

## DEVOLATILIZATION OF COAL BY RAPID HEATING

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### INTRODUCTION

Coal has been used mainly for the generation of electric power to the present time. Now that critical shortages exist in the supply of natural gas for residential heating and industrial usage, a broad effort is being made by industry and government to develop processes for gasifying coal.<sup>1-2/</sup> When these processes are fully developed, they will represent a second major source of coal utilization.

In both combustion and gasification, coal is heated to elevated temperatures, and therefore it inevitably sustains some degree of decomposition prior to or concurrently with other chemical reactions. In the Bureau of Mines' Synthane process,<sup>3-4/</sup> for example, pretreated coal enters the upper, carbonizing section of the gasifier where it undergoes extensive thermal degradation to form char. The reaction products formed at this stage in the process make an important contribution to the overall performance of the gasifier.

For these reasons, research on the devolatilization of coal by rapid heating has been a part of the Bureau's program on gasification. The results presented in this paper represent a continuation of preliminary work that was reported earlier.<sup>5/</sup>

### EXPERIMENTAL

Single pulses of electrical current provide high-speed heating that is needed to measure the thermophysical properties of solids at elevated temperatures,<sup>6/</sup> and of metals in particular.<sup>7-8/</sup> This technique, termed pulse heating, was adopted for devolatilizing coal in the present study. Coal samples were decomposed in vacuo in order to collect and identify the gaseous products. Quantitative measurements of the resultant weight loss of sample after rapid heating, served as a measure of the total volatiles evolved from the coal.

The reaction vessel was essentially a 29/42 tapered ground glass joint sealed on to a pumping system. Suitable vacuum gages, manometers, gas sampling and storage bulbs were attached to the reactor. Total volume of the reactor, including the sampling bulb, amounted to 418 cm.<sup>3</sup> Number 10 copper wires entered the reactor through Kovar-pyrex seals. These copper electrodes terminated in spring clamps which supported the heating element containing the coal sample. Resistive heating elements were made in the form of long, thin cylinders by wrapping 400 mesh stainless steel screen on a mandril. Dimensions of the cylinders were 6 cm in length and 1.2 mm in diameter. In preparation for pulsing, the open ends of the cylinder were completely closed, and the flattened ends inserted into the jaws of the spring clamps.

Current was supplied to the wire screen heating elements by a current controller. This device was an electronic circuit designed to set the initial current flow at a desired value and to allow the current to increase in a predetermined way. Shaping of the current pulse was necessary to compensate for increase in electrical resistance

of the wire and also for radiant heat losses at high temperatures. Typical current values were in the range 15-20 A. The current controller was triggered by a preselected pulse coming from a General Radio unit pulse generator, and current flow continued only for the duration of the timing pulse. Pulse times extended from 65 to 155 msec. A 0.1  $\Omega$  resistor in the current controller converted the current pulse to a voltage pulse which was displayed on a storage-type oscilloscope. Precise values of current and time were measured from the oscilloscope trace.

Coal samples were prepared by cutting out vitrains from lumps of coal. Further upgrading of the vitrains was accomplished by microscopic examination in which coal particles with adhering mineral matter were discarded. Vitrains were chosen for study because they constitute the most abundant and homogeneous component of coal and because they are also low in mineral matter.<sup>9/</sup> It is seen from table 1 that the ash content was less than 2 percent in the Pittsburgh coal and less than 1 percent in the other coals used. A low mineral matter content in the vitrains was desired to avoid ambiguities in the data from possible pyrolysis of mineral matter. The vitrains were ground to a particle size range of 44-53  $\mu\text{m}$  for use in the experiments.

Coals were selected to encompass a rather wide range of rank and volatile matter. Bituminous coals ranged in rank from hvCb to lvb; one subbituminous coal was also studied. Their proximate analyses are given in table 1.

Table 1.--Proximate analyses of vitrains.

