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Published by IPC Science and Technology Press Ltd

# Kinetics of lignite pyrolysis in an entrained-flow, isothermal furnace

Alan W. Scaroni, Philip L. Walker, Jr. and Robert H. Essenhigh\*

Department of Materials Science and Engineering, The Pennsylvania State University,  
University Park, Pennsylvania 16802, USA

(Received 19 December 1979)

An entrained-flow, isothermal furnace was used to study rapid pyrolysis in nitrogen of a Texas lignite. Weight losses for fixed residence times up to 0.4 s were independent of particle size over the range of mean diameter from 41 to 201  $\mu\text{m}$  and increased with temperature elevation over the range 700 to 1000°C. The maximum yield of volatiles, 66.7 wt% of the dry-ash-free coal, was particle size independent and relatively temperature independent over the range of operating conditions. The maximum yield represented a fractional increase of 1.30 over the ASTM volatile matter. This yield enhancement was associated with a reduction in the preponderance of secondary char-forming reactions of the volatiles and not directly with the increase in heating rate from 20°C s<sup>-1</sup> in the ASTM test to > 10<sup>4</sup>°C s<sup>-1</sup> in the isothermal furnace. Pyrolysis was multi-stage; initial rapid devolatilization to 50% weight loss was followed by slower latter-stage devolatilization. First stage pyrolysis could be fitted by a single, first-order kinetic expression whether total weight loss was taken as just that for the first stage or for complete devolatilization. Rate constants for the two cases were  $0.6 \times 10^3 \exp(-45\text{kJ/mol}/RT)$  and  $0.9 \times 10^2 \exp(-32\text{kJ/mol}/RT)$  s<sup>-1</sup>, respectively. One or more additional equations would be necessary to describe the completion of pyrolysis. It is argued that the relatively low activation energy is not necessarily indicative of physical rate control and therefore not necessarily in contradiction with the absence of particle size effects.

In combustors and gasifiers firing pulverized coal, the coal is rapidly heated causing thermal decomposition in association with other chemical reactions. Maximization of the rate of evolution and yield of volatiles reduces reliance on relatively slower heterogeneous gas-solid reactions. As an integral part of the combustion process, pyrolysis influences such parameters as the ignition mechanism, flame stability and heat release along the flame. In the gasification process, depending on the coal and the operating conditions, a significant proportion of the gas yield is the direct result of pyrolysis.

It has been emphasized in recent reviews<sup>1,2</sup> that conditions of rapid heating, often in excess of 10<sup>4</sup>°C s<sup>-1</sup>, are associated with pulverized coal systems. This places stringent requirements on acceptable experimental techniques for studying the kinetics of rapid pyrolysis, stemming partly from the fact that crucial reactions occur in the first few seconds or even milliseconds.<sup>3-6</sup> Two distinct approaches to this problem have evolved. German investigators, in particular, have developed techniques aimed at studying non-isothermal coal pyrolysis. A summary of this work has recently been provided by Jüntgen and van Heek.<sup>7</sup> The more common approach is to study pyrolysis isothermally. Requirements for isothermal pyrolysis studies include controlled rapid heating of the coal, isothermal reaction, variation of reaction time and temperature, and rapid quenching of the char. In essence, it is essential to have an unambiguous reaction history.

It has been previously demonstrated in this laboratory<sup>6</sup> at the entrained-flow, isothermal furnace more or less

satisfies the requirements. Accordingly, a furnace of this type was constructed and used to obtain kinetic data for rapid lignite pyrolysis. In addition, behavioural differences between pyrolysis in the isothermal furnace and in the ASTM volatile matter test were investigated.

## EXPERIMENTAL

### Coal preparation

The as-received coal, a lignite from the Darco Seam in Texas, was crushed, air dried, then ground. The pulverized lignite was size graded by dry sieving and the particle size distribution within each fraction determined using the Rosin-Rammler relation<sup>8</sup>. Analyses for the lignite are given in Table 1.

A feature of the preparation was that mineral matter accumulated in the smaller size fractions; which is reflected in Table 1 as an increase in ash with decrease in mean particle size. It was considered important because it represented a possible coupling of mineral matter effects and particle size effects during pyrolysis.

