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KINETICS OF LIGNITE PYROLYSIS IN FIXED BED AND ENTRAINED
FLOW REACTORS

Technical Report No. 17

By
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MASTER

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COAL RESEARCH SECTION
THE PENNSYLVANIA STATE UNIVERSITY
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ABSTRACT

A laminar flow isothermal furnace has been constructed and used to study lignite pyrolysis in nitrogen at temperatures between 700 and 1000°C. Particles of a Texas lignite (Darco Seam) between 41 and 201 microns in mean diameter, are found to flow down the furnace tube with velocities approximated by the summation of the gas plug-flow velocity and particle free-fall velocities. Some particle shrinkage and density changes occur during pyrolysis. Pyrolysis rate is particle size independent and increases with increase in temperature over the range of operating conditions. Ultimate yield of volatiles in the isothermal furnace, which is calculated from the linear relationship between weight loss and change in proximate volatile matter, is 66% of the original dry-ash-free coal and is particle size independent and relatively temperature independent.

Pyrolysis up to 80% completion fits a single overall first-order reaction equation, but a second equation may be necessary to describe the completion of pyrolysis. Relating first-order rate constants with absolute temperature by the Arrhenius expression yields an activation energy of 7.7 kcal/mole. It is argued that this relatively low value is not necessarily indicative of physical rate control and hence not in contradiction with the absence of particle size effects.

Ultimate yields of volatiles from fixed beds of pulverized coal are smaller than for dispersed particles of the same size. Proximate volatile matter for the lignite is, for example, 51% of the original dry-ash-free coal. Heating rates drop from about 10,000°C/s in the

isothermal furnace to about 20°C/s in the proximate volatile matter test. Pyrolysis rates decrease and display particle size dependency in fixed beds. This implication of physical rate control is attributed to heat transfer limitations. It is proposed that pyrolysis rate and therefore residence time of volatiles in the fixed bed is an important parameter affecting the preponderance of secondary char forming reactions. Also important is the total particle external surface area in the bed. Secondary char formation is considered responsible for yields of volatiles lower than the true volatile content of the lignite as measured in the isothermal furnace.

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1. INTRODUCTION

1.1 Coal Pyrolysis and Its Significance

Combustion of coal is traditionally an important method of satisfying our energy needs. Any future restrictions on supplies of oil and natural gas, either artificial or by exhaustion of reserves, will place an even greater reliance on coal combustion. In addition, it is estimated that coal represents 70% of recoverable fossil fuels in the United States (1) so considerable interest is being shown in coal gasification. Primary attention is directed towards producing clean gaseous fuel as a substitute for natural gas. Impetus stems from the fact that many users of natural gas cannot easily convert to solid fuel and from the considerable advantages associated with the combustion of clean gaseous fuel. It is, in general, easier and cheaper to distribute and burn and causes little, if any, on-site air pollution.

In practical combustion and gasification processes, coal is heated to an elevated temperature causing some degree of thermal decomposition* in association with other chemical reactions. Maximizing the rate of evolution and yield of volatiles by pyrolysis reduces reliance on slow heterogeneous gas-solid reactions. In some practical gasifiers, depending on coal type and experimental conditions, up to 90% of the gas yield can be the direct result of pyrolysis. In combustion processes pyrolysis influences such parameters as ignition

*The terms pyrolysis, thermal decomposition, devolatilization and carbonization are often used synonymously.

mechanism, flame stability and combustion intensity. The stimulation of interest in pyrolysis behavior therefore stems from its application to coal combustion and gasification; two processes which figure prominently in our overall energy scheme.

1.2 Objectives of the Study

The general purpose of the study is to investigate coal pyrolysis under conditions similar to those occurring in pulverized fuel systems. Simulation requires rapid heating of pulverized coal particles dispersed in a gas phase. A technique using a laminar flow of nitrogen in an isothermal furnace has been successfully demonstrated in a previous study (2).

The specific objectives are:

1. To construct a laminar flow isothermal pyrolysis furnace based on an existing design (2) but allowing longer particle residence times and capable of operating at higher temperature.
2. To investigate the effect of particle size and isothermal pyrolysis temperature on rate of pyrolysis and yield of volatiles.
3. To determine the importance of heating rate on maximum yield of volatiles.
4. To explain behavioral differences, if any, between pyrolysis in the isothermal furnace and conventional fixed bed apparatus.
5. To gather kinetic data in order to describe the kinetics of the overall pyrolysis process.

2. HISTORICAL

2.1 Previous Reviews

Literature on coal pyrolysis is voluminous and includes abundant reviews (3-13). Most early data (3-7) refer to coal carbonization under conditions of slow heating, of the order of 1 to 10°C/m, and focus mainly on the quantity and nature of products. Recently, the importance of pyrolysis to pulverized coal flames and gasification systems has been recognized. The result of this recognition is a directional change with emphasis now placed on conditions of rapid heating, above about 1,000°C/s. Later reviews (8-13) differentiate the two heating regimes and concentrate on understanding kinetics of pyrolysis reactions. A recent comprehensive review (12) probably provides the best insight into the state of understanding of pyrolysis under combustion and gasification conditions.

2.2 General Pyrolysis Behavior

General pyrolysis behavior of coal has been known since the early 1900's (14-16). Upon heating, coal begins to decompose, usually at about 350°C, into a carbon rich residue and a volatile fraction relatively richer in hydrogen. Decomposition continues up to a temperature of about 1000°C which, if maintained for an extended period of time, results in almost complete devolatilization. The volatiles are composed of various gases and liquids, the relative proportion of which depend upon the coal type and pyrolysis conditions. Reports originating in the 1960's suggested that rapid heating of the coal enhances the yield of volatiles and changes their composition (17,18). The tar

yield reportedly increases, the gas yield decreases and the volatiles become richer in carbon.

2.3 Techniques for Studying Rapid Pyrolysis

The major difficulty associated with studying rapid pyrolysis is meeting the stringent requirements of the experimental technique. This in part stems from the fact that crucial reactions occur in the first few seconds or even milliseconds (2, 19-21). The requirements include controlled rapid heating, isothermal reaction, rapid quenching, variation of reaction time, ambient gas and coal type, unambiguous reaction history and pressurization.

Projected commercial conditions for gasification processes encompass coal type from lignite to bituminous, temperature from 500 to 1,000°C, heating rates up to 10,000°C/s, particle size from several millimeters to less than 50 microns and pressures up to 100 atmospheres (22). The above temperature limits are probably too low. Two currently available techniques partially satisfy the requirements of a rapid heating pyrolysis system. One technique utilizes a fixed bed of coal while the other employs a flow of coal particles.

Fixed beds of coal are usually held captive in a crucible (23-25), on an electrical grid (17, 19, 26-33), in the wire basket of a thermobalance (34) or as a ring on the inside of a stainless steel pipe (35, 36). Heating rates in crucibles are restricted to about 20°C/s as for the A.S.T.M. proximate volatile matter test (23) and to a few hundred °C/s in the thermobalance (12). Thermal inertia of the stainless steel pipe prohibits rapid quenching of samples in that system. Rapid quenching of samples is also incompatible with monolayer samples

on an electrical grid even though heating rates up to $10,000^{\circ}\text{C/s}$ are attainable. In addition, complications arise from catalytic cracking reactions which deposit carbon on the hot screens (19, 31).