Coal source	Rank	Proximate analysis, percent (mf)		
		Fixed carbon	Volatile matter	Ash
Pocahontas No. 3, W. Va.	lvb	82.4	16.8	0.8
Lower Kittanning, Pa.	mvb	73.8	25.3	0.9
Pittsburgh, Pa.	hvAb	63.1	35.1	1.8
Colchester Illinois No. 2, Ill.	hvCb	51.1	48.0	0.9
Rock Springs No. 7-1/2, Wyo.	Sub A	61.7	37.7	0.6

The temperature attained by the wire screen heating elements was related to the time of current flow by a calibration method. Trial and error determinations were made of the times required to melt pure metal powders of like particle size and amounts as the coal. A number of calibration points were thus established, and it was shown that the temperature at the end of the current pulse was proportional to the time of current flow in the region to 1450° C. The heating rate was therefore constant, and it was determined to be 8250° C/sec.

The experimental procedure for devolatilizing coal samples may now be described. A new (unheated) screen cylinder, containing no coal, was pulsed to 900° C in the reactor which had previously been evacuated. Pre-firing of the screen cylinders is essential because they undergo significant weight losses when they are heated for the first time. Such losses would interfere with measurements made on the coals. However, after the initial heating of a screen cylinder, its weight remains demonstrably constant in further tests. A prefired screen was weighed precisely on a Cahn RG microbalance; approximately 250 µg of coal were inserted into the cylinder, and the combined weight of the screen cylinder and coal sample was again determined precisely on the balance. The weighed coal sample and heating element were placed in the reactor and pumped until the system pressure was reduced to 10<sup>-3</sup> torr. When this reduced pressure was attained, the coal sample was pulse heated to a given temperature. After devolatilization occurred, the coal residue and screen were removed from the reactor and reweighed.

The volume of gases generated during devolatilization was determined from the pressure increase in the reactor. Mass spectrometric analyses of the gases were made at many, but not all, of the different test conditions. In this way, the weight of the gases produced by rapid devolatilization of coal was ascertained.

#### RESULTS AND DISCUSSION

The devolatilization behavior of bituminous coals under rapid heating conditions is shown in figure 1. This figure presents the weight-loss curves of four bituminous coals of different rank over a temperature region from 400° to 1150° C. All of the weight-loss curves have a characteristic shape in common, although they differ in detail. For most of the coals the reaction threshold occurs at 400° C, followed by very rapid decomposition to 600° C. Production of volatile reaction products reaches a peak at relatively low temperatures of 700° to 900°, a finding that should be of considerable importance to those engaged in design of coal gasification equipment. At still higher temperatures the declining trend in the formation of volatiles reverses, and starts to increase again at the highest temperatures of this study.

Some discussion of the low temperature peak in volatile production from bituminous coals is merited because this phenomenon does not occur during slow heating. In the latter case the weight loss increases monotonically with temperature.<sup>10/</sup> The broadest peak is exhibited by the Illinois hvCb coal which has the highest volatile matter content among the coals studied (see table 1). With regard to the higher rank bituminous coals, the peaks become progressively less intense with increase in rank, and the peak position shifts to higher temperatures. In all instances the volatile yield corresponding to the peak in the weight-loss curves was greater than the volatile matter in the coal determined by the ASTM standard method of analysis. These results are demonstrated by the data in table 2, which show that the yield of total volatiles may be increased as much as 36 percent by rapid heating. Supportive evidence for increased yields of volatiles is found in other rapid heating studies.<sup>11-12/</sup>

Consideration of the /cited studies in conjunction with our own leads to the conclusion that the ratio of total volatiles from rapid heating to ASTM volatile content depends not only on the rank of coal, as shown in table 2, but also on the magnitude of the heating rate. One suggested explanation for the appearance of maxima in the weight-loss curves is that of competitive reactions. For example, the bond-breaking reactions that occur in the coal structure and give rise to initial decomposition fragments may well have different temperature dependencies from those of recombination reactions that may form molecules more stable than the parent coal.

