

Studies on Coal Reactivity: Kinetics of Lignite Pyrolysis in Nitrogen at 808°C

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Abstract—Lignites pyrolyzed in nitrogen have provided direct evidence for a two-component model of coal constitution. The pyrolysis was studied in an electrically heated 5.1 cm i.d. laminar-flow furnace using four closely sized cuts (58, 64, 86, and 180 microns). Pyrolysis was under isothermal conditions, at 808°C, for periods up to 1 sec, following a heating period of 95 msec, at 8000°C/sec rate of heating. Pyrolysis times in excess of 200 msec were obtained by recycling, experiments having shown that this did not affect the kinetics. Variations of weight loss with time were found to be in agreement with equations based on a two component model in which two independent parallel reactions are assumed to occur. Notably, weight loss declined approximately exponentially with time, with a sharp break in the lines obtained for pyrolysis times in excess of 200 msec. Slopes of the lines yielded values of the relevant kinetic constants, with Component "I" decomposition dependent on particle size over the range studied, but the slower-reaction of Component "II" being independent of size. The ratio of Component I to Component II is estimated at about 10 to 1. In other results, the proportionality between weight loss and ASTM volatile loss of the char, as first reported by Badzioch and Hawksley was reconfirmed, with Q factors for the coals studied of 1.8 and 2.

INTRODUCTION

account of dwindling native supplies of natural gas and oil, major research and development programs are currently under way in the United States aimed at converting coal into alternate fuels, both liquids and gas. The research programs include numerous fundamental studies of coal reactivity (*e.g.* see ERDA, 1976) designed to aid operation and optimization of the various conversion reactors. Our present work is one of those programs.

The work described in this paper is concerned with gasification, with a focus on pyrolysis; certain results, however, to be described, have interesting parallels with liquefaction. This work is also part of a more general program emphasizing char characterization and reactivity. Pyrolysis is of major importance in gasification, but char reactivity may be even more significant. Char reactivity depends jointly on chemical characteristics, such as the "intrinsic" reactivity of the surface, and on physical characteristics such as specific internal surface areas, open pore volumes, porosities, and densities. The magnitudes of these physical and chemical characteristics after pyrolysis are functions of conditions of pyrolysis such as heating rate, pyrolysis temperature, pyrolysis time, ambient gas, and coal rank or type.

In coal processing, and particularly in gasification, it is now evident that rate of heating (and/or factors allied to it) has particular influence on pyrolysis yields and subsequent char characteristics. To our knowledge, however, the chars produced after rapid heating have not been systematically characterized, and even less attention has been given to relating the ultimate char characteristics to the conditions of pyrolysis. This lacuna therefore provided the incentive for the overall program, with pyrolysis, surface area, porosity, and density measurements on two lignites now completed (and with some further limited results on two bituminous coals), pyrolysis being in nitrogen at 808°C.

In this present paper we described only the pyrolysis results, with the other physical measurements to be reported in a further paper currently in preparation.

Pyrolysis is not, of course, a new subject since it has been of interest for at least 150 years. Only in about the last two decades however, have experimental methods been devised, such as the isothermal furnace method of Badzioch and Hawksley (1970), that would permit measurements with any reasonable degree of precision; and only now is it becoming possible to submit theories of pyrolysis to reasonable experimental test. One such theory

is based on the "Two-Component" hypothesis originally proposed on experimental grounds by Clark and Wheeler (1913) (reviewed in Essenhigh and Howard, 1971). According to this, coal behaves *as if* it consists of two components of different degrees of ease of decomposition (conveniently labelled I and II). There is some further experimental evidence (Essenhigh and Thring, 1958) that Component I splits into Ia and Ib (Essenhigh, 1958), but this is disregarded in this present evaluation.

There are other bases for evaluation of pyrolysis that have also been used in the past. The most common until recently was the assumption of a one-step, first-order decomposition (*e.g.* Van Krevelen *et al.*, 1951) noting that this is still an acceptable first-approximation in some circumstances although its essential inadequacy had been known since 1910 (Clark and Wheeler, 1913). Badzioch and Hawksley (1970) also used this assumption as a starting point, but found that empirical corrections were necessary for their equations to match their results. Anthony *et al.* (1974) adopted Pitt's (1962) prior assumption of a set of reactions requiring a distribution of activation energies. The physical basis for the assumption, however, is arguable other than, maybe, Juntgen and van Heek (1968) evaluation of production of individual constituents. Most recent investigators (Stickler *et al.*, 1976; Ubhayakar, *et al.*, 1977; Kobayashi *et al.*, 1977), on the other hand, seem to favor now some form of "Two-Component" model, with good success in post-evaluation of experimental data.

Past support or evidence for the Two-Component model, however, has been inductive and/or indirect. We report here results believed to be the first direct evidence in support of such a model. This is considered to be the most significant result of this paper.