### Apparatus

Rapid pyrolysis was performed in an entrained-flow, isothermal furnace similar to, but larger than, that described by Nsakala *et al.*<sup>6</sup> which, in turn, was based on the design of Badzioch and Hawksley.<sup>3</sup> Details of the apparatus are provided by Scaroni.<sup>9</sup> It consisted essentially of a vertical tube furnace heated electrically and designed for the injection of a dilute coal stream into the centre of a preheated gas stream. The ensuing mixing resulted in rapid heating of the injected stream, estimated

\* Present address: Department of Mechanical Engineering, The Ohio State University, Columbus, Ohio 43210, USA

Table 1 Analyses of Texas lignite

Code No.	Source area	ASTM rank	Ultimate analysis (wt %)		
				dry	daf
PSOC-412	Darco Seam, Texas	Lignite	C	60.2	71.6
			H	4.5	5.3
			N	1.2	1.4
			S	1.4	1.6
			O	16.8	20.0
			Ash	15.9	—
Mesh size, US standard sieve	Mean diam. ( $\bar{X}$ )	Dispersion ( $n$ )	Proximate analysis (wt %)		
			ASH dry	VM daf	FC daf
60 x 80	201	12.0	10.3	51.2	48.8
70 x 100	160	8.4	10.8	51.2	48.8
100 x 140	111	7.8	10.4	51.1	48.9
140 x 200	79	8.0	12.4	51.0	49.0
200 x 270	52	8.0	12.9	52.1	47.9
270 x 400	41	10.0	15.8	51.0	49.0

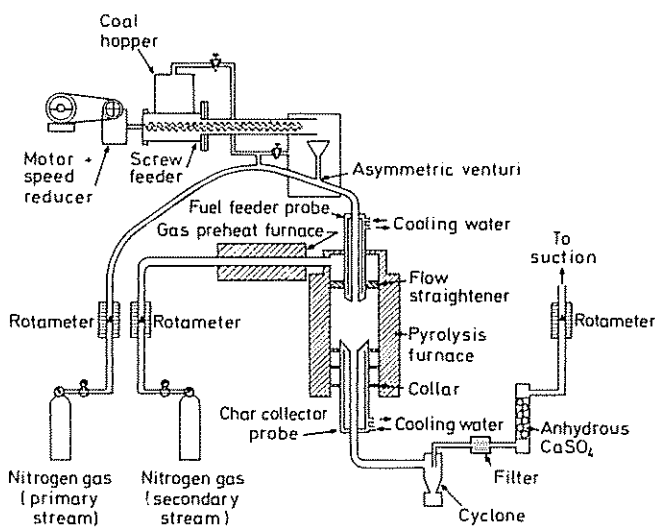


Figure 1 Schematic diagram of entrained-flow, isothermal furnace

to be of the order of  $10^4 \text{ }^\circ\text{C s}^{-1}$ . Careful injector design and the use of a flow straightener minimized migration of coal particles to the furnace tube wall. A water-cooled sampling probe, injected up the axis of the furnace, collected isokinetically and rapidly quenched particles which had flown vertically downward. Quenching rates were calculated to be in excess of  $2 \times 10^4 \text{ }^\circ\text{C s}^{-1}$ .<sup>10</sup> Pyrolysis was contained in an isothermal zone by uniformly heating the furnace tube to the gas preheat temperature. Variation of reaction time was achieved by raising and lowering the collector probe. Char particles were separated from the gas stream in a cyclone separator. A schematic diagram of the equipment is given in Figure 1.

ASTM ash and volatile matter tests were performed in conventional apparatus.<sup>11</sup>

#### Operating conditions

The operating conditions, which are given in Table 2, maintained constant gas velocity down the furnace tube for all experiments. This ensured an approximately constant relation between flow distance and residence time for a given particle size. Low loading of coal ensured that

pyrolysis occurred in the disperse phase with minimal interaction between particles. The constant flow of primary nitrogen was the minimum required for efficient entrainment of the lignite. Optimization of the secondary nitrogen flow rate balanced the conflicting requirements of low flow to increase residence times and high flow to successfully accommodate the cold primary flow without significant temperature drop.

Gas temperatures were measured along the axis of the furnace tube by suction pyrometry. Deviation from the mean operating temperature was never more than  $10^\circ\text{C}$ .

Particle residence times in the isothermal furnace were calculated from particle velocities and flow distances. Cold-flow modelling experiments, presented in detail by Scaroni<sup>9</sup>, indicated that particle velocities were particle size dependent. Adequate prediction to within a maximum error of 10% was achieved by summing the average gas velocity and particle free-fall velocities. Velocity curves for the air-dried lignite are given in Figure 2.

Clearly, the assumption made by others<sup>3,6,10</sup> of equal gas and particle average velocities is not always valid. Its validity depends primarily upon particle size, particle density and average gas velocity. Precise calculation of residence times in the furnace is complicated by the fact that particle density and size change during devolatilization and also that exact gas velocities and flow patterns of the particles are not known. While additional studies are underway to further clarify these points, estimates of maximum errors associated with particle size and density changes have been made.