Coal flow techniques utilize particle free-fall (37-39), entrained flow (2, 21, 40-52) or fluidized beds (18, 53-58). Fluidized beds suffer from problems with agglomerating coals and poor residence time definition. Density changes due to gasification and swelling add considerable complexity to the calculation of free-fall velocities. The problem of density changes is circumvented to some extent in entrained flow systems, particularly if particle free-fall velocities are small compared with the gas velocity. Despite lingering problems with the resolution of residence times for large particles, the laminar flow isothermal furnace most suitably fits the experimental requirements.

The apparatus is essentially an electrical tube furnace designed to inject a dilute coal stream into the center of a preheated gas stream. The ensuing mixing heats the injected stream at a rate of $10,000^{\circ}\text{C/s}$ or faster. The injector is designed to minimize migration and adherence of the coal particles to the furnace tube wall. A water-cooled sampling probe, which is injected up the axis of the furnace, isokinetically collects and rapidly quenches the particle stream. The furnace tube is heated uniformly so that pyrolysis is contained totally in an isothermal region. Variable positioning of the probe adjusts the reaction time. Ambient gases can be easily changed and laminar piston flow provides unambiguous reaction history, at least for small particles.

2.4 Yield of Volatiles

When coal pyrolysis is performed according to an agreed prescription, the proximate volatile matter test for example, results are consistent and reproducible. Deviation from the standard technique, however, usually causes the yield of volatiles to vary. Initially, this behavior was designed out by specification of the precise procedure, but recently interest in the apparently anomalous behavior has revived. Volatile yields exceeding proximate volatile matter have been observed for a range of coals rapidly heated in thin beds or dispersed in gas (2, 17, 20, 21, 28-30, 50). Yields up to 30% in excess of proximate volatile matter are common with one reported excess yield of 100% (50). A few cases of diminished yield under similar conditions are reported (20, 28, 30), but these may be due to insufficient residence time.

Secondary cracking reactions of the volatiles resulting in carbon deposition are associated with packed beds of coal. This is consistent with the observation that the yield of volatiles increases as the bed depth diminishes (2, 19, 25, 59). The argument is basically that the porous bed traps pyrolysis products and provides surface on which they can react. The condition of thinly spread or well dispersed particles associated with rapid pyrolysis techniques discourages secondary char formation thereby causing the observed yield enhancement. While this is the most widely accepted theory (12), it has been proposed that, because of the plastic behavior of some coals, rapidly escaping gases physically carry away fragments of a pyrolysis intermediate (9, 60).

The nature of secondary char forming reactions is relatively unestablished. There is evidence that the primary volatiles are free radicals (61, 62) which polymerize to form coke unless they escape as tar as an intermediate product. Escaping tar may undergo cracking reactions (63). X-ray diffraction shows the existence of soot (64), and it is estimated that about 90% forms on the exterior surface of the particles (52).

In fixed beds the yield of volatiles increases as the heating rate is raised (2). The heating rate elevation is achieved by reducing the sample size or increasing the driving temperature. The accompanying increase in pyrolysis rate can be expected to reduce the preponderance of secondary char forming reactions. For dispersed or monolayer samples, however, the yield of volatiles is substantially independent of heating rate (31). For any situation, therefore, there is no direct evidence that heating rate is the primary cause for variation in the yield of volatiles.

The effect of particle size on the yield of volatiles is also relatively unestablished. Well dispersed lignite particles over the range 50 to 1000 microns and particles of bituminous coal up to 200 microns are reported to display particle size independency (31). Particle size dependency manifested in previous isothermal furnace data (2, 50) may very well be the product of the operating assumptions. This is outlined in detail in Section 5.3. To the knowledge of the author there does not exist an adequate systematical study of particle size effects.

The yield of volatiles increases as the temperature is elevated up to about 1000°C (19, 24, 32, 37, 65, 66). Some volatiles do remain, however, consisting principally of about one percent each of hydrogen and nitrogen (67). These volatile traces evidently require temperatures up to 2,000°C for their removal (13). Reported cases of a reduction in the yield of volatiles at temperatures between 700 and 900°C (27, 29) are attributed to an increase in secondary char formation associated with the experimental technique (12).

The literature permits certain inferences about the yield of volatiles due to coal pyrolysis. For well dispersed particles the yield is substantially independent of particle size up to 1,000 microns for heating rates up to 10,000°C/s. The yield depends, however, upon coal type and final pyrolysis temperature up to 1000°C. For particles contained in packed beds, secondary char forming reactions which occur mainly on particle exteriors cause a reduction in the yield of volatiles. The yield decreases as bed depth increases due to a reduction in heating rate and an increase in the residence time of volatiles in the bed. This is complemented by an increase in the total external surface area of the particles.

2.5 Composition of Volatiles

After drying, the order of appearance of volatile species is formed water, carbon dioxide, carbon monoxide, higher hydrocarbons, ethane, methane and hydrogen (68). The yield of each product depends on coal type (33), final temperature (32, 33) and pressure (17, 32, 33) but is relatively independent of heating rate for monolayer samples over the range 300 to 10,000°C/s (32). Yields of each species increase

monotonically with temperature to a constant value below 1,000°C (32, 33).

2.6 Rate of Pyrolysis

Weight loss versus time curves for pyrolysis of well dispersed particles under rapid heating conditions have been generated for a range of lignite and bituminous coals (2, 11, 21, 31, 50). Weight loss for a specified isothermal pyrolysis time increases with increase in temperature. The role of heating rate is not well understood. One apparent effect of increasing the heating rate is to delay the onset of significant pyrolysis, reasonably described as increasing the pyrolysis temperature. This is demonstrated theoretically using non-isothermal reaction kinetics and confirmed experimentally (26). An apparent consequence of delayed pyrolysis is to prevent significant pyrolysis from occurring during heatup of coal to 808°C at heating rates of about 10,000°C/s (20, 50). There is opposition to this contention, however (19).

The effect of particle size on weight loss with time is relatively unstudied. No effect is reported for 20 and 60 micron particles (20), 35 to 74 micron particles (41) or 60 to 417 micron particles (24). A decrease in pyrolysis rate as particle size increases from 58 to 180 microns is inferred from recent isothermal furnace data (50) but, as previously indicated, data have been analyzed on the basis of suspicious flow assumptions.

2.7 Kinetic Models of Pyrolysis

Models of coal pyrolysis are influenced by views on coal composition (13). The simplest approach is to assume one step degradation

of the coal into volatile matter and carbon residue (20). At the other extreme is the view of an assembly of many varied constituents that decompose independently with further decomposition by the initial pyrolysis products. The overall process is then treated as a statistical assembly of reactions (19, 54). Alternatively, the production of each major volatile species can be modelled (26, 32, 33).

Initially, experimental data were fitted to a single first-order reaction equation in volatile content, assuming the evolution rate to be proportional to the quantity of volatiles remaining (20). The final yield of volatiles is found by correlating the proximate volatile matter of the coal with the residual volatile matter of the char. While fit to a first-order reaction equation is good for a single set of data, the model becomes inadequate if the final yield of volatiles is temperature dependent. First-order rate constants are typically correlated with temperature by the Arrhenius expression.

