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Effects of temperature and atmosphere on the production of light hydrocarbons

Mei-In Melissa Chou
Donald R. Dickerson
Illinois State Geological Survey
Urbana, IL

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PYROLYSIS OF EASTERN GAS SHALE-EFFECTS OF TEMPERATURE AND ATMOSPHERE ON THE PRODUCTION OF LIGHT HYDROCARBONS

Mei-In Melissa Chou and Donald R. Dickerson

Illinois State Geological Survey, Urban, IL

ABOUT THE AUTHORS

Mei-In M. Chou received her B.S. in chemistry at National Taiwan Normal University and her Ph.D. in organometallic chemistry from Michigan State University (1977). Currently she is employed by the Illinois State Geological Survey as Research Associate. She is conducting part of U.S. DOE granted projects "Characterization of Chemical and Physical Properties of Hydrocarbon-bearing Eastern U.S. Shales" and "Characterization of Coal and Coal Residues". Experienced in organic and organometallic chemistry, she is specializing in high vacuum system, atmosphere controlling reaction technique, simple hydrocarbon gas analysis, organic synthesis, transition metal catalysis reaction, and instrumental and method development on the analysis of chemical composition in shale and coal.

Donald R. Dickerson received his B.S. and M.S. degrees in Chemistry and his Ph.D. in Food Chemistry from the University of Illinois. He has had experience as a microanalyst in a commercial microanalytical laboratory. He has been employed at the Illinois State Geological Survey for 26 years, first as an organic microanalytical chemist and later as a research chemist in the synthesis of organic fluorine containing compounds. For the past 10 years, he has been doing research and is the author of several publications dealing with the organic chemistry of petroleum and coal. He is a member of the American Chemical Society and the Illinois State Academy of Science. He has held a number of council offices in the Illinois State Academy of Science and is presently serving as president of the Academy.

ABSTRACT

Samples of black shale from four cores of the New Albany Shale Group (Devonian-Mississippian) from the Illinois Basin in Kentucky and Illinois were used in this study. Sections measuring 4 inches (9 cm) in length were taken from the 4-inch (9-cm) diameter cores and were sealed in canisters for study of released gas. Following the study of released gas, the shale was crushed to <100 mesh for use in the study of the effects of temperature and atmosphere on the pyrolysis of shale.

The correlation coefficients between the quantity of gas released at room temperature from the "canistered" core sections and the organic carbon content, and between the gas released and the total porosity of the shale samples were calculated for the individual cores. The coefficients for the quantity of gas released and the organic carbon content of the four cores were 0.7018(06IL), 0.0023(02IL), 0.8034(04IL), and 0.7531(01KY).

A study was made of the gaseous hydrocarbons produced by pyrolysis of shale at 600°C. Two regression lines could be drawn on the graph of the hydrocarbon gas produced versus the original organic carbon content, one (r^2=0.96) fitting data points for the Illinois cores and the other (r^2=0.92) fitting data points for the Kentucky core.

The composition of the noncondensable hydrocarbon gases produced by heating selected black shale samples at four different temperatures was studied. The formation of alkanes was favored over that of alkenes, particularly at low temperature. Methane, ethane, and ethylene from thermal cracking and higher carbon number alkenes were positively identified in the gases from shale heated to above 120°C.

A study was made of the effect of the pyrolysis atmosphere on the yield of light hydrocarbons (C_1 to C_8), carbon dioxide, carbon monoxide, acetaldehyde, and acetone during thermal degradation of a gram amount of selected shale samples. The effect of various amounts of oxygen in the pyrolysis atmosphere was monitored. The yield of an individual hydrocarbon generally increased with the increase in the oxygen content of the pyrolysis atmosphere until the oxygen content reached the 10 percent level; when the oxygen content was increased above 10 percent, there was a decrease in yield. The yield of carbon dioxide and carbon monoxide increased with the increase in oxygen content of the pyrolysis atmosphere.

Results reported in this study may increase the ability to predict the potential for production of gas from the black shale in the New Albany Group. The study may also provide information useful for improving the quality of the gas produced by pyrolysis of shale.

INTRODUCTION

As part of the Eastern Gas Shale Project of the U.S. Department of Energy, the Illinois State Geological Survey (ISGS) is conducting a number of geologic and geochemical studies[1] of the New Albany Shale Group (Devonian-Mississippian) in the Illinois Basin to evaluate its potential as a source of hydrocarbons. The amount of volatile materials in the shale, their origin, and their continuous formation are of considerable interest with regard to the history and current alteration of shale formation. The present study was undertaken in order to determine the relationships between the light hydrocarbons (C_1 to C_5) released from the shale and the organic carbon content, the pyrolysis temperature, and the molecular oxygen content of the pyrolysis atmosphere. Through observation of the changes—changes that occur when conditions for pyrolysis are changed—in the amounts of CO_2, CO, CH_3CHO, CH_3COCH_3, alkanes, alkenes, and in the alkane to alkene ratios, an insight may be gained into the oxidative processes taking place in the shale during pyrolysis.

EXPERIMENTAL PROCEDURE

Gas released from shale at room temperature

The quantity and composition of gas released at room temperature from specially canned core sections were measured. Ten of the core sections were from drill holes in Christian County, Kentucky (01KY); nine from Effingham County, Illinois (02IL), twenty-nine from Henderson County, Illinois (04IL), and twenty-five from Tazewell County, Illinois (06IL). The locations of these holes are shown in figure 1.

