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The Effect of Fast Neutrons and Gamma Radiation during the Low Temperature Carbonization of Bituminous Coals

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Eight bituminous coals were irradiated with fast neutrons and gamma radiation while under-going carbonization at a heating rate of 6°C/min up to 600°C. The rates of gas evolution and the gas compositions were determined. Irradiation during carbonization was shown to increase the swelling characteristics of the medium and high volatile coals, but no significant effect could be detected on the rate of gas evolution or its composition, the type of coke produced, or the yield of tar.

RELATIVELY little work has been reported in the literature on the irradiation of coal[1-5], and from this work no conclusions can be drawn as to the probable magnitude of the irradiation effects during carbonization. Ionizing radiation may affect the coal and its subsequent carbonization, but it is not certain whether the changes will have practical importance or even be detectable. The present work was conducted to clarify this matter.

EXPERIMENTAL

Eight Pennsylvania bituminous coals were selected for the investigation. Information on the sources, proximate and ultimate analyses are presented in *Tables 1, 2* and *3*.

Table 1. Source of Pennsylvania coal samples

Coal	County	Bed	A.S.T.M. Rank
166	Cambria	Upper Kittanning	Low Volatile
167	Indiana	Lower Kittanning	Medium Volatile
168	Indiana	Upper Freeport	High Volatile A
169	Washington	Pittsburgh	High Volatile A
A	Washington	Pittsburgh	High Volatile A
B	Washington	Pittsburgh	High Volatile A
C	Washington	Thick Freeport	High Volatile A
D	Washington	Pittsburgh	High Volatile A

The Pennsylvania State University reactor used in these experiments is an enriched-uranium water-moderated reactor capable of operating at the time of these experiments, at a maximum power level of 100 kW. This power level is equivalent to a combined dosage of $6\cdot3 \times 10^6$ röntgen/hour of gamma rays, $8\cdot1 \times 10^{11}$ thermal neutrons/cm^2.sec and $7\cdot3 \times 10^{11}$ fast neutrons/cm^2.sec at the face of the fuel elements. Decreasing the power level to 10 kW will decrease the above fluxes by a factor of 10, and at a lower level of 1 kW the

fluxes will be reduced approximately 100-fold from the 100 kW levels. All runs were made at the maximum power level unless stated otherwise.

Precise values for the various fluxes to which the coal samples were subjected are not available due to the geometry of the system and the unknown effective thicknesses of the silica insulation and the boron shield surrounding the coal samples. The dose rates for the centre line position which the coal

Table 2. Proximate analyses (air-dry basis) of coals used

Coal	% Moisture	% VM	% Fixed C	% Ash
166	0·9	16·2	73·6	9·3
167	1·0	26·9	62·1	10·0
168	0·6	28·9	61·2	9·3
169	1·9	38·4	51·9	7·8
A	2·3	38·1	53·1	6·5
B	1·8	36·7	55·6	5·9
C	1·8	36·8	55·2	6·2
D	1·7	38·2	53·4	6·7

Table 3. Ultimate analyses (ash-free basis) of coals used

Coal	% N	% S	% H	% C	% O
166	1·2	1·4	4·1	87·5	5·8
167	1·0	2·5	5·2	85 8	5·5
168	1·0	1·9	5·3	86·8	5·0
169	1·6	1·8	5·5	82·5	8·6
A	1·2	1·4	5·9	81·5	10·0
B	1·3	2·6	5·8	81·5	8·8
C	1·7	1·1	5·9	83·0	8·3
D	1·4	1·5	5·8	82·5	8·8

samples occupied were known from previous measurements, and a total energy absorption of approximately 4×10^3 rads/sec was estimated to result from the reactor when operating[6] at 100 kW. Of this energy, *ca.* 90 per cent was from the absorption of gamma rays and 10 per cent from the absorption of fast neutrons. The slow neutron flux reaching the coal samples was reduced to an insignificant level by absorption in the boron shield.

