THE THERMOCHEMICAL EFFECTS OF GAS-COALS IN PYROLYSIS PROCESS

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INTRODUCTION

The gas-coal is a young bituminous coal. In its organic matter there is a large quantity of thermally unstable constituents. The intense thermal decomposition may be initiated at a temperature as low as slightly above 300°C. Much tar, water of decomposition and gaseous products are liberated sharply (1). These features of thermochemical conversion influence the pyrolysis process.

During pyrolysis, chemical changes and phase transformation are accompanied by certain thermal effects. Chemical reactions occur in opposite directions - degradation and polycondensation. For instance, the high-molecular-weight substances of coal decompose and produce volatile products with low molecular weights, which evolve successively. On the other hand, organic matter remaining in the solid phase will continue to strengthen its linkage between structural units. The thermal effects alternate between exothermic and endothermic during the pyrolysis process. The alternation of thermal effects reflects the nature of chemical interreactions. At each turning point the chemical composition of coal organic matter will undergo a remarkable change.

EXPERIMENTAL PROCEDURE

The thermal effects generated by pyrolytic reactions and phase exchanges under the action of heat may be studied by means of differential thermal analysis (DTA) (2-6). Brief description of DTA experiments are as follows.

About 1g of finely ground coal with a particle size of less than 0.2mm was packed in a porcelain crucible. Another crucible contained the calcined magnesia, which was used as the inert reference. Both crucibles were separately covered with a lid, on which a thermowell was connected. Samples were heated to 850-950°C at a constant rate of 5°C/min. The thermographic curves were plotted by a mirror galvanometer in coordinates of coal temperature versus heating time and temperature difference versus heating time.

To detect chemical changes, the composition of heated coal organic matter at its peak temperature was determined. A series of 10g coal samples were taken and were heated in the same pyrothermograph furnace. The heating was strictly controlled to match that in the DTA tests. When each relative peak temperature was reached, the crucible was immediately taken off the furnace and cooled in the desiccator. The proximate and ultimate analyses of these samples were carried out.

RESULTS AND DISCUSSION

THE GENERALIZATION OF THERMOGRAPHIC PEAKS

DTA curves of several coals studied have shown general characteristics and also have revealed some differences, with respect to peak temperature, peak width, peak altitude and peak shape (Figure 1). Analytic data of these coals are given in Table 1. Coals No. 1 and No. 2 are good caking coals, the others are weakly caking coals.

TABLE 1. ASSAY DATA OF TESTED GAS-COALS

COAL SAMPLE	PROXIMATE ANALYSIS, WT.%				ULTIMATE ANALYSIS, WT.%,DAF				PLASTOMETRIC INDEX*, mm	
	MOISTURE AS DETERMINED	ASH CONTENT (dry)	VOLATILE MATTER (daf)	TOTAL SULFUR (dry)	C	H	N	(O+S)	X	Y
No. 1	1.90	7.86	39.9	3.04	80.51	5.83	1.97	11.69	43	17
No. 2	2.14	12.40	36.5	2.94	81.20	5.59	1.96	11.25	48	14
No. 3	3.29	5.39	46.3	0.52	78.10	5.72	1.94	14.24	40	7
No. 4	4.28	7.08	42.7	0.38	80.48	5.60	2.81	13.11	27	7
No. 5	3.55	9.64	43.9	0.50	80.88	5.90	——	———	40	7-8

*Index X (final shrinkage) and Y (maximum thickness of plastic layer) were determined by special plastometric testing equipment. The value of Y was served as the parameter for measuring the caking capacity of coal.

To interpret the thermograms, the following points should be considered.

1. The primary effect (the first endothermic peak) appears at about 100°C. This effect occurs only in connection with evaporation of physically absorbed water.

2. Above 150°C, the differential curve spreads upward. Its peak temperature indicates the initiation of intense thermal decomposition of organic matter. With respect to gas-coals, the temperature of this peak is located at about 270°C. The temperature of this exothermic peak will be affected by the heating rate. Structural studies had not shown the breakdown of coal structure when it was heated to below 250°C and there was a little possibility of chemical change. Some reactions, such as dehydrogenation, surface oxidation and dehydration, exhibit an exothermic effect (7). At this point water of decomposition is already yielded from gas-coals (1).

3. Beyond 300°C the differential curve starts to decline. The thermal effects of coal pyrolysis show endothermic character as a result of the decomposition reaction, polycondensation of pyrolysis products and phase transformation. The quantity of volatile yield between the second and third peaks makes up almost one half of the total volatile matter.

