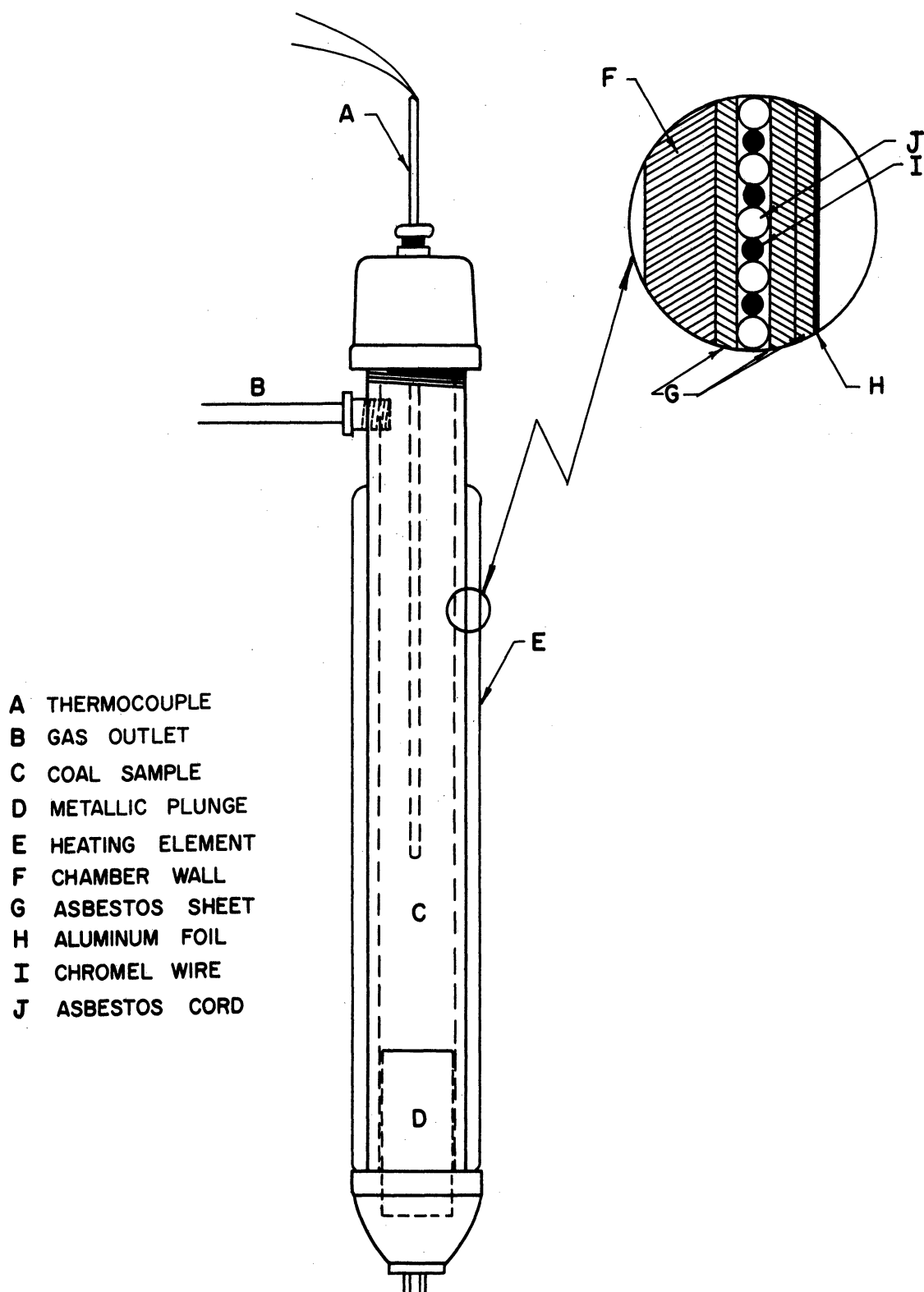


Figure 5. Carbonization Chamber Showing the Heating System

CHAPTER V

METHOD OF OPERATION

Coal was air dried at 105-110°C and ground to pass a 72-mesh B.S. Sieve. The carbonization chamber was charged with 40 gs. of air-dried coal, and tightly closed using silver goop. Gas holder (E) had to be completely filled with a water-glycerin solution before the operation was started. Five cm. of sulfuric acid 0.1N was put in tube (D).