EXPERIMENTAL

Method

The method used to produce the chars for characterization following rapid heating was that of Badzioch and Hawksley (1970). Our equipment is illustrated in Figure 1. The essence is a vertical tube furnace, heated electrically, carrying a stream of down flowing, preheated nitrogen into which finely ground coal is continuously injected. The ground coal is injected at the top of the furnace on the tube axis and carried on a stream of cold nitrogen. Design

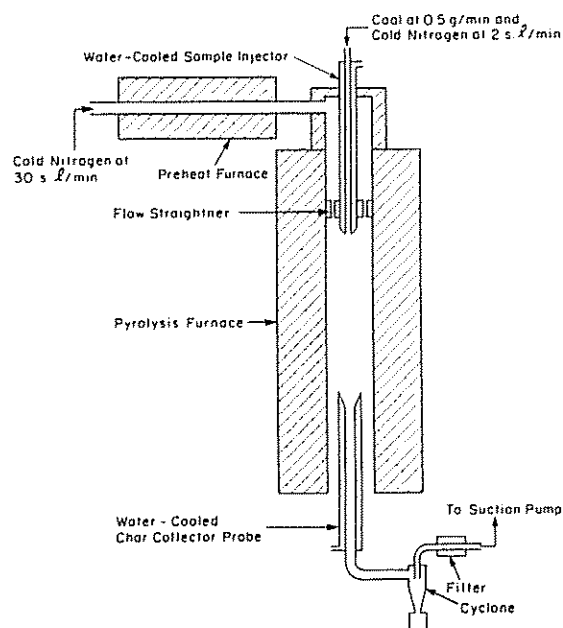


FIGURE 1 Schematic of equipment.

requires that the mass flow of cold nitrogen plus coal is small (ratio 13 to 1) compared with the heated nitrogen so that the cooling effect from addition is also small. Plunging the particles into hot gas also results in rapid heating, estimated in these experiments at 8000 °C/sec. Proper design of the injector reduces radial spread of the particle stream and to a degree keeps the particles off the furnace wall. This is assisted by maintaining laminar flow with velocities high enough (102 cm/sec and $Re = 440$) for gas/particle velocities to be neglected, but otherwise as low as possible to give longest retention times. The particles are captured and quenched in an adjustable, water-cooled sampling tube. Residence time is varied by moving the sampling tube up and down. Maximum residence time was 300 msec, but this was extended to 1.1 sec by recycling as described in more detail below.

Equipment Details

The equipment illustrated in Figure 1 shows a vertical tube furnace, as outlined above, with necessary gas and coal supply and metering equipment. Coal was supplied by an open-spiral screw feeder feeding into a funnel above an asymmetric venturi where the coal was picked up by the cold carrier gas. Char in the furnace stream was picked

up by the water-cooled collector probe and separated from the gas stream by a cyclone and filter.

The (main) pyrolysis furnace consisted of a mullite tube (McDanel MV 30) 58 cm long, 5.1 cm i.d., and 5.7 cm o.d. The electric windings were carried on an outer concentric tube, also MV 30, 51 cm long, 6.4 cm i.d., and 7.0 cm o.d. This was wound with two different sizes of Kanthal A-1 resistance wire for a length of 46 cm at 1.5 windings/cm. This winding was provided with 6 shunt taps to permit adjustment of the temperature profile of the gas in the tube. By appropriate adjustment of the shunts, uniform axial gas temperatures were obtained over a length of 23 cm, as measured by a suction pyrometer, although the wall temperature profiles of the furnace contained marked peaks.

The preheater furnace was also a Mullite (MV 30) tube, 53 cm long, 2 cm i.d., and heated on the outside with Globars.

Temperature of both furnaces was controlled by appropriate controllers (not shown in Figure 1), using chromel/alumel thermocouples as sensors.

The injector tube at the top was water-cooled brass with a 2.5 cm block of 316 stainless around it pierced by 0.6 cm holes to act as a flow straitener for the heated nitrogen stream. Injection of the nitrogen stream was isokinetic with the hot stream for least disturbance (Badzioch and Hawksley, 1970). The injector tube was subsequently fitted with a surrounding refractory tube to prevent thermal shock.

The sampling tube was water cooled with a tapering opening from the tube o.d. of 32 cm down to the i.d. of 0.6 cm. Later, this tube was also fitted with a surrounding refractory tube to prevent thermal shock, which twice cracked the inner main tube of the furnace.

Other details of method and construction are to be found elsewhere (Badzioch and Hawksley, 1970; Nsakala, 1976).

Coals

Four coals have been investigated, with emphasis on two lignites. Analyses are given in Table I. Samples were sized with sieve cuts. Mean (arithmetic) sizes used (not necessarily on all coals) were 58, 64, 86, and 180 microns.

Operating Conditions

All but a few measurements were made at a gas temperature of 808 °C. This was obtained with a

peak wall temperature of 1150 °C which burned out the windings when exceeded. It was appropriate to execute these first experiments at this temperature (808 °C) since secondary graphitization of the char tends to accelerate above about 850 °C so the data thus obtained provide a baseline for comparison with results of future experiments at higher temperatures. At a dilution of 13 to 1, particles heated at about 8000 °C/sec. Flow rates were as follows.

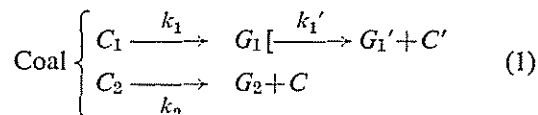
- i) Coal feed, about 0.5 g/min.
- ii) Main nitrogen stream, 30 s.l./min.
- iii) Carrier nitrogen stream, 2 s.l./min.
- iv) Total gas flow, 32 s.l./min.
- v) Collector probe suction rate, 14 s.l./min.

