United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S7-82-027 Sept. 1982

EPA

Project Summary

Rates and Equilibria of Devolatilization and Trace Element Evolution in Coal Pyrolysis

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A laminar flow furnace was used to study the kinetics of devolatilization and evolution of four elements — sulfur, arsenic, lead, and mercury — in the pyrolysis of pulverized coal in nitrogen. The quantities varied in this study included pyrolysis time (170 msec-2 sec), reactor temperature (400-900°C), and parent coals (two low-swelling subbituminous coals and one medium-swelling bituminous coal). Weight losses were estimated using ash as a tracer. A Fisher Sulfur Analyzer was used to analyze the sulfur content of the feed coal and spent char, and atomic absorption spectrophotometry was used to analyze for the remaining three elements.

Weight losses of the coals studied increased significantly with time and temperature and approached different asymptotic values at different temperatures. The devolatilization rates and asymptotic weight losses of the subbituminous coals were lower than those of the bituminous coal. The elements were released in significant quantities during fast pyrolysis as temperature and time increased, with the elemental release from the bituminous coal proceeding more rapidly and to a greater extent than that from the lower rank coals. The emissions of arsenic and lead in subbituminous coal and lead in bituminous coal were found to be proportional to the total volatile matter release, and the emissions of mercury and arsenic in bituminous coal were found to be proportionally greater than the total volatile matter release. The amount of sulfur released was found to be proportional to the amount of dry-ash-free volatile matter released for both coals.

Five kinetic models for devolatilization were tested. Of these, a two-parallel-reaction model due to Kobayashi provided the best correlation of the experimental data for the subbituminous coal, and a distributed activation energy model due to Anthony was found best for the bituminous coal. A single first-order reaction model for elemental release coupled with a model for equilibrium release derived from batch pyrolysis experiments was used to correlate elemental release data.

This Project Summary was developed by EPA's Industrial Environmental Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Coal represents about 70 percent of the recoverable fossil fuel resources in the U.S., and may eventually become our

principal source of hydrocarbon fuel and chemical feedstocks. National recognition of the enormous immediate and long-range potential of coal has resulted in substantial efforts directed toward the development of an economically and environmentally viable coal utilization technology.

Coal conversion to clean gaseous and liquid products is especially attractive for alleviating the growing restrictions on existing consumption patterns. The main approaches to the conversion of coal to gaseous fuels are steam-oxidant gasification, hydrocarbonization, and pyrolysis (devolatilization). In all three processes, pyrolysis plays an important role. When coal is heated in any atmosphere, it releases volatile products. In most coal conversion processes coal is pulverized and subjected to rapid heating which causes a significant rate of devolatilization. The amount of volatile matter produced depends mainly on the type of coal, the temperature of the surrounding gas, the heating rate, the reacting pressure, and the size of the coal particles.

The effluent gases from a coal conversion system contain elements in minor or trace amounts which are toxic to humans, animals, and plants, or cause severe corrosion in coal-fired boilers and gas turbines. These elements may exist as vapor and/or in association with particles in the effluent gases. Studies have been published on the occurrence and distribution of trace elements in different coals and in effluents from coal-fired steam plants and coal gasification plants. The data obtained in these studies provide a good qualitative picture of the pathways of trace and minor element constituents in coal gasification; however, they do not provide the detailed information on reactor conditions needed to predict the thermodynamics and kinetics of the release of these elements.

To estimate the types and quantities of hazardous emissions released in the pyrolysis stage of steam/oxygen gasification or hydrogasification, it is necessary to measure and model the rates and equilibria of both devolatilization and evolution of specific species. In this study, a laminar-flow furnace reactor was used to determine devolatilization and trace element release equilibria for rapid pyrolysis at temperatures up to 900°C. Several existing devolatilization models were fit to the data by nonlinear regression, and the results were used to evaluate and compare the models. In addition, trace element evolution data were fit with a first-order rate law, and the results were used to draw inferences regarding the volatilities of these elements.

Experimental

Preparation of Coal Samples

Experiments were performed on two coals: North Barber No. 8 seam HVC subbituminous coal, Navajo Mine New Mexico (NB8); and Western Kentucky No. 11 HVB bituminous coal (WK11). Table 1 summarizes data on these coals.

Coal samples were crushed in a Bico pulverizer with ceramic plates and in a small porcelain ball mill. The pulverized coal was then size-graded with U.S. standard sieves and a mechanical shaker; the 325-400 mesh size fractions of NB8 and WK11 coals were retained for use in the experiments.

Experimental Equipment

A laminar-flow furnace reactor used by Agreda (1979) was also used in this study. It was designed to:

- Feed coal particles into a reaction zone of known length (residence time).
- Raise the temperature of the coal particles as rapidly as possible (i.e., at a rate greater than 10^4 °C/sec) to the predetermined pyrolysis temperature.
- Quench all the pyrolysis reactions as rapidly as possible following collection to prevent conversion through secondary reactions.
- Separate solid (i.e., char) from gaseous (i.e., volatile matter plus carrier gas) products and prevent volatile matter from depositing on the surface of the solid.

The furnace is made of alumina; it has an ID of 8 cm and is 1 m long. The liner is an alumina tube, 7 cm ID and 0.75 m long. Heat is supplied by a three-zone, 4000-W, 230-V Thermocraft furnace, with a heated length of 47 cm.

In operation, a small carrier flow of cold nitrogen carries the size-graded, finely ground coal from the feeder-hopper into a preheated nitrogen stream passing down through the vertical furnace tube in laminar flow. The furnace tube is held at the same temperature as the preheated main gas. The small carrier gas flow mixes rapidly with the hot gas stream, allowing the particles to be brought rapidly to furnace temperature.

Coal particles travel in a narrow laminar flow streamline along the axis of the furnace and are aspirated into a water-cooled collector. The collector's tapered entry accelerates the aspirated gases to a high-velocity turbulent flow. The consequently high heat transfer rates between the gas and collector wall lead to rapid cooling of the gas and quenching of the devolatilization reactions. Residence time can be varied from 50 to 2000 msec by adjusting the distance between the feeder and the collector and/or adjusting the main gas flow rate. The temperature of the furnace and gas stream can be adjusted up to 1000°C. The pressure of the furnace can be adjusted from atmospheric to 0.4 atm (gauge).

