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Gases Desorbed From Five Coals of Low Gas Content



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GASES DESORBED FROM FIVE COALS OF LOW GAS CONTENT

by

A. G. Kim¹ and L. J. Douglas¹

ABSTRACT

Methane and other hydrocarbon gases, byproducts of coalification, are emitted from coal at widely varying rates and often present ventilation problems during mining. The air in some coal mines apparently contains no methane. To determine if coals from mines which had no history of detectable gas emission contained adsorbed methane, samples of coal at the shaft bottom and at an active face were obtained and placed in sealed metal cylinders. The atmosphere around the coal was sampled and analysed by gas chromatography. Methane, ethane, ethylene, propane, propylene, and butane were found to have been desorbed from these coals. Hydrogen and helium were also detected. An estimate of the amount of residual gas per ton of coal indicated that coal samples from the active face generally contained more adsorbed gas than coal samples obtained from the shaft bottom, although in both instances the total amount of gas was relatively small.

INTRODUCTION

Methane and other hydrocarbon gases are normal byproducts of the coalification process. The amount of methane retained in the coalbed is highly variable and dependent upon many factors--physical, chemical, and geological. The rate of methane emission during mining is related to the concentration of methane in the coalbed. Any methane released into the mine atmosphere must be diluted with air to prevent the formation of an explosive gas mixture. Although it is known that methane continues to be desorbed from coal for long periods of time, in some mine workings there is no evidence of methane emission. Possible explanations for this phenomenon are that either the methane has been completely desorbed from the coal prior to mining, or the rate of methane emission is so low that the concentration of methane in the mine atmosphere (assuming adequate ventilation) is usually negligible. To investigate the first possibility, the experiment described in this report was designed as a simple semiquantitative method for demonstrating the presence or absence of hydrocarbon gases in coals from mines which had no history of methane production.

¹ Chemist.

FORMATION AND RETENTION OF GASES IN COAL

Coalification, the process by which coal is formed, can be described as a series of biochemical and geochemical reactions which transform plant material into a combustible, carbonaceous solid. Methane is the primary gaseous byproduct of this process, but other hydrocarbons, CO_2 , and hydrogen are also produced.

Coalification begins with a biochemical stage during which plant materials are partially decomposed by anaerobic microorganisms, humic substances are formed, and peat accumulates. Also produced during this stage are methane, CO_2 , and trace amounts of ethane, ethylene, propane, propylene, butane, and pentanes. These gases may be retained in the peat by adsorption. Atmospheric nitrogen and oxygen may also be adsorbed on the peat during deposition. Inundation and the deposition of inorganic sediments usually terminates the development of peat and initiates the geochemical phase of coalification.

During the geochemical stage of coalification, the time, temperature, and pressure cause physical and chemical changes in the coal. Rank designations such as lignite, bituminous, and anthracite are roughly equivalent to different stages in a sequential transformation. With increased rank, coal becomes darker and more lustrous. Physical changes are accompanied by an increase in carbon content, aromatic character, and calorific value, and a decrease in moisture, volatile matter, oxygen, and hydrogen content. There are several theoretically possible mechanisms by which gases may be produced during coalification. Methane and other hydrocarbons can be produced by the removal of alkyl side chains from aromatic molecules or by the condensation of straight chain molecules into ring structures. The decomposition of resins and waxes can also yield a mixture of hydrocarbon gases. Hydrogen, also a primary product of coalification, could react with C_2 to C_5 hydrocarbons to form methane. Oxidation of the coal by occluded oxygen results in the formation of CO_2 . Although it is not a reaction product, helium, produced by decay of radioactive minerals, is also present in coal (3-4, 6).² The gas phase in coal, therefore, has been found to be a mixture of methane, the C_2 to C_5 hydrocarbons, CO_2 , oxygen, nitrogen, hydrogen, and helium. However, the postdepositional history of the coalbed affects the amount and composition of the gas retained.

Physically, coal is a highly porous solid with two distinct pore systems. The macropore system consists of cracks and fractures; the micropore system is similar to a molecular sieve structure with an average pore diameter of 5 to 20 Å. Gases in the coalbed can exist as free gas in the macropore system or adsorbed on the surface of the micropores. The diffusion coefficient, activation energy of desorption, adsorbate density, permeability, surface area, and pressure control the rate at which gas can flow from the micropores. Flow in cracks and fractures depends upon pressure, the degree of fracturing, and the permeability of adjacent strata. Emission from the bed into a mine is

²Underlined numbers in parentheses refer to items in the list of references at the end of this report.

generally diffusion controlled; the rate of emission is given by Fick's law:

$$\frac{dq}{dt} = DA \frac{dC}{dL}$$

where dq/dt is the volume flow rate, D is the diffusion coefficient, A is the area, C is the concentration of gas, and L is the diffusion path length.