The shale core sample (approximately 4 inches (9 cm) in height and 4 inches (9 cm) in diameter) was sealed in a 2800-mL aluminum resealable canister as soon as possible after the core had been brought to the surface and the sample cut. Each canister was equipped with a rubber septum-sealed valve. The canistered samples were stored in a room with a constant temperature of 21°C for approximately 3 to 4 months. Hydrocarbons that had been formed by natural processes, e.g., by microbial degradation of organic matter, and had remained trapped in the shale until the core was cut were released to the headspace of the canister. The pressure inside the canisters was monitored periodically with a mercury manometer. The gas yield was calculated from the volume of the canister headspace and the pressure of the gas. The composition of the gases was determined with a Beckman GC-4 gas chromatograph equipped with a hot wire detector and a flame ionization detector. A CTR column (Alltech Associates, Inc.), with the injector at 100°C, and temperature programmed from 60° to 180°C at 16°C/min was used with the hot-wire detector at 185°C. A Chromosorb 102 column with the injector at 100°C and temperature programmed from 50° to 150°C at 16°C/min was used with the flame-ionization detector at 175°C.

Yield of gaseous hydrocarbons (C_1 to C_5) from pyrolysis of shale

Thirty shale samples were studied. Eight of the samples were from the core from Christian County, Kentucky, six were from Effingham County, eight were from Henderson County, and eight were from Tazewell County, Illinois.

A 250-mg sample of pulverized shale (<100 mesh) was weighed into a custom-made pyrex tube (7 in. x 0.7 in. ID). The tube was sealed with a rubber serum cap secured with a wire band. The sample was degassed with a small hypodermic needle, and the tube was then placed in a pre-heated (600°C) electric tube furnace for 5 minutes. A known amount of pure cyclopropane was injected into each sample tube for use as an internal standard. The gases that were noncondensable at 29 ± 1°C were sampled from the headspace and analyzed on a Perkin-Elmer 3920B gas chromatograph equipped with a flame ionization detector and interfaced with a Perkin-Elmer Sigma 10 data system. A stainless steel column (6 ft x .125 in. [2M x 3 mm ID]) packed with Chromosorb 102 (80/100 mesh) was used. The inlet and detector temperatures were 200° and 250°C, respectively, and the column temperature was programmed from 40°C to 180°C at 8°C/min and was held at the upper temperature for 8 minutes. The flow of helium carrier gas was 20 mL/min.

A blank was run to be certain that all the gas in the tube came from the shale. A small amount, however, may have come from indigenous gas trapped in the pore structure of the shale. Figure 2 shows the gas chromatogram of a representative gas sample separated on the Chromosorb 102 column. The yield of pyrolysis products was determined by integration of the chromatograms and was calculated by using the Sigma 10 data system.

Effect of temperature on the pyrolysis of shale

A shale sample taken from a section of the drill hole in Christian County, Kentucky, which was 2182 to 2249 ft below the surface, was used in this study.

The temperatures selected for pyrolysis were 60°, 145°, 300°, and 450°C. Small portions (0.5 to 1 g) of pulverized shale sample (<100 mesh) were weighed into pyrex tubes. Each tube was sealed with a rubber serum cap secured with a wire band as previously described.

A silicon oil bath was used to heat the samples to 60° and 145°C, and an electric furnace was employed for higher temperatures. The heating time was always 18 hours. The gas compositions were analyzed by gas chromatography using a Chromosorb 102 column and were checked with a Carbopack C/ 0.2 percent CW 1500 column; operating conditions were the same as described in the preceding section. Figure 3 shows a typical GC trace of a gas sample separated on the Carbopack C/ 0.2 percent CW 1500 column.

Effect of molecular oxygen on the pyrolysis of shales

A shale sample taken from the core from the drill hole in Effingham County, Illinois, at 3,053 ft below the surface was used in this study.

One-gram amounts of samples of pulverized shale were weighed into pyrex tubes and sealed as described above. The bulk of the air in the sample tube was exchanged for a gas mixture of known composition by evacuating the tube and filling it with oxygen and nitrogen in the desired proportions. The percentage of oxygen in the sample tube was checked by gas chromatography before pyrolysis.

All samples were pyrolyzed at 450°C for 15 minutes. The headspace gases, with an added internal standard, were measured by gas chromatography on both a Chromosorb 102 and a Carbopack C/

0.2 percent CW 1500 column. The operating conditions were as described previously. A 5A Molecular Sieve column was also used for separation of the hydrocarbons and the products of oxidation. Conditions for the chromatography were: injection port at 200°C; column oven with initial hold of 3 minutes at 40°C and then programmed from 40° to 260°C at 20°C/min and held at 260°C for 10 minutes; hot wire detector at 300°C; helium carrier gas at 30 mL/min flow rate. The identification of the components of the gas was confirmed by GC-MS analysis.

RESULTS AND DISCUSSION

Gas released from shale at room temperature

For the four cores studied, correlation coefficients were calculated for the relationship of the quantity of gas released from the "canistered" core sections at room temperature to the organic carbon content and total porosity of the shale. The correlation coefficients (r^2) of the organic carbon content with the quantity of gas released, for the four cores, were 0.70(06IL), 0.002(02IL), 0.80(04IL), and 0.75(01KY). The Illinois State Geological Survey made porosity measurements (at 100°C) on some of the 77 samples, and the results have been reported elsewhere[2] (see table 1). The correlation coefficients between the porosity and the released gas for the four cores were 0.19, 0.30, 0.16, and 0.02, respectively. The amount of gas released from shale at room temperature did not appear to be related to the porosity of the shale.