Table 2.--Increased volatiles from rapid pyrolysis.

Coal source	Volatile matter content		Increase factor
	by ASTM analysis	from peak weight loss	
Pocahontas No. 3	16.8	18.5	1.10
Lower Kittanning	25.3	30.8	1.22
Pittsburgh	35.1	47.9	1.36
Colchester Ill. No. 2	48.0	55.8	1.16
Rock Springs No. 7-1/2	37.7	42.4 (plateau)	1.12

In contrast to the results obtained with bituminous coals, the weight-loss curve of subbituminous coal exhibited no peak; instead, it reached what might be called a plateau in figure 2. From 800° to 1000° C the volatile yield remained level at about 42 weight percent of the coal. Beyond this region the production of volatiles increased sharply. The fact that the devolatilization curve of subbituminous A coal differs distinctly from those of bituminous coals indicates a need for more work with other subbituminous coals and lignites. Low rank materials such as these are of interest in coal gasification because their reserves are abundant and because they are situated in deposits with shallow ground cover.

The gases arising from rapid pyrolysis of coal vitrains have been examined by mass spectrometric analysis. The major components in the gas are H<sub>2</sub>, CH<sub>4</sub> and CO. Lesser amounts of CO<sub>2</sub> and the higher molecular weight hydrocarbons (up to C<sub>6</sub>) are also present. Hydrocarbons are present as both saturates and unsaturates with the notable exception of acetylene. Traces of aromatics such as benzene, toluene and xylene are found as well as sulfur in the form of H<sub>2</sub>S. The absence of acetylene, which has been found in appreciable quantity in some rapid heating processes<sup>13-14</sup> is most likely due to the lower temperatures and lower heating rate employed in our experiments.

Temperature profiles of the individual gases from pyrolysis of Pittsburgh vitrain are shown in figure 3. Here it is seen that the molar percentages of  $\text{CO}_2$ ,  $\text{CH}_4$  and the  $\text{C}_2\text{-C}_4$  hydrocarbons decrease with increasing reaction temperature. The functional dependence of  $\text{H}_2$  and  $\text{CO}$  on temperature is more complex.  $\text{H}_2$  production starts at 31.5 mole percent at  $700^\circ\text{C}$  and increases to a maximum value of 67.0 percent at  $990^\circ\text{C}$ . Further increase in temperature causes a small but real decrease in its concentration.  $\text{CO}$  concentration changes in an opposite manner to  $\text{H}_2$ . A minimum  $\text{CO}$  value of 12.0 mole percent is achieved at about the same temperature at which the maximum  $\text{H}_2$  concentration occurred. The gas composition data are given on a  $\text{H}_2\text{O-O}_2\text{-N}_2$ -free basis.

In addition to the gases produced by rapid devolatilization of coal, heavier products, referred to as tar, also form. This material condenses on the walls of the reactor and is visible as/brown stain on the glass. Because the quantity of tar from a single experiment is so small, it has not been measured nor has it been chemically analyzed. However, the quantity of tar can be obtained indirectly by subtracting the weight of the gases from the total volatiles, i.e. the weight loss of the coal. Results of such calculations for Pittsburgh vitrain are shown in figure 4 in which the experimentally determined curves for "total volatiles" and for "gas" have first been drawn. The curve for "tar" is of course determined by the difference calculation. The curves show that tar formation is favored by low decomposition temperatures and that tar is in fact the main product at all temperatures up to  $1000^\circ\text{C}$ . Above  $1000^\circ$  the amount of gas exceeds the amount of tar even though the total volatile yield is still below the peak yield obtained at  $700^\circ\text{C}$ . Further correlations of product yields with rank and temperature parameters have been made and will be published later.