The total volume of gas released per mass of coal (V_t) is

$$V_t = A [1 - \exp(t/t_0)^n] \text{ for } 1 > n > 0,$$

where A is the initial gas content of the coal, t_0 is a time constant, t is the time elapsed since the start of emission, and n is an empirical constant. With time, the volume of gas emitted increases; the rate of emission decreases as the volume of gas retained in the coal decreases (1-2, 8).

EXPERIMENTAL METHOD

Basically the experimental method consisted of placing samples of coal in a sealed container, allowing gas in the coal to desorb, sampling the atmosphere in the container, and analysing it by gas chromatography. Coal samples were obtained from six mines in five coalbeds (table 1). All mines had no history of gas emission. In the majority, samples were taken both at the active face to obtain freshly mined coal, and from the shaft where the coal had been exposed for relatively long periods of time. The coal was sealed in a cylinder of either cast iron or aluminum (fig. 1); in the top of the cylinder were a pressure gage and a valve. Volume of the cylinder was approximately 0.1 cubic foot. Cylinders were weighed before and after coal samples were collected, and the difference was taken as the weight of the coal.

TABLE 1. - Description of coal samples

Sample	Coal seam	Location	Sample obtained	Rank
1	Upper Freeport.....	Preston County, W. Va..	Face.....	HvAb
2	Laramie No. 3.....	Weld County, Colo.....	Shaft.....	SubB
3	do.....	do.....	Face.....	SubB
4	do.....	do.....	Shaft.....	SubB
5	do.....	do.....	Face.....	SubB
6	Uncorrelated bed.....	Lucas County, Iowa.....	Shaft.....	HvCb
7	do.....	do.....	Face.....	HvCb
8	No. 1 (Rock Island)...	Mercer County, Ill.....	Shaft.....	HvCb
9	do.....	do.....	Face.....	HvCb
10	Mammoth.....	Monroe County, Iowa....	Shaft.....	HvCb
11	do.....	do.....	Face.....	HvCb

In the laboratory, a Hamilton³ lecture bottle septum was attached to the valve on the cylinder. The valve was opened and a sample of the gas in the

³Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

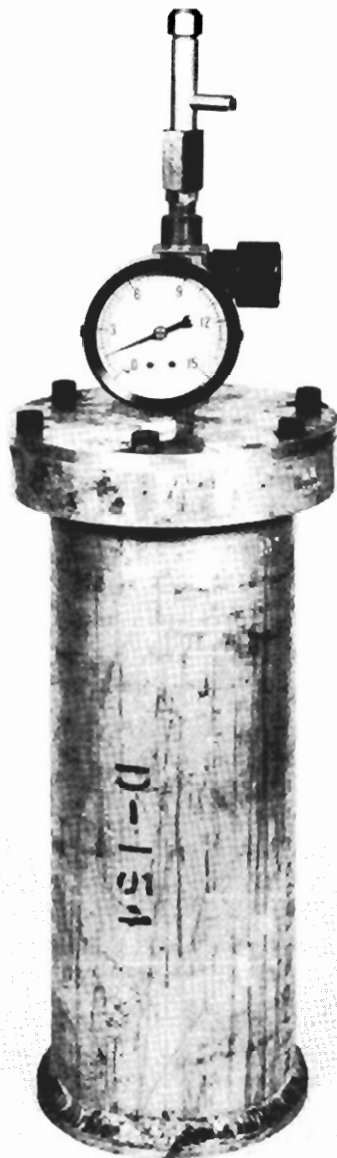


FIGURE 1. - Cylinder containing coal sample.

cylinder was withdrawn with a gastight syringe, then injected into a gas chromatograph. Two gas samples were used for each complete analysis. The first was injected onto a Porapak column; a flame ionization detector was used to identify the hydrocarbons. The second gas sample was injected onto another Porapak column which separated air from CO_2 ; a molecular sieve column separated the air into H_2 , He, O_2 , and N_2 . These gases were detected by a thermal conductivity detector (7). Sensitivity of the analysis was 0.0001 percent for hydrocarbons and 0.01 percent for inorganic gases. Hydrocarbons, H_2 , and He were calculated by comparison with a standard gas mixture. Oxygen, nitrogen, and CO_2 were calculated using thermal conductivity response factors from the literature. Analyses were repeated periodically for 3 months.