A water-jacketed stainless steel collector is used to collect the char particles following pyrolysis. A thermostated reservoir (90-100°C) supplies cooling water to the collectors. The hot water cooling system prevents tars from condensing on the chars, which would seriously affect the precision of weight

Table 1. *Coal Characterization Data*

Coal Characterization				Proximate Analysis			
Coal	Code	Rank	FSI	Moisture	Ash	Volatile	Fixed
NM No. 8	NB8	HVC	0.5	10.09	18.32	33.80	37.79
W.K. No. 11	WK11	HVB	2.5	6.34	15.02	34.67	43.97

	Ultimate Analysis (%)				Sulfur Forms (%)		
	C	N	H	S	Pyritic	Sulfatic	Organic
NM No. 8	55.18	1.21	4.12	0.73	0.31	0.0	0.42
W.K. No. 11	60.07	1.775	4.28	4.64	2.63	0.14	1.87

loss estimates. An electromagnetic vibrator is used at the bottom of the collector to prevent char particles from sticking to the collector walls.

Experiments and Results

Two coals were pyrolyzed in the laminar flow reactor (see Table 1): North Barber No. 8 (NB8, low-swelling New Mexico subbituminous coal) and Western Kentucky No. 11 (WK11, medium-swelling bituminous coal). A total of 47 runs were carried out, the first 28 of which were with NB8 coal at 500-900°C.

To calculate weight losses, ash was used as a tie element between the feed coal and spent char, with a correction applied to account for ash losses. The weight losses are shown in Figures 1 and 2 for NB8 and WK11 coals, respectively, NB8 (low-swelling coal) exhibited a much lower devolatilization rate than WK11 (medium-swelling coal) at a given temperature. At higher temperatures, equilibrium was achieved within tens of milliseconds for WK11 coal; NB8 coal required hundreds of milliseconds.

Modeling

Experimental weight loss data obtained for NB8 and WK11 coals and data for Montana Rosebud subbituminous coal obtained by Agreda et al. (1979) were correlated with five models: a single first-order reaction model (both isothermal and nonisothermal reactor operation being considered separately), Badzioch and Hawksley's (1970) isothermal model, Kobayashi's (1976) nonisothermal two-reaction model, and Anthony's (1974, 1975, 1976) nonisothermal infinite parallel reactions model. For the last three models, the parameters proposed by the model developers were first used; then, for all models, the parameters were adjusted to obtain least-squares fits to the data. In the latter calculations, an initial set of model parameters was chosen, weight losses were evaluated at a series of times and temperatures corresponding to experimental data points, and the unweighted sum of squares of residuals

$$SSE = [V^*_{exp} - V^*_{model}]^2 \qquad (1)$$

was calculated. Then the model parameters were systematically varied to determine the set that minimized SSE. For the isothermal first-order model, the parameters were estimated by logarithmic transformation followed by linear regression; for the others, either a Gauss-Marquardt nonlinear regression or Pattern Search algorithm was used, depending on whether or not derivatives of the expression for V* with respect to the model parameters could be determined analytically.

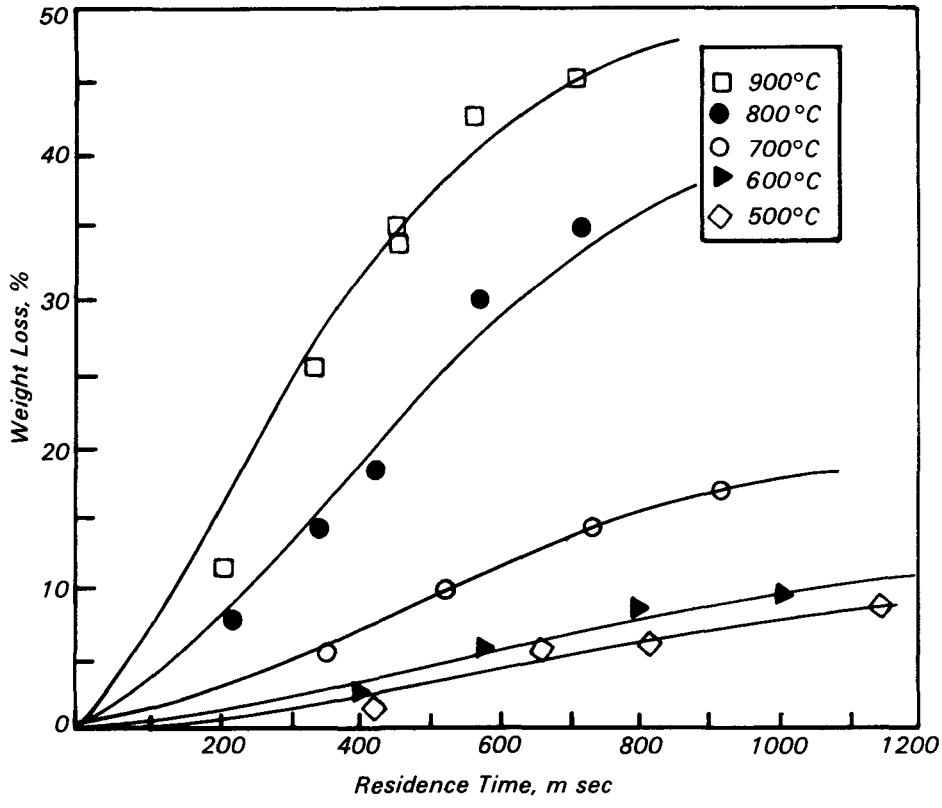

Figure 1. Dry ash-free weight loss for NB8 coal.

Equilibrium Devolatilization

An important parameter of the models is the equilibrium or asymptotic weight loss at the reaction temperature. This quantity can be obtained either from batch pyrolysis data or from long residence time data in the laminar flow reactor. Duhne (1977) has shown that asymptotic equilibrium values for physical and chemical processes can be estimated from an equation of the form

$$V^* = \frac{d}{t_R} + V_f^*, \; V^* > 0.67 V_f^* \qquad (2)$$

where V* is the weight loss on a dry ash-free (d.a.f.) basis, V_f^* is the long-time asymptotic limit of this quantity, t_R is the residence time, and d = a constant. V*, plotted versus $1/t_R$, should approach a straight line at low values of the abscissa with the intercept equal to V_f^*.

Plots of this type were generated for Montana Rosebud (MRS) (Agreda et al., 1979) and WK11 coals. The resulting values of V_f^* are listed in Table 2, along with batch pyrolysis equilibrium values obtained by Agreda et al. (1979). NB8 coal did not come close enough to equilibrium in the LFR experiments for the given procedure to be used. The batch values shown in Table 2 were used for all kinetic modeling for this coal.