Table 2 Operating conditions

	Gas preheat and wall temperature ( $^\circ\text{C}$ )			
	700	800	900	1000
Coal feed rate ( $\text{g min}^{-1}$ )	1.0	1.0	1.0	1.0
Mean gas velocity ( $\text{m s}^{-1}$ )	1.12	1.12	1.12	1.12
Secondary/Primary nitrogen	16.7	15.0	13.7	12.5
Coal loading (wt %)	2.2	2.5	2.7	2.9

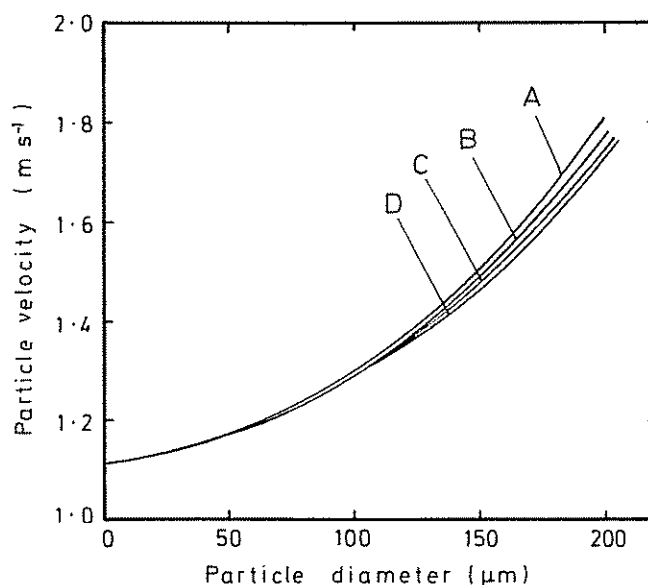


Figure 2 Variation of particle velocity of air-dried lignite with particle diameter and gas temperature. A, 700; B, 800; C, 900; D, 1000°C



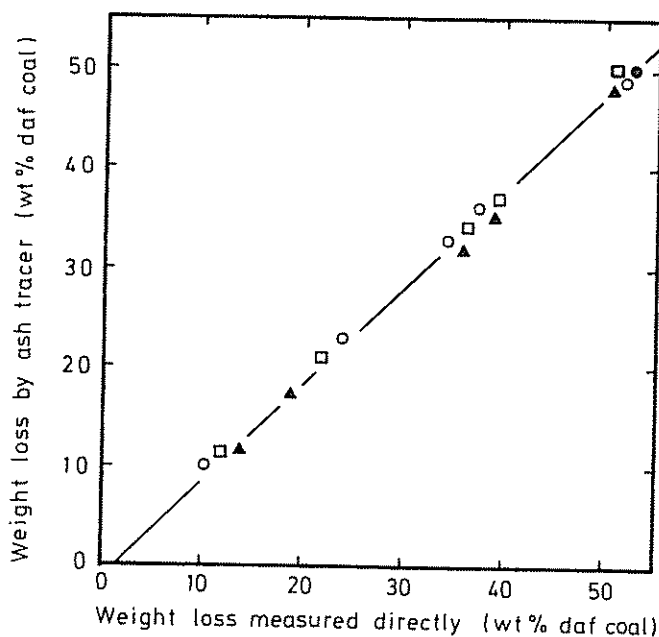


Figure 3 Relationship between weight loss measured directly and determined using ash as a tracer;  $\bar{X}$   $\mu\text{m}$ :  $\blacktriangle$ , 201;  $\circ$ , 160;  $\bullet$ , 111;  $\square$ , 79

It has been previously shown<sup>1,2</sup> and substantiated in this investigation that lignite particles do not decrepitate significantly during rapid pyrolysis. Furthermore, weight loss does not occur at constant (mercury) density or constant particle size. Rather, particles undergo simultaneous density and particle size reduction, each to a lesser extent than would occur in the absence of the other. If weight loss in the furnace were to occur at constant density causing maximum particle shrinkage, then particle velocities calculated on the basis of the air-dried lignite would be in maximum error. For the largest particles used in this investigation, 201  $\mu\text{m}$  in diameter, experiencing the maximum weight loss, 50% of the daf coal, the error in calculation of the instantaneous velocity at the point of maximum weight loss would be 15%. The error in intermediate residence times would be considerably less. Since this illustration is a worst-case situation that does not in fact occur, the present method of calculating residence times is considered adequate.