About 8 grams of char were needed for the subsequent proximate (V.M. and ash) analysis, and for the gas adsorption and density measurements. Maximum run time to obtain the necessary samples was up to 3 hours per station in the pyrolysis tube.

Preliminary Experiments

These included initial cold model tests to determine the injector probe and flow straitener design that would minimize radial spread of the particles (see Nsakala, 1976), as well as temperature measurements to determine conditions for uniform gas temperatures. In other experiments, the Pittsburgh Seam bituminous coal (E-5, see Table I) was found difficult to handle because it plugged the collector tube. This coal has a free swelling index of 5. In consequence, most further experiments were limited to the other (non or weakly swelling) coals.

THEORETICAL The reaction scheme used, based on the Two-Component hypothesis, (Clark and Wheeler, 1913; Essenhigh, 1958; Essenhigh and Howard, 1971) is as follows:



where C_1 and C_2 represent the quantities of initial Components I and II left at time t after reaction has started, with Component I transformed to gas, G_1 , alone, in a primary reaction with velocity constant k_1 ; and Component II transformed to gas, G_2 , and char, C , in a parallel primary reaction with velocity

TABLE 1
Analyses of coals

Coal identification			Analysis (in weight percent)						Free swelling index
Code No.	Source area	ASTM rank range	Proximate analysis ^c	(dry)	(daf) ^a	Ultimate analysis ^b	(dry)	(daf) ^a	
PSOC-90	Lower Seam, Savage Mine, Montana	Lignite	Volatile matter	39.9	43.5	C	64.8	71.6	0
			Fixed carbon	51.7	56.5	H	4.4	4.9	
			Ash	8.4	—	N	0.7	0.8	
						S	0.3	0.3	
						O	20.3	22.4	
			Ash				9.5	—	
PSOC-246	Coteau Seam, Glen Harold Mine, North Dakota	Lignite	Volatile matter	43.7	47.5	C	64.1	71.0	0
			Fixed carbon	48.3	52.5	H	4.4	4.9	
			Ash	8.0	—	N	1.4	1.6	
						S	0.6	0.6	
						O	19.8	21.9	
			Ash				9.7	—	
PSOC-296	Ohio No. 5 Lower Kittaning Seam, Five Points Mine, Ohio	HVA	Volatile matter	35.6	42.9	C	67.2	82.1	1.5
			Fixed carbon	47.3	57.1	H	4.7	5.7	
			Ash	17.1	—	N	2.1	2.6	
						S	0.1	0.1	
						O	7.5	9.5	
			Ash				18.2	—	
E-5	Pittsburgh Seam, Mathies Mine, Pennsylvania	HV	Volatile matter	37.7	40.1	C	77.3	82.8	~5.0
			Fixed carbon	56.3	59.9	H	5.2	5.6	
			Ash	6.0	—	N	1.4	1.5	
						S	1.5	1.6	
						O	8.0	8.5	
			Ash				6.6	—	

^a daf = dry-ash-free; ^b Data obtained from the Penn State University Coal Data Base; ^c Proximate analysis for size graded materials (200 × 325 mesh for E-5; 200 × 270 mesh for PSOC-90, PSOC-246, and PSOC-296).

constant k_2 . This parallels similar schemes used by others (Stickler *et al.*, 1976; Ubhayakar *et al.*, 1977; Kobayashi *et al.*, 1977), a difference in principle being their assumption that char is formed in a first stage by both reactions. Our view is that there is evidence (Essenhigh and Thring, 1958; Essenhigh and Howard, 1971) that C_1 forms only gas (G_1) initially, but G_1 is then the only source of char from secondary cracking, indicated in the reaction scheme (I) by transformation of G_1 in a secondary reaction to G_1' and char C' . Secondary cracking is neglected here (but see Ubhayakar *et al.*, 1977).

If the Components I and II decompose by independent, first-order reactions (velocity constants k_1 and k_2), and writing C_1^0 and C_2^0 for the initial concentrations of the components, the

variation of C_1 and C_2 with time are

$$C_1 = C_1^0 \exp(-k_1 t) \quad (1a)$$

$$C_2 = C_2^0 \exp(-k_2 t) \quad (1b)$$

The weight loss $\Delta W = G_1 + G_2$ where $G_1 = (C_1^0 - C_1)$ and $G_2 = [(C_2^0 - C_2) - C']$. If α is a proportioning factor between G_2 and C given by $\alpha G_2 = C$ we have for ΔW

$$\Delta W = C_1^0(1 - \exp[-k_1 t]) + [C_2^0/(1 + \alpha)] \times (1 - \exp[-k_2 t]) \quad (2)$$

At infinite time the maximum weight loss is ΔW_∞ where

$$\Delta W_\infty = C_1^0 + C_2^0 / (1 + \alpha) \quad (3)$$

Rearranging, we find

$$1 - \Delta W / \Delta W_\infty = (C_1^0 / \Delta W_\infty) \exp(-k_1 t) \\ + (1 - C_1^0 / \Delta W_\infty) \exp(-k_2 t) \quad (4)$$