For the Effingham County core (02IL), there is considerable scatter to the points in the plot of the data for the released gas yield versus the organic carbon content (fig. 4). This may be explained in part by the fact that in this area the black shale overlies an oil pool. The composition of the gas released from the shale was essentially identical to that of the gas released from a producing oil well nearby. This indicates that most of the gas migrated into the shale rather than being indigenous to it.

There was good correlation between the amount of gas released and the organic carbon content for the other three cores; however, the correlation was not as good as that between the organic carbon content and the gas released upon pyrolysis of the shales, as established in the next section of results. The poorer correlation between indigenous volatile material and organic carbon content may be due, in part, to the fact that the amount of gas in the core is a function not only of the amount of gas formed over geologic time periods, but also of the amount that remained trapped in the shale. It is also possible that the trapped gases may have originated elsewhere and migrated into the shale in question. Other geologic factors may be operative as well.

The correlation of the gas released with the organic carbon content and the lack of correlation between the gas released and the porosity is in agreement with the findings of Kalyoncu et al.[3] and Snyder et al.[4]

Yield of gaseous hydrocarbons (C_1 to C_5) from pyrolysis of shales

The relationship of the gas yield from the pyrolysis of shale at 600°C with the organic carbon content of shales is shown in figure 5. There is a direct correlation between the gaseous hydrocarbon yield and the organic carbon content. Despite some scatter of data points, two regression lines can be drawn through the points in figure 5. One (r^2=0.96) closely fits data points for Illinois drilling hole cores and the other (r^2=0.92) follows data points for the Kentucky drill hole core only. For all data points the correlation coefficient (r^2) is 0.86. The reason that the Kentucky core produced more hydrocarbon gas than the Illinois cores per unit of organic carbon content has not been accounted for. A difference in the nature of the organic matter or the existence of a special mineral-surface catalytic reaction may be the cause. Of these four drilling holes, only the one in Kentucky appeared to have the potential to be an economical gas-producing well.

Effect of temperature on the pyrolysis of shale

Samples of shale from the core from a drilling hole in Christian County, Kentucky, were pyrolyzed at 60°, 145°, 300°, and 450°C for 18 hours. The long pyrolysis time was chosen in order to accumulate a sufficient amount of gas for analysis at a comparatively low temperature (60°C). Pyrolyses over an eighteen-hour period could not be carried out at temperatures higher than 450°C because of possible damage to the rubber septum seal. The average values of the relative hydrocarbon yields from several determinations at each temperature are presented in table 2. Typical GC traces obtained at 60° and at 300°C are shown in figure 6. At 60°C the hydrocarbon products were mostly alkanes; alkenes were in trace amounts only. The yields of C_1 and C_2 hydrocarbons from thermal cracking and of higher carbon number alkenes are substantially increased as the temperature of pyrolysis is raised to 300°C. The alkane/alkene ratios for C_2 to C_5 hydrocarbons as a function of pyrolysis temperature are shown in figure 7. The ratios for C_2, C_3, C_4, and C_5 hydrocarbons show that conditions for the formation of these alkenes are more favorable at high temperatures[3].

The total yield of gases (C_1 to C_5) increases fairly rapidly as the temperature of pyrolysis is increased (fig. 8). The increase in yield is dramatic at a pyrolysis temperature of 450°C.

The trends observed in this study can be related to the trends observed in the study of the effects of molecular oxygen on pyrolysis (see fig. 9). The data may also provide information on the type of hydrocarbons that exist in the shale.

Effect of molecular oxygen on the pyrolysis of shale

The yields of products obtained from heating shale at 450°C for 15 minutes with various percentages of oxygen in the pyrolysis atmosphere are presented in table 3. The products are comprised of C_1 to C_8 hydrocarbons and include CH_3COCH_3, CH_3CHO, CO, and CO_2. The yield of each hydrocarbon generally increases with an increase in oxygen content of the pyrolysis atmosphere until the oxygen content reaches 10 percent.

Figure 9 shows the ratio of alkanes to alkenes produced for carbon numbers 2 through 6, as a function of the oxygen content in the pyrolysis atmosphere. The plot of the alkane to alkene ratio for C_2 shows that the alkene formation becomes relatively more favorable as the oxygen content increases. For C_3, C_4 C_5, and C_6, alkene formation becomes only slightly more favorable relatively, as the oxygen content becomes higher in the pyrolysis atmosphere.

The higher oxygen levels will result in higher surface temperature because of oxidation. Thus an effect of oxygen is to lower the pyrolysis temperature at which the maximum level of evolution of organic gases occurs. Whether the trends in yields observed are the same at different temperatures is under investigation. Information concerning the effect of controlling both the temperature and the quantity of molecular oxygen on the pyrolysis of shale should prove very helpful for optimizing shale retorting operations.

The yields of CO_2, CO, CH_3CHO, and CH_3COCH_3 as a function of the oxygen content of the pyrolysis atmosphere are given in figure 10. The yields of CO_2, CO, and CH_3COCH_3 increase significantly as the percentage of oxygen increases in the pyrolysis atmosphere.

