

ISOTHERMAL FURNACE STUDIES OF THE KINETICS OF LIGNITE PYROLYSIS

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INTRODUCTION

In practical pulverized coal combustors and gasifiers, pyrolysis occurs in conjunction with rapid heating of the coal; heating rates in excess of 1,000°C/s being common. One apparent consequence of rapid heating is that crucial reactions occur in the first few seconds or even milliseconds (1-3). This is partially responsible for the stringent requirements associated with an acceptable experimental technique for studying the kinetics of rapid coal pyrolysis. The requirements include controlled rapid heating, isothermal reaction, variation of reaction time and rapid quenching. In essence, it is essential to have unambiguous reaction history.

Two of the techniques currently in use more or less satisfy the requirements. One employs essentially monolayer samples heated on an electrical grid (1), and the other utilizes a flow of coal particles injected into a preheated gas stream (2,3). The latter technique is used in this laboratory. The kinetics of pyrolysis are most conveniently studied using an inert atmosphere as the pyrolyzing medium. This has the effect of decoupling pyrolysis reactions from other heterogeneous gas/solid reactions that occur when a reactive atmosphere such as H₂ is used. Present data are for isothermal pyrolysis in N₂ of a lignite from the Darco Seam in Texas. Temperatures vary from 700 to 1,000°C and particle size fractions, from 60 x 80 to 270 to 400 mesh.

EXPERIMENTAL

Pyrolysis is performed in an entrained flow, isothermal furnace similar to that described by Nsakala and co-workers (3) which, in turn, is based on the design of Badzioch and Hawksley (4). It is, in essence, a vertical reactor heated electrically and for the injection of a dilute coal stream into the center of a preheated gas stream. The ensuing mixing heats the injected stream at a rate of about 10,000°C/s. The injector is designed to minimize migration and adherence of coal particles to the furnace tube wall. A water-cooled sampling probe, which is inserted up the axis of the furnace, collects and rapidly quenches the particle stream. The reactor tube is heated uniformly so that pyrolysis is essentially contained in an isothermal region. Variable positioning of the sampling probe adjusts the reaction time. A schematic of the equipment is shown in Figure 1 and the operating conditions are given in Table 1.

Weight loss due to pyrolysis is determined using proximate ash as a tracer. Data are corrected for the error associated with this technique. For the Darco lignite the error is less than 10% and is thought to result from the loss of sulfur during pyrolysis (5). The proximate analysis of the lignite is given in Table 2. Particle size fractions are separated by dry sieving and characterized by the Rosin-Rammler technique (6).

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TABLE 1. OPERATING CONDITIONS

	<u>Gas and Wall Temperature, °C</u>			
	<u>700</u>	<u>800</u>	<u>900</u>	<u>1,000</u>
Coal Feed Rate, g/min	1.0	1.0	1.0	1.0
Mean Gas Velocity, m/s	1.12	1.12	1.12	1.12
Secondary/Primary N ₂	16.7	15.0	13.7	12.5
Coal Loading, wt%	2.2	2.5	2.7	2.9
Gas Reynolds Number	458	391	339	298

TABLE 2. PROXIMATE ANALYSIS OF THE DARCO LIGNITE

	<u>as-received</u>	<u>dry</u>	<u>daf</u>
Moisture, %	22.4	-	-
Ash, %	12.4	15.9	-
Volatile Matter, %	33.3	43.0	50.2
Fixed Carbon, %	31.9	41.1	49.8

Equilibrium Moisture = 39.8%

RESULTS

A typical weight loss versus time curve is shown in Figure 2 for isothermal pyrolysis at 900°C. Weight loss, hence pyrolysis rate, is independent of particle size over the range 60 x 80 to 270 x 400 mesh. The corresponding range in mean particle size is 40 to 200 μm . Similar curves are obtained at 700, 800 and 1,000°C.

The maximum potential weight loss in the isothermal furnace is not measurable by a single pass because of the restricted residence time. It is calculated by the method of Badzioch and Hawksley (4). This involves establishing a relationship between the change in proximate volatile matter between the original dry-ash-free coal and char and weight loss due to pyrolysis. The derived relationship is linear; it is essentially particle size (Figure 3) and temperature independent (Figure 4) for the range of operating conditions. The maximum weight loss is 66% of the daf coal, representing a fractional increase of 1.3 over the proximate volatile matter. The weight loss achieved by a single pass in the isothermal furnace at 1,000°C and a total residence time of 0.4 s is 50% of the daf coal, indicating about 80% completion of pyrolysis.

A first-order plot for pyrolysis at 900°C is shown in Figure 5. A feature of the curve is the apparent delay in the onset of pyrolysis during heat-up of the particles. This is in agreement with the findings of Jüntgen and Van Heek (7). Correlating first-order rate constants by the Arrhenius expression (Figure 6) yields a pseudo activation energy of 7.7 kcal/mole and a pre-exponential factor of 92 s^{-1} .