The existence of a W-shape peak expresses the situation of coal in plastic stage. As illustrated in Figure 2, there is little difference in the appearance of differential curves between the original coal and the fast preheated (50°C/min) to 280°C coal. It shows that deep destruction has not taken place during the fast heating of coal. However, on the thermogram of char, a similar W-shape peak disappears. The curve is smooth before the temperature reaches 536°C. This is because the primary decomposition and evolution of volatile matter and the phase conversion essentially have been completed. Therefore the existence of that W-shape peak is characteristic of the plastic state. The phenomenon of exothermic effect within a W-shape peak might also be affected by the increase in thermal conductivity when the particles became agglomerated. In essence, the first dip of the curve occurs when coal softens and changes to a plastic state. The second dip occurs during resolidification of the plastic mass.

4. The general thermal effect becomes clearly exothermic at temperatures of 510-550°C. The rise of the curve indicates the formation of a semi-hard structure. This secondary carbonization, accompanied by liberation of residual hydrogen from the periphery of aromatic clusters, in every case gives rise to an exothermic peak.

5. At temperatures above 760°C, slight endothermic effects could be observed. These effects are due to further regulation in the arrangement of hexagonal carbon network.

6. The effect of mineral matters under high temperatures may be reflected on the thermogram. The thermogram of coal sample No. 2 with a 20% lime additive is shown in Figure 3. To a certain degree, mineral matters affect thermal decomposition of organic matter. Particularly at temperature ranges of 750-850°C, there appears an obvious endothermic effect, which is characteristic of this additive.

CONSTITUENT CHANGES OF NONVOLATILIZED MATERIAL

The chemical reaction of thermal decomposition of gas-coal organic matter is extremely complex. While it is difficult to postulate the thermochemical reactions, the study of constituent alternation of gas-coal organic matter is helpful in explaining the mechanism of thermal decomposition.

Elemental composition data of nonvolatilized material from gas-coals No. 1 and No. 2 heated to each characteristic peak temperature are given in Tables 2 and 3. R_{HC} is the ratio of total hydrogen and carbon to total content of other elements. The hydrogen-containing grade (f_H) is the atomic ratio of hydrogen to carbon. The carbonization grade (f_C) is an index of the atomic ratio of carbon to noncarbon elements. This ratio for the original coal is assigned an index value of 1.0. The aromaticity (fa) is calculated according to Van Krevelen and Schuyer's formula (8).

These two gas-coals begin to decompose at about 270°C. It appears that thermochemical decomposition is initiated from hydrogen- and oxygen-rich groups. As data indicate, the hydrogen content of nonvolatilized material decreases sharply as the pyrolysis process proceeds. On the contrary, the main part of the carbon ring structure is strengthened because of the polycondensation reaction. The carbonization grade of nonvolatilized material increases steadily with the increase of temperature. For coal sample No. 1, carbon-to-hydrogen ratio changes from $C_6H_{5.2}$, approximated to the aromatic composition of benzene, to $C_6H_{0.9}$. As shown in Figure 4, fc rises from 0.722 to 0.999 and eventually stabilizes.

The carbonization process is carried out simultaneously with dehydrogenation. This is shown by the decreasing hydrogen-containing grade. Meanwhile, the carbonization of condensed carbon rings exhibits an aromatizing characteristic, as indicated by the increase of aromaticity. So it may be presumed that chemical structure changes only in the direction of high polycondensation of aromatic rings.

CONSTITUENT CHANGES IN VOLATILIZED MATERIAL

As a result of thermochemical decomposition, certain fractions of coal organic matter turn into volatile matter. The changes in volatile matter content of gas-coals No. 1 and No. 2 are listed in Tables 2 and 3.

As previously stated that in the temperature range between the second and third peaks, i.e. 258-435°C for gas-coal No. 1 and 274-438°C for gas-coal No. 2, the evolving rate of volatile products is higher than in other ranges. The higher evolution rate for gas-coal No. 2 appears in a higher temperature interval ranging from 372°C to 438°C. It shows that gas-coal No. 2 probably has a higher thermal stability than gas-coal No. 1.

The devolatilization process may be divided into three stages. Referring to the DTA curve for gas-coal No. 1, temperature ranges for the three stages are 20-435°C, 435-530°C and beyond 530°C. The chemical composition of evolved volatilized material changes significantly, depending on the various temperature ranges. These data are listed in Tables 4 and 5. Where, Cv, Hv, (O+S)v and Nv are contents of carbon, hydrogen, oxygen and sulfur, and nitrogen in volatilized material in wt.% respectively, δC, δH, $\delta(O+S)$ and δN (wt.%, daf) are the quantities of each element converted into volatile products in certain temperature ranges.