The general design and significant dimensions of the furnace used for carbonizing the coal samples are shown in *Figure 1*. This comprises an outer fused quartz container 36 in. high by 2¾ in. in diameter. Inside this container, the heating element is wound on a fused quartz tube permitting ¼ in. of insulation with Santocel A. Over the whole area of the heater (*ca.* 12 in.), a 2 mm layer of boron was cemented. Within the heater tube a further layer of *ca.* 2 mm thickness of boron was packed between the heater wall and a concentric fused quartz tube. The power leads from the heater were '2S aluminium' insulated for the first 15 ft with quartz tubing and thereafter by

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Tygon plastic tubing. A chromel–alumel thermocouple was employed, the first 6 ft were insulated in quartz tubing and thereafter in plastic. Re-calibration showed this thermocouple to be unaffected by irradiation. Both the power and the thermocouple leads were connected to a Leeds–Northrup programme controller which gave linear heating rates of 3° or 6°C/min and then held the furnace at the soaking temperature of 600°C.
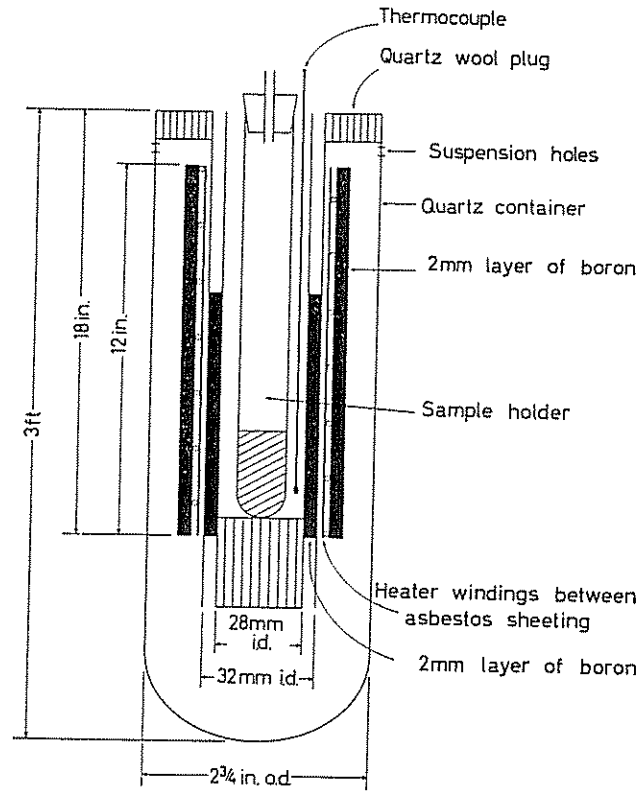

Figure 1. Carbonization furnace

Two '2S aluminium' wires were used for suspending the furnace during loading and unloading operations. During irradiation, the furnace was situated at the base of a 3 in. i.d. aluminium tube, *ca.* 28 ft high. The aluminium tube protected the furnace from the water in the reactor and enabled accurate positioning of the furnace with respect to the fuel elements. When in place, the furnace was submerged *ca.* 24 ft in water.

The sample holder was placed inside the furnace and was connected by a rubber bung to 4 ft of quartz tubing, the upper end of which terminated in a Y. Tygon tubing was used for the remaining connections to an absorption train comprising a sulphuric acid absorption bulb, followed by a calcium chloride U-tube, caustic potash bulb, and another calcium chloride U-tube.

The absorption train was connected to a Beckman chromatograph employing a 6 ft length of Linde 13X molecular sieves with argon as the carrier gas.

The chromatograph was used to detect hydrogen, oxygen, nitrogen, methane and carbon monoxide. From the chromatograph the evolved gas passed to a calibrated gasometer maintained at a reduced pressure of 6 in. of water. The total length of gas line from the sample holder to the gasometer was *ca.* 50 ft. *Figure 2* is a flow sheet of the complete apparatus.
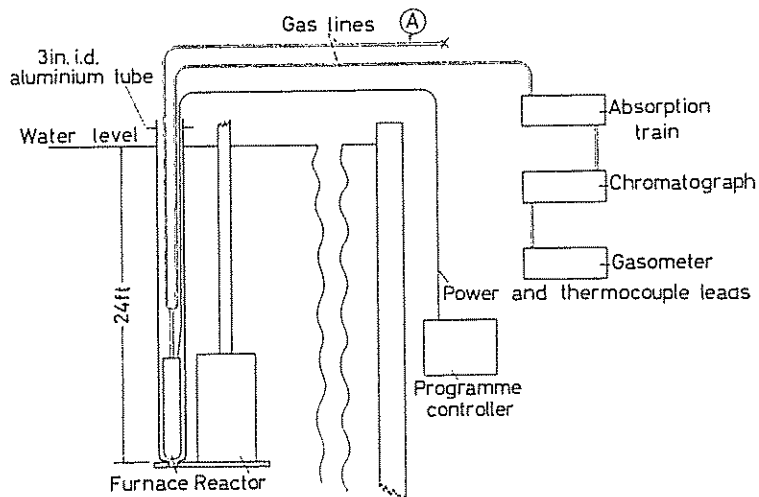