The weight loss at infinite time, ΔW_∞ , may be found by comparison of the measured weight loss with the VM analysis of the char residue measured by ASTM. This follows from an empirical correlation found by Badzioch and Hawksley (1970), for which Gray *et al.* (1974) obtained a simple theoretical basis, according to which the weight loss (ΔW) measured in their flow experiments was proportional to the loss of volatile matter corrected to an effective loss from the original coal (ΔV), thus

$$\Delta W = Q \cdot \Delta V = Q(V_0 - V_c) \quad (5)$$

where V_0 is the volatile percentage in the coal as measured by the ASTM analysis, and V_c is the VM content of the char. The factor Q is a multiplier reflecting, according to Gray *et al.* (1974), the effect of carbon capture in secondary cracking in the ASTM volatile matter determination. This capture effect is minimized or eliminated in low density dispersions of coal in air (but can become significant in air dispersions as the cloud (particle) density is increased—see Ubhayakar *et al.* (1977). At $V_c = 0$, $\Delta V = V_0$ and we have

$$\Delta W_\infty = Q \cdot V_0 \quad (6)$$

The original empirical expression and the derivation of equation (5) included an intercept term, ΔW_0 , but this is evidently small and may be neglected.

RESULTS

General Behavior

Loss in weight of the coal flowing through the furnace was determined as a function of time, and Figure 2 illustrates the typical results obtained in

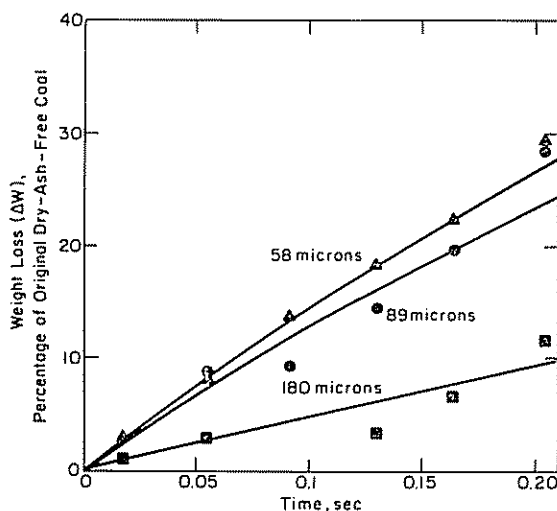


FIGURE 2 Variation of weight loss with isothermal pyrolysis time for PSOC-90 (\blacktriangle) $\bar{x} = 58 \mu\text{m}$, (\bullet) $\bar{x} = 89 \mu\text{m}$, (\blacksquare) $\bar{x} = 180 \mu\text{m}$.

most cases. The example is for the lignite, PSOC-90, for three particle sizes. Time was initially measured from the point of entry and calculated by assuming uniform velocity at constant temperature (808 °C) for the bulk of the flow (although 1/13th by weight was heating up). Weight loss was found to start at a false origin (as also found by Badzioch and Hawksley, 1970) 95 msec after entry. In Figure 2 this heating period has been subtracted out. Weight loss was determined using ash as a tracer in the conventional manner: this involved measuring the ratio of combustible to ash in the char samples, obtained by ashing.

Estimates (Nsakala, 1976) of heating rates of particles plunged into hot gas indicate that even at 8000 °C/sec heating rate no significant temperature gradient exists in the particles on reaching reactor temperature (808 °C) after 95 msec.

Reproducibility of Weight Loss Measurements

The variation in weight loss between successive determinations was examined by comparing five repeat measurements at two particle sizes of the Ohio bituminous coal (PSOC-296). The results, given in Table 2, were compared using the methods for small number statistics described by Dean and Dixon (1951). As indicated in Table 2, reproducibility at the 95 percent confidence limit is to within ± 2 percentage points, which is acceptable.

TABLE 2
Accuracy of weight loss results at 95 percent confidence limits for PSOC-296

Size (microns)	Percent ash in coal (dry basis)	Percent ash in chars (dry basis)	Weight loss (percent of original dry-ash-free coal)
64	17.1	19.9	17.1 ± 1.8
180	16.7	18.6	11.8 ± 1.4

Relation Between Volatile Loss and Weight Loss

In the char samples taken from the furnace the volatile matter remaining in the char (V_c) was determined by conventional ASTM analysis. Figure 3 illustrates the results of plotting ΔW against $(V_0 - V_c)$, testing Eq. (5), for three particle sizes of PSOC-90. This substantiates the equation under test (with a small, but negligible intercept). The slope yields the Q -factor (of value 2 for this coal, and independent of particle size). This value of Q was then used with the ASTM value for V_0 to obtain ΔW_∞ by Eq. (6). The values of Q and ΔW_∞ for the two coals PSOC-90 and 246 are listed in Table 3 with other data obtained as described below.

Effects of Heat-up Time and Recycle

Samples of some chars were recycled through the furnace one or more times with two objectives in view: to examine the influence of the heating up time on the pyrolytic loss of weight; and to determine the feasibility of extending the reaction time by recycling. To test the effects of recycle, the weight loss obtained in a given once-through transit time was compared with the weight loss for the same isothermal and cumulative transit time in-

