

PYROLYSIS OF THE ARGONNE PREMIUM COALS UNDER SLOW HEATING CONDITIONS

M.A. Serio, P.R. Solomon, and R.M. Carangelo

Advanced Fuel Research, Inc., 87 Church St., East Hartford, CT 06108 USA

INTRODUCTION

The establishment of the Argonne Premium Sample Bank (1) will allow more meaningful comparisons to be made between pyrolysis studies from different laboratories. This sample bank also provides a good suite of coals for examining rank dependent phenomena, such as the kinetics of primary gas evolution. A recent "general" model of coal pyrolysis proposed by our research group (2-4) has as one of its assumptions that the kinetics of primary product evolution are rank-insensitive. This assumption was tested by a thorough examination of our data from experiments where only coal type was varied as well as data from similar experiments in the literature (5). The conclusion was that, with few exceptions, the kinetic rate constants for individual species evolved from coals pyrolyzed under the same conditions show little variation with rank. However, this conclusion remains controversial. The Argonne premium samples provide an opportunity to further test this assumption with a set of coals that was designed to cover a wide range of coal types. A slow, constant heating rate experiment was used, which is the most sensitive to rate variations.

A second controversial area is the importance of heating rate on the volatile product yield and distribution. Evidence has been presented which suggests no intrinsic effect of heating rate on pyrolysis yields (6) and other studies have indicated the converse to be true (7,8). However, often these studies have been done under sufficiently different experimental conditions that direct comparisons are difficult. Our own work has indicated a role for heating rate on tar yields for bituminous coals and on tar molecular weight distributions for lignites (3,9). We plan to extend this work to the Argonne coals in order to better establish these trends. The current paper is concerned primarily with pyrolysis of the Argonne coals under slow heating conditions in a unique TG-FTIR instrument developed in our laboratory. Results from slow heating rate pyrolysis into a FIMS apparatus are also presented. Experiments have also been done under rapid heating conditions. These will be the subject of another paper.

EXPERIMENTAL

Coal Properties - Elemental data are given for the Argonne coals in Table I. This information was obtained from Ref. 1.

TABLE 1 - ELEMENTAL ANALYSES OF ARGONNE PREMIUM COAL SAMPLES (1)

	%daf basis			% dry basis	
	C	H	O	S	Ash
1. Pocahontas	91	4.7	3	0.9	5
2. Upper Freeport	87	5.5	4	2.8	13
3. Pittsburgh #8	83	5.8	8	1.6	9
4. Upper Kanawha	81	5.5	11	0.6	20
5. Utah Blind Canyon	79	6.0	13	0.5	5
6. Illinois No. 6	77	5.7	10	5.4	16
7. Wyodak	74	5.1	19	0.5	8
8. Beulah-Zap	73	5.3	21	0.8	6

TG-FTIR - The apparatus is the TG/PLUS offered by Bomem, Inc.. It consists of a sample suspended from a balance in a gas stream within a furnace. As the sample is heated, the evolving tars and gases are carried out of the furnace directly into a 5 cm diameter gas cell (heated to 150°C) for analysis by FT-IR. The TG/PLUS couples a Dupont 951 TGA with a Bomem Michelson 100 FT-IR spectrometer.

The apparatus is designed to carry evolved products from the furnace to the gas cell over a short path to minimize secondary reactions or condensation on cell walls. In addition, the furnace geometry, the sample size, the sweep gas and flow rate have been chosen to ensure that the condensable products form a submicron aerosol mist. This size aerosol has two advantages: 1) the particles follow the gas stream lines, thus minimizing condensation; and 2) the particles produce little scattering in the mid I.R., so the condensable products can be analyzed directly in the FT-IR cell.

The FT-IR can obtain spectra every 30 seconds to determine quantitatively the evolution rate and composition of most pyrolysis products. The system allows the sample to be heated in a gas flow of selected composition on a pre-programmed temperature profile at rates between 1°C min⁻¹ and 100°C min⁻¹ up to a temperature between 20 and 1000°C and held for a specified time. The system continuously monitors: 1) the time-dependent evolution of the gases (including specific identification of the individual species such as CO, CO₂, H₂O, CH₄, C₂H₄, C₂H₂, benzene, heavy paraffins, heavy olefins, HCN, HCl, NH₃, NO, NO₂, SO₂, CS₂, COS, CH₃OH, CH₃CHO and CH₃COCH₃); 2) the tar evolution rate and its infrared spectrum with identifiable bands from the functional groups; and 3) weight of the non-volatile material (char plus mineral components). An analysis of C, H, N and S in the residue at the end of the pyrolysis experiment can be obtained by introducing oxygen to burn the residue and analyzing the combustion products.

For the experiments reported here, approximately 35mg of each coal sample was heated at 30°C/min, first to 150°C for drying and then to 900°C for pyrolysis. Additional details on the TG-FTIR apparatus can be found in Refs. 10 and 11.