Figure 2. Apparatus in position for irradiation

The coal samples were ground to − 40 mesh (U.S.) and stored under nitrogen until required. Twenty-gramme samples were packed in quartz containers (*ca.* 18 in. long × 22 mm i.d.) to a depth of about 8·5 cm, and the remainder of the container was packed with quartz wool. The filled container was placed in the furnace (the upper 6 in. of the container was outside the heating zone and served as a tar trap), connected to the gas lines by a rubber bung, and the system flushed for 12 hours. The flushing, which consisted of passing argon into gas line A and out through the gasometer, removed the air almost completely from the gas lines, absorption train and chromatograph column before carbonization was started. Complete removal of air from the sample holder was not achieved.

The total time for carbonization was 3 h for the 6°C/min heating rate and 8 h for 3°C/min heating rate. Throughout these periods, samples of gas were withdrawn from the system and analysed by the chromatograph. About 700 ml of argon (the volume of the gas lines) was displaced before any detectable gas was evolved which usually occurred at a furnace temperature of *ca.* 500° to 550°C. While the rate of evolution recorded corresponds approximately with the furnace temperature observed, the gas samples taken at specific furnace temperatures refer to furnace temperatures below those reported. In all experiments the first detectable gas contained appreciable

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quantities of air, presumably left in the sample holder after flushing. In subsequent samples of gas no oxygen could be detected, and only about one per cent of nitrogen was detected, which was assumed to have been evolved from the coal. Gas samples could be taken every ten minutes for analysis, so that a reasonable relation of time and temperature to gas composition could be recorded. The rate of evolution was computed from the time and temperature of every 100 ml of gas evolved. Multiplicate runs were within the experimental error, i.e. $\pm$ 5 per cent in gas volume and $\pm$ 10 per cent in gas composition.

One week after irradiation the contact activity of the samples was sufficiently low to permit handling with the minimum of precaution. The sample holder was cut to separate the tar from the coke, both sections weighed and the tar trap placed in a 850°C oven for 3 h. The loss in weight was taken as tar. The coke was removed from its section of the container; the container was cleaned, dried and re-weighed and the difference was taken as coke.

On selected cokes, reactivity to air at 600°C, surface areas from nitrogen adsorption at 78°K, and crystallographic parameters from x-ray diffraction studies were obtained.
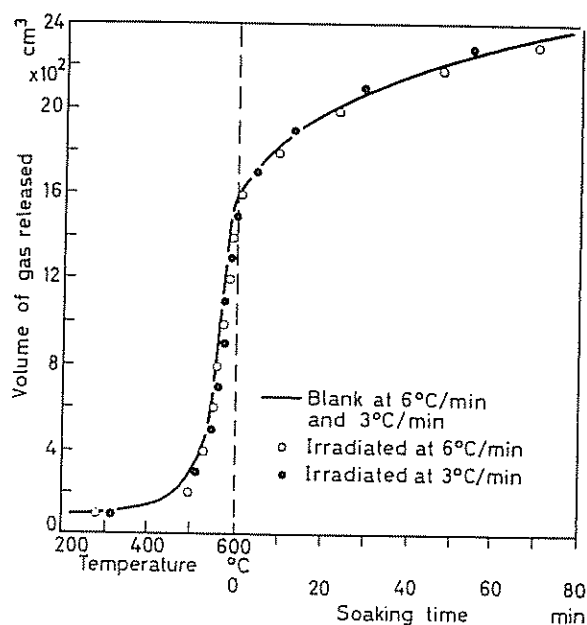

Figure 3. Gas release from coal 166

Although the temperature/gas composition was arbitrary and peculiar to the apparatus, as were the coke expansions and tar yields, the results were reproducible and adequate for the comparison of irradiated and unirradiated samples.