TABLE 2. CONSTITUENT CHANGES OF NONVOLATILIZED MATERIAL DURING HEATING OF COAL SAMPLE NO. 1

TYPE OF ANALYSIS DATA	PEAK TEMPERATURE, °C						
	ORIGINAL COAL	258	435	482	530	760	COKE
Volatile Matter*, VMo, %	39.9	34.1	15.6	12.3	7.63	3.71	1.32
Evolving Rate of Volatile Matter (ΔVMo/°C) X 100		3.6	10.4	7.0	9.7	1.7	1.3
Composition of non-volatilized material, %, daf							
Carbon	80.51	82.20	84.04	84.70	86.70	91.60	94.20
Hydrogen	5.83	5.51	4.11	3.51	3.11	1.93	1.19
Oxygen & Sulfur	11.69	10.29	9.57	9.40	7.85	4.18	2.74
Nitrogen	1.97	2.00	2.28	2.39	2.34	2.29	1.87
R_{HC}	6.3	7.1	7.4	7.5	8.8	14.4	20.7
f_H	0.87	0.81	0.59	0.50	0.43	0.25	0.15
f_C	1.00	1.09	1.44	1.65	1.92	3.23	5.27
fa	0.722	0.771	0.937	0.962	0.999	0.999	1.00

$$*VMo = \frac{\text{Weight of VM of nonvolatilized sample}}{\text{Weight of original coal sample, daf}}$$

TABLE 3. CONSTITUENT CHANGES OF NONVOLATILIZED MATERIAL DURING HEATING OF COAL SAMPLE NO. 2

TYPE OF ANALYSIS DATA	PEAK TEMPERATURE, °C							
	ORIGINAL COAL	274	372	438	514	563	735	COKE
Volatile Matter*, VMo, %	36.5	34.4	25.7	15.4	11.8	11.0	5.41	1.91
Evolving Rate of Volatile Matter (ΔVMo/°C) X 100		1.2	8.9	15.6	4.7	1.6	3.3	1.6
Composition of non-volatilized material, %, daf								
Carbon	81.20	82.11	82.50	84.77	85.18	87.44	90.76	94.27
Hydrogen	5.59	4.95	4.25	3.30	3.20	2.86	1.83	0.70
Oxygen & Sulfur	11.25	10.95	11.12	9.70	9.37	7.59	5.20	3.11
Nitrogen	1.96	1.99	2.13	2.23	2.19	2.11	2.21	1.92
R_{HC}	6.5	6.7	6.5	7.4	7.7	9.3	12.5	19.0
f_H	0.82	0.73	0.62	0.47	0.45	0.39	0.24	0.09
f_C	1.00	1.13	1.29	1.65	1.72	2.00	3.11	7.26
fa	0.757	0.770	0.854	0.936	0.973	0.957	0.988	0.998

TABLE 4. CHEMICAL COMPOSITION OF VOLATILIZED MATERIAL RELEASED FROM HEATING GAS-COAL NO. 1

CHEMICAL COMPOSITION	TEMPERATURE RANGE, °C		
	20-435	435-530	BEYOND 530
Element Converted, Wt.%, daf			
δC	11.30	5.01	2.85
δH	2.44	1.13	1.50
δ(O+S)	3.71	2.21	3.98
δN	0.08	0.17	0.50
Elemental Composition, %			
Cv	64.46	58.80	32.28
Hv	13.92	13.26	16.98
(O+S)v	21.16	25.94	45.08
Nv	0.46	2.00	5.66
Atomic Ratio			
C	5.4	4.9	2.7
H	13.9	13.3	17.0
O	1.3	1.6	2.8

TABLE 5. CHEMICAL COMPOSITION OF VOLATILIZED MATERIAL RELEASED FROM HEATING COAL SAMPLE NO. 2

CHEMICAL COMPOSITION	TEMPERATURE RANGE, °C		
	20-438	438-563	BEYOND 563
Element Converted, Wt.%, daf			
δC	9.93	4.03	3.59
δH	2.82	0.54	1.69
δ(O+S)	2.98	2.33	3.80
δN	0.06	0.07	0.13
Elemental Composition, %			
Cv	62.87	57.82	38.98
Hv	17.86	7.75	18.35
(O+S)v	18.87	33.43	41.26
Nv	0.40	1.00	1.41
Atomic Ratio			
C	5.2	4.8	3.2
H	17.9	7.8	18.3
O	1.2	2.1	2.6

Although carbon evolves during the pyrolysis of coal, most of the carbon remains nonvolatilized. Referring to Tables 6 and 7, only about 25% of the carbon in coal sample No. 1 converts into volatile products, and 21.6% of carbon in coal sample No. 2 converts into volatile products. Furthermore, the evolution of volatile carbon is relatively concentrated in the 270-550°C temperature range. Below 270°C, carbon hardly participates in devolatlilization.