An alternative model consists of two competing overall reactions, both first-order with different pseudo activation energies. One reaction is assumed dominant at relatively low temperatures with the other increasing in domination as the temperature increases, requiring that the latter have a higher pseudo activation energy. There are minor variations (21, 52, 69) to the basic model (50) presented here.

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 , in a primary reaction with velocity constant k_1 ; and Component II transformed into gas, G_2 , and char, C , in a parallel primary reaction with velocity constant k_2 . This two reaction model successfully accounts for any effect of temperature on the yield of volatiles.

The probability of several consecutive or competing reactions is recognized and modelled by a distribution of activation energies (19, 54). One objection to this approach is that the large number of adjustable constants virtually ensures fit to any data. Another approach is to model the production of individual volatile species, each by a one step first-order rate equation (32). Monitoring nine volatile species produces good agreement with the distribution of activation energies model.

Observed values of activation energy for the single step first-order model are typically less than 20 kcal/mole (31). This has led to inferences that mass transfer is the rate controlling step (70). However, a multistep model giving an activation energy distribution around 50 kcal/mole can be modelled by a single step activation energy of 10 kcal/mole (19). This is consistent with a theoretical demonstration for reactions under non-isothermal conditions (71). It is difficult on other grounds as well to attach any physical significance to derived activation energies (11). As an example, for the Arrhenius expression to be applied to an experimentally determined rate constant, the constant must vary with reciprocal absolute temperature according to an exponential law. This is true for gas and liquid phase reactions where the Maxwell-Boltzmann distribution of energies,

and thus activated and non-activated molecules, applies, but the rate constant/temperature relationship may not necessarily be the same in pyrolysis reactions. Other circumstances may lead to an Arrhenius type relationship between rate constant and temperature leading to an ambiguous activation energy calculation (72).

The significance of physical factors, internal and external heat and mass transfer, can be determined to some extent by experimentation. The most revealing test is the effect of particle size variation on the rate of pyrolysis. An absence of particle size effects in a flow system such as that of the isothermal furnace eliminates the existence of physical rate control except possibly for mass transfer control in the micropores of a microporous solid such as coal. Theoretical estimates of heat and mass transfer during pyrolysis are dubious due, in part, to the necessity of making assumptions of values for coal properties. These property values are not well known for coals and even less is known about their dependency on the transformation of coal into char. Nevertheless, the results of typical calculations are worth noting.

For a heating rate of $10,000^{\circ}\text{C/s}$, calculations predict that internal heat transfer effects are not significant for particles below 200 microns (73). Coal particles heated by convection are estimated to reach 95% of final temperature, 900°C , in 0.06 s for 100 micron particles and 0.24 s for 200 micron particles (11). Internal mass transport effects are reported for 300 to 5000 micron particles (74) but disappear for smaller particle sizes (41).

3. THEORETICAL

3.1 Use of Proximate Ash as a Tracer

Weight loss by coal due to pyrolysis can be determined using proximate ash as a tracer. The theoretical derivation is as follows:

For the original coal

$$W_a = A_o W_{\text{Coal}} / 100$$

where W_a = weight of ash, g

W_{Coal} = initial weight of dry coal, g

A_o = proximate ash in dry coal, %

For chars produced by pyrolysis

$$W_a' = A' W_{\text{Char}} / 100$$

where W_a' = weight of ash, g

W_{Char} = initial weight of dry char, g

A' = proximate ash in dry char, %

The basic assumption associated with using proximate ash as a tracer is that for two coal samples of equal weight, the weight of ash produced from an original sample equals the weight of ash produced from a char of the other sample. That is,

$$W_a = W_a'$$

Therefore

$$W_{\text{Coal}} = A' W_{\text{Char}} / A_o \quad 1.$$

Weight loss, ΔW as % daf coal is

$$\Delta W = 100 - 100 [W_{\text{Char}} (100 - A') / W_{\text{Coal}} (100 - A_o)] \quad 2.$$

Combining equations 1 and 2 yields

$$\Delta W = 100 - [100A_0/(100-A_0)] [(100-A')/A'] \quad 3.$$

3.2 Change in Proximate Volatile Matter

The proximate volatile matter of a char can be related to the change in proximate volatile matter between the original coal and the char. From equation 3, the char yield, Y as % daf coal is

$$Y = [100A_0/(100-A_0)] [(100-A')/A'] \quad 4.$$

The proximate volatile matter of the char, X as % daf char is related to that on a dry basis, VM' by

$$X = VM' [100/(100-A')] \quad 5.$$

Combining equations 4 and 5 yields

$$R = [(100A_0)/(100-A_0)] [VM'/A']$$

where R = proximate volatile matter of the char as %
original daf coal

Therefore,

$$\begin{aligned} \Delta V &= VM_0 - R \\ &= VM_0 - [(100A_0)/(100-A_0)] (VM'/A') \end{aligned}$$

where ΔV = change in proximate volatile matter between
original coal and char as % daf coal

VM_0 = proximate volatile matter of coal as %
daf coal

3.3 Reaction Kinetics

The derivation is presented for the model consisting of two independent overall reactions, both first-order with different pseudo activation energies (50). That is

where C_1 and C_2 represent the quantities of initial Components I and II left at time t after pyrolysis has started, with Component I transformed to gas, G_1 , alone and Component II transformed to gas, G_2 , and char C . For decomposition by independent first-order reactions with velocity constants k_1 and k_2 , and writing C_1 and C_2 for the initial concentrations of the components, the variation of C_1 and C_2 with time is given by

$$C_1 = C_1^{\circ} \exp(-k_1 t)$$

$$C_2 = C_2^{\circ} \exp(-k_2 t)$$

$$\text{Weight loss, } \Delta W = G_1 + G_2$$

$$\text{where } G_1 = (C_1^{\circ} - C_1)$$

$$G_2 = [(C_2^{\circ} - C_2) - C]$$

If α is a proportioning factor between G_2 and C given by $\alpha G_2 = C$, then

$$\Delta W = C_1^{\circ} [1 - \exp(-k_1 t)] + [C_2^{\circ} / (1 + \alpha)] \times [1 - \exp(-k_2 t)]$$

At infinite time the maximum weight loss is ΔW_{∞} where

$$\Delta W_{\infty} = C_1^{\circ} + C_2^{\circ} / (1 + \alpha)$$

Rearranging,

$$1 - \Delta W / \Delta W_{\infty} = (C_1^{\circ} / \Delta W_{\infty}) \exp(-k_1 t) + (1 - C_1^{\circ} / \Delta W_{\infty}) \exp(-k_2 t)$$

4. EXPERIMENTAL

4.1 Coal Preparation

The as-received coal, a lignite from the Darco Seam in Texas, is crushed in a General Purpose Mill (Fisher Scientific Company, Pittsburgh, Pa.), air dried, then ground in a Hammer Screen Mill (Model 48356, Raymond Pulverizer Division of Combustion Engineering Co., Chicago, Ill.). The pulverized coal is size graded by dry sieving in a Rotap Sieve Shaker (Model 20482, W.S. Tyler Co., Cleveland, Ohio).