The fact that the asymptotic and equilibrium weight loss estimates shown in Table 2 differ is not surprising. In the case of the MRS coal, the equilibrium values appear to be higher than the asymptotic values. This result is consistent with the finding of Horton (1979), who reviewed the fast pyrolysis data of several researchers and noted that a quasi-equilibrium is reached before the particles are quenched, but that additional devolatilization occurs when the quenched char particles are reheated in a batch reactor.

With WK11 coal, the equilibrium values stay higher than the asymptotic values at temperatures below 700°C. This can be explained by the caking characteristics of this coal. Caking coals

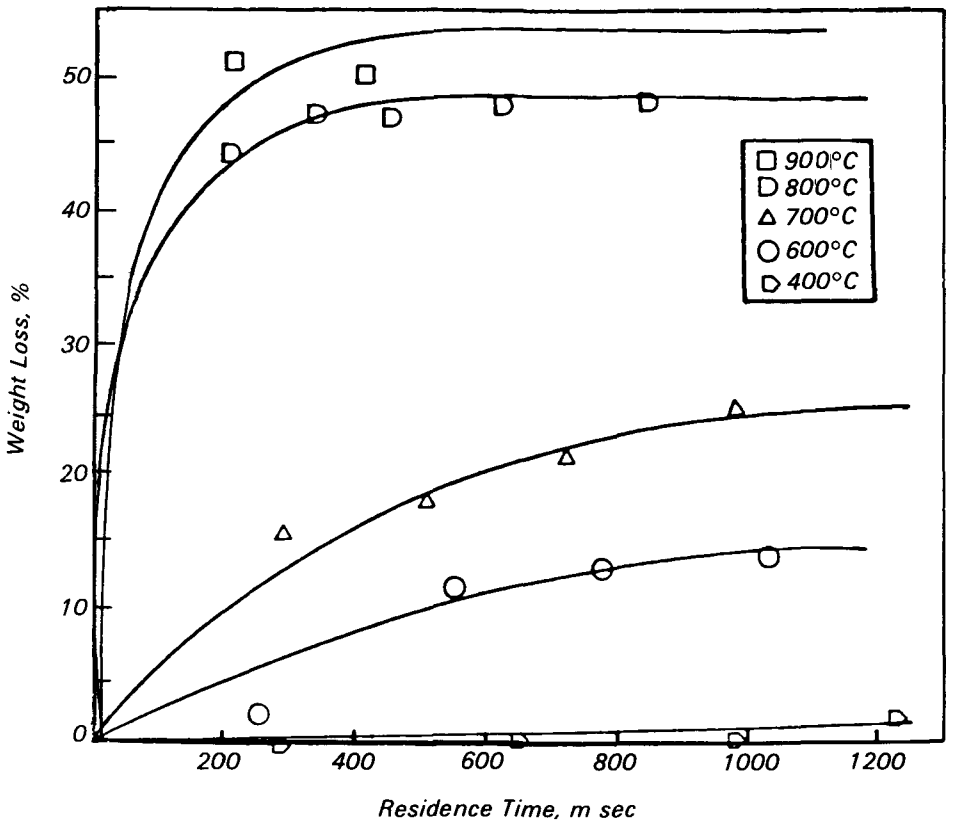

Figure 2. Dry ash-free weight loss for WK11 coal.

often devolatilize with the formation of bubbles and then resolidify during batch pyrolysis, while in fast pyrolysis the structure of the coal particles is deformed as the volatile matter is removed. Therefore, after caking (about 700°C), the fast pyrolysis asymptotic weight losses should be higher than the batch pyrolysis equilibrium values.

The values of V_f^* determined above (from the LFR measurements for MRS and WK11 and from batch measurements for NB8) were fitted versus T with a fourth-order polynomial:

$$V_f^*/100 = B_0 + B_1T' + B_2T'^2 + B_3T'^3 + B_4T'^4 \quad (3)$$

where T' = T(°C)/100. The coefficients of this polynomial for the three coals are shown in Table 3.

Devolatilization Rate Models

The devolatilization rate data collected for all three coals studied were fitted with the five cited models. Some of the models presume a fixed (temperature-independent) equilibrium volatiles yield. Fits were obtained for these models, both with and without this assumption; for the latter, equilibrium yields (determined as described above) were substituted. For isothermal models, the reactor temperature was assumed constant but the residence time was corrected to account for the time required to heat the particles following their entry into the reactor. For nonisothermal models, the true temperature-time history of the particles in the reactor was substituted into the model equations. For the Badzioch-Hawksley, Kobayashi, and Anthony models, the fits obtained by regression were compared with the fits provided by the model parameters suggested by the proponents.

The following cases were examined:

- Single first-order reaction — isothermal, fitted parameters.
- Single first-order reaction — nonisothermal, fitted parameters.
- Badzioch-Hawksley model — isothermal, variable equilibrium yield, fitted and original parameters.
- Kobayashi model — nonisothermal, fixed and variable equilibrium yield, original and fitted parameters.
- Anthony model — nonisothermal, fixed and variable equilibrium yield, original and fitted parameters.

Complete descriptions of the models and the modeling procedures used, and tabulations and plots of the results, are given in the full report. The paragraphs that follow discuss the principal findings and summarize the conclusions.

Comparative listings of the model parameters (both original and fitted) and the sum of squares of residuals for all five models and all three coals are given in Tables 4-6. As indicated by the smaller values of SSE, the fitted isothermal models (single first-order reaction model and Badzioch-Hawksley model) provide reasonable correlations of the experimental data. However, the arbitrary specification of an isothermal reaction time limits the flexibility required to describe nonisothermal pyrolysis in any reactor, and leads to anomalously low activation energies. Therefore, these two models were eliminated from further consideration.