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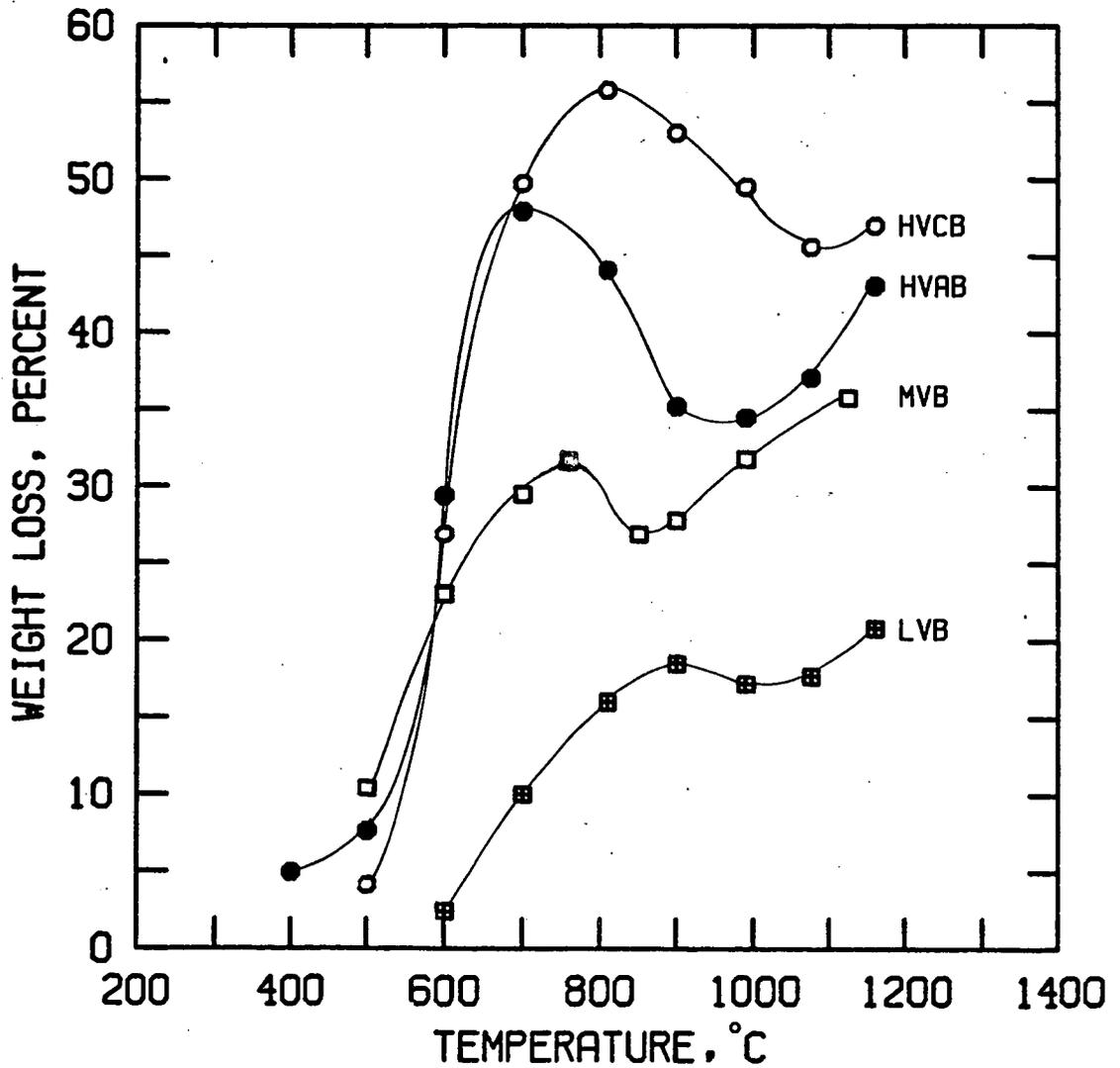


Figure 1.--Devolatilization of bituminous coals by rapid heating.