#### Ash as a tracer

The furnace design precluded the use of direct material balances for determining weight losses due to pyrolysis. This derived from the fact that some char bypassed the collector probe and some adhered to inner probe surfaces. Collection efficiencies were typically 70 to 80%. This necessitated the use of ASTM ash as a tracer for determining weight losses.<sup>3,5,10</sup> This technique is errorless only if mineral matter in the lignite does not undergo transformations during pyrolysis which would cause a yield variation from the ASTM ash of the coal upon subsequent ashing of the char.

Experimental ash yields from short residence time chars were, in some cases, lower than yields obtained by ashing the raw coal, reflected in weight loss calculations as apparent weight gain. Sporadic instances of apparent weight gains of up to 1% of the daf coal could be attributed to the reproducibility of the ash analyses, but consistent occurrences required an alternative explanation.

Crucible experiments in the ashing furnaces where weight losses could be directly measured showed that the use of ash as a tracer consistently underestimated actual weight losses. This is in agreement with the data of others<sup>5</sup>, and may be due to the loss of sulphur during pyrolysis which would otherwise be fixed during ASTM ashing. Typical data are shown in Figure 3, and are represented empirically by the rectilinear relation:

$$\text{Actual weight loss} = 1.031 (\text{Ash tracer weight loss}) + 1.70$$

with weight losses expressed as % daf coal. The relation was essentially particle size and temperature independent over the range of operating conditions. It was used to correct isothermal furnace data. Its application eliminated the occurrences of apparent weight gain during the early stages of pyrolysis.

## RESULTS AND DISCUSSION

### Weight loss in the isothermal furnace

A typical weight loss versus time plot is shown in Figure 4a for pyrolysis in nitrogen at 900°C over the range of particle size. Datum points are representative of at least duplicate ash determinations on duplicate chars. Error bars represent reproducibility at the 95% confidence level. Similar curves were generated at 700, 800 and 1000°C and best-fit lines are given in Figure 4b.

There was a characteristic delay time before the onset of significant pyrolysis associated with heating of the par-

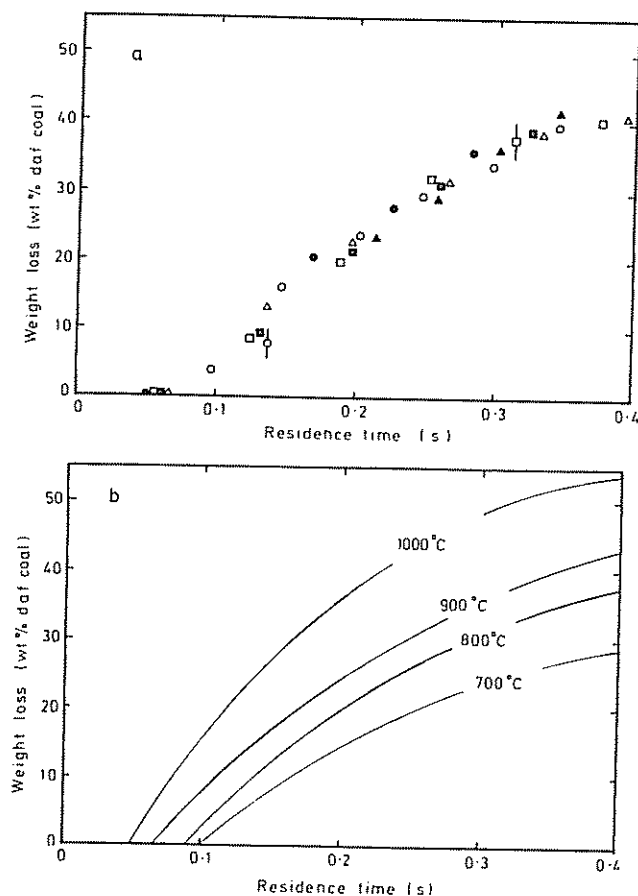


Figure 4 (a) Weight loss as a function of residence time at 900°C;  $\bar{X}$   $\mu\text{m}$ :  $\blacktriangle$ , 201;  $\circ$ , 160;  $\bullet$ , 111;  $\square$ , 79;  $\blacksquare$ , 52;  $\triangle$ , 41. (b) Effect of temperature on weight loss as a function of residence time