The results obtained for the models of Anthony (1974) and Kobayashi (1976) are best understood in light of the differences between these two models:

- Anthony postulates an infinite number of parallel first-order reactions, with a common frequency factor for all rate laws and a Gaussian distribution of activation energies. Kobayashi postulates two parallel first-order reactions, with different stoichiometric extents, frequency factors, and activation energies for each reaction.
- Anthony's model has three adjustable parameters: the frequency factor and the mean and standard deviation of the Gaussian distribution of activation energies. However, indications are that the model is relatively insensitive to the value of the frequency factor, so that this parameter may be set to an arbitrary value, and the fitting performed by adjusting only two variables. Kobayashi's model has six adjustable parameters: two stoichiometric extents, two frequency factors, and two activation energies.
- The data on which Anthony's model was based were obtained in an electrically heated wire grid reactor; experiments by Suuberg et al (1978) that appeared to confirm the validity of the model were

Table 2. *Equilibrium and Asymptotic D.A.F. Weight Losses for WK11 and MRS Coals*

Coal	Temperature, °C	Asymptotic(O) Equilibrium(X)	Weight Loss, % V_t
WK11	400	0	2.94
		X	12.94
WK11	600	0	17.65
		X	38.76
WK11	800	0	49.90
		X	44.67
WK11	900	0	52.90
		X	46.50
MRS	300	0	0.85
		X	3.27
MRS	400	0	6.76
		X	11.63
MRS	600	0	13.44
		X	33.42
MRS	800	0	37.40
		X	41.73
MRS	900	0	39.27
		X	46.85
NB8	300	X	3.27
NB8	400	X	11.63
NB8	600	X	33.42
NB8	800	X	41.73
NB8	900	X	44.23

Table 3. *Coefficients of the Fourth-Order Polynomial for Asymptotic Weight Loss*

Coal	B_0	B_1	B_2	B_3	B_4
MRS	-1.783	1.1411	-0.2590	0.02479	-0.0008233
WK11	-4.291	2.691	-0.5927	0.05477	-0.001775
NB8	1.052	-0.7150	0.1615	-0.01367	0.0004044

performed on the same type of apparatus. The difficulties associated with this approach are uncertainty of heating time, inability to quench the pyrolysis rapidly, and resolidification of volatile matter during cooling. On the other hand, Kobayashi's experiments were performed in a laminar flow reactor, similar to the one used in the present study. Numerous problems arise in experiments of this type, such as ash loss errors and tar recondensation on the collected char. The principal advantages offered by the LFR are precise control over residence time and extremely low heating and quench times compared to those characteristic of the heated grid.

A comparison of the predictions of both models is shown in Figure 3. A coal with the properties of Montana Rosebud subbituminous is used as the basis of comparison. Devolatilization curves predicted by both models are shown for 600°C, corresponding to a relatively low pyrolysis temperature, and 800°C, a moderate-to-high temperature. The model parameters are those suggested by Anthony (1974) and Kobayashi (1976). The predictions of the two models are seen to be quite different: Anthony's model predicts that equilibrium is reached in a few hundred milliseconds, while Kobayashi's model predicts an increasing trend even at long residence times. At all temperatures, Anthony's model predictions are consistently above Kobayashi's model predictions.

The observed differences are consistent with the previous observations regarding the two models. Anthony let his coal samples remain in the heated grid reactor for a few seconds after the heater was turned off. Therefore, his weight loss values should reach equilibrium during this period of time and stay higher than those of Kobayashi.

Results obtained for the parameters determined by fitting Anthony's model to our data have been compared with results based on Anthony's original model parameters. The fitted parameters for the medium-swelling high rank coal (WK11) are close to Anthony's values, although the spread of the fitted activation energy distribution is narrower than Anthony's. On the other hand, contradicting Anthony's prediction, the fitted parameters for NB8 and MRS coals suggest that a single reaction with a low activation energy dominates the decomposition of low-swelling low-rank coals. However, this result does not eliminate the possibility that the pyrolysis may be better described as a finite set of decomposition reactions with different activation energies.

Kobayashi's model has this possibility. However, for this model as well, the values of the fitted parameters for all three coals imply that a low activation energy first-order reaction dominates the overall pyrolysis between 400 and 900°C. The rate constants for the first reaction (K_1) at 900°C obtained from the parameters in Tables 4-6 are one to two orders of magnitude greater than those for the second reaction (K_2), with the disparity increasing as the temperature decreases and the coal rank increases. Thus, adding a second reaction with a high activation energy makes little difference for a medium-swelling high-rank coal like WK11 and essentially no difference for low-swelling low-rank coals like MRS and NB8.

The conclusion is that at below 1000°C, pyrolysis of MRS and NB8 coals (and presumably of other low-swelling low-rank coals) is well described by a single first-order decomposition rate law; replacing this law by a discrete set of reactions with higher activation energies does not improve the fit significantly, and replacing it with a continuous distribution of high activation energies makes the fit worse. This conclusion basically supports the findings of Kobayashi and is inconsistent with those of Anthony and Suuberg. On the other hand, Anthony's model is quite consistent with our results for the pyrolysis of a medium-swelling high-rank coal, although the standard deviation of our activation energy distribution

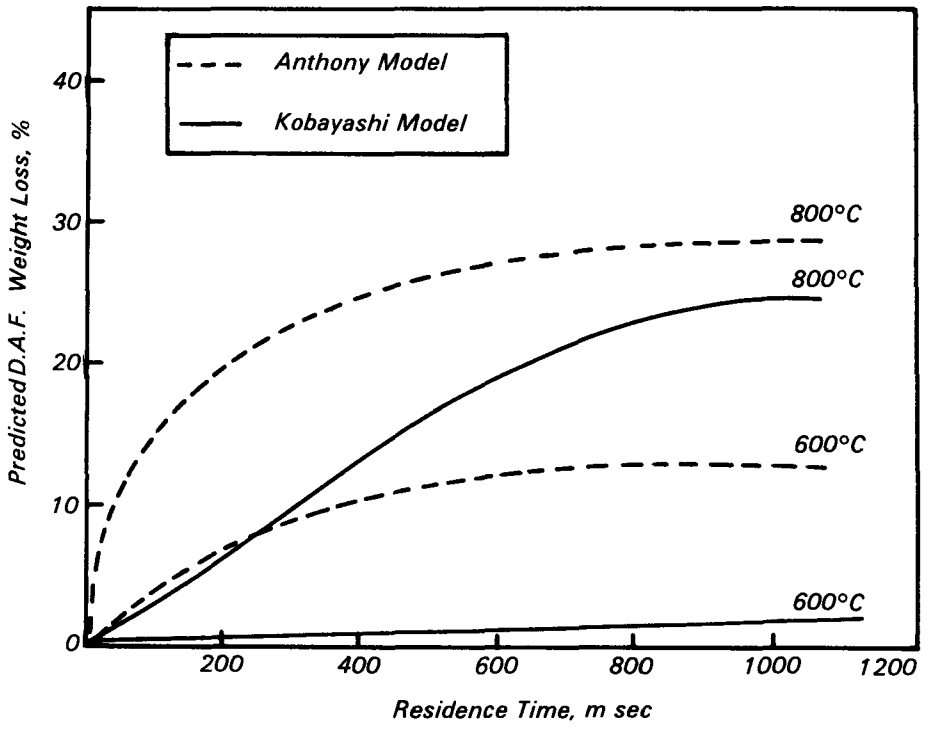

Figure 3. Comparison of Anthony and Kobayashi model predictions.

is substantially lower than that found by Anthony.