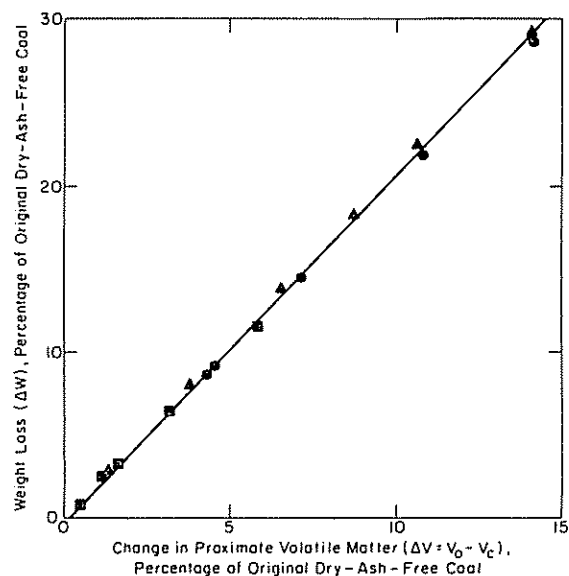


FIGURE 3 Variation of weight loss with change in ASTM volatile matter of char for Montana lignite (PSOC-90, 43.50 percent VM) (\blacktriangle) $\bar{x} = 58 \mu\text{m}$, (\bullet) $\bar{x} = 89 \mu\text{m}$, (\blacksquare) $\bar{x} = 180 \mu\text{m}$.

volving one recycle. Typical results are summarized in Table 4 (with explanation of the results below), for PSOC-246 at four different particle sizes. A once-through isothermal transit time of 205 msec could be accommodated, involving, of course, a pre-heating period of 95 msec for a total transit time of 300 msec.

Table 4 summarizes the following conditions for comparison. Line 1 gives weight loss of a sample that was removed after 55 msec of isothermal exposure and then recycled for the same conditions. Isothermal exposure was therefore 2×55 msec = 110 msec, with 2×95 (= 190) msec of heating time for a total cumulative residence time

TABLE 3
Results for pyrolysis of lignites in laminar flow furnace at 808 °C

Coal	Size (microns)	Q	k_1 (sec ⁻¹)	k_2 (sec ⁻¹)	ΔW_∞ (percent, daf)	G_1 (percent, daf)	G_2 (percent, daf)	α	C_1	C_2
PSOC-246	64	1.8	2.38	0.30	86	32	6	0.24	25	75
	86	1.8	1.74	0.41	86	25	15	0.21	15	85
	180	1.8	0.84	0.39	86	13	21	0.18	4	96
PSOC-90	58	2.0	1.94	—	87	29	—	—	—	—
	89	2.0	1.62	—	87	29	—	—	—	—
	180	2.0	0.61	—	87	12	—	—	—	—

TABLE 4
Effect of recycling on weight loss for PSOC-246

Recycle condition	Isothermal time (msec)	Total time (msec)	Weight loss, percent of original dry-ash-free coal			
			$\bar{x} = 64 \mu\text{m}$	$\bar{x} = 86 \mu\text{m}$	$\bar{x} = 127 \mu\text{m}$	$\bar{x} = 180 \mu\text{m}$
1) once	110	300	10.1	11.4		3.7
2) once	205	395	30.5	19.0	18.1	12.7
3) none	205	300	31.6	25.2	18.5	13.0

of 300 msec. Line 2 gives weight loss for a sample recycled once for the same (190 msec) heating time duration, but the isothermal exposure time was increased to $2 \times 102.5 = 205$ msec., for a total exposure time of 395 msec. Line 3 is for the once-through sample at 95 msec heating time and 205 msec isothermal exposure, for a total exposure time of 300 msec. The conclusion is self-evident: weight losses were comparable (with some question on the 86 micron fraction) for equal isothermal exposure time (lines 2 and 3); weight losses were clearly far from comparable at equal total exposure time (lines 1 and 3). It is concluded, as others have previously (Badzioch and Hawksley, 1970) that there is no detectable or significant weight loss during either the heating or the cooling period: even more significant, the pyrolysis mechanism is evidently unaffected at this temperature by the reaction being interrupted.

Effect of Increased Reaction Time

Advantage was taken of the conclusions of the recycling experiments to extend the isothermal reaction time to one second. Figure 4 is typical of the results obtained (for PSOC-246): as can be

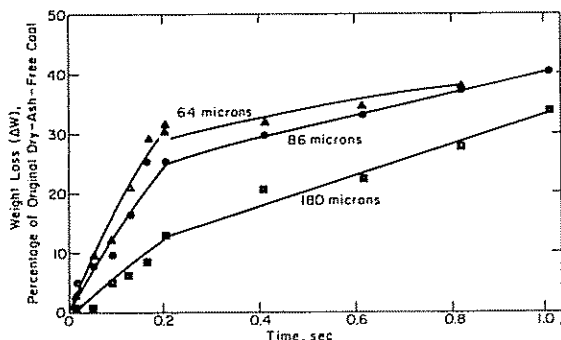


FIGURE 4 Variation of weight loss with isothermal pyrolysis time for North Dakota lignite (PSOC-246, 47.5 percent VM) (\blacktriangle) $\bar{x} = 58 \mu\text{m}$, (\bullet) $\bar{x} = 89 \mu\text{m}$, (\blacksquare) $\bar{x} = 180 \mu\text{m}$.

seen, the extended reaction time brought out a significantly different trend in the weight loss behavior, with a marked break in the line for all three particle sizes shown—and with the location of the break at a reaction time that is somewhat independent of particle size.

Such a break in a cumulative reaction curve is characteristic of two independent parallel reactions, hinting at decomposition of two independent components.

EVALUATION OF RESULTS

Kinetic Equations Evaluation

The weight loss results were evaluated in terms of the kinetic equation 4 and the phenomenological model (1) on which the equation is based.