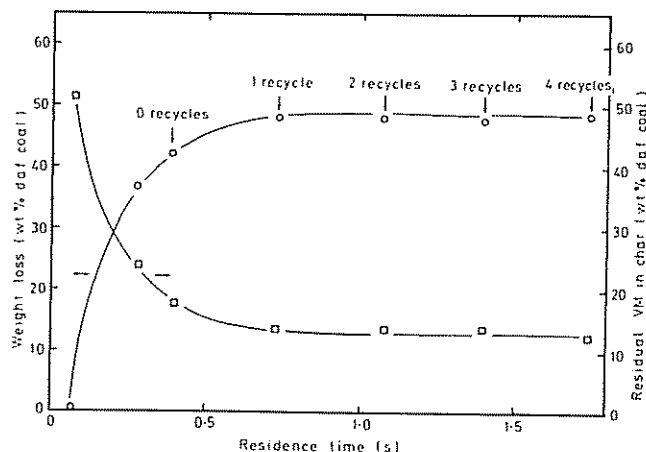


Figure 5 Variation of weight loss and residual ASTM volatile matter in char as a function of cumulative residence time upon recycling at 950°C,  $\bar{X} = 160 \mu\text{m}$

ticles. Pyrolysis then proceeded such that, for a given residence time, weight loss increased with increase in temperature. In addition, weight loss was independent of particle size over the range of mean particle diameter from 41 to 201  $\mu\text{m}$ .

The absence of particle size effects essentially implies the absence of internal heat and mass transfer control of the pyrolysis, except possibly for mass transfer control in the micropores of the lignite. This stems from the fact that the microporosity may not be altered significantly during the grinding procedure. Such diffusion control is unlikely, however, owing to the violent nature of the pyrolysis under the operating conditions; i.e. scanning electron micrographs showed the existence of cracks and fissures in preponderance in the chars which were not evident in the raw lignite. In addition, external physical rate control is absent based on the previously noted fact that particle velocities, hence relative particle/gas velocities and boundary layer thicknesses, are particle size dependent. The implication is, therefore, that pyrolysis was occurring in the chemically controlled regime.

#### Maximum weight loss for isothermal furnace conditions

It was important for several reasons to determine the maximum potential weight loss under isothermal furnace conditions. It is an important parameter required to model the kinetics of pyrolysis and it has practical significance to combustors and gasifiers in which it is advantageous to maximize the yield of volatiles. This parameter was not measurable directly by a single pass of the lignite through the furnace because of limited residence time. Recycling of the char was potentially a feasible technique for achieving maximum weight loss.

The effect of recycling the char at 950°C is shown in Figure 5. After 1 recycle and a cumulative weight loss of nearly 50% of the daf coal, insignificant additional weight loss occurred on further recycling. The chars still contained, however, ASTM volatile matter representing about 12% of the daf coal. It became apparent, since the ASTM test is conducted for a period of 7 min, that a significantly longer residence time than could be reasonably achieved by recycling was required for the completion of pyrolysis in the isothermal furnace. The implication is that the pyrolysis was multistage in nature; initial rapid devolatilization followed by slower latter-

stage devolatilization. This is in agreement with the hypotheses of others,<sup>6,13</sup> who proposed two-stage devolatilization. Further data are required to determine if the fraction of the total volatile matter representing the rapidly evolved component is rank dependent.

An alternative to directly measuring the maximum potential weight loss was to calculate it based on measurement of a standard property which changed regularly with weight loss in the isothermal furnace. It has been previously demonstrated that change in ASTM volatile matter between the original daf coal and the daf char is one property which correlates well with weight loss.<sup>3,6</sup> The relation for the Texas lignite is shown in Figure 6, and is represented by

$$\Delta W = 1.30 \Delta V$$

where:  $\Delta W$ , weight loss, % daf coal; and  $\Delta V$ , change in ASTM volatile matter between coal and char, % daf coal. The relation was essentially temperature and particle size independent over the range of operating conditions.

The maximum potential weight loss,  $\Delta W_x$ , as % daf coal, is obtained from the rectilinear relation when there is no ASTM volatile matter remaining in the char. For the Texas lignite,  $\Delta W_x$  is 66.7% of the daf coal.