The cold junction of the thermocouple was in ice and initial operating temperature for each run was about room temperature.

The terminals of the heating wire were connected to power, and a final inspection of the flow lines and valves was made before starting the operation.

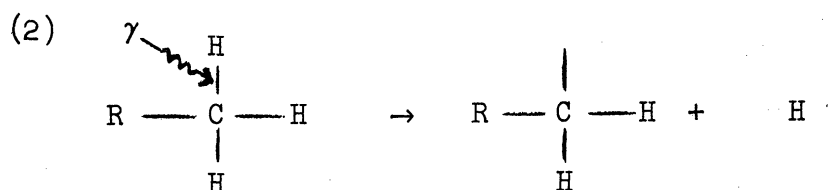
For radiation runs, the apparatus was placed in the high-radiation room and the carbonization chamber was arranged to fit into the center of the cobalt source, when this was raised. When the carbonization chamber is in the center of the source, the coal sample receives about 850,000 RPH.

The heating procedure consisted of a rapid temperature increase up to 300°C followed by a controlled increase of five degrees per minute. This was attained by using a SECO Powerstat, and a typical time-temperature history, shown in Table I. See also Figure 6.

The length of the run, 150 minutes, was kept constant for the three different carbonization temperatures. During the experiment, periodic volume readings were made to keep track of the time-volume behavior. Graphics illustrating these parameters are shown in Figure 7

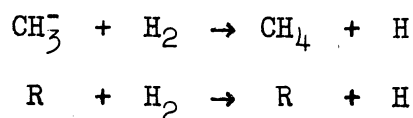
- (1) The density of the gaseous phase is low when compared with the solid sample and therefore the frequency of gamma-interaction with molecules decreases proportionately.
- (2) The time of exposure of the gas molecules is rather short, since they occupy just a small portion of the chamber and shortly leave the region of high radiation.

C. Some tendency of gamma-radiation breaking the bonds of CH_3 -radicals attached to higher molecules, rather than freeing hydrogen atoms, is observed at 600°C . This can be represented by the following reactions



where R can represent one of the complex hydrocarbon radicals present in the coal.

Reaction (1) could be followed by



and the hydrogen atoms would react with some other free radicals, being ultimately absorbed. The formation of CH_2^\cdot radicals also can be expected but in smaller amounts. CH_2^\cdot

for several runs.

At the end of the experiment, twenty or thirty minutes were allowed to cool the system. The final volume, adjusted atmospheric pressure, was then recorded. The next step consisted of weighing the solid and liquid products and analyzing the released gases. With this data it was then possible to estimate the balance of materials and thereby the quantitative success of the experiment.

Gas analyses were made by two independent procedures: by means of an Orsat analyzer the percentage of H_2 , CO , CO_2 and O_2 were determined; in addition a gas-chromatographic analysis was carried out to evaluate the quantitative composition of CH_4 , C_2H_2 and higher hydrocarbons. The correlation of both these results gives a fairly accurate picture of the gas composition and further enables us to make the balance of materials.

The carbonization chamber and parts (D) and (C) were carefully washed with acetone after each run in order to assure a reliable quantitative analysis.

Lack of time and facilities prevented us from making an analysis of the solid and liquid products.