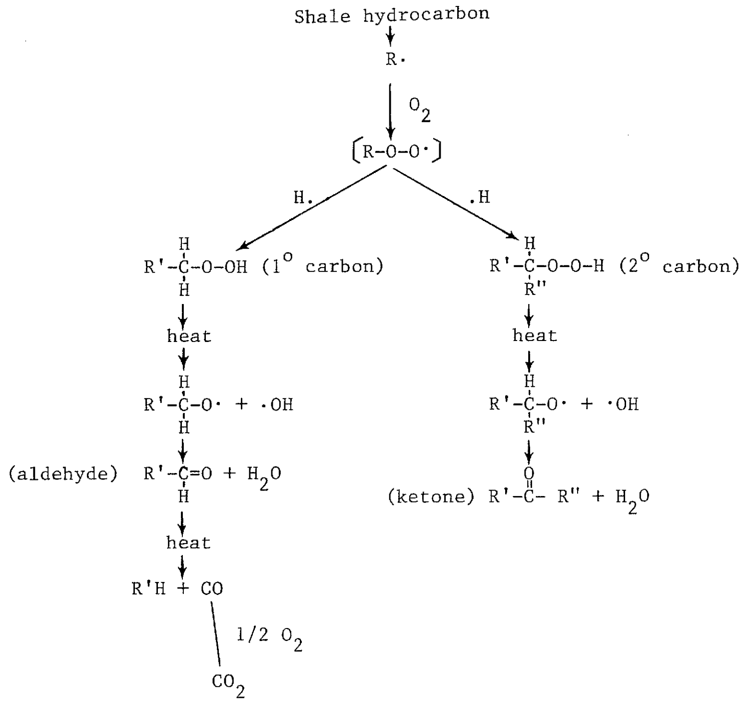
Many details of the complex reaction involved in the oxidation of hydrocarbons by moleuclar oxygen have not yet been elucidated. It is commonly accepted that a chain mechanism is operative[5,6] and that one of the first products formed is a hydroperoxide that may be oxidized further or decomposed thermally, thereby to initiate new chains. It is also known that these intermediates are responsible for the increased yield of oxygenated compounds in the thermolysis of hydrocarbons in higher oxygen concentrations.[5,6] Most likely, oxidation proceeds by the pathways shown on the diagram at the top of the next page. In the initial reaction hydroperoxide radicals are formed by combination of the organic free radicals (formed by thermolysis from shale hydrocarbons) and molecular oxygen, and further thermolysis reactions produce aldehyde and ketone molecules.

CONCLUSIONS

Our study of the gas released from shale at ambient temperature shows that the amount of gas released is highly dependent on the organic carbon content and is not limited by the porosity of the shale. For the shales studied, the organic carbon content of a given shale appears to be a much better indicator of the potential for gas production from shale than does porosity data. There may be other geological factors, however, that play an important role in the production of gas from shale.

About twenty times more gas was produced from the shale by high temperature pyrolysis than was obtained by natural release at ambient temperature. The yield of hydrocarbons in pyrolysis showed a higher degree of dependence on the organic carbon content of a given shale than was found for ambient temperature gas release. This may be true, in part, because the gas produced by pyrolysis was not affected by geologically controlled factors.

In the study of the effects of temperature on pyrolysis, data showed that the yield of the total quantity of light hydrocarbons (C_1 to C_5) was increased the most for pyrolysis temperatures above 300°C, and the relative proportion of alkene to alkane produced for a given carbon number increased as the pyrolysis temperature was increased. The same trend was observed in the study of



the effect of the presence of molecular oxygen on the pyrolysis of shale. The proportion of alkenes to alkanes that were produced for a given carbon number increased as the oxygen content of the atmosphere was increased; however, except for C_2, the increase in the relative production of alkene to alkane was not very significant. The quantity of any individual hydrocarbon that was produced generally increased as the oxygen content increased in pyrolysis atmosphere until the oxygen content reached 10 percent; thereafter there was a decrease in yield as the process of combustion became more significant. A plot of the effect of oxygen on the formation of CO and CO_2 had a point of inflection at about the 10 percent oxygen level. Possibly, the presence of some molecular oxygen could lower the pyrolysis temperature needed to produce a gas of desired composition. The study of the effect of molecular oxygen at different temperatures of pyrolysis and the determination of gases other than hydrocarbons formed in pyrolysis of shale at different temperatures would be helpful in order to test this conclusion. Moreover this additional study could be used to determine the changes that occur in the composition of the light gases produced from the organic matter in shales as temperature and atmosphere of pyrolysis are varied.

ACKNOWLEDGEMENTS

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TABLE 1

Linear regression analysis on the amount of gas released from shale at room temperature and the porosity of shale.

Core and sample #	Depth to top of sample (ft)	Y Gas released, cu ft/cu ft$_{\text{shale}}$	X Porosity (%)	$y = a_2 + bx$ r^2*
06IL-16C1	1053.15	0.0067	11.8	
19C1	1083.20	0.0321	11.3	
20C1	1093.35	0.0277	6.8	0.19
02IL-01C1	3011.4	0.30	7.0	
04C1	3033.0	0.29	4.6	
07C1	3085.5	0.57	7.0	
08C1	3096.5	0.51	6.66	0.30
04IL-10C1	413.5	0.0089	15.7	
20C1	513.4	0.0329	13.4	
29C1	604.5	0.0013	9.1	0.16
01KY-01C1	2182.25	1.47	3.6	
04C1	2230.20	0.39	4.2	
05C1	2240.10	0.76	2.7	
06C1	2250.00	0.09	2.9	0.02
			Overall	0.35

*r^2 = the correlation coefficient

TABLE 2

Relative percentages of hydrocarbons (C_1 to C_5) produced in the pyrolysis of shale from a drill hole at Christian County, Kentucky, at selected temperatures for 18 hours.