DISCUSSION

Successful description of the kinetics of pyrolysis up to 80% completion by a single first-order reaction equation is not inconsistent with the need for a second equation to describe the completion of pyrolysis as postulated by Nsakala and co-workers (3). This derives from the fact that the second component devolatilization is associated mainly with H₂ liberation (8), which on a weight basis accounts for only about 5% of the daf coal.

The relatively low pseudo activation energy is consistent with the data presented by Anthony and Howard (9). The absence of particle size effects on the rate of pyrolysis for the Darco lignite essentially implies the absence of significant heat and mass transfer effects. Since low activation energies are usually associated with these physical factors, an alternative explanation is required here. Howard and co-workers (1,9) provide a probable explanation in terms of a distribution of activation energies for the generation of different volatile species. They obtain an activation energy of about 10 kcal/mole in a single-step correlation and about 50 kcal/mole in a multistep model.

SUMMARY

The present work further demonstrates the suitability of the entrained flow isothermal furnace for studying the kinetics of lignite pyrolysis. Under rapid heating conditions there is a delay in the onset on significant pyrolysis during particle heat-up. For the Darco lignite, pyrolysis up to 80% completion follows a single first-order reaction equation; but a second equation may be necessary to describe the completion of pyrolysis. The relatively low activation energy of less than 10 kcal/mole and the absence of significant particle size effects are not necessarily inconsistent, as the former may not necessarily indicate physical rate control.

ACKNOWLEDGEMENTS

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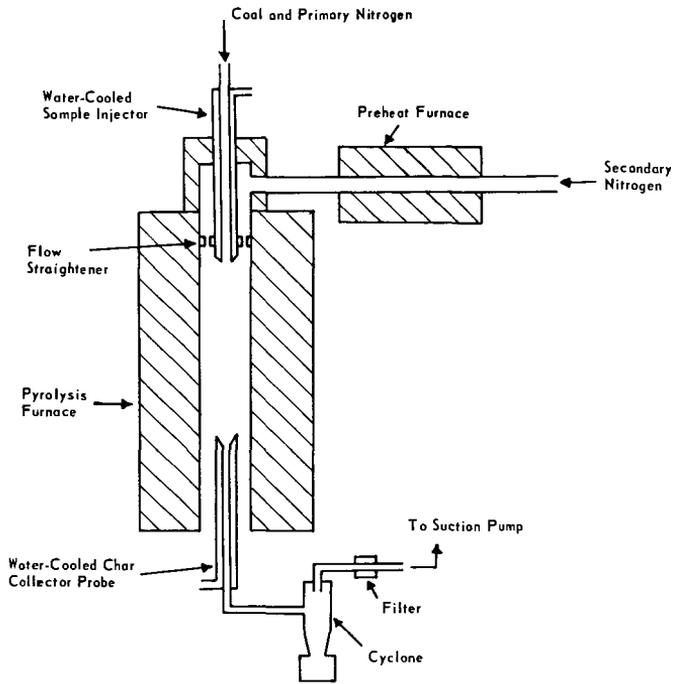


Figure 1. SCHEMATIC OF EQUIPMENT

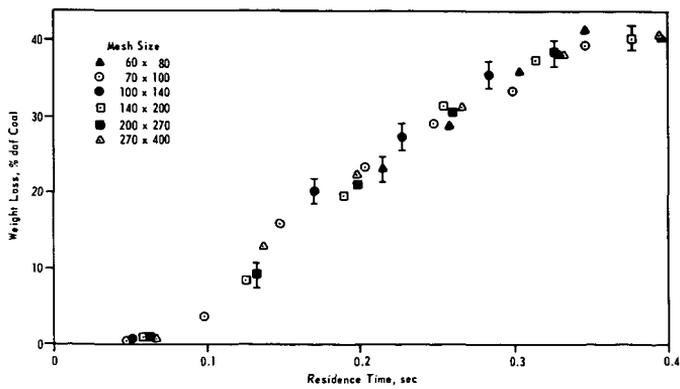


Figure 2. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME OF LIGNITE IN REACTOR AT 900°C