The particle size distribution within each size grade is determined using the Rosin-Rammler relation (75) which, although intended specifically for analytical description of the fineness of coal powders, is as useful as the available alternatives for expressing the fineness of pulverized coal (76).

4.2 Coal Characterization

The coal is characterized in detail by the Coal Research Section of The Pennsylvania State University. This includes rank calculations, petrographic and chemical data, caking and mechanical properties and mine and seam information. Chemical data include proximate, ultimate, elemental and ash analyses and sulfur forms.

In addition, proximate analyses are performed on each size grade of the pulverized coal, essentially following the A.S.T.M. procedure (23). This involves the determination of moisture, ash, volatile matter and, by difference, fixed carbon. Reproducibility tests allow statistical confidence limits (77) to be placed on proximate analysis data.

4.3 Experimental Setup

The experimental setup for studying rapid pyrolysis is shown in Figure 1 and is based on that used by Nsakala (2) which, in turn, is a modification of the design of Badzioch and Hawksley (20). Specific components have been redesigned to improve on basic limitations encountered previously.

The requirements of an experimental method for studying rapid pyrolysis were discussed in Section 2.3 where it was indicated that the laminar flow isothermal furnace best satisfies the requirements. Ancillary equipment servicing the isothermal furnace include coal feeder, gas supply, char sampling and temperature monitoring systems.

4.4 Pyrolysis Furnace

The furnace used by Nsakala (2) was limited by a 30 cm isothermal zone and an operating gas temperature of 808°C. The present furnace, which is shown in Figure 2, is designed for an isothermal zone of 60 cm and an operating gas temperature of 1000°C. To achieve this the physical dimensions of the furnace were increased and the heat supply system replaced.

Equally spaced in the annulus of two concentric mullite tubes (Type MV30, McDanel Refractory Porcelain Co., Beaver Falls, Pa.) are four silicon carbide resistance heating elements (Type RR, I²R Element Company, Lancaster, N.Y.). Transite boards hold the tubes in position. The elements, which are powered from a variable voltage autotransformer (Model 9T92Y51G2, General Electric Co., Johnstown, Pa.) maintain the inner tube at constant temperature. Heat loss from the outer tube is minimized by insulation (Fiberfrax LoCon Felt,

Figure 1. EXPERIMENTAL SETUP FOR RAPID PYROLYSIS STUDIES

Figure 2. PYROLYSIS FURNACE

Carborundum Co., Niagara Falls, N.Y.). The insulation is supported by an outer housing of 304 stainless steel and transite boards at both ends. A sliding thermocouple (100% Pt/90% Pt, 10% Rh) connects to a recorder (Model 19311, Honeywell Inc., Fort Washington, Pa.) and provides a permanent record of the history of the inner tube temperature.

4.5 Gas Supply System

Gas cylinders provide a metered flow of primary and secondary nitrogen. The small primary flow serves the coal feeder system and remains at ambient temperature until injection into the furnace. The larger secondary flow is raised to the furnace temperature in the preheater prior to injection into the furnace. In the preheater, which is shown in Figure 3, heat is supplied by four silicon carbide heating elements to nitrogen flowing through the inner tube. Radial heat losses are reduced by insulation. A thermocouple at the outlet provides an approximate measurement of the preheat temperature while the inner tube temperature is monitored by a sliding thermocouple. A T-shaped stainless steel adapter, which is shown in Figure 4, provides passage for the preheated secondary nitrogen into the furnace tube. Laminar flow in the furnace tube is enhanced by a stainless steel flow straightener which is illustrated in Figure 4(b).

4.6 Coal Feeder System

Primary nitrogen entrains coal, which is fed by the screw feeder shown in Figure 5(a), in a galvanized steel asymmetric venturi, which is illustrated in Figure 5(b). The entrained coal is injected into the furnace through a water-cooled brass probe (Figure 6) which is

Figure 3. GAS PREHEAT FURNACE

Figure 4. MISCELLANEOUS DEVICES

(a) Screw Feeder (Measurements in cm)

$$AA' = 1.27$$

(b) Asymmetric Venturi (Measurements in cm)

$$\theta_1 = 21^\circ, \theta_2 = 12^\circ, \theta_3 = 45^\circ$$

Figure 5. COAL FEEDER SYSTEM

Figure 6. WATER-COOLED FEEDER PROBE

held in position by the T-shaped adapter and centered in the furnace tube by the flow straightener. The portion of the probe projecting into the furnace is fitted inside a mullite tube to prevent excessive cooling of the secondary nitrogen. The coal feed rate varies with the rotating speed of the stainless steel screw feeder. The screw speed is controlled by a motor and speed reducer. The screw feeder design encourages uniform delivery and dispersion of coal particles (2).

4.7 Char Sampling System

A water-cooled brass sampling probe, which is shown in Figure 7, is externally lined with a mullite tube and positioned inside the furnace tube by stainless steel collars [Figure 4(c)]. Vacuum, which is applied to the probe by a vacuum pump, aspirates char particles which are subsequently separated from the gas in a stainless steel cyclone (Figure 8). Design calculations and collection efficiency data for the cyclone are presented by Nsakala (2). The collection efficiency is in excess of 99% for particles as small as 44 microns.

4.8 Temperature Monitoring System

Gas temperatures in the furnace are measured by suction pyrometry. This technique minimizes errors due to wall radiation and convective resistance encountered by bare thermocouples (78). The thermocouple is shielded from wall radiation by a ceramic shield and a ceramic sheath and convective heat transfer to the thermocouple is enhanced by increasing the velocity of gas passing the thermocouple bead. Gas velocity is controlled by the variation of suction. The suction pyrometer is shown in Figure 9.

Figure 7. WATER-COOLED CHAR COLLECTOR PROBE

(a) Proportions of Cyclone

(b) Dimensions (in cm) of Cyclone

Figure 8. CYCLONE FOR CHAR SEPARATION

Figure 9. SUCTION PYROMETER

4.9 Experimental Principle

Coal particles, which are entrained in a small flow of primary nitrogen so as to be in a disperse phase, are maintained at ambient temperature prior to injection into the furnace tube by passage through a water-cooled probe. On clearing the tip of the probe, coal particles and primary nitrogen are rapidly heated to the furnace temperature. Convective mixing is the predominant heat transfer mechanism although the particles are also exposed to wall radiation. Isothermal pyrolysis occurs as the particles flow vertically downward due to gravity and entrainment, essentially following a laminar streamline. Isothermal conditions are maintained by equalizing the wall and gas preheat temperatures.

Char particles are sampled isokinetically and quenched rapidly in the water-cooled collector probe. Rapid cooling, which is estimated to be of the order of $10,000^{\circ}\text{C/s}$ (2), effectively quenches pyrolysis reactions. Representative samples of char are separated in the cyclone for subsequent analyses. Residence times at furnace temperature are varied by raising and lowering the collector probe.