	Pyrolysis temperature (°C)			
Composition	60° (%)	145° (%)	300° (%)	450° (%)
methane	1.7	1.8	20.2	18.8
ethylene	-	1.1	7.0	6.6
ethane	0.1	2.0	13.8	15.8
propylene	0.1	1.7	10.7	11.7
propane	12.7	12.9	15.6	15.9
i-butane	5.0	8.7	6.4	3.5
1-butene	-	0.7	3.0	8.0
n-butane	51.0	40.9	16.9	18.2
1-pentene	-	0.3	0.5	0.5
n-pentane	29.4	29.8	6.0	1.4

TABLE 3

Composition of product obtained from heating shale at $450^{\circ}C$ for 15 minutes with various percentages of oxygen in the pyrolysis atmoshpere.

Constituent	Yield of hydrocarbons (X 10^{-5} g/g shale)				
	O_2 in pyrolysis atmosphere				
	1.48%	5.1%	10.11%	15.16%	20.0%
methane	78.93	91.60	119.56	81.76	86.29
ethylene	17.96	21.01	27.97	21.66	23.80
ethane	68.20	75.94	92.61	67.42	68.03
propylene	35.86	40.89	50.19	38.73	38.87
propane	47.77	50.84	60.04	45.92	44.77
butenes	22.97	24.77	29.26	23.25	22.15
i-butane	4.00	4.29	5.01	3.86	3.66
n-butane	24.19	26.00	30.04	23.08	21.76
cyclopentane	0.56	0.63	0.65	0.55	0.43
pentenes	11.54	12.72	14.70	10.97	9.90
i-pentane neo-pentane	7.82	8.67	10.40	7.58	6.95
n-pentane	7.45	7.73	8.33	6.44	5.78
cyclohexane methyl-cyclohexane	0.70	0.73	0.62	0.56	0.44
hexenes	3.73	4.00	4.05	3.25	3.05
i-hexane & isomers	3.67	3.81	3.71	3.19	2.93
n-hexane	2.41	2.45	2.44	1.96	1.86
benzene	1.72	1.72	1.71	1.44	1.37
C_7's	5.70	5.62	4.59	6.48	3.75
C_8's	1.98	1.54	0.73	1.05	0.89
acetone	0.41	0.59	1.27	1.57	2.27
CH_3CHO	11.17	14.13	15.86	37.70	33.49
CO	6.03	9.77	37.29	70.09	84.27
CO_2	14.16	21.78	84.05	140.23	161.96
Total	378.93	431.23	605.08	598.74	628.67

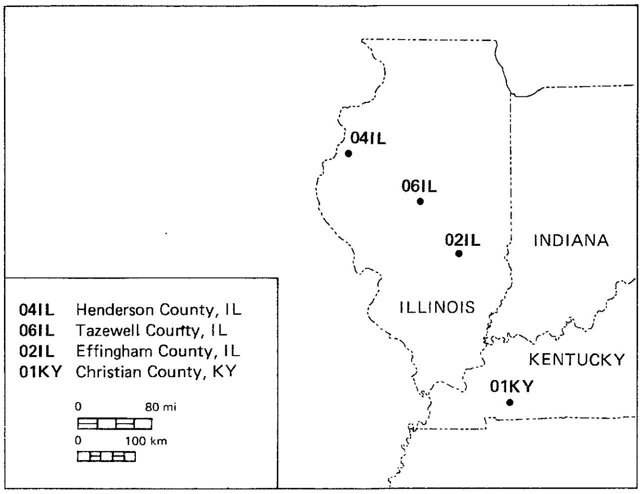

Figure 1. Location of wells.

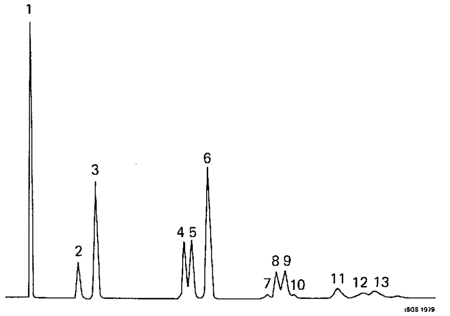

Figure 2. GC trace of light hydrocarbon gases from shale pyrolysis. Column: stainless steel 2m x 3mm I.D. Chromasorb 102. Temperature programmed from 40°C to 180°C (held at 180°C for 8 minutes). Hydrocarbon gases: (1) Methane, (2) Ethylene, (3) Ethane, (4) Propylene, (5) Propane, (6) Cyclopropane (std.), (7) iso-Butane, (8) 1-Butene, (9) Butane, (10) 2-Butenes, (11) Acetone, (12) 1-Pentene, and (13) Pentane.