RESULTS

Analyses of gas samples for O_2 , N_2 , CO_2 , H_2 , He, and the C_1 to C_5 hydrocarbons are summarized in table 2. Air, trapped in the cylinder when the coal samples were obtained, was the major component of the gas. With time some of the coal was oxidized, resulting in a decrease in the percentage of oxygen and an increase in the amount of CO_2 . The percentage of hydrogen, helium, and hydrocarbons remained relatively constant with time. Helium was desorbed from only two samples, one obtained in the shaft (No. 7) and one from the active face (No. 10). Hydrogen was detected in the gas from all face samples and in the gas from two of the five

shaft samples. Methane was desorbed from all samples, as was ethane. Small amounts of ethylene and propane-propylene were detected; only trace amounts of butane were found and no pentanes were detected in the desorbed gas. The amount of hydrogen and hydrocarbons desorbed was greater from coals obtained at the face than from coal samples obtained in the shaft. Since desorption is a continuous process, the concentration of gas within the coal would be lower in coals that had been exposed for longer periods.

TABLE 2. - Average composition of gas, percent

Sample ¹	1	2	3	4	5	6	7	8	9	10	11
O ₂	4.59	6.65	5.11	9.07	4.04	2.04	2.71	2.40	3.21	6.61	6.02
N ₂	92.34	84.45	93.93	84.02	93.37	86.29	95.79	90.57	93.79	80.65	93.21
CO ₂	2.11	8.90	.59	6.91	2.00	11.67	1.43	7.03	.93	12.73	.66
H ₂	.92	Tr	.37	.0002	.56	ND	.01	ND	.07	ND	.06
He.....	ND	ND	ND	ND	ND	ND	.02	ND	ND	.01	ND
CH ₄	.0436	.0039	.0039	.0017	.0360	.0031	.0382	.0052	1.94	.0038	.0443
C ₂ H ₆	.0002	.0002	.0006	.0002	.0003	.0005	.0005	.0005	.0594	.0006	.0047
C ₂ H ₄	Tr	.0002	.0002	.0003	.0002	Tr	Tr	.0001	ND	Tr	.0016
C ₃ H ₈ ²	Tr	.0002	.0003	.0002	.0001	.0003	Tr	.0001	.0001	.0003	.0004
C ₃ H ₆ ²	ND	ND	ND	ND	ND	ND	ND	Tr	ND	Tr	.0003
C ₄ H ₁₀	ND	ND	ND	ND	ND	ND	ND	Tr	ND	Tr	.0003
Total..	100.0038	100.0045	100.0050	100.0024	99.9966	100.0039	99.9987	100.0059	99.9995	100.0047	100.0013

ND--Not detected.

Tr--<0.001 percent (trace).

¹Sample numbers refer to table 1.

²Propane-propylene elute from gas chromatograph as 1 peak.

Assuming that oxygen and nitrogen are related to air in the cylinder and CO_2 is formed by oxidation of the coal, the hydrogen, helium, and hydrocarbons were considered the gases actually desorbed from the coal. The relative composition of the desorbed gas is given in table 3.

Since hydrogen constituted an unusually large percentage of the gas from most of the coals, the possibility that the hydrogen was formed during the experiment was considered. One possible mechanism involved the formation of sulfuric acid from pyrite in the coal. If the acid reacted with the metal cylinder, hydrogen would have been produced. There was no correlation between either the sulfate or pyritic sulfur of the coal and the hydrogen content, and the cylinders showed no signs of corrosion. The possibility that the hydrogen was a byproduct of the oxidation of the coal was also considered. No relationship was found between the concentrations of CO_2 and H_2 . With one exception, the gas samples from coals obtained at the face contained substantially more hydrogen than gases from coals obtained in the shaft, indicating that despite the anomalously high concentration, hydrogen was desorbed from the coal. However, the origin of the hydrogen could not be unequivocally established with this experimental method.

Previous analyses have shown that the hydrocarbon gas desorbed from coal with a high gas content usually consists of over 95 percent methane; the concentrations of C_2 to C_5 alkanes generally decrease with increasing molecular weight. Ethylene and propylene are the only alkenes detected, and only at low concentrations. In the hydrocarbon gas desorbed from coals of low gas content, methane was the major component, but in the majority of samples it constituted less than 90 percent of the hydrocarbon gas (table 4). In four of the five pairs of samples, gas from face coal contained a higher percentage of methane than gas from the shaft coals. Ethane was the second most abundant hydrocarbon. The relative amounts of ethylene and propane-propylene varied. Butane was detected occasionally; pentane was not found in the desorbed gas.

The lower flammability limit for methane is 5 percent. When other combustible gases are present with methane, the flammability limit of the mixture depends upon the proportion and flammability limit of each gas (5, 9). The lower flammability limit for the mixture of hydrocarbon gases desorbed from the low-gas-content coals generally falls between 4 and 5 percent. If hydrogen is included in the calculation of the lower flammability limit, it again falls between 4 and 5 percent (table 5).