As described above, the limiting weight loss, ΔW_{∞} was obtained by algebraic extrapolation of Figure 3, using Eq. (6). Agreement with Eq. (4) was then examined by plotting $\ln(1 - \Delta W / \Delta W_{\infty})$ against time, t , as illustrated in Figures 5 and 6. The results are reasonably in agreement with the equation. Figure 5 (for PSOC-90) shows only two straight lines for two particle sizes, consistent with evidence for only a single decomposition. Figure 6, however, (for PSOC-246) shows reasonable correspondence to the behavior described by Eq. (4), with the curves for each particle size well represented by two straight lines. This is characteristic of two independent parallel reactions having substantially different rate constants. This is interpreted as support for the existence of the Components I and II.

Effect of Particle Size on Pyrolysis Rates

The results illustrated in Figures 5 and 6 provide interesting information on the different effects of

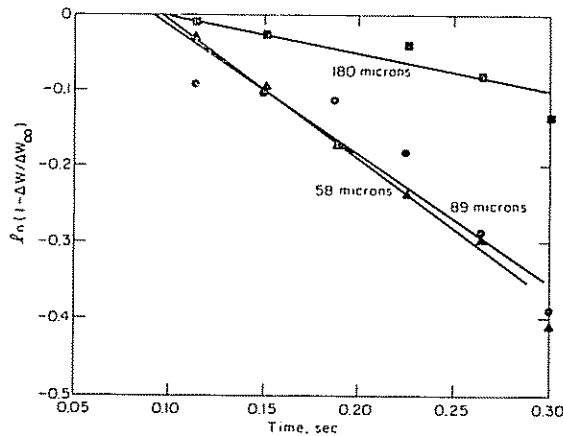


FIGURE 5 Variation of $\ln(1 - \Delta W/\Delta W_\infty)$ with cumulative residence time in the pyrolysis furnace for Montana lignite (PSOC-90, 43.5 percent VM) (\blacktriangle) $\bar{x} = 58 \mu\text{m}$, (\bullet) $\bar{x} = 89 \mu\text{m}$, (\blacksquare) $\bar{x} = 180 \mu\text{m}$.

particle size on the two reactions. Figure 5 and the initial stages of Figure 6 show marked dependence on particle size. The slower, Component II decomposition, on the other hand is evidently insensitive to particle size.

This behavior can be compared with other results. As discussed in more detail elsewhere (Gray *et al.*, 1974; Essenhigh, 1977) it is generally accepted that the rate of escape of volatiles is influenced by diffusion out of the char particle, and thus depend-

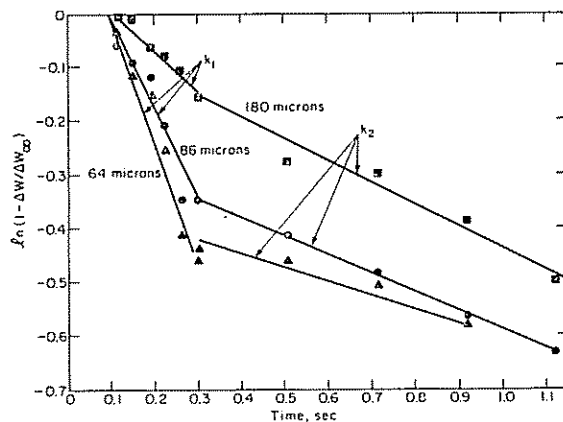


FIGURE 6 Variation in $\ln(1 - \Delta W/\Delta W_\infty)$ with cumulative residence time in the pyrolysis furnace for North Dakota lignite (PSOC-246, 47.5 percent VM) (\blacktriangle) $\bar{x} = 64 \mu\text{m}$, (\bullet) $\bar{x} = 86 \mu\text{m}$, (\blacksquare) $\bar{x} = 180 \mu\text{m}$.

ent on particle size, down to about 100 microns. Escape is generally believed to be substantially independent of particle size below 50 microns, with a transition zone from one regime to the other between 50 and 100 microns.

The results described above are in broad agreement with this picture, with added significant detail. The particle sizes used are in the transition range. Empirically, the velocity constants of PSOC-246 for k_1 vary approximately inversely with particle diameter. In contrast, the Component II decomposition is evidently so relatively slow that diffusional escape is no barrier of significance and the kinetic constants are effectively independent of particle size.

It is interesting, therefore, that Eq. (4) appears to describe the overall behavior quite well even though it is predicated on such rapid escape of the volatiles that diffusional effects are presumed to be small. There is clear need to investigate the effect of particle size over a greater range, both at larger and smaller sizes.

Coefficient and Constant Values

Taking Eq. (4) and the agreement to it at its face value, nevertheless, it is possible to extract values for the additional coefficients, C_1^0 , C_2^0 , and a . If conditions show weight loss independent of particle size. Extrapolation of the Component II decomposition line back to the decomposition origin ($t = 0$) would yield the value of $(1 - C_1^0/\Delta W_\infty)$, and hence $C_2^0/(1+a)(\Delta W_\infty)$ from Eq. (3). However, $(100 - \Delta W_\infty) = C_\infty$, the maximum primary char yield, and manipulation generates: $(C_\infty/a) = C_2^0/(1+a)$, from which a and hence C_2^0 may be obtained under the particle size invariance requirement.