FIMS - Molecular weight distributions of the primary pyrolysis tars were determined at SRI, International using the Field Ionization Mass Spectrometry (FIMS) apparatus described by St. John et al. (12). The samples were heated at 0.05°C/sec in a vacuum chamber.

RESULTS AND DISCUSSION

The quantitative gas evolution plots from all eight coals are presented in

Figs. 1-6 for tars plus aliphatics, CH₄, CO₂, CO, SO₂ and H₂O respectively. The coals are arranged on each plot according to the rank order given in Table 1. The actual temperature-time profiles are given on the first plot in each figure.

The results show how the structure of the product gas evolution curves varies from simple in the case of hydrocarbons to complex in the case of oxygenated species. One reason is that the latter are likely to be influenced by mineral decomposition peaks. Of course this can be assessed to a large extent by running demineralized samples, which we are in the process of doing.

In order to determine how well pyrolysis of the Argonne coals agreed with the assumption of rank-insensitive kinetics, a compilation was made of the temperatures for maximum evolution rate for the evolution of the most consistently prominent peaks for each gaseous product. This was difficult in some cases because of the fact that numerous "subpeaks", shoulders and minor peaks were often present. However, it was the usual case that an identifiable peak appeared in the same temperature vicinity for each coal. The results of this analysis are tabulated in Table 2.

In general, the standard deviations are greatest for oxygenated gases (CO₂, CO, SO₂, H₂O) compared to hydrocarbon gases (CH₄, tar/aliphatics). This phenomena was also observed previously (5). If one assumes a 50 Kcal/mole activation energy, a range in the peak temperature of 40°C corresponds to a factor of 5 in the rate while a range in the peak temperature of 65°C corresponds to a factor of 10 (5). It appears that about one-half of the 10 products show a variation of x5 or less, while one-half show a variation of x10 or less.

An interesting feature of the tar evolution curves in Fig. 1 is a low temperature evolution peak which is probably due to unattached guest molecules in the coal. These are most apparent in the Pittsburgh and Upper Freeport evolution curves. A comparison of the infrared spectra obtained at the low and high temperature peaks is presented in Fig. 7. The spectrum taken at the early peak (Fig. 7b) has been scaled up to compare to the spectrum from the later peak (Fig. 7c). The earlier peak appears to have a slightly higher aliphatic to aromatic content compared to the later peak. This would be consistent with the concept of some guest polymethylene in the coal, perhaps mixed with small molecules more representative of the coal's average organic structure.

FIMS Analysis

Molecular weight distributions of coals were obtained at SRI International using the Field Ionization Mass Spectrometry (FIMS) apparatus described by St. John et al. (11). The coal samples were pyrolyzed directly in the FIMS apparatus. The FIMS technique produces little fragmentation of the evolved tars and so provides a good determination of the tar molecular weight distribution. Figures 8 and 9 present the weight loss of six of the eight Argonne coals heated in the FIMS apparatus at 0.05°C/sec.

The spectra show a distinct progression from low to high rank. The highest rank coals, Pocahontas (Fig. 8a) and Upper Freeport (Fig. 8b) both show low intensities at low molecular weights (100 - 200 amu). This suggests few one and two ring clusters. The intensity in the 200 - 600 amu range, however, suggests the presence of three, four and higher ring cluster sizes and dimers and trimers of these. The low yield for the Pocahontas is due to its higher bond energies (525°C tar peak in Fig. 1) and lower number of small ring clusters capable of being volatilized.

The intermediate rank coals, Pittsburgh (Fig. 9a), Utah (Fig. 9b) and Upper Knawha (Fig. 8c) all have similar molecular weight distributions showing substantial intensities in the 100 to 200 amu region indicative of one and two ring clusters as well as in the 200 to 600 amu range.

The low rank coal, Myodak (Fig. 9c) shows high intensity between 100 and 200 amu, but substantially lower intensity above 200 amu. This is typical of the Zap lignite also, and has been explained by extensive cross linking related to carboxyl groups in low rank coals (4).

CONCLUSIONS

1. For most species there is a trend of increasing evolution temperature with increasing rank. However, the variations are small enough that the assumption of rank-insensitive kinetics is a good first approximation for nearly all of the major volatile products.
2. There is a systematic variation in the tar molecular weight distribution with rank. Higher rank coals show greater intensity in the high molecular weight range (200-600 amu), while lower rank coals show greater intensity in the lower molecular weight range (100-200 amu).

ACKNOWLEDGMENTS

This work was supported under DOE Contract DE-AC21086MC23075. Justin L. Beeson is the Project Manager.