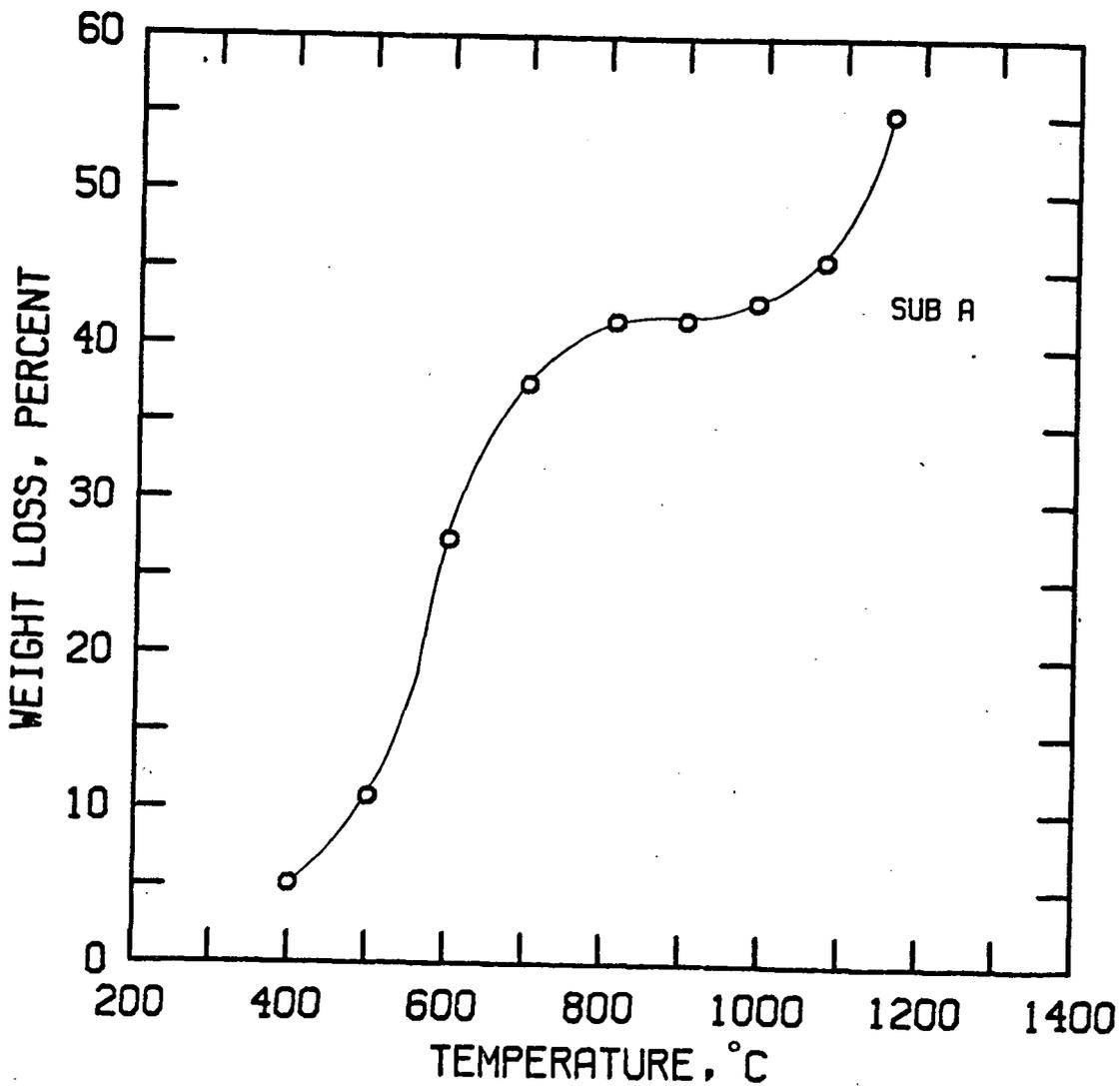


Figure 2.--Devolatilization of a subbituminous coal by rapid heating.