RESULTS AND DISCUSSION

All the unirradiated coals have the same type of gas evolution curve. The majority of the gas is evolved at a constant rate up to the soaking temperature, as indicated by the linear section of the curve in Figure 3. When the soaking

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temperature is reached, the rate of gas evolution steadily decreases and after one hour it becomes very low. No effect of heating rate in the range 3°C to 6°C/min could be detected with coal No. 166 (as indicated in *Figure 3*) and thereafter only the 6°C/min heating rate was used. Both the linear gas evolution/temperature relation below the soaking temperature and the absence of heating rate effects are similar to the rate of release of volatile matter from anthracite[7].

Only two of the eight coals showed significant changes in gas evolution rates on irradiation. Both gave lower rates of evolution resulting in *ca*. 25 per cent decreases in volume of gas for coals 167 and 168, respectively. This reduction in gas evolution is not due to a reduction in volatiles, but merely is an indirect indication of enhanced swelling which will be discussed shortly.
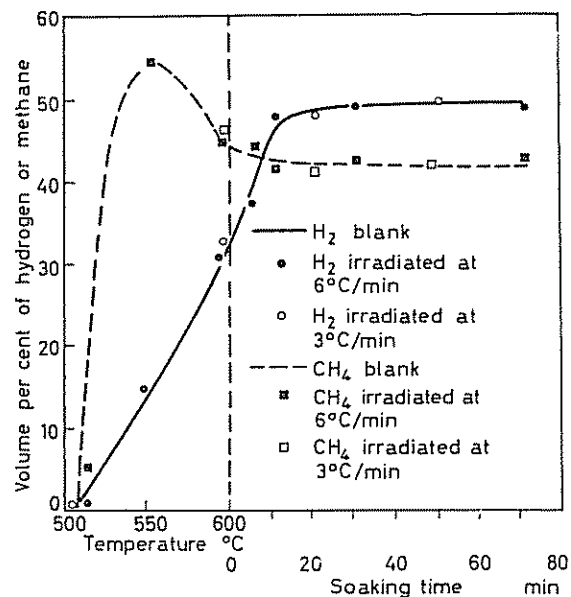

Figure 4. Hydrogen and methane concentrations in gas evolved from coal 166

Figures 4 and *5* are selected plots showing the relation between gas composition, temperature and soaking time for runs with and without radiation. As previously mentioned the composition/temperature relationships are peculiar to the apparatus employed and in fact the temperatures quoted are well above the probable temperatures at which any given gas composition was evolved. Once gas evolution commences, hydrogen and methane constitute *ca*. 90 per cent of the gas detected by the chromatograph. The remaining constituents were nitrogen at a concentration of 1 to 2 per cent and carbon monoxide at 2 to 3 per cent. Ammonia, carbon dioxide, water vapour, and hydrogen sulphide were absorbed in the absorption train; of these, only ammonia and hydrogen sulphide were estimated. Very poor reproducibility was obtained for both gases. This may be due to the length of the connections

which permitted reaction with the plastic tubing and the partial absorption of these gases by condensing volatiles. It appears that irradiation had no effect on the amount of free ammonia evolved. On the other hand, irradiation may decrease slightly the amount of hydrogen sulphide recovered although these results are still inconclusive. The greatest decrease observed was 20 per cent (0·30 to 0·23 wt H_2S/wt of coal) for coal 169. The total concentration of other low molecular weight hydrocarbons was not more than a few per cent.
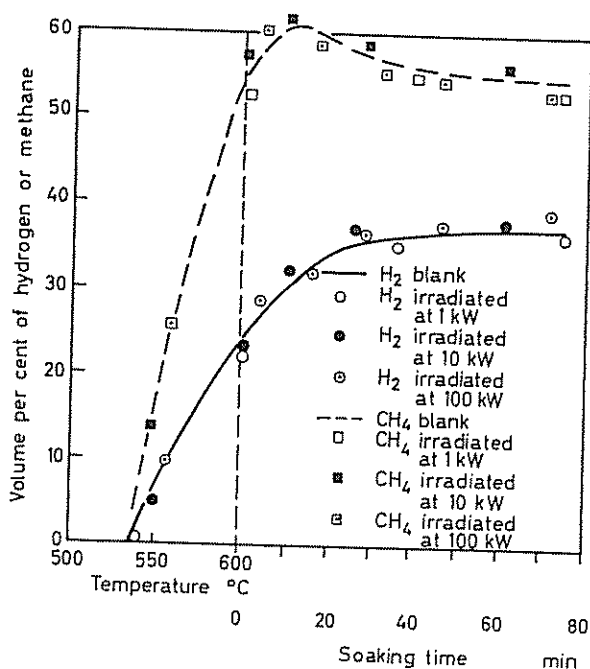