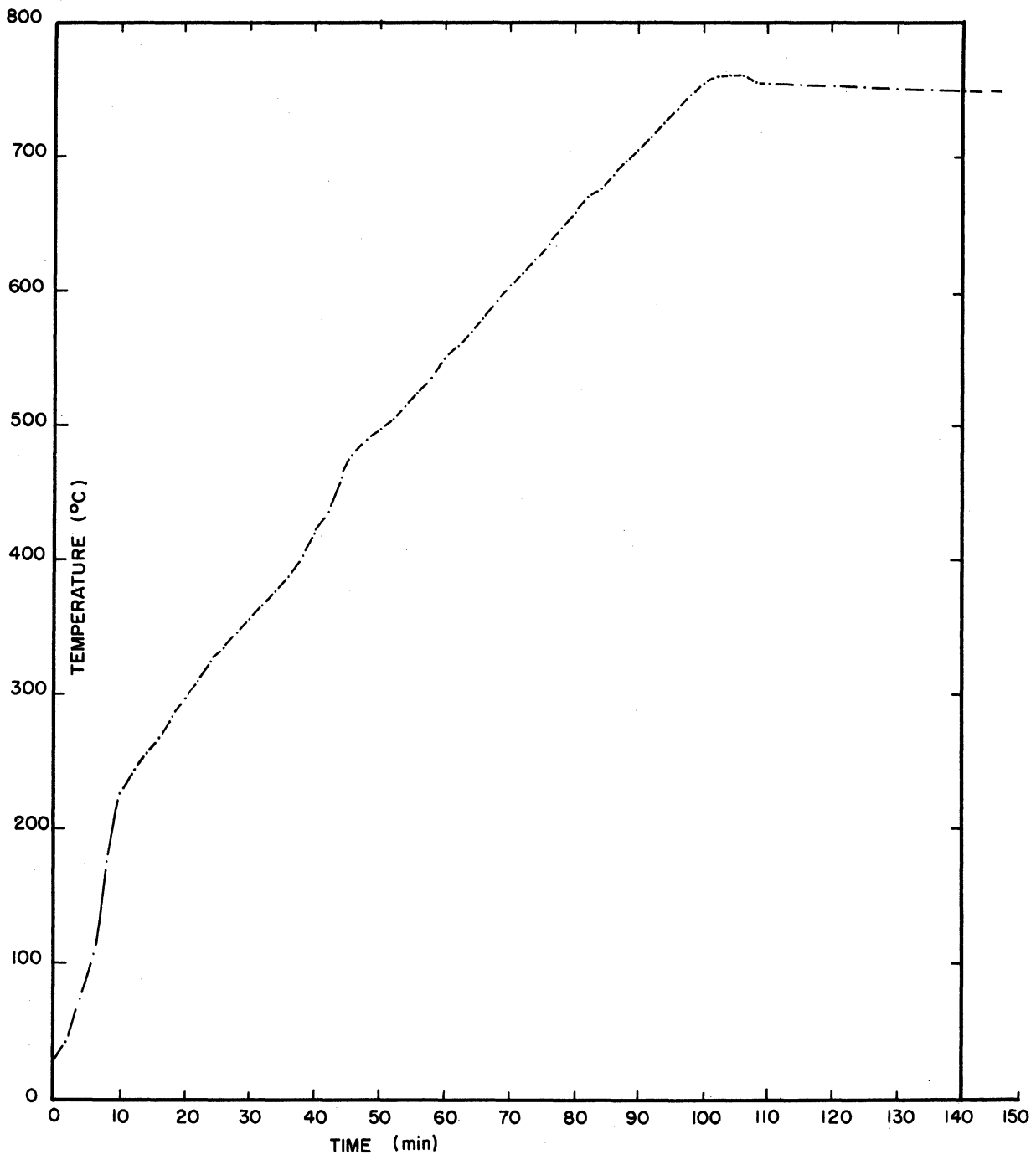


Figure 6. Typical Temperature History. Run 750-809

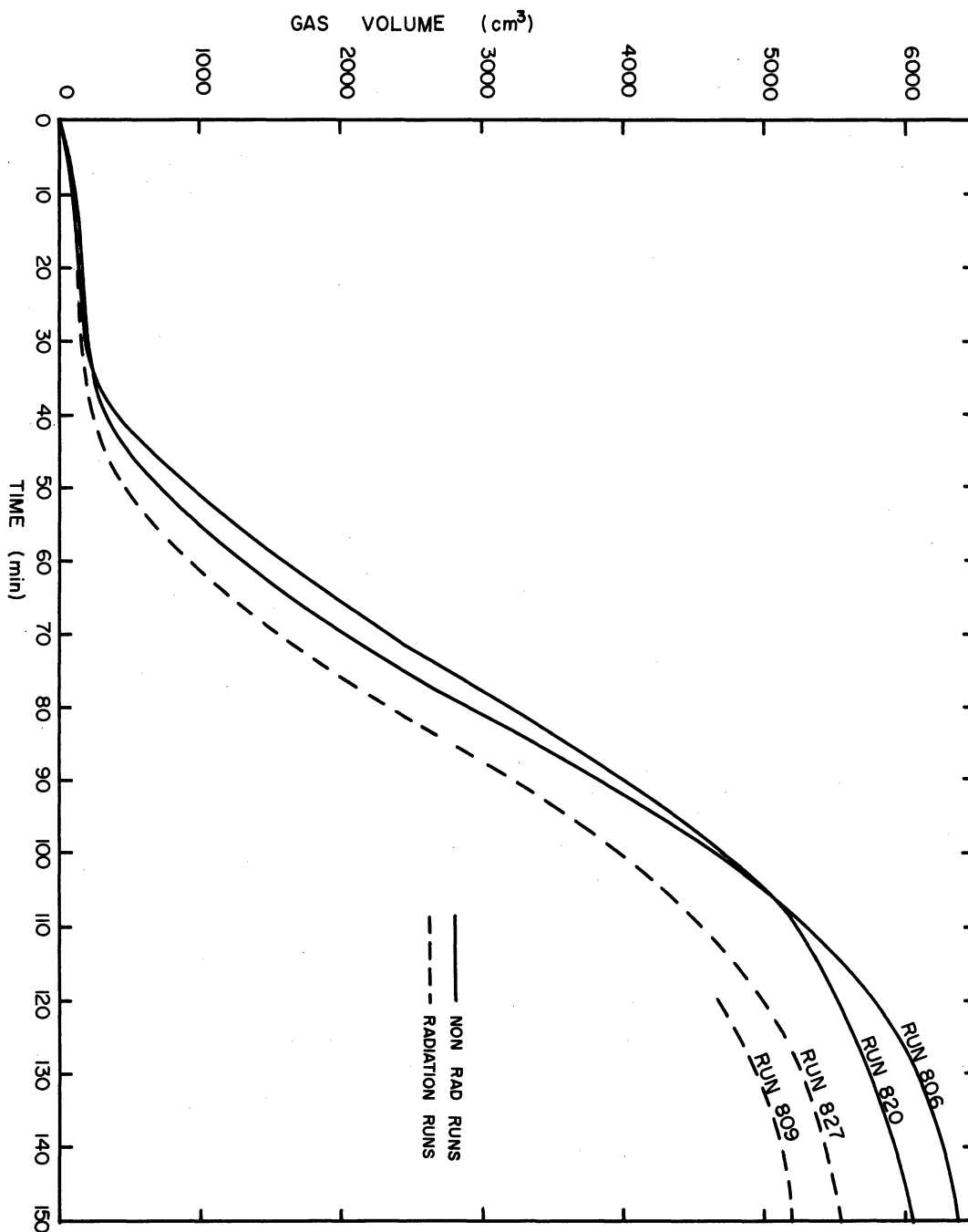


Figure 7. Time-Volume Curves at 750°C Runs

CHAPTER VI

INTERPRETATION OF DATA

Results from runs made at 450°C did not seem to throw much light on the problem; therefore, emphasis was placed on higher temperature runs.

Volume of Gas Released

At 600°C the volume released did not give any conclusive difference, since the radiation runs gave intermediate values, as may be observed in Tables II and III. However, at 750°C both radiation runs gave lower amounts of gases.

H₂ Content

The observed difference is small at 600°C, but at 750°C there is a definite decrease under radiation.

CH₄ Content

There were contradictory results in this matter. At 600°C, there was a slight increase in radiation runs, while at 750°C there was a decrease. (The decrease at 750°C was smaller than the increase at 600°C).

CO Content

The analysis revealed some increase in CO released when the runs were made under radiation.

Content of Other Species

From the series of runs made it is not possible to draw any conclusive result about variations of CO₂, O₂, C₂H₆ and higher hydrocarbons.

Solid Product or Cokes

In general, the weight of the cokes follows a correlated relationship with the volume of gas released. Further results concerned with possible changes in structural and/or mechanical properties are likely to be encountered, when a complete analysis of the collected samples is made.