The extent of pyrolysis is most easily determined by measuring weight loss by the solid phase. However, direct material balances are not accurate since some char bypasses the collector probe and small quantities adhere to probe surfaces. Weight loss is determined using ash, which is mineral matter of the coal oxidized under standard conditions, as a tracer. An inert atmosphere of nitrogen is used to decouple pyrolysis reactions from heterogeneous gas/solid reactions occurring in a reactive gas.

4.10 Operating Conditions

The operating conditions, which appear in Table 1, maintain constant gas velocity in the furnace tube. This maintains an approximately

Table 1. Operating Conditions

	Gas and Wall Temperature, °C			
	700	800	900	1000
Coal Feed Rate, g/m	1.0	1.0	1.0	1.0
Mean Gas Velocity, m/s	1.12	1.12	1.12	1.12
Secondary/Primary Nitrogen	16.7	15.0	13.7	12.5
Coal Loading, Weight %	2.2	2.5	2.7	2.9
Gas Reynolds Number	458	391	339	298

constant relationship between flow distance and residence time for a specified particle size over the operating temperature range. Reynolds numbers indicate that the flow is always laminar and coal loading is kept low to ensure a disperse phase. The flow of primary nitrogen is kept constant and is the minimum required for efficient entrainment of the coal. Optimization of the secondary nitrogen flow rate balances the conflicting requirements of low flow to increase residence times and high flow to successfully accommodate the cold primary flow without significant temperature drop.

5. RESULTS AND DISCUSSION

5.1 Gas Temperatures

For the flow conditions of Table 1 the maximum gas temperature recorded by the thermocouple at the preheater exit is about 600°C. This is considerably below the design value of 1000°C. The heat transfer problem arises not from a lack of temperature driving force since the wall temperature exceeds 1100°C, but from a deficiency in heat transfer surface. Packing the preheater inner tube with mullite rods to increase surface area improves but does not eliminate the problem. Consequently, for operating temperatures above 700°C it is necessary to utilize the upper section of the furnace tube to achieve the required incremental temperature rise. This effectively shortens the maximum isothermal zone from the design length of 61.0 cm to 45.7 cm, thereby reducing residence times proportionally. Gas temperature profiles are obtained by suction pyrometry and are shown in Figure 10.

5.2 Char Sampling Efficiency

Radial dispersion of coal particles flowing down the furnace tube causes reduction in char sampling efficiency. This is simply the result of radially displaced particles missing the entrance to the collector probe. Sampling efficiency per se is of little importance as long as sufficient sample is collected to satisfy the requirements of subsequent analyses. It does provide, however, a quantitative measure of the visual observation that very little particle migration to the furnace tube wall occurs. If the radial velocity of particles

Figure 10. TEMPERATURE PROFILES IN PYROLYSIS FURNACE

Figure 11. VARIATION OF CHAR SAMPLING EFFICIENCY WITH POSITION OF COLLECTOR PROBE

is of sufficient magnitude, migration to and possibly reflection from the furnace tube wall will occur. The situation then exists where particle residence times based on flow down a vertical streamline are erroneous.

Sampling efficiency, however, is relatively independent of the collector probe position as shown in Figure 11. This implies insignificant reflection of particles from the furnace tube wall.

The absolute value of sampling efficiency, about 75%, is considerably in excess of that predicted theoretically for uniform radial dispersion of the particles. Based on the area ratio of the collector probe and the furnace tube, the theoretically calculated sampling efficiency for uniform radial dispersion is 32%. The experimental sampling efficiency of 75% indicates that three-quarters of the coal flows essentially vertically downward. The residence time history of the other quarter of the coal is of little consequence since it is not sampled and subsequently analyzed.

5.3 Particle Velocities in the Isothermal Furnace

The mean gas velocity in the isothermal furnace is maintained constant at 1.12 m/s for all operating temperatures by adjusting the volumetric flow rate. It is common in isothermal furnace studies (2, 20) to assume that injected coal particles are entrained in the vertical downward flow of preheated gas and travel with the same velocity as the gas. It is further assumed (2) that the gas is in plug-flow and that the mean gas velocity represents particle velocities at all points in the furnace. Invoking these assumptions allows convenient estimation of particle residence times as a function of

reaction distance. The validity of such assumptions, however, is questionable particularly for particles with free-fall velocities which are significant in comparison to the gas velocity. This results, in part, from the fact that particle velocities consist essentially of two additive components: one component is due to entrainment or drag force exerted by the flowing gas and the other is due to the force of gravity. The latter component increases in significance as the particle size increases.

The basic inconvenience associated with calculating free-fall velocities is that the drag force is proportional to the relative velocity between the particle and gas. Since the particle velocity is the required unknown, the implication is an iterative calculating procedure. A technique is available, however, which allows direct computation of free-fall velocities and its use is illustrated in Appendix A. Summing particle free-fall velocities and the gas plug-flow velocity produces the theoretical curve of Figure 12. It is apparent that as the particle diameter increases the free-fall velocity component becomes increasingly important. The error associated with the plug-flow approximation is, for example, 7% for 41 micron particles and 45% for 160 micron particles.

Experimental velocities indicated in Figure 12 are mean velocities obtained by timing the flow of particles down a 365 cm tube with similar diameter to the furnace tube. The flowing nitrogen is at room temperature and constant velocity of 1.12 m/s. Agreement is respectable between experimental data and the theoretical curve obtained by summing the plug-flow gas velocity and particle free-fall

Figure 12. COMPARISON BETWEEN PARTICLE VELOCITIES IN NITROGEN AT 20°C MEASURED EXPERIMENTALLY AND CALCULATED THEORETICALLY FOR DIFFERENT MODELS

velocities. The dependency of particle velocities on gas temperature as shown in Figure 13 is a direct reflection of the important gas properties, density and viscosity. These properties are given in Table 2 for the range of operating temperatures. Particle velocities decrease as the gas temperature rises. The curves of Figure 13 are used to determine particle residence times in the isothermal furnace.

Table 2. Nitrogen Properties

Temperature, °C	Density, ρ 10^4 g/cm^3	Viscosity, μ 10^4 g/s cm
20	11.14	1.75
700	3.51	3.39
800	3.18	4.17
900	2.91	4.40
1000	2.68	4.61

Two assumptions invoked in calculating the curves of Figure 13 are constant particle size and constant particle density. Both have some inherent error. For no shrinkage by 201 micron particles, for example, 45% weight loss due to pyrolysis causes an overestimation of the instantaneous velocity of about 10% as a result of the reduction in density. On the other hand, 45% weight loss at constant density produces particle shrinkage to 154 microns and overestimation of the instantaneous velocity by about 12%. These estimates are for solid spherical particles undergoing maximum weight loss for the experimental conditions. The significant conclusion is that assumptions of constant

Figure 13. VARIATION OF PARTICLE VELOCITIES IN PYROLYSIS FURNACE WITH PARTICLE DIAMETER AND GAS TEMPERATURE

particle size and constant particle density generate a maximum error at maximum weight loss of about 10 to 12% in the estimation of residence times.

It is acknowledged that the calculating method is an approximate one. It does not, for example, have the sophistication to predict the effect of cloud density on particle velocities. It is, however, a considerable improvement on the plug-flow assumption and in the absence of a more detailed investigation is considered necessarily acceptable.