We are aware of the fact that the evidence obtained by Suuberg et al. (1978) on coal pyrolysis product distributions supports the notion that devolatilization is governed by a set of reactions with varying activation energies. We are currently modifying our laminar-flow reactor to permit measurement of gas product compositions, and so to determine whether this too is a reflection of the difference between the heated grid and the laminar-flow reactor types. For now, the contradiction must remain unresolved.

Elemental Release

Among the potentially hazardous trace and minor elements in coals, sulfur is present in the greatest amount, and mercury, arsenic, and lead are perhaps the most volatile (Agreda, 1979). These elements were therefore selected as the subjects of this study.

Experiments and Results

Proximate, ultimate, and trace/minor element analyses were carried out on the coals and chars produced. The trace element determinations were performed by atomic absorption spectrophotometry. Every effort was made to ensure the accuracy and precision of the analyses and to eliminate any bias in the data due to instrument drift or analysis bias. Certified standards were run concurrently with the samples for almost every analyte. If the analysis of the standard did agree with the certified value, the entire lot of analyses was discarded and new analyses made.

The weight loss data discussed in the preceding section were used in the following equations to calculate the fractional retention of elements in chars. Figures 4-7 show the fractional retention of the elements as functions of residence time and temperature. The solid lines in Figures 4 and 5 are model predictions to be discussed later. The trends are clear for the four elements except in the case of mercury in NB8 coal. These figures clearly show that the kinetics of elemental release differ considerably from the low-swelling subbituminous coal to the medium-swelling bituminous coal, with the release in the latter coal being more rapid and proceeding to a greater extent. This is not unexpected since the devolatilization rates and perhaps the mechanisms are quite different. The devolatilization of high- or medium-swelling coals (caking coals) is often accompanied by deformation of the coal structure and the formation of a highly porous char containing entrapped bubbles. It is likely that trace and minor elements leave the char particles in significant quantities during the deformation and resolidification of the char particles. The element retentions greater than 100% observed in Figure 4 are physically impossible and suggest that errors remain in the weight loss estimates after correcting for ash loss.

Correlations and Modeling

As a first step toward the modeling of elemental release, the retention and loss values for all four elements were linearly regressed with time and temperature. The null hypotheses that the slopes with respect to time and temperature equal zero were tested statistically. The detailed results are given by Kau (1980). Inferences about element volatilities drawn from these results include:

- The emissions of arsenic and lead in NB8 coal and lead in WK11 coal are proportional to the total volatile matter release from 400 to 900°C.
- The emissions of sulfur, mercury and arsenic in WK11 coal and sulfur in NB8 coal are proportionally greater than the total volatile matter release from 400 to 900°C.
- The emissions of all four elements in both coals increase as temperature increases from 400 to 900°C except for mercury in NB8 coal, for which the scatter was too great for a trend to be observed.
- The elemental release of mercury in NB8 coal and arsenic and mercury in WK11 coal increase as the residence time increases from 170 to 1200 msec. The results indicate that temperature appears to be more important than residence time in determining the extent of elemental release during pyrolysis of the coals studied from 400 to 900°C and at residence times from 170 to 1200 msec.

Despite the scatter in the data and the uncertainties in the sampling, analysis, and calculation of process parameters, efforts have been made to model elemental release in coals during fast pyrolysis. Agreda et al. (1979) proposed a first-order release model coupled with equilibrium release parameters determined in batch pyrolysis studies to correlate the results from LFR experi-

Table 4. *Comparison of Model Parameters and SSE Values (MRS)*

Model	Isothermal Yes	Isothermal No	Equivalent Yield Fixed	Equivalent Yield Variable	Parameters Fixed	Parameters Fitted	Parameter Values	SSE
Single First-Order	X			X		X	B_0 = 93.5(l/sec) E_0 = 8.7(kcal/mole)	413
		X		X		X	B_0 = 7677(l/sec) E_0 = 18(kcal/mole)	242
Badzioch and Hawksley	X			X	X		K_1 = 0.001031 K_2 = 589 Q = 1.8 A = 8.36 × 10^4(l/sec) B = 8.9(kcal/mole)	2184
	X			X		X	K_1 = 0.001031 K_2 = 589 Q = 1.8 A = 906(l/sec) P = 6 37(kcal/mole)	194
Kobayashi		X	X		X		a_2 = 1.0 B_1 = 2 × 10^5(l/sec) B_2 = 1.3 × 10^7(l/sec) E_1 = 25(kcal/mole) E_2 = 40(kcal/mole)	270
		X		X		X	a_2 = 1.0 B_1 = 6030(l/sec) E_1 = 18(kcal/mole) B_2 = 6.6 × 10^6(l/sec) E_2 = 40(kcal/mole)	590 230
Anthony		X	X		X		K_O = 1.0 × 10^{10}(l/sec) V* = 47% E_O = 48.7(kcal/mole) s = 9.36(kcal/mole)	1079
		X		X	X		K_O = 1.0 × 10^{13}(l/sec) E_O = 48.7(kcal/mole) s = 9.36(kcal/mole)	588
		X		X		X	K_O = 1.0 × 10^{13}(l/sec) E_O = 18.9(kcal/mole) s = 1.0 × 10^{-3}(kcal/mole)	227

ments. The solid lines shown in Figures 4 and 5 are the predictions of this model. No fitting was done for the other elements in NB8 coal or for any elements in WK11 coal because of the high degree of scatter of the data. Details of the calculations and results are given in the full report.

Conclusions

- Several models can be used to fit most of the devolatilization rate data obtained in this study with more or less equivalent degrees of success; in fact, a model consisting of a single first-order decomposition reaction is as good as any of the more complex models for the two low-rank coals studied and not too much worse than the best of the models for the bituminous coal. Moreover, the single reaction model parameter values for both low-rank coals are quite similar: the pre-exponential factor is roughly 7750(s^{-1}), and the corresponding activation energy is 18 kcal/mole.
- All fitting studies support the notion that the kinetics of low-rank coal pyrolysis are dominated by a single first-order reaction with a low activation energy. This contradicts the findings of Anthony (1974) and Suuberg et al. (1978), whose results support the conclusion that pyrolysis is in reality a series of parallel reactions with activation energies distributed over a much higher range. On the other hand, the data obtained in this study for the bituminous coal are quite consistent with Anthony's picture, albeit the spread of the activation energy distribution is narrower than that proposed by Anthony.
- Kobayashi's model with its original parameters does a reasonable job of representing the pyrolysis of the two low-rank coals studied. Improvements can be made by ad-