Correlations of the variation of H_2 with respect to CH_4 and higher hydrocarbons were made and are shown in Figure 8.

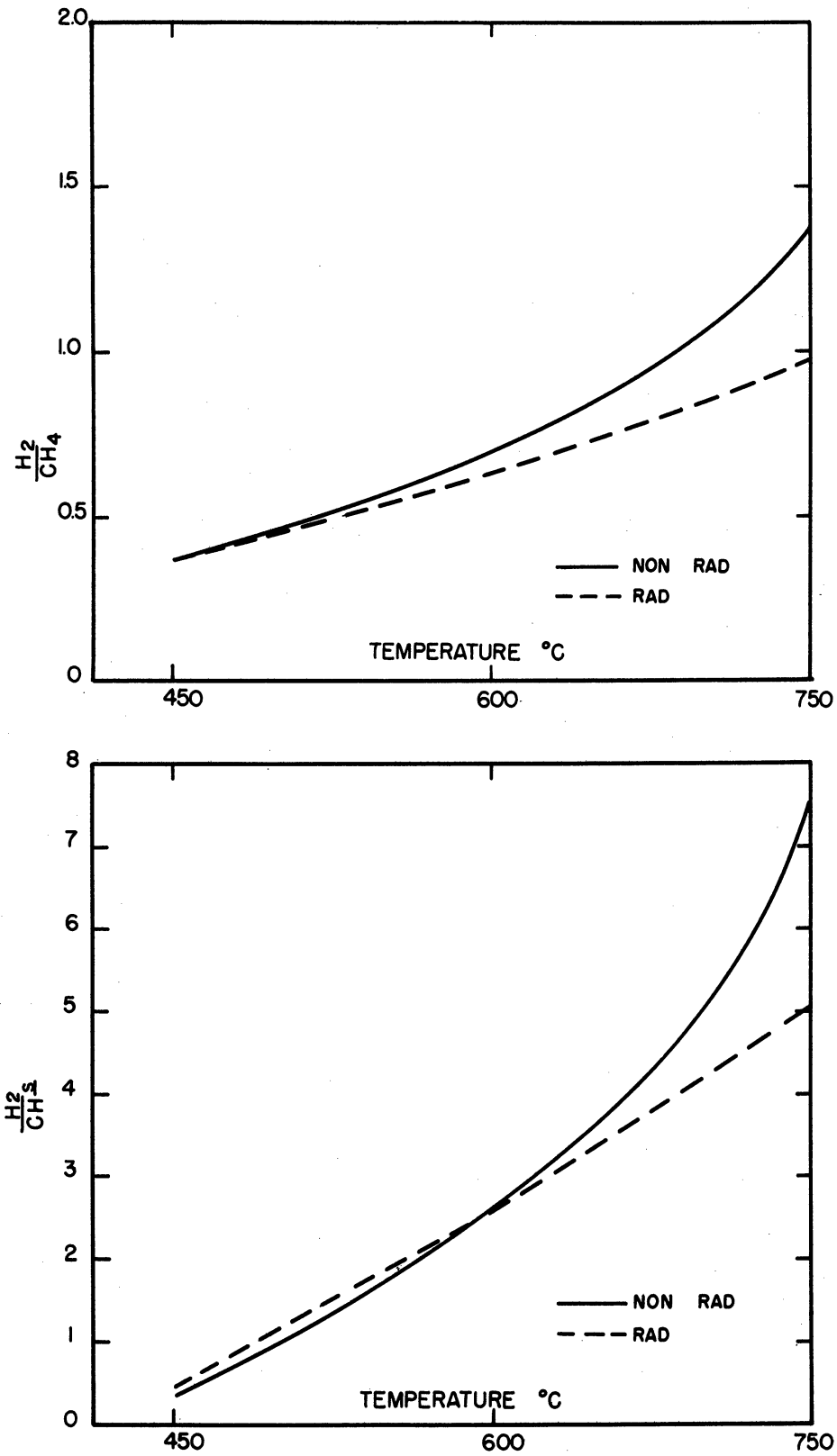


Figure 8. Changes of Gas Composition at Different Temperatures

CHAPTER VII

CONCLUSIONS

An early study of the data gave indications of a decrease in the ratio $\frac{H_2}{CH_4}$ which is inferred from data given in terms of percentages of the volume released. Plots of H_2/CH_4 and H_2/HCS vs. Temperature are shown in Figure 9.