REFERENCES

1. Vorres, K.S., ACS Fuel Chem Div. Preprints, **32**(4), 221 (1987).
2. Solomon, P.S., Hamblen, D.G., Deshpande, G.V. and Serio, M.A., 1987 Int. Conf. on Coal Science, p. 601, Maastricht, The Netherlands, (Oct. 26-30, 1987).
3. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A. and Deshpande, G.V., ACS Fuel Div. Preprint, **32**(3), 83 (1987).
4. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A. and Deshpande, G.V., Combustion and Flame, **71**, 137 (1988).
5. Solomon, P.R. and Hamblen, D.G., Prog. Energy Combust. Sci., **9**, 323 (1983).
6. Howard, J.B., Chemistry of Coal Utilization, (M.A. Elliott, Ed.), John Wiley, NY, Chapter 12, p. 665 (1981).
7. Niksa, S., Heyd, L.E., Russel, W.B. and Saville, D.A., 20th Symp. (Int) on Combustion, The Combustion Institute, University of Michigan, Ann Arbor, MI, pp. 1445-1453 (August 12-17, 1984).
8. Gribbins-Matham, J. and Kandigoti, R., ACS Fuel Div. Preprints, **32**(4), 318 (1987).

9. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A. and Deshpande, G.V., "A General Model of Coal Devolatilization", submitted to Energy and Fuel (1987).
10. Carangelo, R.M., Solomon, P.R. and Gerson, D.J., Fuel, 66, 960 (1987).
11. Whelan, J.K., Solomon, P.R., Deshpande, G.V., and Carangelo, R.M., Energy and Fuels, 2, 65, (1988).
12. St. John, G.A., Buttrill, Jr., S.E. and Anbar, M., ACS Symposium Series, 71, 223 (1978).

TABLE 2
 Comparison of Temperatures for Maximum Evolution Rate for Volatile
 Products from Pyrolysis of the Argonne Premium Coals

SPECIES	PEAK #	POCAHONTAS	UPPER FREEPORT	PITTSBURGH	UPPER KNAWAH	UTAH	ILLINOIS	WYODAK	ZAP	AVERAGE
SO ₂	1	-	-	375	375	375	360	360	330	363 ± 20
CO ₂	1	-	435	420	465	465	435	435	420	439 ± 19
CO	1	495	525	-	465	465	450	435	465	470 ± 30
Tar/ Aliphatics	1	525	510	485	485	485	470	465	465	485 ± 22
H ₂ O	1	585	555	510	525	495	525	495	495	525 ± 32
CH ₄	1	570	555	555	555	555	555	555	570	560 ± 7
SO ₂	2	600	615	615	600	615	585	570	600	600 ± 16
CO ₂	2	705	750	705	660	735	735	690	615	700 ± 45
CO	2	780	795	795	765	705	780	795	765	773 ± 30
H ₂ O	2	815	840	795	795	825	765	-	-	807 ± 28