The ratio of Component I and II in PSOC-246 is estimated at about 10 to 1. The ratio of gas yields G_1/G_2 , however, is somewhat lower, at about 3 to 1.

The results so far obtained yield intercept values that are particle size dependent. The range in particle size is too small at present for the particle size dependency to be established so that extrapolation to particle size independency would be possible. An alternate method for determining the factors is described in the section following, however, drawing on results obtained by Badzioch and Hawksley that are assumed for purposes of estimation, to be comparable. The estimates of C_1^0 , C_2^0 , a , G_1 , and G_2 are given in Table 3.

DISCUSSION

Comparison with Badzioch and Hawksley Empirical Equation

Badzioch and Hawksley (1970) adopted or implied a one-step, first-order decomposition reaction, but found it necessary to add an empirical correction factor, C^* , so that their rate expression could be written

$$\Delta V/V_0 = (1 - C^*)(1 - \exp[-k_1 t]) \quad (7)$$

where $V_0 = V_0$ in our nomenclature, and from Eqs. (5) and (6) we have $\Delta V/V_0 = \Delta W/\Delta W_\infty$.

We now show that our rate Eq. (2) has the form of approximately of Eq. (7) at short t . Rewriting Eq. (2) or (4) in the form

$$\begin{aligned} \Delta W/\Delta W_\infty &= \Delta V/V_0 \\ &= \{1 - (1 - C_1^0/\Delta W_\infty)(1 - [1 - \exp(-k_2 t)]/[1 - \exp(k_1 t)])\} (1 - \exp[-k_1 t]) \end{aligned} \quad (8)$$

which has the form of Eq. (7) with

$$C^* = (1 - C_1^0/\Delta W_\infty)(1 - [1 - \exp(-k_2 t)]/[1 - \exp(-k_1 t)]) \quad (9)$$

and for small t , expanding the exponentials we have

$$C^* = (1 - C_1^0/\Delta W_\infty)(1 - k_2/k_1) < 1 \quad (10)$$

If k_1 and k_2 have similar temperature coefficients and/or the ratio k_2/k_1 is small, C^* will be insensitive to or independent of temperature. For lignites, Badzioch and Hawksley reported C^* was constant with a value of 0.14. From our Table 3 we find $k_2/k_1 = 0.12$ to 0.5, with the ratio diminishing with particle diameter. Adopting $C^* = 0.14$, this gives us a value for C_1^0 of 77 ± 5 percent.

We can also write

$$C^* = (1 - C_1^0/\Delta W_\infty) \times (1 - [k_2^0/k_1^0] \exp[-(E_2 - E_1)/RT]) \quad (11)$$

for comparison with Badzioch and Hawksley's empirical expression

$$C^* = C^*_0 \exp(-KT) \quad (12)$$

Both expressions show C^* declining with increasing T . Equation (12) is for a curve that is concave

upwards. Equation (11), however, will only describe a concave upward curve if $(E_2 - E_1)$ is very small, of the order of 5 kJ. We do not conclude, however, that $E_1 \approx E_2$. Rather, we feel that the empirical method of fitting to their results used by Badzioch and Hawksley has disguised the true trend. Clearly, there is scope for a re-examination of their data.

Influence of Pyrolysis Rate Constants on Loss During Heat Up

Lacking necessary variations in temperature we do not have the data to determine the activation energies and frequency factors for the reactions directly. We can, however, set limits that are considerably informative. Since we write, as is common

$$k = k_0 \exp(-E/RT) \quad (13)$$

we use the experimental values of k at the known temperature to set limits on k_0 and E for the two reactions. We have then explored by calculation two aspects of behavior: first, the limiting value of E at the arbitrarily chosen value of $k_0 = 10^{13} \text{ sec}^{-1}$ that will allow heat up at $8000^\circ\text{C}/\text{sec}$ with only 1 percent loss of volatiles in 95 msec.; and second, the variation of E with k_0 for the same loss restriction on heating up. The results are illustrated in Figures 7 and 8.

Figure 7 shows the variation of fractional weight loss with time assuming a linear rise in temperature to 808°C which is then held constant. The frequency factor k_0 was held fixed at 10^{13} sec^{-1} and E was varied from 167 kJ/mole (40 kcal/mole) to

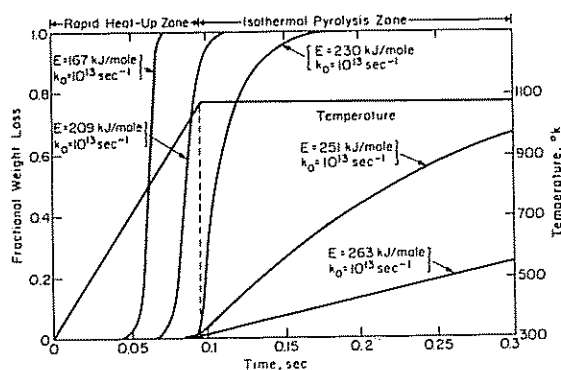


FIGURE 7 Calculated variation of fractional weight loss of volatile with time for a one-step first order reaction with $k_0 = 10^{13} \text{ sec}^{-1}$ and variable values of E —see Eq. (13).