It can be noticed, however, that these curves follow a pattern that is established by the hydrogen itself, which shows an appreciable increase in volume released when the runs are made under radiation.

In general the mechanisms involved in the processes are quite difficult to interpret. The most interesting fact is the cited decrease in hydrogen. The complexity of the chemical reactions that take place in coal carbonization makes the problem more difficult.

On the basis of the exploratory purpose of this work, it is pertinent to postulate some of the possible mechanisms as well as pointing out some effects of radiation.

- A. The decrease of H_2 produced can be caused by a polymerizing effect of gamma-radiation. This polymerization would hinder the release of H_2 . Such an effect would produce more complicated hydrocarbon molecules in the coal itself. One way of checking this possibility will be by means of the complete analysis of the cokes produced.
- B. The radiation can be expected to produce an effect either before or at the very instant of the gas evolution. It is quite unlikely that radiation has much effect in the gaseous phase itself because:

radicals would eventually increase the amount of hydrocarbons in the gas released. In some work (that has been done here, under the guidance of Dr. J. J. Martin) dealing with the effect of radiation upon hydrocarbons of high molecular weight an increase in methane formation has been observed. This mechanism (Reaction (1)) could account partly for the results, at least at 600°C, reported here. At 750°, however, this effect could be counterbalanced by some other mechanism that we are not able to determine as yet. (Such as the polymerizing effect cited in B-(1)).