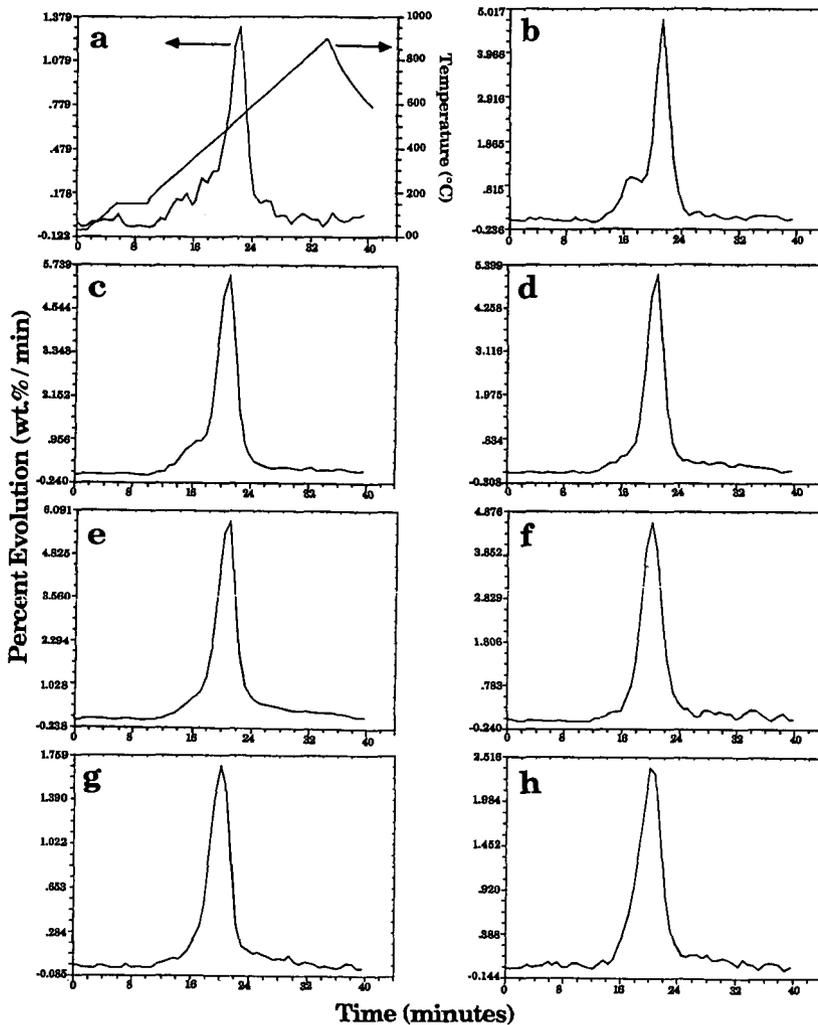


Figure 1. Evolution Rate for Tars/Aliphatic from the Eight Argonne Coals in a TG-FTIR at 0.5°C/s. a) Pocahontas; b) Upper Freeport; c) Pittsburgh; d) Upper Knawha; e) Utah Blind Canyon; f) Illinois No. 6; g) Wyodak; h) Zap.

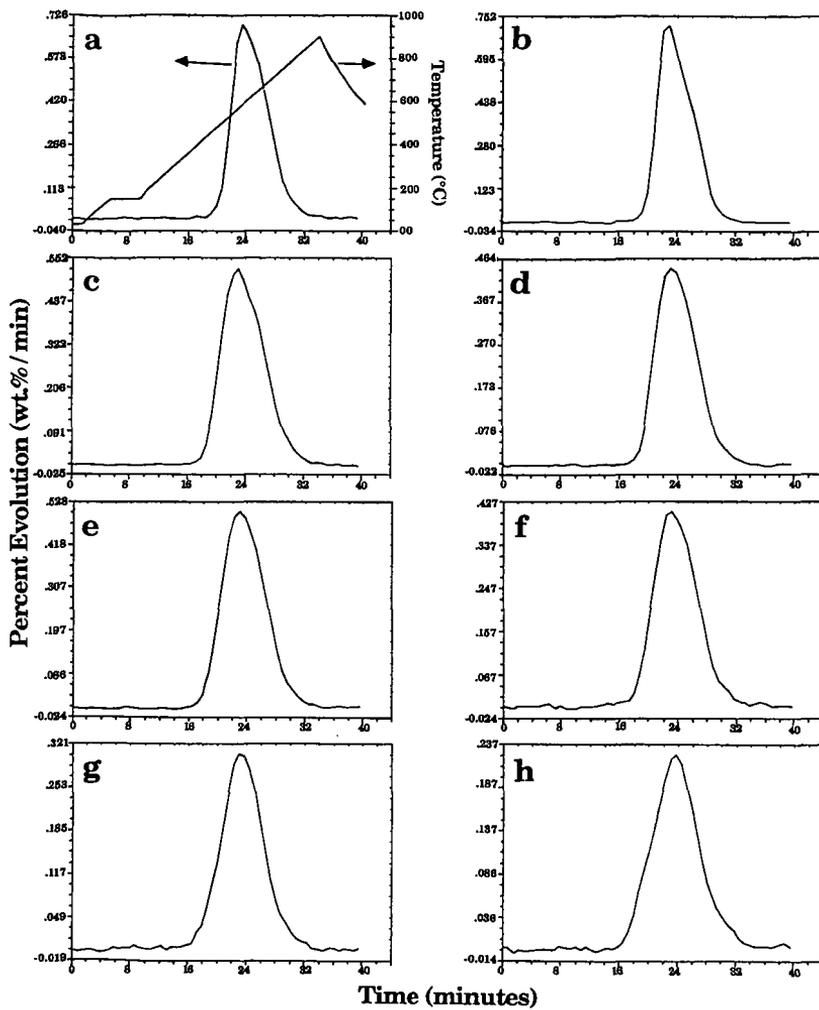


Figure 2. Evolution Rate for CH_4 from the Eight Argonne Coals in a TG-FTIR at 0.5°C/s . a) Pocahontas; b) Upper Freeport; c) Pittsburgh; d) Upper Knawha; e) Utah Blind Canyon; f) Illinois No. 6; g) Wyodak; h) Zap.