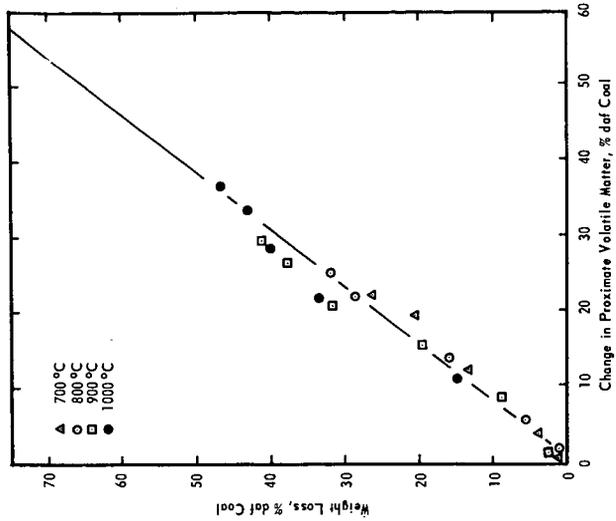


Figure 4. VARIATION OF WEIGHT LOSS IN ISOTHERMAL FURNACE WITH CHANGE IN PROXIMATE VOLATILE MATTER BETWEEN COAL AND CHAR FOR 140 x 200 MESH SIZE FRACTION

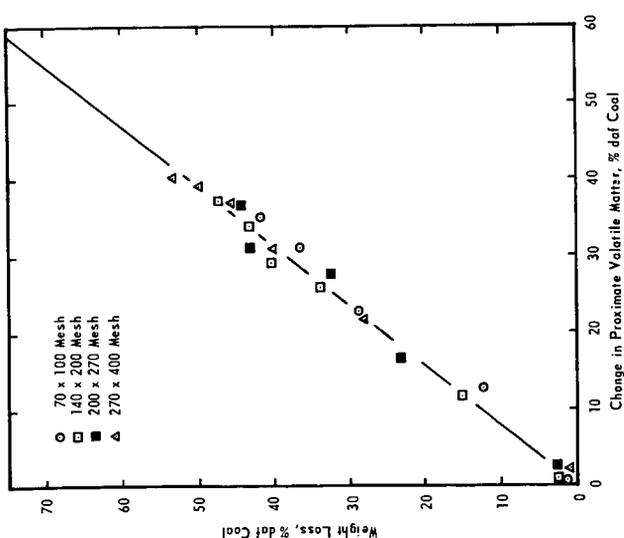


Figure 3. VARIATION OF WEIGHT LOSS IN ISOTHERMAL FURNACE AT 1,000°C WITH CHANGE IN PROXIMATE VOLATILE MATTER BETWEEN COAL AND CHAR

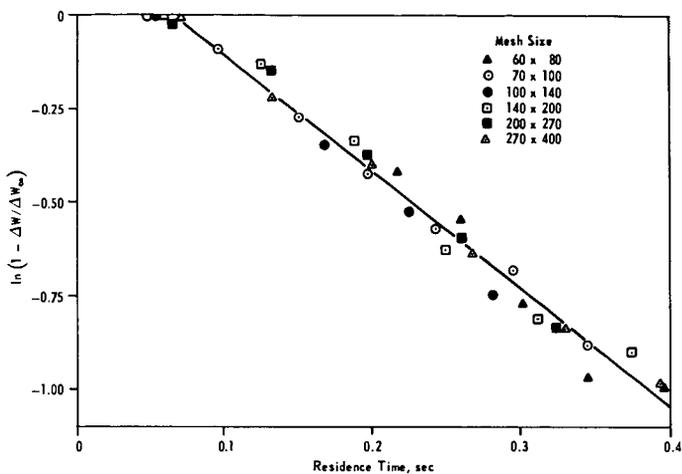


Figure 5. FIRST ORDER PLOT FOR DEVOLATILIZATION WEIGHT LOSS FOR LIGNITE AT 900°C

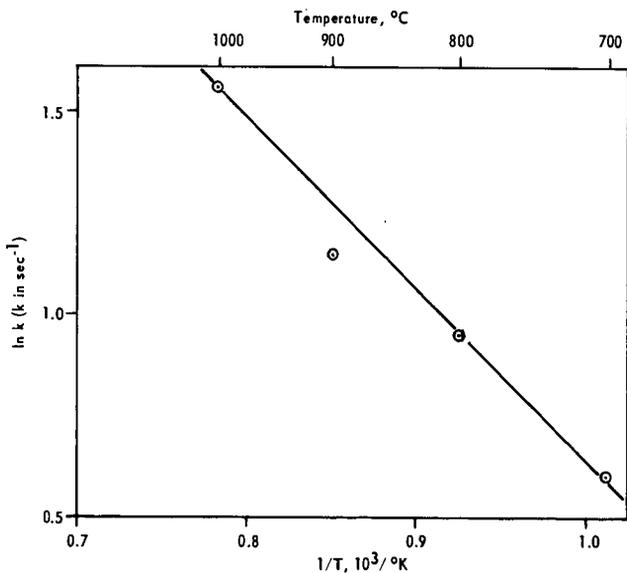


Figure 6. ARRHENIUS PLOT FOR LIGNITE DEVOLATILIZATION TREATED AS ONE STEP, FIRST-ORDER REACTION