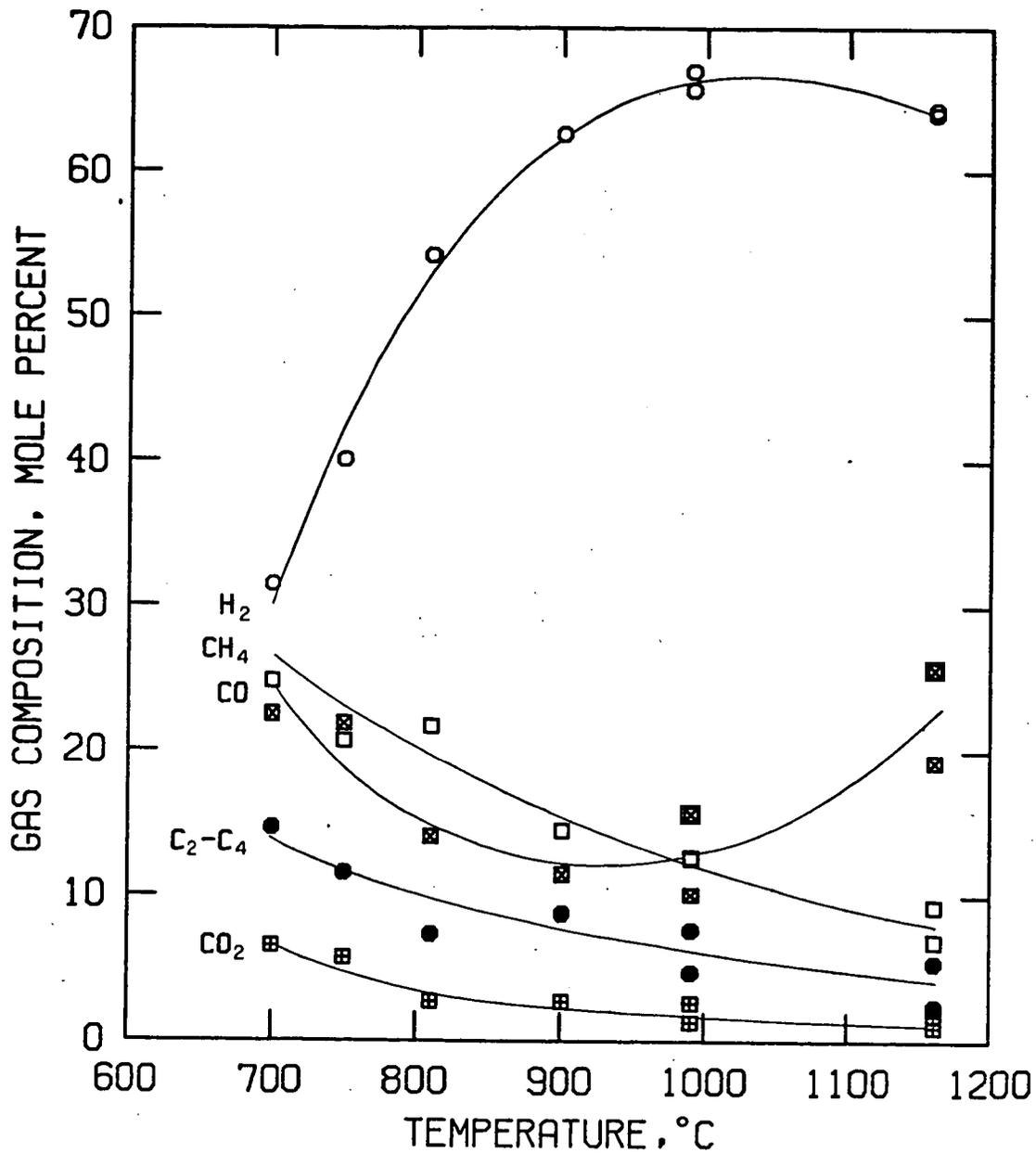


Figure 3.--Composition of gas from devolatilization of Pittsburgh hvAb coal.