5.4 Coal Characterization

The coal studied exclusively is a Darco Texas lignite from the United States Gulf Province. It is designated PSOC-412 by the Coal Research Section of The Pennsylvania State University and characterization by that section is presented in Table 3.

Three basic properties of the lignite prompt its selection as a coal to study. Firstly, the proximate volatile matter is sufficiently high to ensure significant weight loss in the isothermal furnace. In addition, the high proximate ash content allows convenient application of the ash tracer technique for calculating weight loss due to pyrolysis. Finally, the non-swelling nature of the coal minimizes particle size changes during pyrolysis and reduces the possibility of clogging in the experimental apparatus.

Preparation of the lignite following the procedure of Section 4.1 produces a range of particle sizes. Characterization by the Rosin-Rammler technique (75) is presented in Table 4 for six size fractions. Use of the technique is illustrated elsewhere for a similar lignite (2).

Table 3. Coal Data Base

Identification PS0C-412

Darco Texas lignite

Chemical Data

Proximate Analysis

	as-received	dry	daf	dmmf*
% Moisture	22.4	-	-	-
% Ash	12.4	15.9	-	-
% Volatile Matter	33.3	43.0	51.1	50.2
% Fixed Carbon	31.9	41.1	48.9	49.8

* Parr mm = 18.0%

Ultimate Analysis

	as-received	dry	daf	dmmf
% Carbon	46.7	60.2	71.6	73.4
% Hydrogen	3.5*	4.5	5.3	5.5
% Nitrogen	0.9	1.2	1.4	1.5
% Total Sulfur	1.1	1.4	1.6	-
% Oxygen	13.1*	16.8	20.0	19.7

*excludes moisture

Sulfur Forms

	% pyritic	% sulfatic	% organic
dry	0.38	0.07	0.93
daf	0.45	0.08	1.11

Table 3. (Continued)

Calorific Value

(Gross, kcal/kg)

	as-received	dry
mm containing	4,504	5,807
mm free (Parr)	5,199	7,032

(Net, kcal/kg)

dmmf

6,806

Petrographic Data

Maceral Analysis (White Light Analysis)

	Ulm- inite	Humo- detrinite	Gel- inite	Corpo- huminite	Spor- inite
dmmf, vol%	71.5	12.9	0.7	0.8	1.4
dry, wt %	58.7	10.6	0.6	0.7	1.1
	Res- inite	Fus- inite	Semi- fusinite	Mac- rinite	Sclero- inite
dmmf, vol %	0.1	5.2	4.3	3.0	0.1
dry, wt %	0.1	4.3	3.5	2.5	0.1

Caking and Mechanical Properties

Hardgrove Grindability	85.1
Vickers Hardness Number	4.0
Free Swelling Index	0.0
Ash Fusion Temperature, Fluid	1332°C

Table 3. (Continued)

Major Element Analysis

	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO
oxide % of hta	40.7	21.9	1.13	13.2	2.17
Element % dry coal	2.2	1.4	0.08	1.1	0.15
	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃
oxide % of hta	8.80	0.38	1.49	0.04	10.0
Element % dry coal	0.74	0.03	0.15	0.002	1.4

Table 4. Particle Size Fractions

Mesh Size (U.S. Standard Sieve)	Mean Diameter $\bar{X}$ microns	90% Larger Than X_1 microns	90% Smaller Than X_2 microns	Dispersion Parameter n
60 x 80	201	180	225	12.0
70 x 100	160	130	185	8.4
100 x 140	111	90	130	7.8
140 x 200	79	67	92	8.0
200 x 270	52	41	61	8.0
270 x 400	41	33	47	10.0

The upper median diameter of 201 microns represents almost a factor of five increase in size over the lower median diameter of 41 microns. This is considered sufficient to detect property changes with particle size.

Proximate analyses for the size fractions are given in Table 5. As shown in Figure 14 proximate ash increases with decrease in particle size. This is normally associated with the grinding procedure which causes accumulation of mineral matter in the finer size fractions. Proximate volatile matter when expressed on a daf basis is relatively independent of particle size as shown in Figure 15.

General pyrolysis behavior of the lignite is shown in Figure 16 as a function of temperature. Data are obtained by following the proximate analysis method in all aspects except the specified furnace temperature of 950°C. Pyrolysis begins below a temperature of 250°C and is essentially complete by about 800°C. Initiation of pyrolysis at relatively low temperatures and subsequent early completion is characteristic of highly volatile lignites.

It is convenient and economical to dry samples in air rather than nitrogen prior to ash and volatile matter determinations. This results, however, in consistent underestimation of the moisture content as shown in Figure 17. In all probability this is caused by weight gain by the lignite during drying in air due to oxygen chemisorption. Quantitatively, the effect is insignificant in comparison with the overall experimental accuracy.

Reproducibility data for proximate analyses are presented statistically for each size fraction in Table 6. Confidence levels for the mean are set at 95% as is typical for coal analysis. In

Table 5. Proximate Analyses of Size Fractions

Mesh Size (U.S. Standard Sieve)	% Moisture	% Ash	% Volatile Matter dry	Matter daf	% Fixed Carbon dry	Carbon daf
60 x 80	15.2	10.3	45.9	51.2	43.8	48.8
70 x 100	15.2	10.8	45.7	51.2	43.5	48.8
100 x 140	14.0	10.4	45.8	51.1	43.8	48.9
140 x 200	12.2	12.4	44.7	51.0	42.9	49.0
200 x 270	12.0	12.9	45.4	52.1	41.7	47.9
270 x 400	9.0	15.8	42.9	51.0	41.3	49.0

Table 6. Reproducibility of Proximate Analyses

Mesh Size (U.S. Standard Sieve)	# of Tests	Mean	95% Confidence Limits
Ash, % daf coal			
60 x 80	10	10.3	± 0.10
70 x 100	9	10.8	± 0.16
100 x 140	12	10.4	± 0.08
140 x 200	6	12.4	± 0.12
200 x 270	8	12.9	± 0.08
270 x 400	7	15.8	± 0.24

Table 6. (Continued)

Volatile Matter, % daf coal			
60 x 80	9	45.9	± 0.18
70 x 100	6	45.7	± 0.22
100 x 140	6	45.8	± 0.16
140 x 200	5	44.7	± 0.39
200 x 270	5	45.4	± 0.35
270 x 400	5	42.9	± 0.47

Table 7. Reproducibility of Isothermal Furnace Data

Mesh Size (U.S. Standard Sieve)	# of Tests	Weight Loss % daf coal	95% Confidence Levels	
			Exp.	Calc. from Prox. Ash
70 x 100*	8	7.5	± 0.7	± 1.3
100 x 140**	8	13.1	± 1.3	± 1.0
200 x 270***	6	33.0	± 2.2	± 1.0

* 0.13 s at 900°C

** 0.17 s at 800°C

*** 0.33 s at 800°C

Figure 14. PROXIMATE ASH AS A FUNCTION OF MEAN PARTICLE SIZE

Figure 15. PROXIMATE VOLATILE MATTER AS A FUNCTION OF MEAN PARTICLE SIZE

Figure 16. VOLATILE MATTER AS A FUNCTION OF FINAL TEMPERATURE AS DETERMINED USING PROXIMATE ANALYSIS METHOD

Figure 17. MOISTURE AS A FUNCTION OF MEAN PARTICLE SIZE FOR DRYING IN AIR AND NITROGEN AT 105°C

Table 7 the significance of the confidence limits to data of weight loss in the isothermal furnace is shown. For 7.5% mean weight loss the scatter can be explained entirely in terms of reproducibility of proximate ash determinations. At 33% mean weight loss, however, only about half of the scatter can be attributed to this cause. The remainder is associated with the operating technique of the isothermal furnace.