TABLE 6. DECOMPOSITION AND DEVOLATILIZATION RATES OF EACH ELEMENT IN HEATED GAS-COAL NO. 1*

RATE OF ELEMENTAL DECOMPOSITION, %	PEAK TEMPERATURE, °C					
	258	435	482	530	760	COKE
ΔC	——	14.0	18.9	21.4	22.5	25.0
ΔH	6.0	41.7	53.3	61.2	77.4	86.8
Δ(O+S)	12.9	31.7	38.2	50.6	75.6	84.5

*

$$\Delta C = \frac{\text{Weight of carbon devolatilized}}{\text{Weight of carbon in original coal sample}} \times 100\%$$

$$\Delta H = \frac{\text{Weight of hydrogen devolatilized}}{\text{Weight of hydrogen in original coal sample}} \times 100\%$$

$$\Delta(O+S) = \frac{\text{Total weight of oxygen and sulfur devolatilized}}{\text{Total weight of oxygen and sulfur in original coal sample}} \times 100\%$$

TABLE 7. DECOMPOSITION AND DEVOLATILIZATION RATES OF EACH ELEMENT IN HEATED GAS-COAL NO. 2

RATE OF ELEMENTAL DECOMPOSITION, %	PEAK TEMPERATURE, °C						
	274	372	438	514	563	735	COKE
ΔC	1.4	5.7	12.3	15.7	17.2	18.6	21.6
ΔH	13.4	29.1	50.5	53.1	60.1	76.0	90.4
Δ(O+S)	3.7	6.9	26.5	29.6	47.3	66.4	81.0

Hydrogen plays an important role in the coal pyrolysis process. The basis of pyrolytic change may be looked at as a redistribution of hydrogen among newly formed products (1). Large quantities of hydrogen are consumed for the formation of water, hydrogen sulphide and ammonia. The remaining hydrogen, called free hydrogen, is necessary for the yield of tarry products and for the formation of fusible matter in the plastic stage. The amount of liquid phase and the degree of softening increase with increasing amounts of free hydrogen in the coal. For coal sample No. 2, which produces a more stable plastic mass, the quantity of hydrogen evolved at the second stage (plastic stage) is lower than that in sample No. 1.

The free hydrogen may be better preserved in plastic mass under pressure. It has been proven by experiment that up to 600°C, plastic coal briquettes gave off less hydrogen than the same coal packed in a loose mass (9). Thus, pressurization is extremely important in the destructive hydrogenation of coal. In the conventional pyrolysis process, however, the nonvolatile part of carbon cannot be devolatilized because of a lack of thorough structural destruction. Furthermore, the amount of free hydrogen is limited, thus it is impossible to yield a great deal of liquid products.

After 550°C, the quantity of devolatilizable hydrogen is still sizable. It holds three-fourths of the total atomic amount of various elements (Tables 4 and 5). In a small degree, carbon converts into volatile products. At this stage volatile products should be light gaseous products, such as hydrogen and methane. Clearly, the production of liquid products by either pyrolysis or other conversion processes may be controlled only before reaching the exothermic peak within the W-shape (Figure 1).

CONCLUSIONS

1. This study of thermographical curves and corresponding assay data of gas-coals at peak temperatures has shown that thermal effects were closely connected with the decomposition of coal organic matter and its changes in chemical composition.

2. After the second peak (exothermic) temperature, gas-coals started to decompose intensely. Thermal decomposition was initiated from hydrogen- and oxygen-rich thermally unstable constituents.

3. The evolution of volatile carbon from solid substances was concentrated in the temperature range between the second and third peaks. The control of thermal decomposition before reaching the exothermic peak within the W-shape is of great importance. Improving interreaction between volatile carbon and free hydrogen, coal pyrolysis and other coal conversion processes could be improved to yield a greater amount of hydrocarbon products.

4. Beyond the second endothermic peak within the W-shape, the atomic ratio of carbon to the sum of other elements in nonvolatilized material increased markedly. The aromaticity of nonvolatilized material tends to increase with the rise of the carbonization degree.