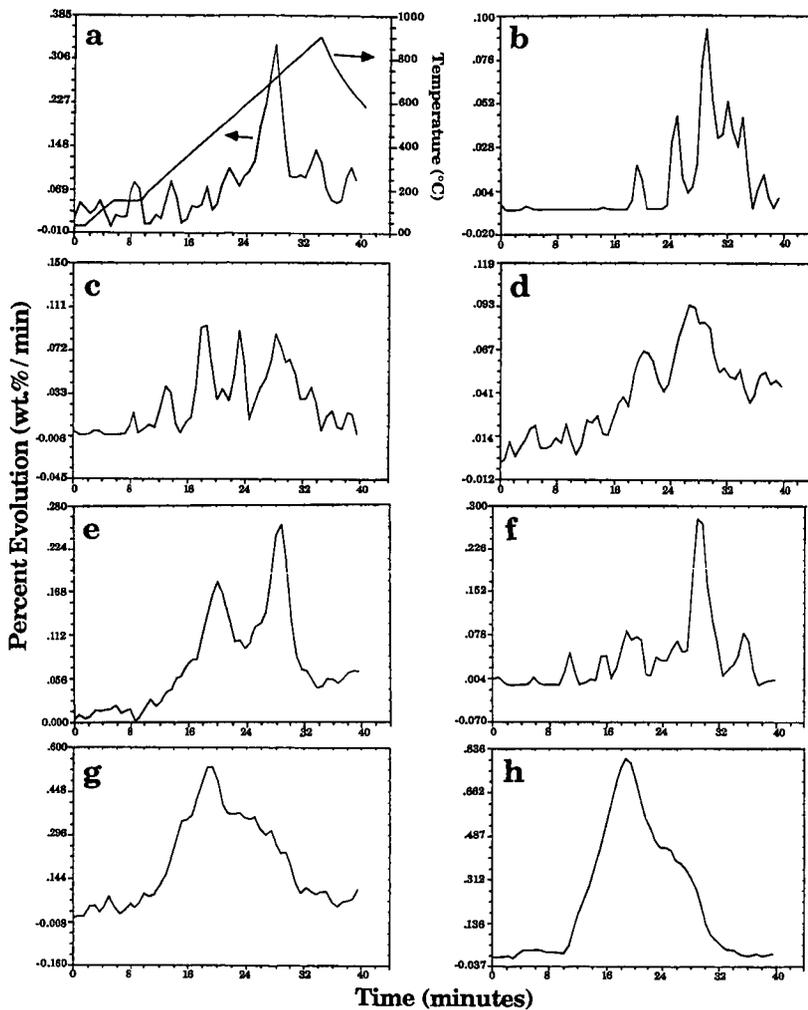


Figure 3. Evolution Rate for CO_2 from the Eight Argonne Coals in a TG-FTIR at 0.5°C/s . a) Pocahontas; b) Upper Freeport; c) Pittsburgh; d) Upper Knawha; e) Utah Blind Canyon; f) Illinois No. 6; g) Wyodak; h) Zap.

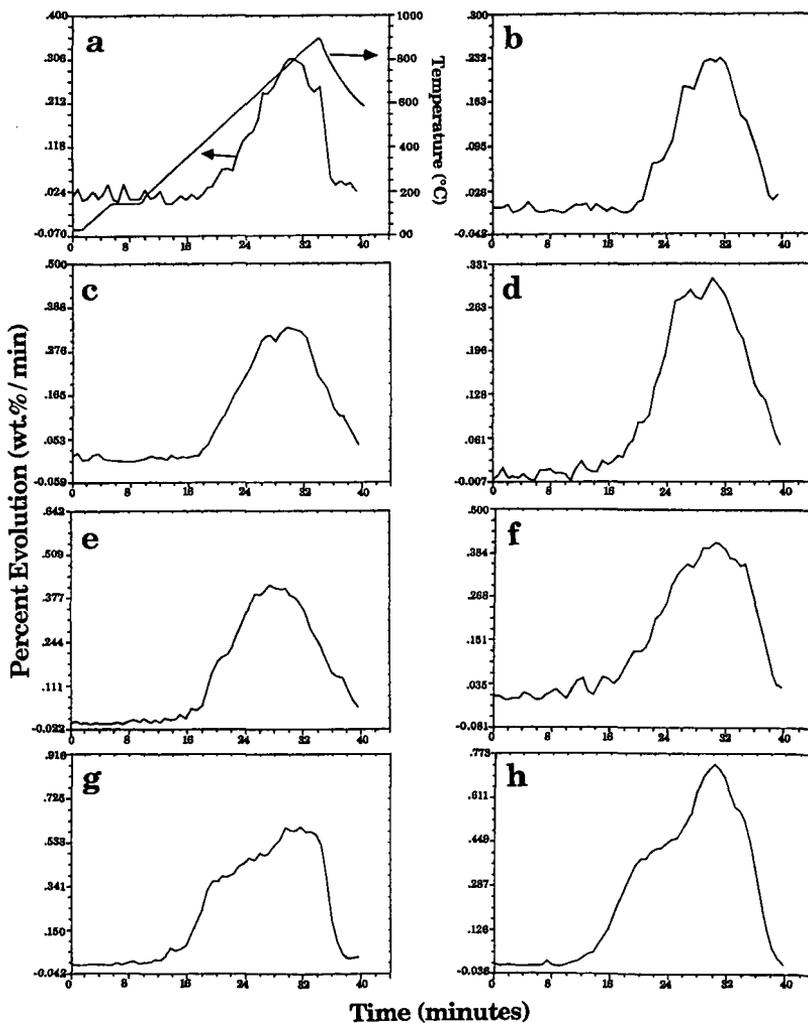


Figure 4. Evolution Rate for CO from the Eight Argonne Coals in a TG-FTIR at 0.5°C/s. a) Pocahontas; b) Upper Freeport; c) Pittsburgh; d) Upper Knawha; e) Utah Blind Canyon; f) Illinois No. 6; g) Wyodak; h) Zap.