The coal samples used in this experiment were obtained from mines which did not have detectable gas emissions. Since a mixture of combustible gases is being desorbed from the coals, the rate of desorption must be very low, and the rate of desorption is related to the volume of gas in the coal. To obtain an estimate of the amount of gas in the coal, the volume of gas in the cylinder was calculated. This, multiplied by the proportion of hydrocarbons and hydrogen (table 2), divided by the weight of the coal, was considered a minimum value for the residual gas in the coal (table 6). Since there are insufficient data about residual gas in coal, these numbers cannot be related to an "average" gas content of coal.

TABLE 3. - Air- and CO₂-free composition of gas, percent

Sample ¹	1	2	3	4	5	6	7	8	9	10	11
H ₂	95.45	1.10	98.67	7.69	93.87	ND	14.53	ND	3.38	67.57	53.91
He	ND	ND	ND	ND	ND	ND	29.07	ND	ND	ND	ND
CH ₄	4.52	85.71	1.04	65.38	6.03	78.48	55.52	87.40	93.74	25.68	39.80
C ₂ H ₆	.02	4.40	.16	7.69	.05	12.66	.73	8.40	2.87	4.05	4.22
C ₂ H ₄	.005	4.40	.05	11.54	.03	1.27	.07	1.68	ND	.34	1.44
C ₃ H ₆ ²	}	4.40	.08	7.69	.02	7.59	.07	1.68	.005	2.03	.36
C ₃ H ₈ ²		ND	ND	ND	ND	ND	ND	.84	ND	.34	.27
C ₄ H ₁₀		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total	100.00	100.01	100.00	99.99	100.00	100.00	99.99	100.00	99.995	100.01	100.00

ND--Not detected.

¹ Sample numbers refer to table 1.² Propane-propylene elute from gas chromatograph as 1 peak.

TABLE 4. - Relative composition of hydrocarbon gas, percent

Sample ¹	1	2	3	4	5	6	7	8	9	10	11
CH ₄	99.32	86.67	78.00	70.83	98.36	78.48	98.45	87.40	97.02	79.17	86.35
C ₂ H ₆	.46	4.44	12.00	8.33	.82	12.66	1.29	8.40	2.97	12.50	9.16
C ₂ H ₄	.11	4.44	6.00	12.50	.55	1.27	.13	1.68	ND	1.04	3.12
C ₃ H ₆ ²	}	4.44	4.00	8.33	.27	7.59	.13	1.68	.005	6.25	.78
C ₃ H ₈ ²		ND	ND	ND	ND	ND	ND	.84	ND	1.04	.58
C ₄ H ₁₀		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total	100.00	99.99	100.00	99.99	100.00	100.00	100.00	100.00	99.995	100.00	99.99

ND--Not detected.

¹ Sample numbers refer to table 1.² Propane-propylene elute from gas chromatograph as 1 peak.

TABLE 5. - Lower flammability limit of gas mixtures

Sample ¹	Hydrocarbons, percent in air	Hydrocarbons + H ₂ , percent in air
1	4.98	4.04
2	4.47	4.43
3	4.20	4.03
4	3.94	3.94
5	4.92	4.05
6	4.20	4.20
7	4.95	4.41
8	4.64	4.64
9	4.90	4.86
10	4.19	4.05
11	4.52	4.23

¹ Sample numbers refer to table 1.TABLE 6. - Estimated residual hydrocarbons and hydrogen in coal

Sample ¹	Weight of coal, g	True specific gravity	Residual hydrocarbons, ft ³ /ton	Residual hydrogen, ft ³ /ton
1	2,168	1.38	0.0072	0.151
2	1,634	1.48	.0014	-
3	1,625	1.43	.0015	.113
4	1,712	1.49	.0007	.00005
5	1,615	1.45	.0114	.175
6	1,533	1.46	.0012	-
7	1,202	1.43	.0168	.004
8	1,648	1.44	.0015	-
9	1,691	1.56	.524	.018
10	1,498	1.54	.0015	-
11	1,563	1.43	.0145	.017

¹ Sample numbers refer to table 1.

CONCLUSION

Although the methods used were fairly simple, this experiment did demonstrate that methane and other hydrocarbons are contained in coals from which there is no apparent methane emission. Ethane, ethylene, propane, propylene, butane, and hydrogen in addition to methane were detected in the desorbed gas. The estimated amount of residual gas is small. However, lack of critical data about the gas content of coal prevents making comparisons between the residual gas content of low-gas and "normal" coals.

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