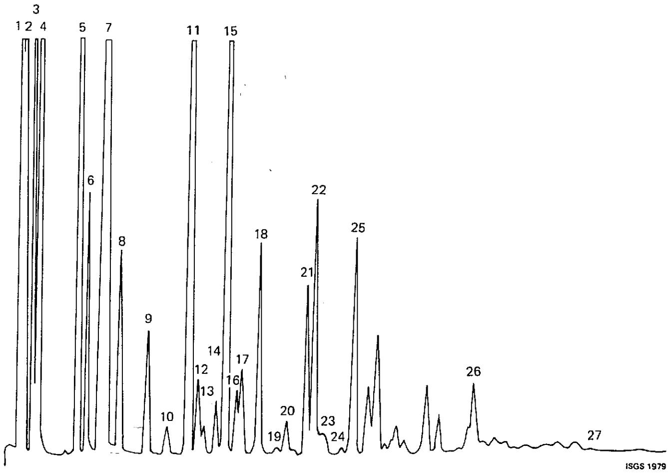

Figure 3. GC trace of light hydrocarbon gases from shale pyrolysis. Column: stainless steel 2m x 3mm I.D. Carbopack C/0.2 percent CW 1500. Temperature programmed from 40°C to 180°C (held at 180°C for 10 minutes). Hydrocarbon gases: (1) Methane, (2) Ethane and Ethylene, (3) Cyclopropane (std.), (4) Propane and propylene, (5) iso-Butane, (6) 1-Butene, (7) n-Butane, (8) Neopentane, (9) Cyclopentane, (10) saturated C_5, (11) iso-Pentane, (12) 1-Pentene, (13) cis-2-Pentene, (14) trans-2-Pentene, (15) n-Pentane, (16) iso-Pentene, (17) Cyclohexane, (18) Methyl-Cyclopentane, (19), (20) saturated iso-Hexane isomers, (21) iso-Hexane, (22) Benzene, (23) 1-Hexene, (24) trans-2-Hexene, (25) n-Hexane, (26) n-Heptane, and (27) n-Octane.

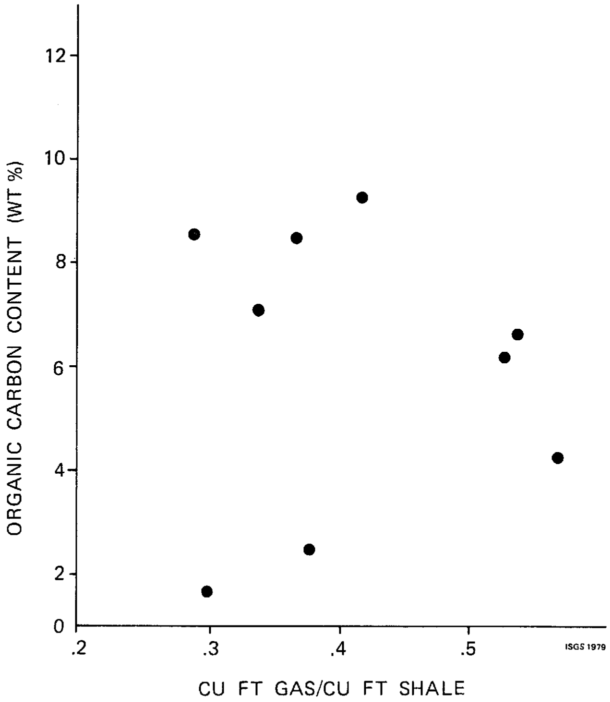

Figure 4. The organic carbon content versus the volume of gas released at room temperature from shale samples taken at 10-foot intervals from the core at Effingham County, Illinois.