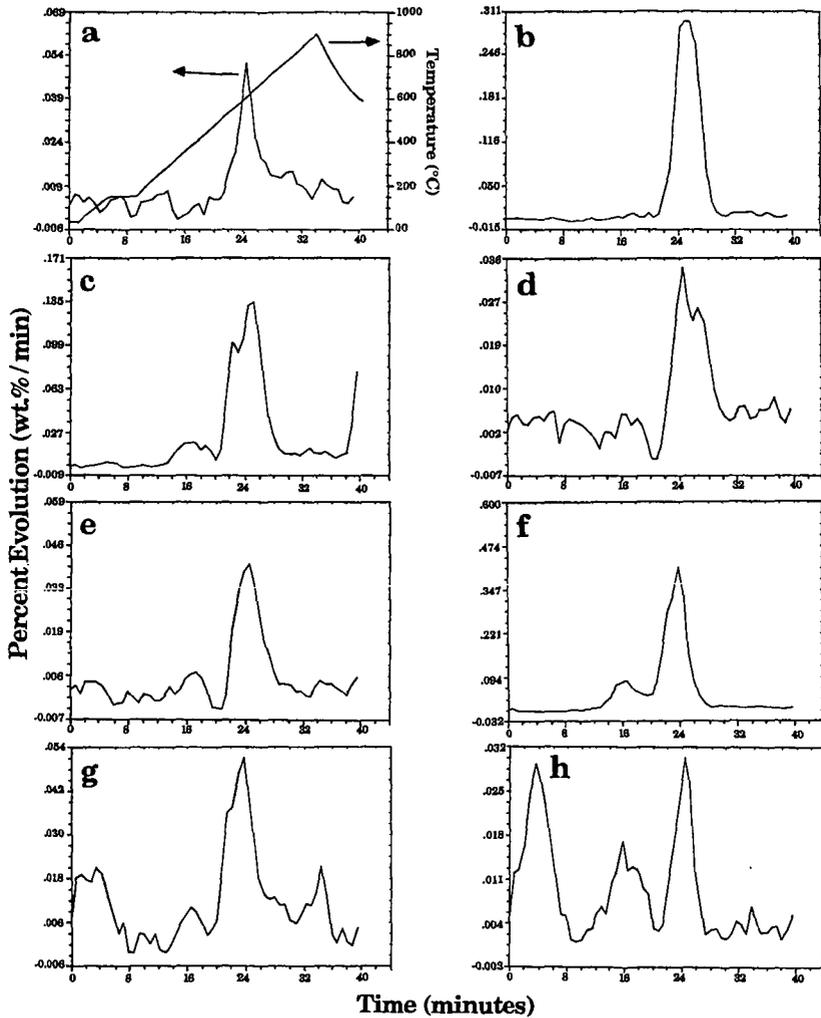


Figure 5. Evolution Rate for SO_2 from the Eight Argonne Coals in a TG-FTIR at 0.5°C/s . a) Pocahontas; b) Upper Freeport; c) Pittsburgh; d) Upper Knawha; e) Utah Blind Canyon; f) Illinois No. 6; g) Wyodak; h) Zap.