D. Increase of C_2H_6 in the radiation runs is doubtful.

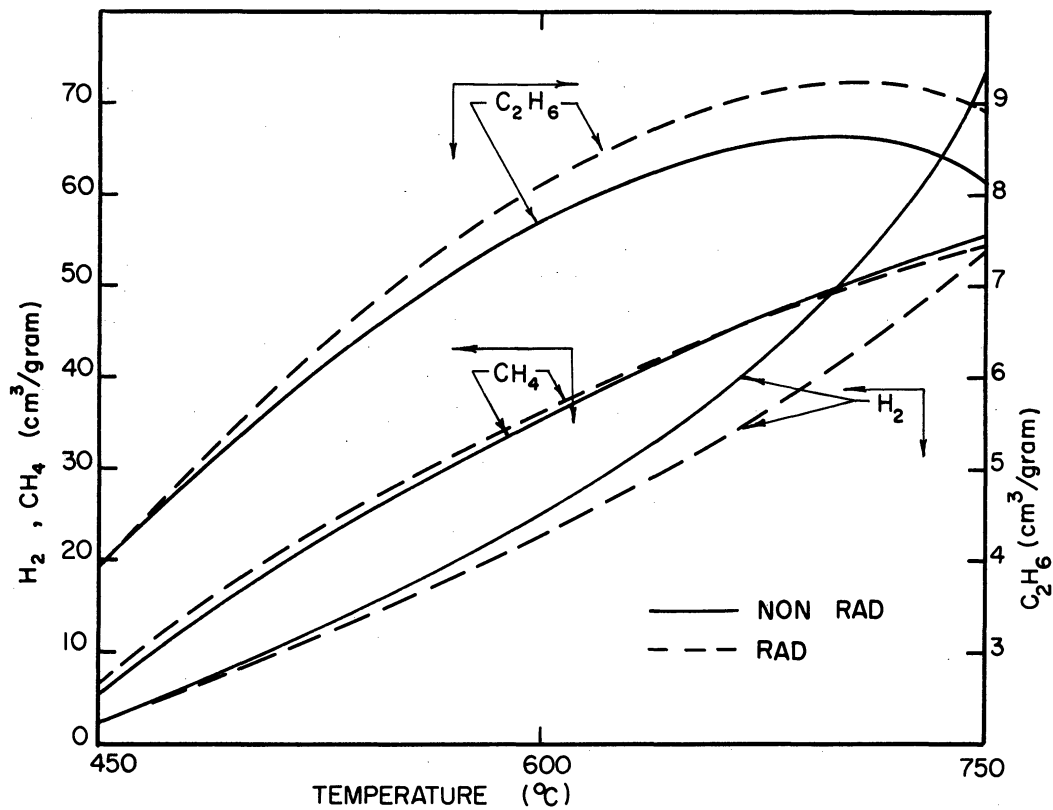


Figure 9a. Influence of Radiation Upon $\frac{H_2}{CH_4}$

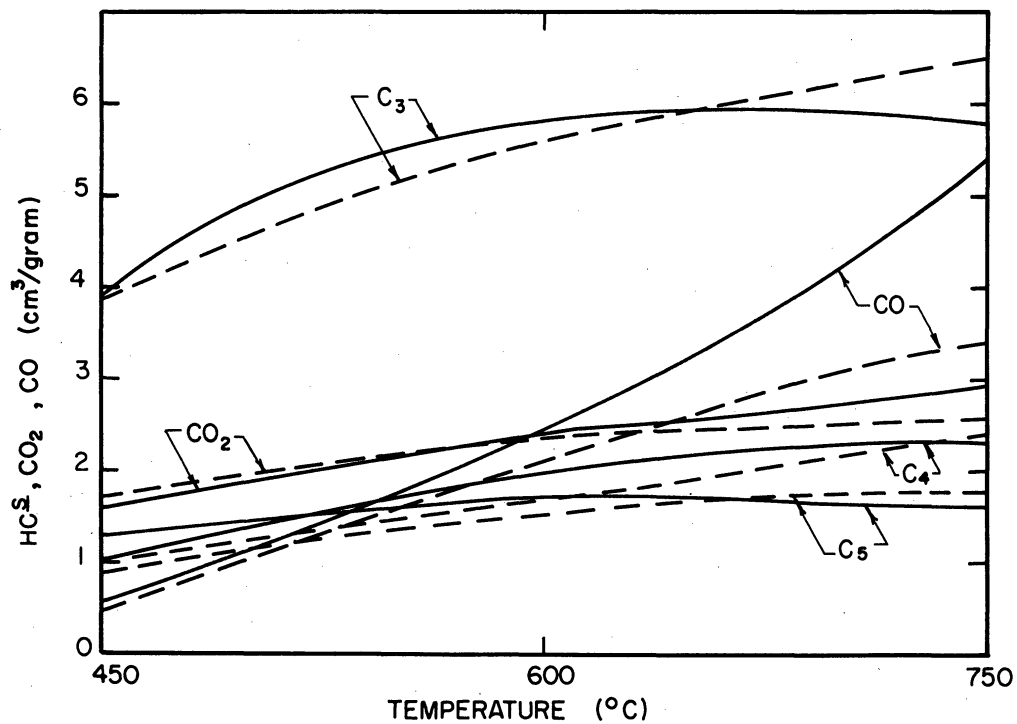


Figure 9b. Influence of Radiation Upon $\frac{H_2}{CH_4}$

TABLE I

TIME-TEMPERATURE DATA IN A RADIATION RUN

TIME (min.)	TEMP. (°C)	Δ T	TIME (min.)	TEMP. (°C)	Δ T
0	30	-	62	560	9
2	42	12	64	571	11
4	74	32	66	582	11
6	108	34	68	594	12
8	177	69	70	605	11
10	227	50	72	614	9
12	243	16	74	624	10
14	256	13	76	636	12
16	268	12	78	648	12
18	283	15	80	660	12
20	298	15	82	671	11
22	310	12	84	678	7
24	323	13	86	688	10
26	335	12	88	699	10
28	347	12	90	708	10
30	357	10	92	717	9
32	367	10	94	728	11
34	377	10	96	737	9
36	389	12	98	748	11
38	404	15	100	755	7
40	422	18	102	760	5
42	438	16	104	761	1
44	462	24	106	760	-1
46	480	18	108	756	-4
48	490	10	110	755	-1
50	498	8	115	754	-1
52	505	7	120	754	-0
54	514	9	125	753	-1
56	528	14	130	750	-
58	539	11	140	750	-
60	551	12	150	750	-