Table 5. *Comparison of Model Parameters and SSE Values (NB8)*[a]

Model	Isothermal Yes	Isothermal No	Equivalent Yield Fixed	Equivalent Yield Variable	Parameters Fixed	Parameters Fitted	Parameter Values	SSE
Single First-Order	X			X		X	B_0 = 353 (l/sec) E_0 = 11.3 (kcal/mole)	397
		X		X		X	B_0 = 7853(l/sec) E_0 = 18 (kcal/mole)	154
Badzioch and Hawksley	X			X	X		$K_1 = 2.55 \times 10^{-3}$ K_2 = 471 Q = 1.2 A = 8.36×10^4 (l/sec) B = 8.9(kcal/mole)	11281
	X			X		X	$K_1 = 2.55 \times 10^{-3}$ K_2 = 471 Q = 1.2 A = 4335 (l/sec) B = 84. (kcal/mole)	134
Kobayashi			X			X	a_2 = 1.0 $B_1 = 2.0 \times 10^5$ (l/sec) E_1 = 25 (kcal/mole)	722
		X						
				X	X		$B_2 = 1.3 \times 10^7$ (l/sec) E_2 = 40 (kcal/mole)	679
		X		X		X	a_2 = 1.0 B_1 = 7530 (l/sec) E_1 = 18 (kcal/mole) $B_2 = 1.44 \times 10^6$ (l/sec) E_2 = 40(kcal/mole)	160
Anthony		X	X			X	$K_0 = 1.0 \times 10^{10}$(l/sec) V_1*= 49% E_0 = 49.38 (kcal/mole) s = 0.36 (kcal/mole)	1341
		X		X	X		K_0 = 1.0 × 10 (l/sec) E_0 = 48.7 (kcal/mole) s = 9.36 (kcal/mole)	953
		X		X		X	$K_0 = 1.0 \times 10^{13}$ (l/sec) E_0 = 18.9 (kcal/mole) s = 0.16 (kcal/mole)	246

[a]*Batch equilibrium yields used for V_1**

justing the parameter values, but not to the extent that the original values are discredited. Anthony's model appears to be superior for describing the pyrolysis of high-rank coals.

- Anthony's model with its original parameters fails to fit the data for any of the coals studied. Considerable improvements are obtained for bituminous coal by allowing the asymptotic weight loss to vary with temperature, and decreasing the standard deviation of the activation energy distribution. However, for low-rank coals, the model is consistently outperformed by a single first-order decomposition reaction model with a low activation energy.
- The contradiction between the results obtained here for low-rank coals and those of Anthony (1974) and Suuberg, et al. (1978) has not yet been resolved, although it may be attributable to the difference between the operating characteristics of laminar flow reactors (such as those used in this study and by Kobayashi) of electrically heated grid reactors (such as those used by Anthony and Suuberg).
- Sulfur, mercury, lead, and arsenic are released in significant quantities during fast pyrolysis; the release is completed in tenths of seconds. The release of these elements from low-swelling coal is quite different from that in medium-swelling coal, with elements being released much more rapidly and to greater extents from the latter.
- The emissions of arsenic and lead in NB8 coal and lead in WK11 coal are proportional to the total volatile matter release, and the emissions of mercury and arsenic in WK11

Table 6. Comparison of Model Parameters and SSE Values (WK11)

Model	Isothermal Yes	Isothermal No	Equilibrium Yield Fixed	Equilibrium Yield Variable	Parameters Fixed	Parameters Fitted	Parameter Values	SSE
Single First-Order	X			X		X	B_0 = 6320(l/sec) E_0 = 14.2 (kcal/mole)	597
		X		X		X	B_0 = 16035(l/sec) E_0 = 19.12(kcal/mole)	439
Badzioch and Hawksley	X			X	X		$K_1 = 1.930 \times 10^{-3}$ K_2 = 676 Q = 1.8 $A = 6.1 \times 10^7$ (l/sec) B = 16.3 (kcal/mole)	1143
	X			X		X	$K_1 = 1.938 \times 10^{-3}$ K_2 = 676 Q = 1.8 $A = 6.1 \times 10^7$ (l/sec) B = 16.3 (kcal/mole)	513
Kobayashi		X	X		X		a_2 = 1.0 $B_1 = 2.0 \times 10^5$ (l/sec) $B_2 = 1.3 \times 10^7$ (l/sec) E_1 = 25 (kcal/mole) E_2 = 40 (kcal/mole)	7679
		X		X		X		4681
		X		X	X		a_2 = 1.0 $B_1 = 4.8 \times 10^4$(l/sec) E_1 = 18 (kcal/mole) $B_2 = 5.0 \times 10^6$ (l/sec) E_2 = 40 (kcal/mole)	394
Anthony		X	X		X		$K_o = 1.0 \times 10^{13}$ (l/sec) V^*_1 = 48% E_o = 54.8 (kcal/mole) s = 17.2 (kcal/mole)	2842
		X		X	X		$K_o = 1.67 \times 10^{13}$ (l/sec) E_o = 54.8 (kcal/mole) s = 17.2 (kcal/mole)	670
				X		X	E_o = 55.2 (kcal/mole) s = 6.18 (kcal/mole)	243

coal are proportionally greater than the total volatile matter release. The amount of sulfur release was nearly directly proportional to the amount of dry-ash-free volatile matter released for NB8 and WK11 coals. This confirms the findings of Agreda et al. (1979).

- The kinetics of sulfur and lead release for NB8 coal can be modeled using a first-order reaction model coupled with a model for equilibrium release derived from batch pyrolysis experiments. The lack of precision in the retentions of other volatile trace elements prevented the meaningful determination of kinetic parameters for the release of these elements.

Recommendations

The most important addition to the work performed in this study is the sampling and chromatographic analysis of the gases produced in both the batch and laminar flow reactors. Gas samples should be analyzed for major components by thermal conductivity detection, for trace hydrocarbons by flame ionization detection, and for trace sulfur gases by flame photometry. The results will elucidate the mechanism of pyrolysis, and will shed light on the presently unresolved contradiction between the results favoring the single first-order decomposition rate law and the distributed activation energy model.

The procedures for trace element sampling and analysis should be refined to afford a greater degree of experimental precision, and the modeling efforts commenced in this study should be continued. The list of elements studied should be extended to cover a wider range of species that are both volatile and potentially hazardous, such as selenium, beryllium, antimony, and vanadium.