5.5 Sample Weight Effects in Proximate Analyses

Proximate ash and volatile matter analyses specify a sample weight of one gram (23). It is convenient and sometimes necessary to use considerably smaller samples. Necessity originates from the sparking behavior of highly reactive lignites under the conditions of the proximate volatile matter test. The effect on ash yield of reducing the sample weight but otherwise following the proximate procedure is shown in Figure 18. Using one gram of sample produces one standard yield of ash. Reproducibility limits for the proximate ash test at the 95% confidence level are included in Figure 18. It is apparent that below a sample weight of about 0.3 gram, ash yields tend to diminish. This is probably due to the magnified effect of small ash losses from the crucible during handling. To maintain constant reproducibility sample weights in excess of 0.3 g are used whenever possible. No particle size effects on deviation from the standard ash yield are apparent over the range 41 to 201 microns.

In proximate volatile matter tests one gram of sample contained in a standard lidded crucible is pyrolyzed by plunging the crucible and contents into a standard furnace preheated to 950°C. For highly

Figure 18. EFFECT OF SAMPLE WEIGHT ON ASH CONTENT AS DETERMINED USING THE PROXIMATE PROCEDURE

Figure 19. FRACTIONAL YIELD OF VOLATILES AFTER 15 SECONDS OF THE PROXIMATE VOLATILE MATTER TEST AS A FUNCTION OF SAMPLE WEIGHT

volatile coals prone to sparking a two step temperature rise is recommended; initial pyrolysis at 600°C followed by elevation to 950°C. Even when the latter technique is employed, it is difficult to prevent size fractions of PSOC-412 coal and char below about 60 microns in mean diameter from sparking significantly. This creates difficulty in consistently obtaining proximate volatile matter data. Sparking is suppressed, however, by reducing the sample weight below the specified one gram.

Quantitatively, sparking is observed as the phenomenon accompanying rapid pressure rise in the crucible. The loose-fitting lid is violently ejected and sample is lost by entrainment in the escaping volatiles. Sparking is controlled more or less by two parameters; quantity of volatiles potentially in the coal and their rate of evolution. For PSOC-412 lignite the quantity of volatiles is essentially independent of particle size, as shown in Figure 15, suggesting that sparking in the smaller size fractions is the result of more rapid pyrolysis. This is confirmed in Figure 19 which indicates greater devolatilization by the smaller size fraction after an intermediate pyrolysis time. Data represent weight loss due to pyrolysis after a residence time of 15 s in the proximate volatile matter furnace. Almost no significance can be placed on the absolute value of the residence time since pyrolysis continues for an unmeasurable time period after removal of the sample from the furnace. The fixed residence time is only useful for comparative purposes. It is apparent from Figure 19 that there is a particle size effect above about 0.4 g.

The effectiveness of reducing sample weight as a means of suppressing sparking can be inferred from Figure 20. Assuming constant composition of the volatiles, the mass yield of volatiles is proportional to the volumetric yield which is an important sparking parameter. Sample weight reduction below one gram for the sparking size fraction, 270 x 400 mesh causes an initial increase in the volumetric yield due possibly to an increase in the rate of pyrolysis. Further reduction in sample size, however, causes a decrease in the volumetric yield due to the overwhelming effect of reduction of the potential quantity of volatiles in the crucible. Data are consistent with the qualitative observations that the 70 x 100 mesh size fraction does not spark for any sample weight up to one gram and that sparking for the 270 x 400 mesh size fraction essentially ceases for sample weights below 0.2 g.

The particle size and sample weight dependency of pyrolysis rate demonstrated in Figure 19 are consistent with physical rate control. Particle size dependency is consistent with internal mass transfer control but the disappearance of dependency below sample weights of about 0.2 g is difficult to explain. Sample size dependency is also consistent with mass transport control through the packed bed of coal, but one would expect the dependency to diminish and eventually disappear as the sample size is reduced. It is difficult, therefore, to match the data with mass transfer control. Heat transfer, on the other hand, is more likely to play a major role. Pyrolysis for the first few seconds of the test is non-isothermal suggesting heating rate dependency of the pyrolysis rate. The predominant heat transfer mechanism is conduction between particles and with the walls of the

Figure 20. WEIGHT YIELD OF VOLATILES AFTER 15 SECONDS OF THE PROXIMATE VOLATILE MATTER TEST AS A FUNCTION OF SAMPLE WEIGHT

crucible. Sample size reduction diminishes conduction distances thereby increasing the heating rate. Particle size effects are more difficult to explain but conceivably are due to enhanced contact between particles and with the walls for the smaller size fractions.

The effect of sample weight on the ultimate yield of volatiles is shown in Figure 21. Reducing the sample weight below the proximate analysis specification of one gram causes a yield enhancement, represented in Figure 21 as a fractional increase above the proximate yield. As postulated elsewhere (25) and discussed below, the yield for an infinitely small sample probably represents the true yield with the proximate volatile matter being the anomalous yield. There is no observed particle size effect on the yield enhancement, as illustrated in Figure 21 which is used to normalize all data obtained with less than one gram of sample. The sample weight effect, or more strictly the bed geometry effect, is postulated to be associated with the preponderance of secondary char forming reactions of the volatiles (25). According to the postulate, the bed acts as a trap for the volatiles and provides surface to enhance secondary pyrolysis reactions which produce carbon deposition. The implication, therefore, is that char deposition results from surface rather than gas phase reactions. It follows that additional important parameters are the specific activity of the surface and the residence time of the volatiles in the bed. The latter parameter, together with the total surface area, controls the number of collisions that a molecule of volatile matter makes with the surface. The former parameter controls, in part, the fraction of collisions which result in reaction and carbon deposition.

Figure 21. EFFECT OF SAMPLE WEIGHT ON ULTIMATE YIELD OF VOLATILES AS DETERMINED USING THE PROXIMATE PROCEDURE

Based on comparable data for a similar lignite (2), the internal (CO_2 adsorption) to geometric area ratio for a 201 micron particle is about 8,000. However, the ratio of the internal surface area of a single particle to the geometric area of one gram of particles is only about 0.05. This ratio is considerably reduced if a single pore path in the particle is considered instead of the total internal surface area. It is the area of the pore walls that an escaping volatile matter molecule is exposed to on its passage out of the particle. Assuming successive diffusion through a typical micropore, transitional pore and macropore system of diameters 5, 500 and 5,000 Å respectively and with length to diameter ratios of 5, the total pore wall area exposed to an escaping volatile matter molecule is 10^{-12} m^2 . The ratio of the pore wall area to the geometric area of the bed is then 10^{-10} . This ratio is important if the bed is considered to be fluidized. For a stationary bed, however, a volatile matter molecule must diffuse out of a typical pore system in the bed. For illustrative purposes, the length can be assumed equal to the bed depth and the diameter equal to the particle size. For one gram of 201 micron particles, a typical internal pore area to bed pore area ratio is 10^{-6} . The relevance is that, assuming no diffusion of liberated volatiles back into pores, the overwhelming majority of surface available to secondary cracking reactions is the external particle surface.