TABLE II
RESULTS OF NON-RADIATION RUNS

Temp. (°C)	450	600	600	750	750
Run#	806	801	823	806	820
Coke (gs)	36.77	33.84	33.49	32.60	31.72
Tars (gs)	1.20	4.20	1.48	-	2.39
H ₂ O (gs)	3.80	-	1.35	-	1.70
Gas Vol ($\frac{\text{cm}^3 \text{ of gas}}{\text{gr. of coal sample}}$)	20	85.75	80.0	159.50	151.25
H ₂	2.14	24.44	25.04	73.69	72.45
CO ₂	1.60	2.31	2.40	3.35	2.42
O ₂	-	-	0.88	1.12	0.91
CO	0.58	2.83	2.24	6.06	4.69
CH ₄	5.76	36.96	33.60	53.43	56.72
C ₂ H ₆	3.86	9.26	6.24	9.33	7.11
C ₃	3.82	6.69	4.98	6.86	4.84
C ₄	1.02	1.54	2.52	3.38	1.36
C ₅	1.30	1.29	1.98	2.26	1.06

TABLE III
RESULTS OF RADIATION RUNS

Temp. (°C)	450	600	600	750	750
Run #	805	802	825	809	827
Cokes (gs)	36.24	34.57	33.04	33.37	33.175
Tars (gs)	1.0	2.9	1.40	1.78	1.645
H ₂ O (gs)	2.6	4.0	1.30	1.66	1.49
Gas Vol $\left(\frac{\text{cm}^3 \text{ of gas}}{\text{gr. of coal sample}}\right)$	21.25	76.50	86.25	130.00	138.75
H ₂	2.55	21.80	24.15	50.83	56.89
CO ₂	1.74	2.14	2.59	2.34	2.77
O ₂	-	-	1.38	1.30	0.69
CO	0.53	2.60	1.72	2.21	4.58
CH ₄	6.88	33.05	39.93	56.16	52.31
C ₂ H ₆	3.95	8.26	7.76	8.45	9.16
C ₃	3.76	5.74	5.43	5.33	7.63
C ₄	1.00	1.45	1.98	1.87	2.84
C ₅	0.85	1.45	1.47	1.51	2.01

CHAPTER VIII

APPENDIX

BALANCE OF MATERIAL -

In order to evaluate the reliability of the experiments, material balances were made in most of the runs. The procedure was as follows: Solid and liquid products were weighed on the analytic scale. Released gas was allowed to cool and, the volume reading was made at room temperature.

After the Orsat and Gas-Chromatography analysis, the composition data was used to calculate the weight of the gas mixture. Using the concept of average molecular weight, the expression

$$pV = \frac{m}{M_{av}} RT \quad (1)$$

can be used and m , the weight, found in grams. It is assumed that the mixture behaves ideally.

This procedure can be illustrated in the case of run 750-809 (radiation run).

Weight of cokes:	33,370	
Weight of tars:	1,785	
Weight of H ₂ O:	<u>1,665</u>	
	36,820	grams

The average molecular weight

$$M_{av} = x_A M_A + x_B M_B + x_C M_C + \quad (2)$$

was calculated for all the components encountered in the gas mixture. In our case:

H ₂	-----	0.391 x 2	=	0.782
CO ₂	-----	0.018 x 44	=	0.790
O ₂	-----	0.010 x 32	=	0.320
CO	-----	0.017 x 28	=	0.476
CH ₄	-----	0.432 x 16	=	6.920
C ₂ H ₆	-----	0.065 x 30	=	1.950
C ₃	-----	0.041 x 44	=	1.800
C ₄	-----	0.014 x 58	=	0.810
C ₅	-----	0.012 x 70	=	0.840
				<u>14.688</u>
				= Mav.

Solving equation (1) for

$$M = \frac{pV}{RT} Mav$$

where p = 1 atm.

V = 5200 cm.

R = 82.05 cm. atm./°K mol.

T = 300°K

Mav = 14,688

$$\text{therefore } m = \frac{1 \times 5200}{82.05 \times 300} \times 14.688$$

$$m = 3.1 \text{ gs.}$$

The total weight of the products is

coke and liquids 36.820

weight of the gas 3.100

39.920 grs.

A loss of 0.080 grams (0.2% of 40 grams) was found, which is a satisfactory result.

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