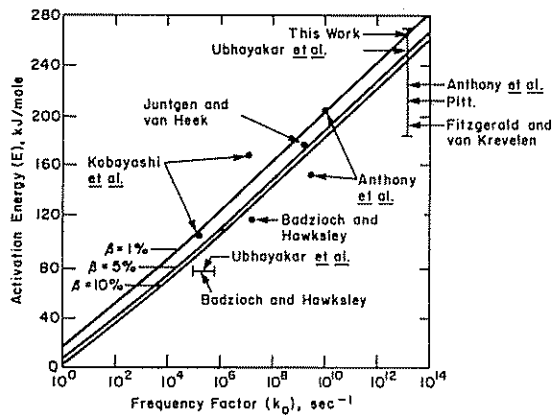


FIGURE 8 Variation of frequency factor with activation energy for 1, 5, and 10 percent loss of volatiles in 95 msec at 8000°C/sec heating rate.

263 kJ/mole (63 kcal/mole). It is clear from this that E must exceed 230 kJ/mole (55 kcal/mole) for $k_0 = 10^{13} \text{ sec}^{-1}$ if the experimental finding of negligible loss of volatiles on heating up is to hold.

Equally obviously, this limit value of 230 kJ/mole is dependent on the choice of k_0 . The frequency factor was therefore varied from 10^0 to 10^{14} sec^{-1} , and again the limit value of E was determined, in this instance for three levels of loss, 1 percent, 5 percent and 10 percent ($=\beta$). The results are illustrated in Figure 8, which also includes values of k_0 and E reported by others—see Table 5.

It will be seen from Figure 8 that in spite of a range of four decades in the experimentally reported values of k_0 , the values of E so match that the reaction rates are still somewhat comparable. At the same time, however, there is clearly much need and scope for improvement in the accuracy of measurement.

Comparison with Liquefaction Theories

Equations for liquefaction behavior show close parallels to the pyrolysis equations examined in this paper. Most commonly used models (Curran *et al.*, 1967; Hill *et al.*, 1966; Weller *et al.*, 1951; Oele, *et al.*, 1951; Liebenberg and Pothier, 1973; Wisler, 1968) assume either a sequential set of reactions where each product becomes the reactant for the next reaction, or that there is a set of parallel reactions. Experimentally, good support has been obtained for two independent, parallel, first order reactions (Curran *et al.*, 1967) and the rate expression obtained is identical with our Eq. (4). Liquefaction then shows further complications as products of the first reaction step become reactants (paralleling the secondary pyrolysis reaction of G_1 to produce char).

The overall parallelism of the behavior is striking and also supports a Two-Component model. It is not evidence, of course, that the component division are the same in pyrolysis and liquefaction,

TABLE 5
Kinetic constants: A survey

Authors	Frequency factor (k_0), sec^{-1}	Activation energy (E) kJ/mole	Comments
Fitzgerald and van Krevelen 1959	1.67×10^{13}	192.53	—
Pitt, 1962	1.67×10^{13}	146–314	Sharp maximum peak for activation energy: 209–230 kJ/mole
Juntgen and van Heek, 1968	1.67×10^9	175.9	—
Badzioch and Hawksley, 1970	$(0.836 - 5.68) \times 10^5$	73.6	Weakly and highly swelling coals
	1.79×10^7	116.7	Anthracite
Anthony <i>et al.</i> , 1974	1.67×10^{13}	230–255	—
Anthony <i>et al.</i> , 1974	1.07×10^{10}	203.65 ± 39.21	Experimental values for a lignite
		154.12 ± 17.47	Experimental values for a bituminous coal
		234 ± 46	Theoretical values for a lignite
		213 ± 29	Theoretical values for a bituminous coal
Kobayashi <i>et al.</i> , 1977	2×10^5	105	First of two competing reactions
	1.3×10^7	167	Second of two competing reactions
Nsakala, N., 1976	10^{13}	263	—
Ubhayakar <i>et al.</i> , 1977	3.7×10^5	73.6	First of two competing reactions
	1.46×10^{13}	251	Second of two competing reactions

but by Occams Razor this, as the simplest assumption, is the best to adopt at present for purposes of developing working theories of coal behavior.

CONCLUSIONS

Pyrolysis of six lignite coal particles at constant temperature follows the same general trends reported by others. At the heating and cooling rates involved no evidence for reaction during heating or cooling was obtained, as reported by others (Badzioch and Hawksley, 1970), which provides implications on limits on activation energies. Also as reported by others, weight loss under these experimental conditions substantially exceed the VM percentage of the coals determined by ASTM analysis, and with weight loss proportional to ASTM volatile loss from the char formed.

More significantly, evidence was obtained for two stage pyrolysis, for pyrolysis times exceeding 0.2 sec. This behavior was consistent with a Two-Component model of coal constitution, and in agreement with the equations based on the model. This is believed to be the first direct evidence in support of such a model although it was first proposed about 60 years ago. Evidence for such a model, however, has tended in the past to be indirect and/or inductive.

The Component I decomposition was found to be particle size dependent down to the smallest particles examined (58 microns) with indications that this dependence would continue to particle sizes much smaller than 50 microns, which has been considered the upper limit of independence in the past. The Component II decomposition by contrast, appears to be independent of size, up to the largest particle size examined (180 microns), which is invading the region normally assumed to be rate limited by diffusional escape.

We submit these results as evidence in support of a working model of coal constitution that can be as a target for test in future experiments.

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