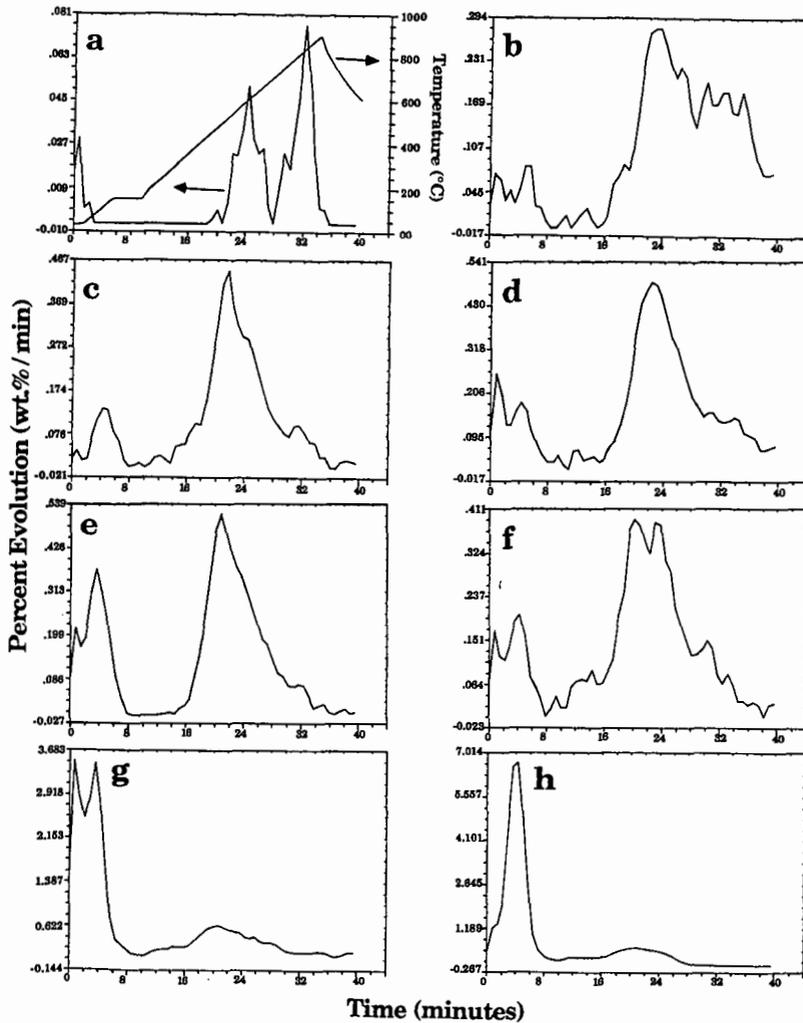


Figure 6. Evolution Rate for H₂O from the Eight Argonne Coals in a TG-FTIR at 0.5°C/s. a) Pocahontas; b) Upper Freeport; c) Pittsburgh; d) Upper Knawha; e) Utah Blind Canyon; f) Illinois No. 6; g) Wyodak; h) Zap.

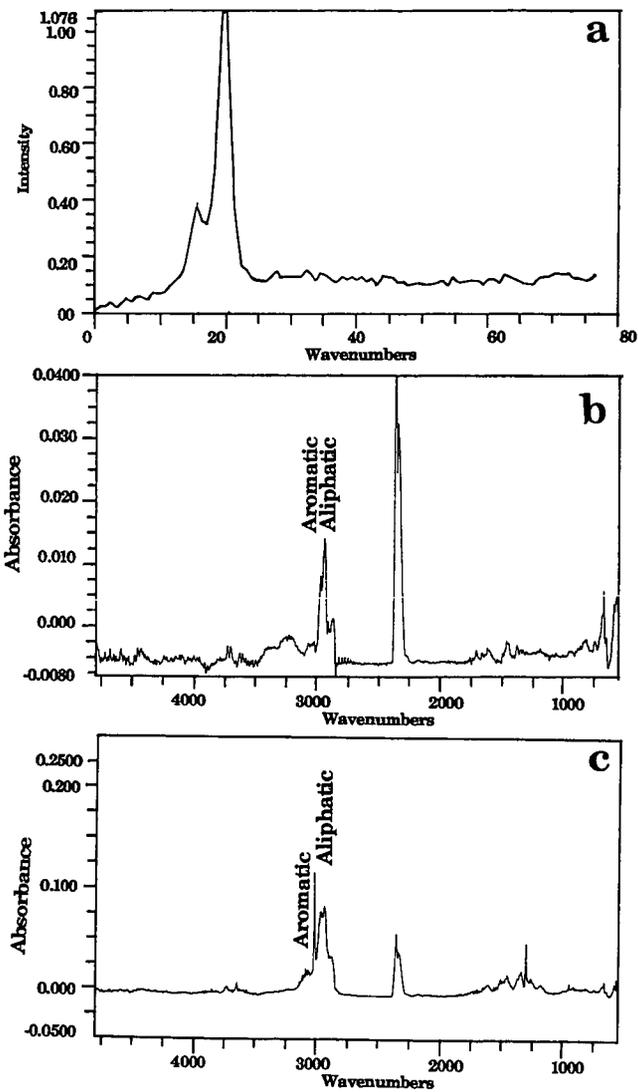


Figure 7. Spectrum of Products Evolved in Pyrolysis. a) Rate for Tar Evolution showing two Peaks, b) Spectrum at First Peak and c) Spectrum at Second Peak.