#### Enhancement in yield of volatiles

The slope of Figure 6, 1.30 for this lignite, represents the fractional yield enhancement over the ASTM volatile matter and has been called the Q factor.<sup>3,13</sup> Others have observed similar enhancements.<sup>3,5,6,13</sup> Two of the basic operating differences which exist between the isothermal furnace and the ASTM volatile matter test which could account for the yield variation are heating rate and bed size. The isothermal furnace operates in the disperse phase

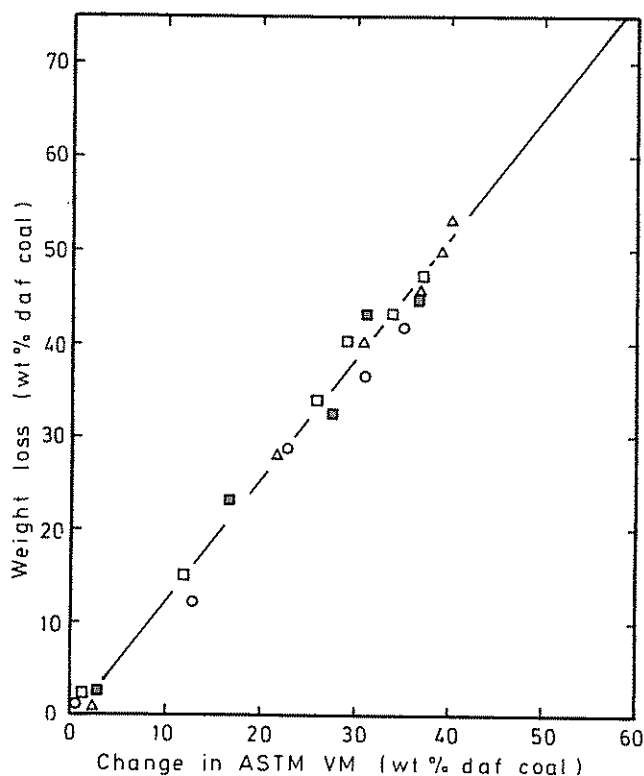


Figure 6 Variation of weight loss at 1000°C with change in ASTM volatile matter;  $\bar{X} \mu\text{m}$ : ○, 160; □, 79; ■, 52; △, 41

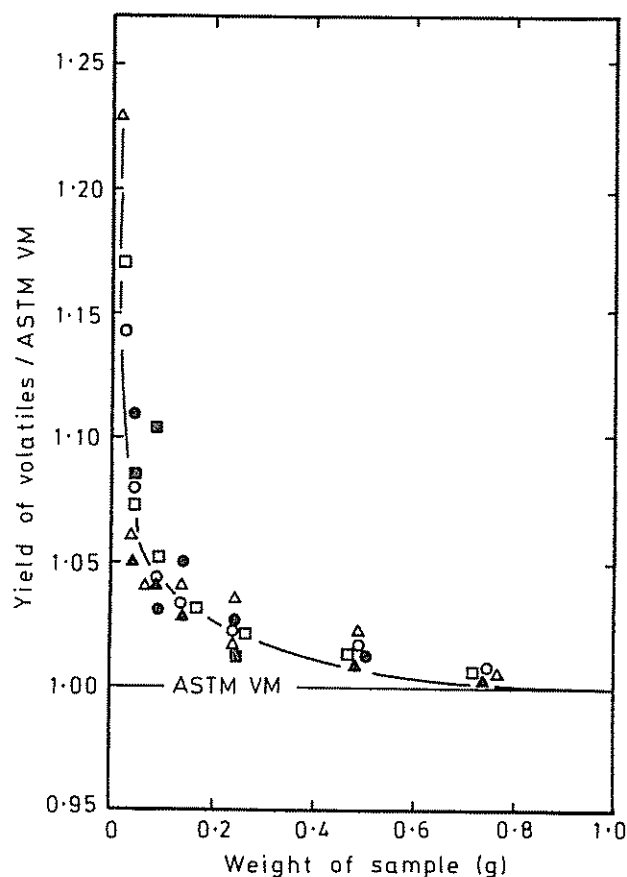


Figure 7 Effect of sample weight on yield of volatiles for crucible experiments at 950°C;  $\bar{X}$   $\mu\text{m}$ : ▲, 201; ○, 160; ●, 111; □, 79; ■, 52; △, 41

with heating rates of the order of  $10^4^\circ\text{C s}^{-1}$ . In the ASTM test, heating rates are  $\approx 20^\circ\text{C s}^{-1}$ <sup>14</sup>; and the sample is, in essence, a miniature fixed bed.

The effect of reducing sample weight, in effect the bed depth, during the ASTM volatile matter test is shown in Figure 7 for the Texas lignite. There was an enhancement in the yield of volatiles as the sample weight was reduced. Similar behaviour was observed by Gray *et al.*<sup>14</sup> The enhancement factor for a sample weight of 0.025 g is 1.23 over the standard yield. Further sample size reduction was not practical in the crucible apparatus. The observed enhancement is slightly lower than that occurring in the disperse phase of the isothermal furnace.