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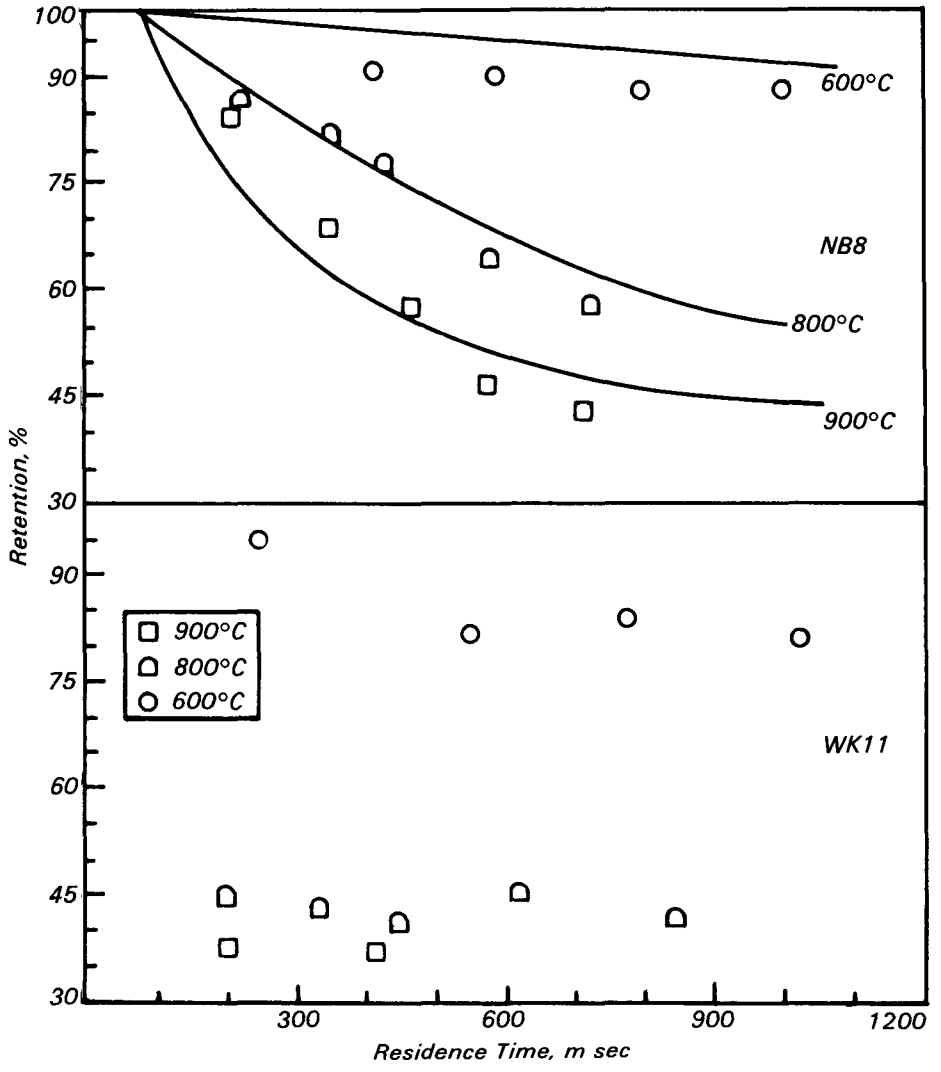

Figure 4. *Sulfur retention in LFR chars.*

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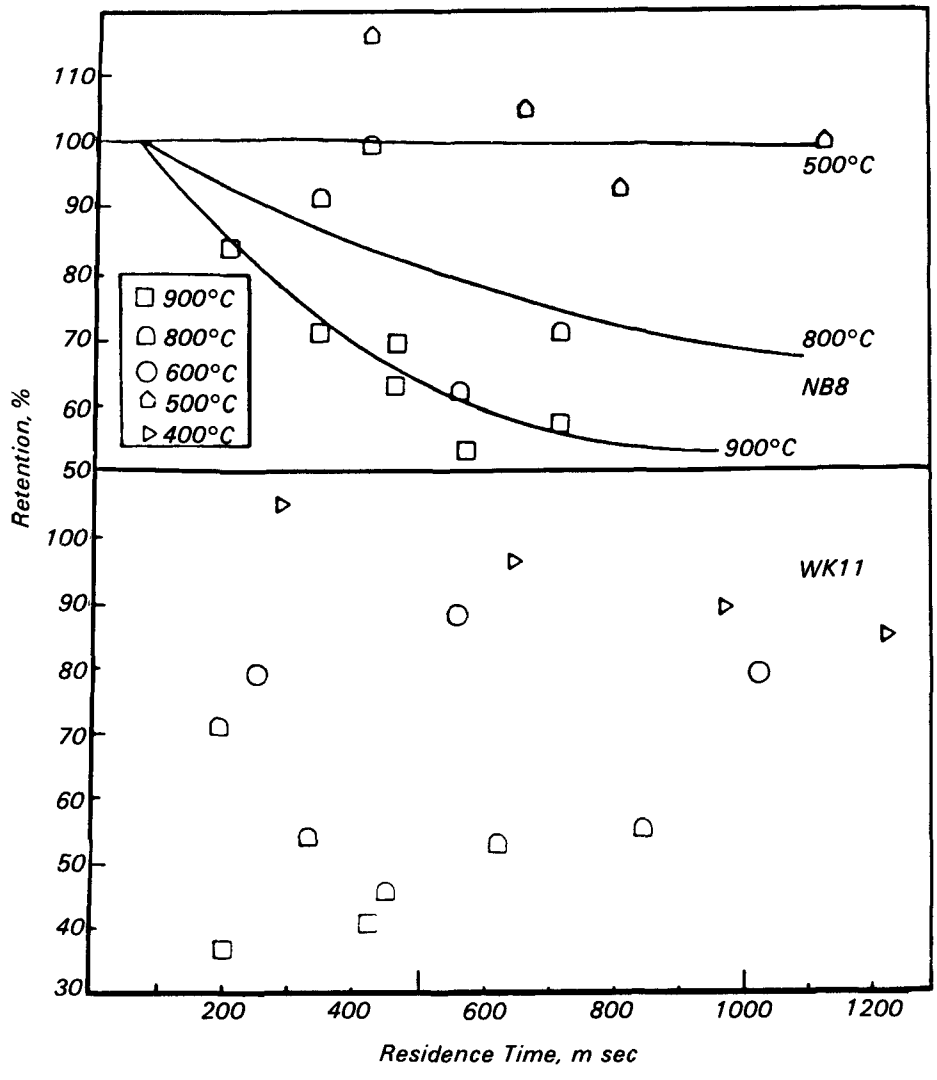