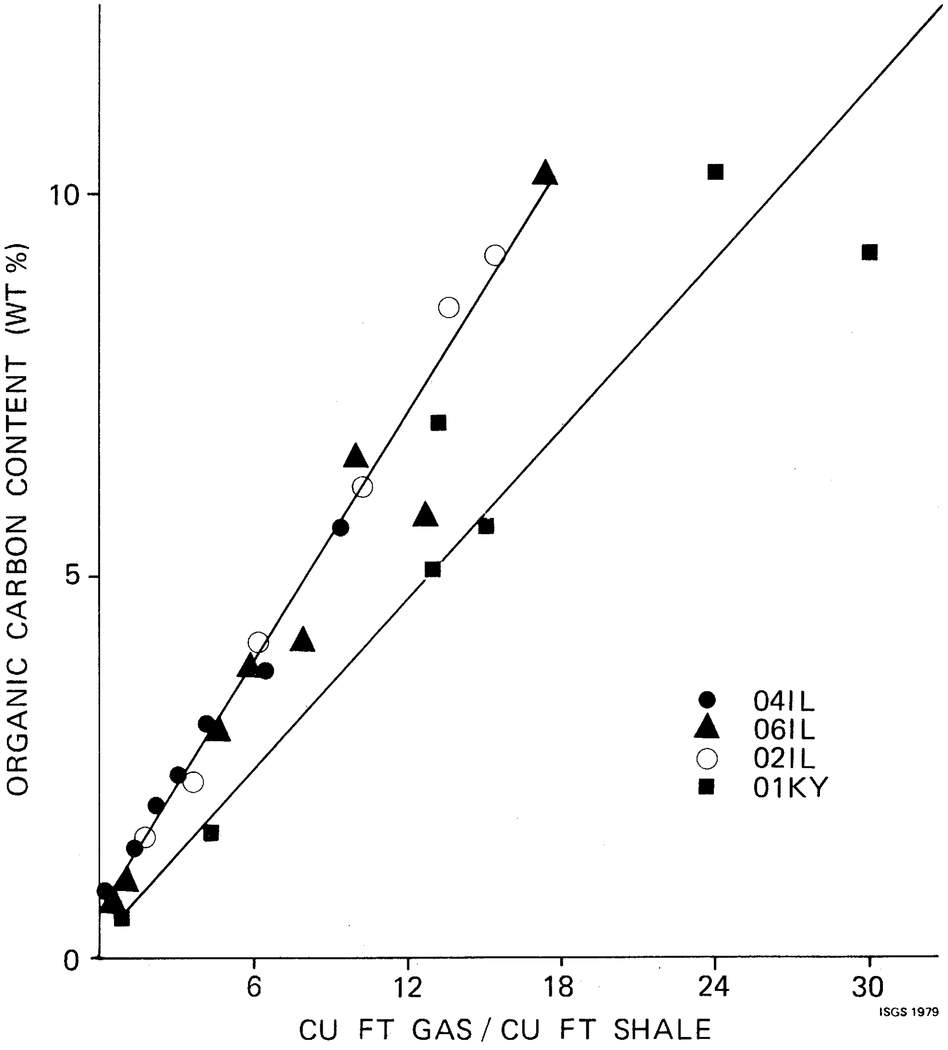

Figure 5. The relationship of the gas yield from pyrolysis of shale at 600°C to the organic carbon content of the shale.

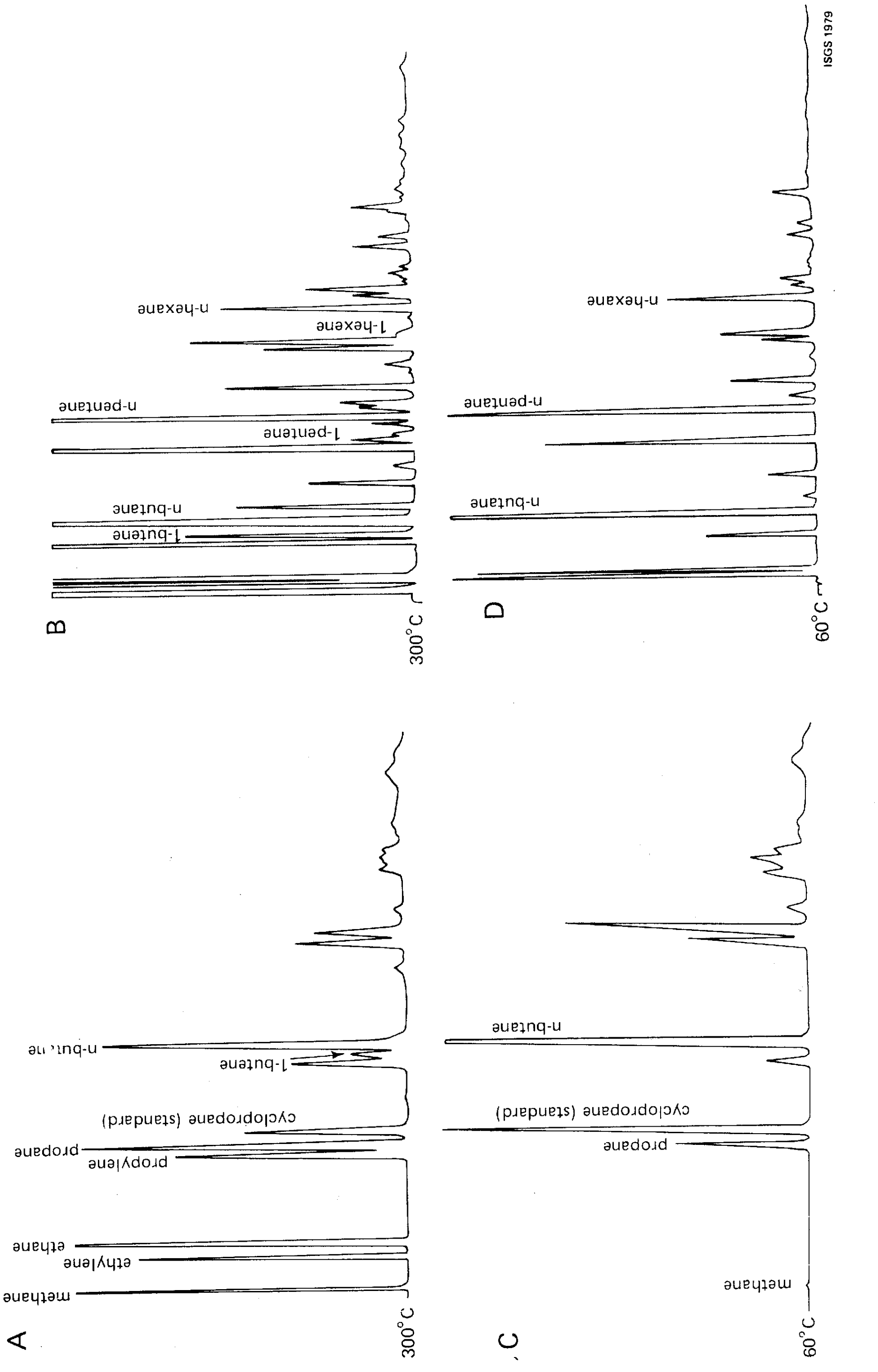

Figure 6. Typical GC trace of gaseous products from shale pyrolysis at 60°C (C, D) and at 300°C (A, B). A and C—Chromasorb 102 column; B and D—Carbopack C/0.2 percent CW 1500 column.