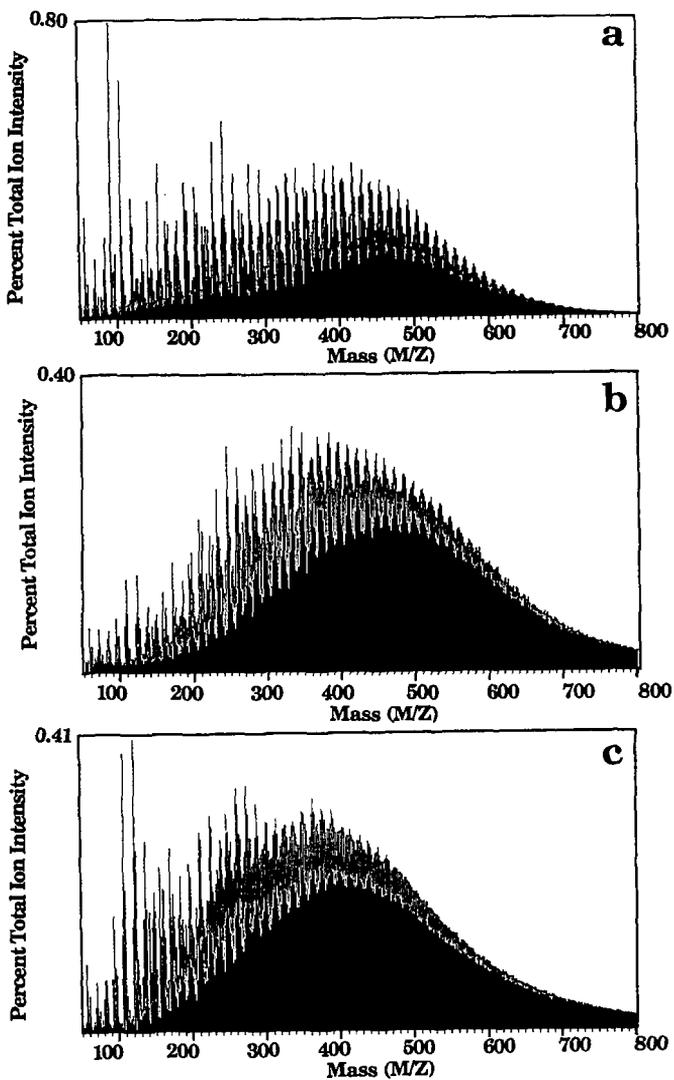


Figure 8. Tar Molecular Weight Distributions for Three Argonne Coals Pyrolyzed in the SRI FIMS Apparatus at 0.05°C/s. a) Pocahontas; b) Upper Freeport; c) Pittsburgh.

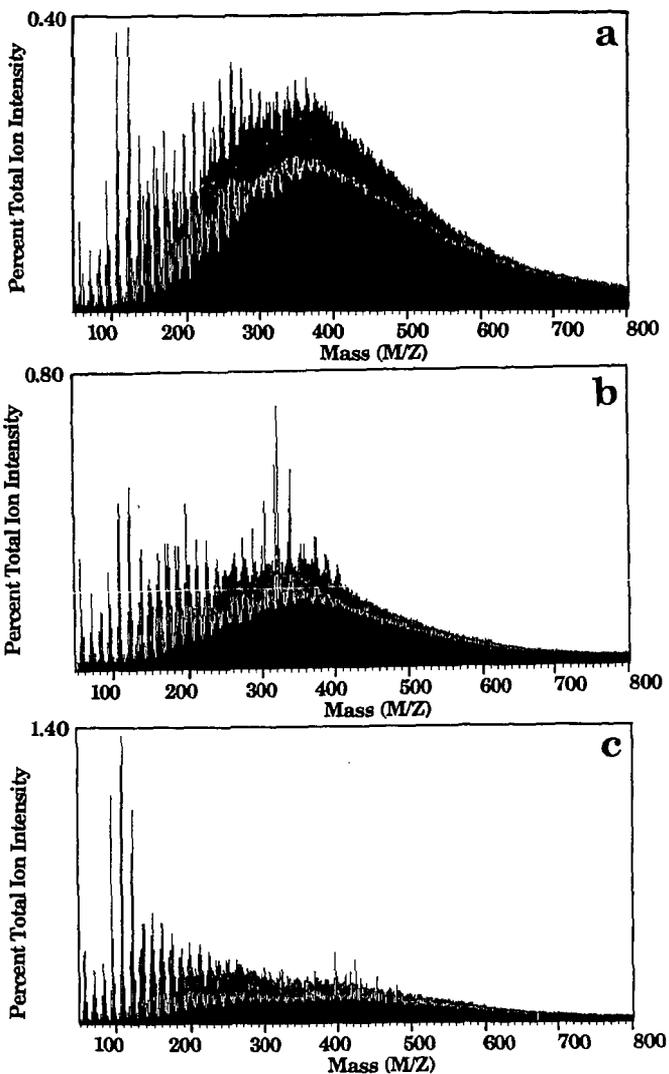


Figure 9. Tar Molecular Weight Distributions for Three Argonne Coals Pyrolyzed in the SRI FIMS Apparatus at 0.05°C/s. a) Upper Knawha; b) Utah Blind Canyon; c) Wyodak.