It has been postulated that the sample weight effect is associated with the preponderance of secondary char-forming reactions of the primary volatiles. As sample weight increases, the bed increasingly acts as a trap for the volatiles and provides a surface on which secondary reactions deposit carbon. In such a case, an important parameter controlling the preponderance of secondary reactions would be the number of collisions between a molecule of volatile matter and the surface. It can be shown by simple calculation that the predominant area available for carbon deposition is the external surface of the particles.<sup>9</sup>

An expected increase in average heating rate with reduction in sample size, however, made it difficult to decouple heating rate effects from sample weight effects. This decoupling was achieved by the addition of additives to the lignite sample which were essentially inert to pyrolysis under the operating conditions. The additives,

size graded Saran char and petroleum coke, were previously devolatilized to constant weight. The total sample weight was maintained constant at 0.6 g in all tests to ensure essentially constant heating rate. Typical results for the  $70 \times 100$  US mesh size fraction are given in Figure 8. The yield of volatiles was always lower in the presence of the additive.

The yield, in addition, was to a large extent independent of the type of additive. This implies that there was no significant diffusion of the volatiles into, and reaction in, the pores of the additives. This derives from the fact that the additives have markedly dissimilar total surface areas,  $1000 \text{ m}^2 \text{ g}^{-1}$  for the Saran char and  $1.5 \text{ m}^2 \text{ g}^{-1}$  for the petroleum coke as measured by  $\text{CO}_2$  adsorption at 298 K. This further demonstrates the importance of the external surface area.

Logical extrapolation of the data implies that it is the disperse phase operating mode of the isothermal furnace which is the cause of the yield enhancement. There is no evidence to support a direct heating rate effect.

#### Kinetics of pyrolysis

A typical first-order plot for initial rapid pyrolysis of the lignite is shown in Figure 9 for pyrolysis at 900°C. This plot has been constructed using the maximum potential weight loss,  $\Delta W_{\infty}$ , of 66.7% of the daf coal. Use of this value is in accordance with the theory developed by Nsakala *et al.*<sup>6</sup> for two stage devolatilization. First-order plots based on the weight loss due only to the initial rapid devolatilization also displayed rectilinear behaviour. This limiting weight loss is also expected to be temperature independent; however, this expectation has not yet been confirmed experimentally. In this study, the limiting weight loss for the first stage of devolatilization was taken at 50.0% of the daf coal, as measured at 950°C (Figure 5).

The rectilinearity seen in Figure 9 indicates that pyrolysis up to 75% of completion is modelled reasonably by a single, first-order reaction equation. This is not inconsistent with the need for one or more additional equations to describe the completion of pyrolysis by

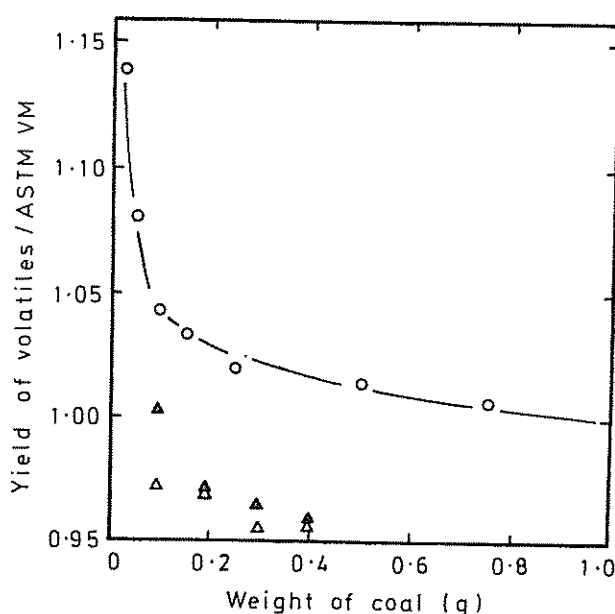


Figure 8 Effect of additives on yield of volatiles for crucible experiments at 950°C,  $\bar{X} = 160 \mu\text{m}$ : ○, lignite; ▲, lignite + Saran char; △, lignite + petroleum coke