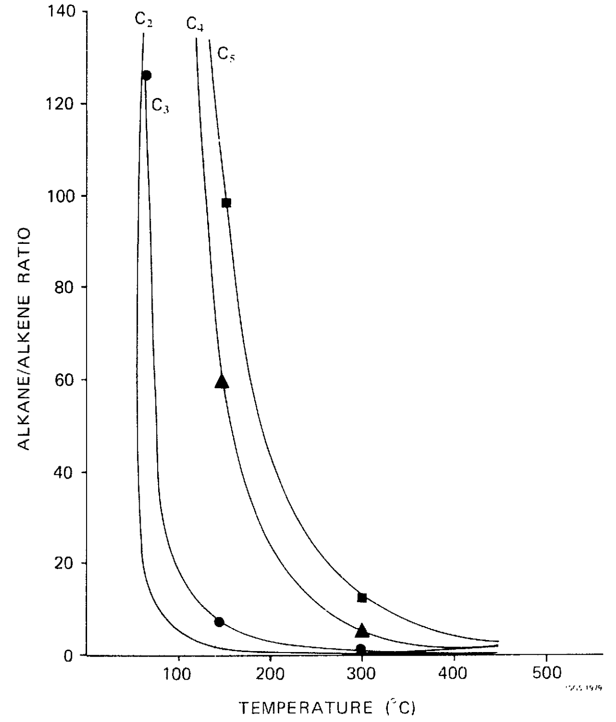

Figure 7. The alkane/alkene ratio of the hydrocarbons produced by pyrolysis of shale as a function of temperature.

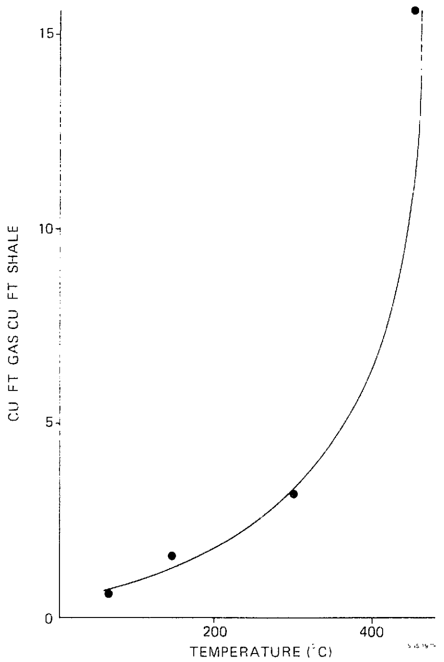

Figure 8. The total yield of hydrocarbons (C_1-C_5) produced from shale as a function of pyrolysis temperature.

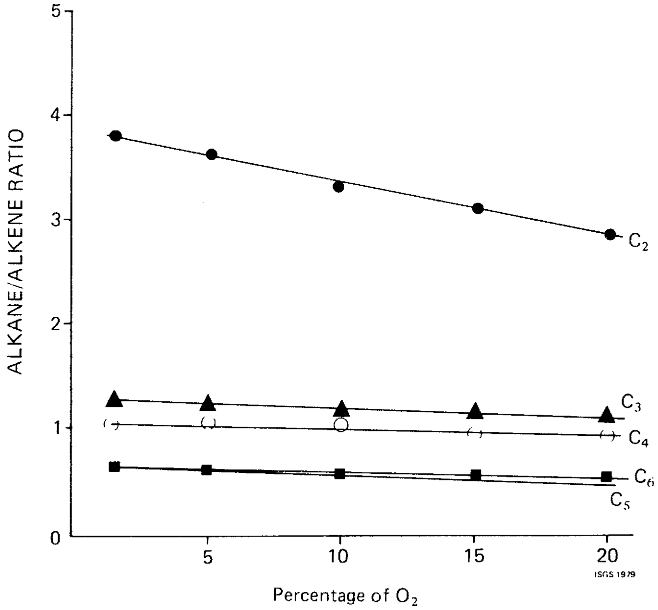

Figure 9. The alkane/alkene ratio of hydrocarbons produced by the pyrolysis of shale as a function of the percentage of oxygen in the pyrolysis atmosphere.

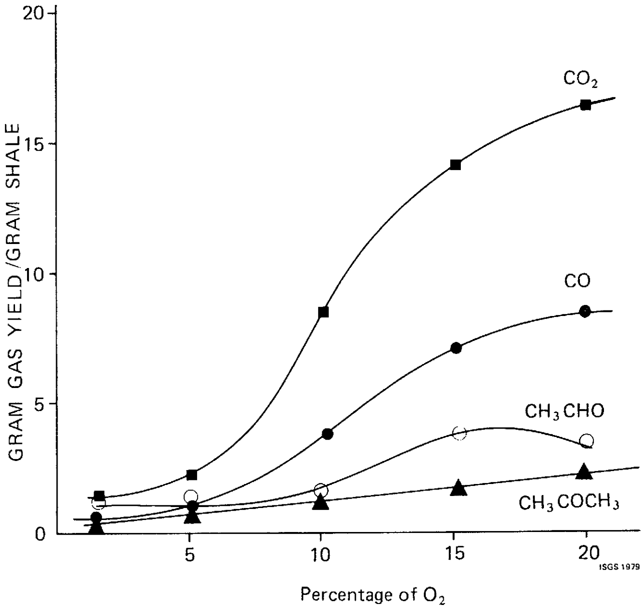

Figure 10. The yield ($\times10^{-4}$) of CO_2, CO, CH_3CHO, and the yield ($\times10^{-5}$) of CH_3COCH_3 produced by the pyrolysis of shale as a function of the percentage of oxygen in the pyrolysis atmosphere.

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