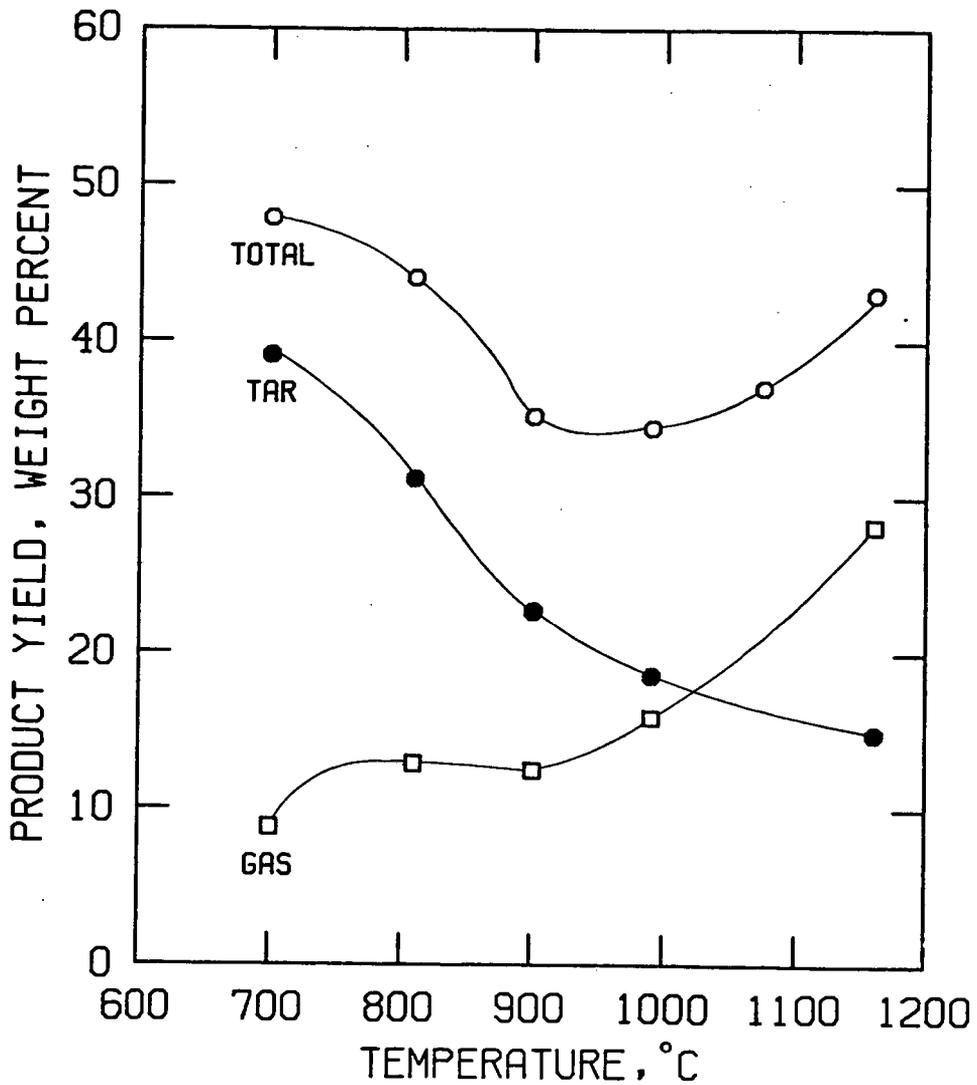


Figure 4.--Yields of tar and gas from devolatilization of Pittsburgh hvAb coal.