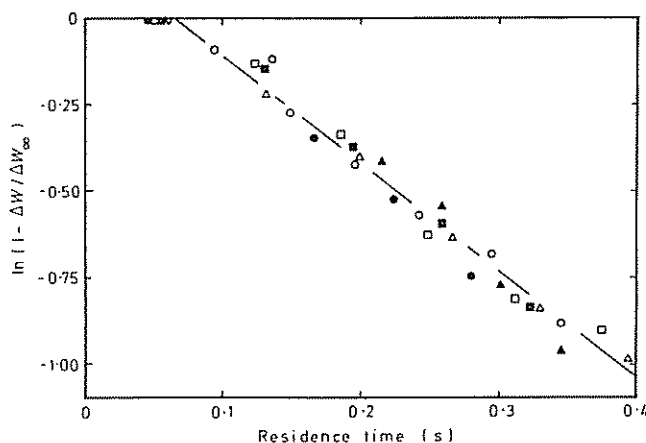


Figure 9 First-order plot for devolatilization at 900°C;  $\bar{X}$   $\mu\text{m}$ :  $\blacktriangle$ , 201;  $\circ$ , 160;  $\bullet$ , 111;  $\square$ , 79;  $\blacksquare$ , 52;  $\triangle$ , 41. Plots based on  $\Delta W_\infty$  for complete devolatilization

slower latter-stage devolatilization, as proposed by Nsakala *et al.*<sup>6</sup>. This is because the latter devolatilization may be mainly associated with the liberation of hydrogen,<sup>15</sup> which on a weight basis accounts for only about 5% of the daf coal.

Figure 9 further illustrates the characteristic delay in the onset of pyrolysis which is associated with particle heat-up. Average heating rates based on the delay time vary between  $10^4$  and  $2 \times 10^4$  °C s<sup>-1</sup> depending on the operating temperature. The apparent lack of weight loss during heat-up at these high heating rates is in agreement with the calculations of Jüntgen and van Heek<sup>16</sup>, who show a theoretically calculated shift of pyrolysis reactions to higher temperatures as the heating rate is increased.

First-order constants calculated from rectilinear plots, e.g. Figure 9, were used to construct the Arrhenius plot of Figure 10 which suggests an apparent activation energy of 32 kJ mol<sup>-1</sup> and apparent frequency factor of  $0.9 \times 10^2$  s<sup>-1</sup>. The corresponding values when using the limiting weight loss in the first stage of devolatilization as  $\Delta W_\infty$  are 45 kJ mol<sup>-1</sup> and  $0.6 \times 10^3$  s<sup>-1</sup>. Little physical significance can be attached to either of the derived activation energies because pyrolysis is a combination of numerous chemical reactions each with a characteristic activation energy and frequency factor.

The relatively low apparent activation energy is consistent with the data of others for lignite pyrolysis.<sup>1</sup> The absence of particle size effects on the rate of pyrolysis was previously interpreted to imply the absence of significant heat and mass transfer effects. Since low activation energies are usually associated with these factors, an alternative explanation is required. Howard *et al.*<sup>1,4</sup> provide a probable explanation in terms of a distribution of activation energies for the generation of different volatile species. They obtained an activation energy of  $\approx 40$  kJ mol<sup>-1</sup> in a single step correlation and  $\approx 200$  kJ mol<sup>-1</sup> in a multistep model. The implication is that for a complex process like pyrolysis, a low activation energy may not necessarily indicate physical rate control.

#### ACKNOWLEDGEMENT

The research on which this paper is based was supported by the United States Department of Energy on Contract

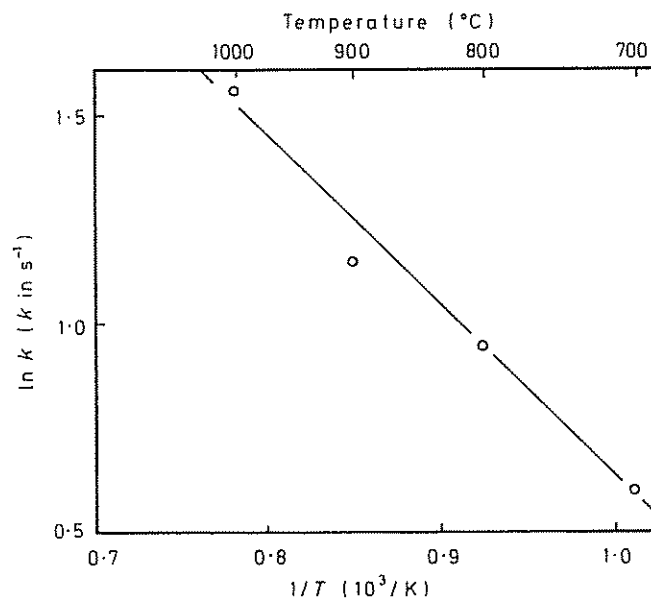


Figure 10 Arrhenius plot for initial devolatilization treated as one-step, first-order reaction. Rate constants obtained from plots, e.g. Figure 9

E(48-19)-2030. Professor W. Spackman, Jr. supplied the lignite studied.

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