Figure 5. *Lead retention in LFR chars.*

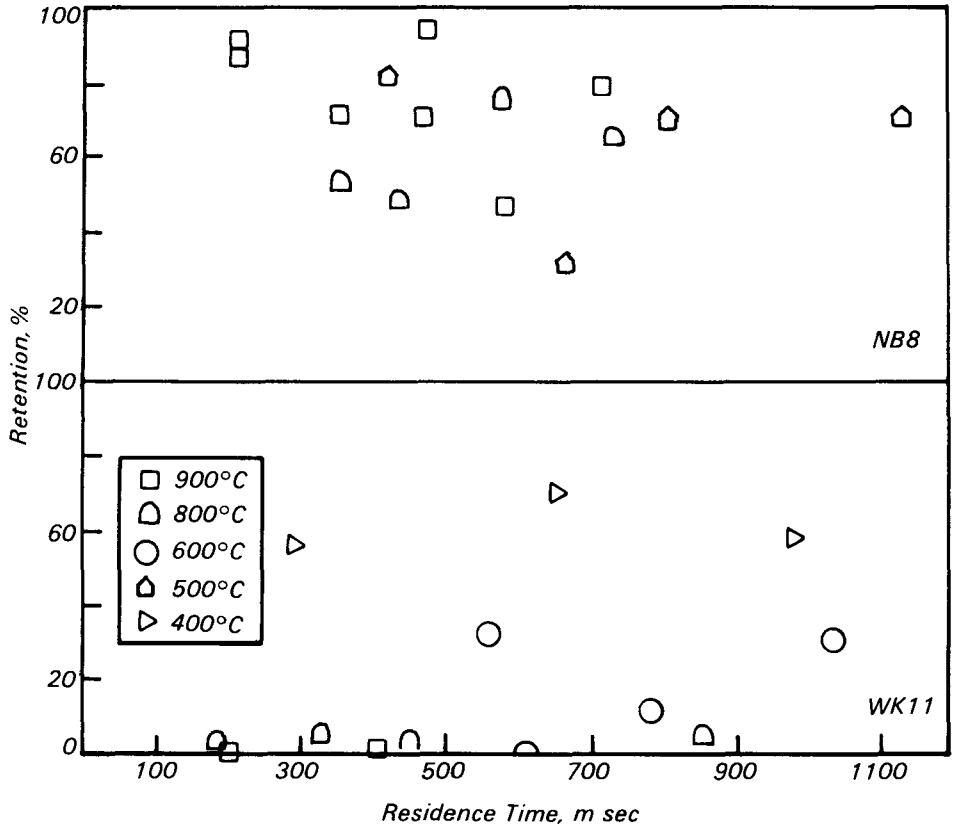

Figure 6. *Mercury retention in LFR chars.*

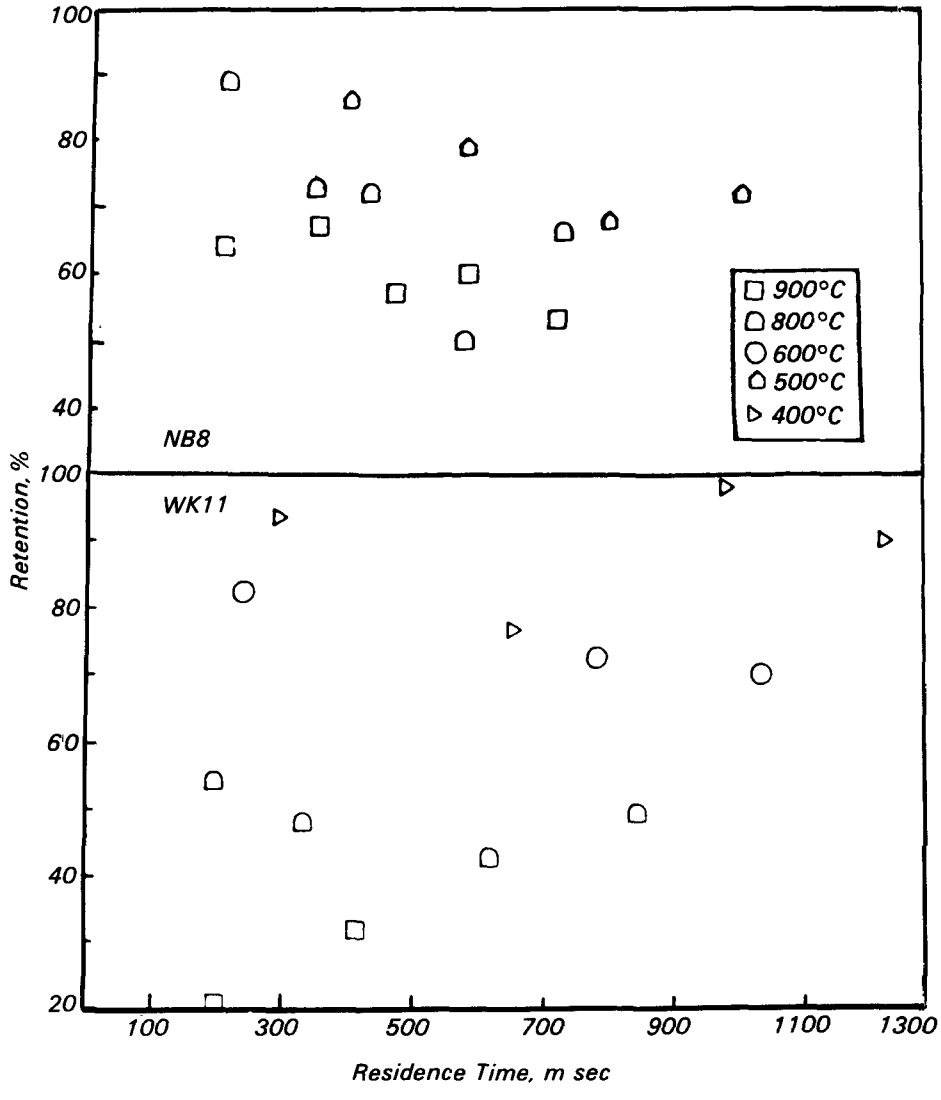

Figure 7. *Arsenic retention in LFR chars.*

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The complete report, entitled "Rates and Equilibria of Devolatilization and Trace Element Evolution in Coal Pyrolysis," (Order No. PB 82-260 944; Cost: $12.00, subject to change) will be available only from:
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