REFERENCES

1. Wang, Zhaoxiong, Journal of Tienjin University, No. 13, 27 (1963), (in Chinese).

2. Wang, Zhaoxiong, Chemical World, No. 5, 224 (1962), (in Chinese).

3. Pope, M.I., et al., Differential Thermal Analysis, London (1977).

4. Shou, J.K., et al., Proceedings of 11th IECEC, 300 (1976).

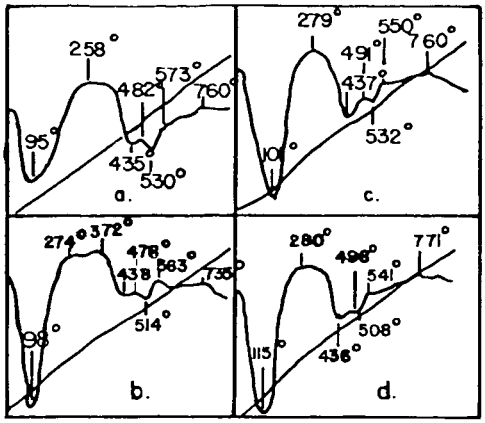
5. Heilpern, S., Thermal Analysis, Vol. 3, 283, London (1974).

6. Arseneau, D.F., et al., Proceedings of the Coal and Coke Sessions, 28th Can. Chem. Eng. Conf., 56 (1978).

7. Takekawa, T., et al., Fuel, 57, 797 (1978).

8. Francis, W., Coal, London (1961).

9. Gryaznov, N.S., et al., Koks i Khimiya, No. 6, 1 (1975).



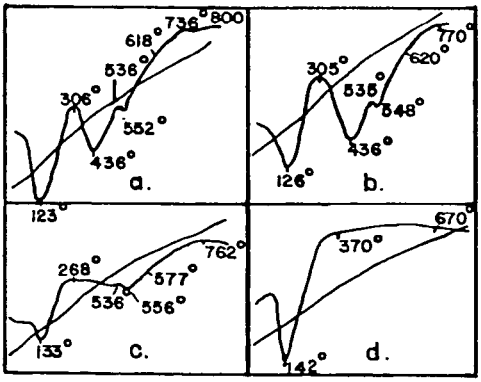
a. Coal Sample No. 1

b. Coal Sample No. 2

c. Coal Sample No. 3

d. Coal Sample No. 4

FIGURE 1. THERMOGRAMS OF GAS-COALS



a. Original Coal

b. Fast Preheated Coal

c. Char From Preheated Coal

d. Coke From Preheated Coal

FIGURE 2. THERMOGRAMS OF GAS-COAL SAMPLE NO. 5

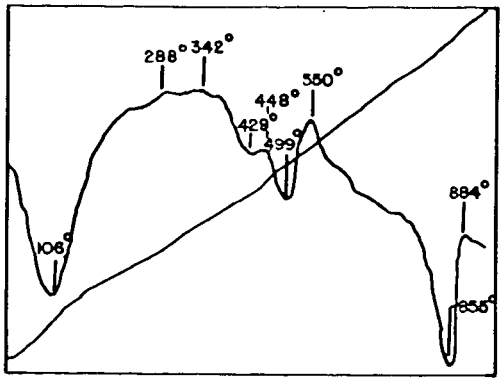


FIGURE 3. THERMOGRAM OF GAS-COAL SAMPLE NO. 2 WITH LIME ADDITIVE

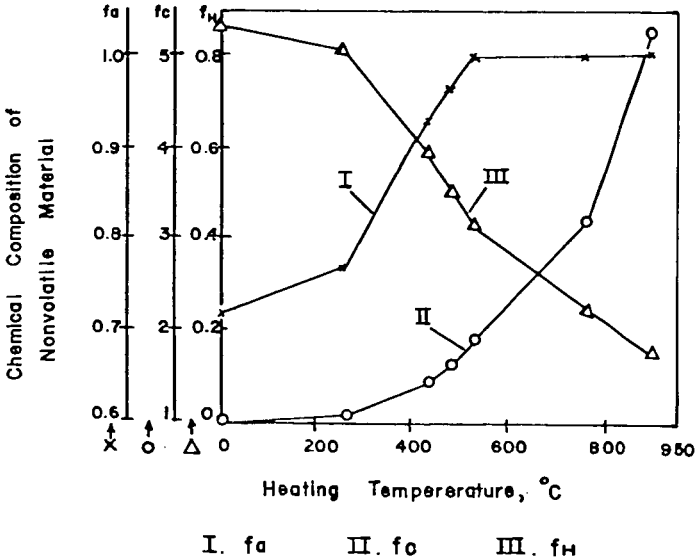


FIGURE 4. CHANGES OF AROMATICITY, CARBONIZATION GRADE AND HYDROGEN-CONTAINING GRADE OF COAL SAMPLE NO. 1 WITH HEATING TEMPERATURE