Figure 5. *Hydrogen and methane concentrations in gas evolved from coal 168*

Considering the unirradiated samples, both hydrogen and methane were evolved from all the coals in a similar manner. Within the limits of measurement, they appeared to be initially evolved at the same temperature, although the first trace of hydrogen could often be detected in the absence of methane. This was probably due to the greater sensitivity of the chromatographic instrument for hydrogen and to a diffusion effect. Once evolution had commenced, the rate of evolution of methane was greater than that for hydrogen. A maximum concentration of methane between 47 and 62 per cent was reached, followed by a fairly rapid decrease in concentration and thereafter by a steady or slightly declining concentration. Hydrogen, while showing a less spectacular initial rate of release, did not exhibit a maximum but increased steadily throughout the remainder of the run.

Within experimental error, the irradiated samples gave the same concentration–temperature–time profiles as the unirradiated samples.

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The yields of coke and tar for the unirradiated and irradiated coals are summarized in *Table 4*. Making allowance for the evolved gases, there is an overall mass discrepancy of *ca*. 5 per cent. This discrepancy is believed to be due largely to a combination of the method of determining the coke and tar yields and the inefficiency of the tar trap. The tar trap allowed the passage of water vapour and other volatiles which condensed in the quartz and plastic tubing of the gas line connections. However, the method is adequate for the comparison of coke and tar yields from irradiated and unirradiated low

Table 4. Coke and tar yields from coals during carbonization

Coal	Coke, % w/w of coal		Tar, % w/w of coal	
	Blank	Irradiated	Blank	Irradiated
166	89·1 (89·4)*	89·3 (89·4)*	3·6 (3·0)*	3·8 (2·4)*
167	86·5	91·0†	6·9	5·7
168	86·3	92·0†	7·6	5·1
169	74·0	74·0	14·9	14·8
A	74·0	73·9	16·0	16·1
B	75·7	75·6	14·3	14·3
C	76·9	77·0	13·3	13·2
D	75·4	75·4	14·8	14·7

* Obtained at a heating rate of 3°C/min, all other results obtained at a heating rate of 6°C/min.
† Expanded beyond the main heating volume of the furnace and includes partially coked coal.

Table 5. Effect of irradiation during carbonization on swelling of coals

Coal	Length of coke sample, cm	
	Blank	Irradiated
166	10·1 11·2*	10·1 11·2*
167	33·0	36·0
168	32·0	32·0 (1 kW)† 32·0 (10 kW)† 36·0
169	17·5	19·5
A	22·5	25·0
B	19·5	24·0
C	21·5	25·5
D	22·5	26·5

* Obtained at a heating rate of 3°C/min, all other samples heated at 6°C/min.
† All irradiations carried out at 100 kW power level unless otherwise stated.

temperature carbonization. Furthermore, it is reasonable to conclude that any effect that irradiation may have on the condensable volatiles is restricted to a very small part of it, as the majority of the material condensing in the gas lines appeared to be water. As can be seen, no significant change occurs in the coke or tar yield on irradiation. The two apparent exceptions to this (coals 167 and 168) are undoubtedly due to the expansion of these coals beyond the main heating zone of the furnace with resultant incomplete carbonization.

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The effect of irradiation on swelling is summarized in *Table 5*. With the exception of coal 166, which is a poorly coking coal, all the coals exhibit a definite increase in their swelling characteristics on irradiation at a power level of 100 kW during carbonization. The importance of power level on swelling is demonstrated with coal 168, however. At power levels of 1 and 10 kW, irradiation does not increase swelling.

The cokes obtained from coals 166, 168 and C were examined for reactivity in air at 600°C using the method of P. L. WALKER, Jr and J. R. NICHOLS[8]. The x-ray diffraction patterns and BET surface areas were also obtained. No significant changes in the cokes could be detected by any of these methods.

CONCLUSIONS

The only significant effect of irradiation during the course of low temperature carbonization is the enhancement of the swelling characteristics of the medium and high volatile coals examined. Furthermore, this effect is only observed above a threshold energy absorption value. The mechanism by which swelling of the coals is increased by irradiation during carbonization is not yet clearly understood.

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