The ratio of geometric areas for 41 and 201 micron particles is about 5.0. There is no significant difference, however, in proximate volatile matter as illustrated in Figure 15. A counter-effect, postulated to be the increase in pyrolysis rate causing a reduction in

residence time of the volatiles in the fixed bed and hence a reduction in the number of collisions between a molecule of volatile matter and the surface, is deemed responsible for the yield invariance. It may not always be the case that the effects counter balance exactly. Sample size reduction decreases both the available surface and contact times.

The importance of external surface is demonstrated in subsidiary experiments. Samples of 70 x 100 mesh Saran char and petroleum coke, previously devolatilized under proximate analysis conditions, are added as inert fillers by mixing with samples of PSOC-412 lignite weighing between 0.1 and 0.4 g. The combined weight of the crucible is always 0.6 g. Results are shown in Figure 22. For each run the heating rate and external surface area are essentially equivalent to those for 0.6 g of coal. The potential quantity of volatiles, however, varies from 17 to 67% of the quantity in 0.6 g of coal. Hence, the residence time of volatiles in the bed is always longer when inert filler is present. Assuming equal specific activities of the surfaces, it is apparent from Figure 22 that residence time is an important parameter controlling the preponderance of secondary char formation. The relative independence of the yield on type of filler implies insignificant diffusion into, and reaction in, the filler pores. This derives from the fact that the fillers have markedly dissimilar total (CO_2) surface areas, about $1,000 \text{ m}^2/\text{g}$ for the Saran char and about $1.5 \text{ m}^2/\text{g}$ for the petroleum coke.

Figure 22 also shows data for the addition of alumina chips to various weights of coal sample. The total surface area of the alumina chips is only about 10 cm^2 and is negligible in comparison with the

Figure 22. EFFECT OF INERT ADDITIVES ON YIELD OF VOLATILES FOR 70 x 100 MESH SIZE FRACTION

total external surface area of the coal or the combined areas of coal and filler. A slight yield enhancement is observed with the addition of the chips particularly for small sample sizes. Interpretation of the data, however, is complicated by a probable change in heat transfer. Thermal conductivity data for coal, particularly lignites, are scarce, but a value of 10^{-3} cal/s cm°C is not unreasonable for room temperature (66). This is two orders of magnitude less than the value for the alumina chips. It is possible, therefore, that the observed yield enhancement is due, in part, to an increase in pyrolysis rate which reduces the associated residence time of the volatiles.

5.6 Ash Tracer Technique

The ash tracer technique for estimating weight loss in the isothermal furnace is errorless only if mineral matter in the lignite does not undergo transformation in the isothermal furnace which causes a yield change upon subsequent ashing. Experimental ash yields from short residence time chars are in some cases lower than yields obtained by direct ashing of the raw coal. This is reflected in weight loss calculations as apparent weight gain. Sporadic instances of apparent weight gains of up to one percent of the original dry-ash-free coal can be attributed to the reproducibility of proximate ash analyses. Consistent occurrences, however, require alternative explanation.

The proximate volatile matter furnace is a convenient apparatus for comparing weight loss data obtained by direct material balances with data obtained using ash as a tracer. The procedure involves ashing chars produced at a variety of temperatures. Consistent underestimation of weight loss occurs when ash is used as a tracer as shown in Figure 23

Figure 23. COMPARISON BETWEEN WEIGHT LOSS DETERMINED BY MATERIAL BALANCE AND ASH AS A TRACER FOR 70 x 100 MESH COAL

Figure 24. COMPARISON BETWEEN WEIGHT LOSS DETERMINED BY MATERIAL BALANCE AND ASH AS A TRACER AS A FUNCTION OF PARTICLE SIZE FOR PYROLYSIS AT 950°C

for a range of weight loss and Figure 24 for a range of particle size. For 41 data points collected over the temperature range 300 to 950°C and particle size range 41 to 201 microns, there is an approximately linear relationship between weight loss as measured by the two techniques. The relationship, which is illustrated for convenience by 16 data points in Figure 25, is

$$\text{Actual Weight Loss} = 1.031 \text{ Ash Tracer Weight Loss} + 1.70$$

where weight losses are expressed as percent original daf coal. The relationship is reasonably assumed to apply to data from the isothermal furnace and its application eliminates the occurrence of apparent weight gain during the early stages of pyrolysis.

Computations of change in proximate volatile matter between the original coal and a char suffer from a similar error. The relationship, which is illustrated in Figure 26, is

$$\begin{array}{rcl} \text{Actual Change in Proximate} & & \text{Ash Tracer Change in} \\ \text{Volatile Matter} & = 1.010 & \text{Proximate Volatile Matter} + 0.71 \end{array}$$

The relationships demonstrate mutual consistency in that weight loss of 1.70% of the original daf coal represents a change in proximate volatile matter of 0.71% on the same basis.

It is apparent from Table 3 that the mineral matter of the lignite undergoes about 11% weight loss on proximate ashing. This is due to loss of water by clays and CO₂ by carbonates, for example. An important distinction, however, is that error associated with using ash as a tracer involves differential yields after ashing the mineral matter. The data indicate maximum weight change in ash content of 5% as shown in Figure 27. This is consistent with other published data for a lignite (21). PSOC-412 lignite contains 1% organic sulfur on a

Figure 25. RELATIONSHIP BETWEEN WEIGHT LOSS BY MATERIAL BALANCE AND ASH TRACER

Figure 26. RELATIONSHIP BETWEEN CHANGE IN PROXIMATE VOLATILE MATTER BY MATERIAL BALANCE AND ASH TRACER

Figure 27. REDUCTION IN ASH YIELD AS A FUNCTION OF WEIGHT LOSS BY COAL DUE TO PYROLYSIS FOR 70 x 100 MESH

dry basis. Conceivably, a fraction of this is expelled during pyrolysis as H_2S , COS or in tars. It is apparent from Table 3 that the total sulfur content of PSOC-412 is fixed in the proximate ash presumably by highly dispersed exchangeable cations, mainly calcium and potassium in this case (80). Loss of about 50% of the organic sulfur during pyrolysis would produce the calculated 5% reduction in proximate ash.

5.7 Weight Loss in the Isothermal Furnace

Weight loss by the lignite in the isothermal furnace is shown in Table 8 for a range of temperature, reaction distance and particle size. Data are corrected for the error associated with using ash as a tracer. Reaction distances are transformed into residence times for the operating conditions outlined in Table 1 using the velocity curves of Figure 13. Weight loss is shown as a function of residence time in Figures 28 to 31 for the four operating temperatures. In general, a data point represents weight loss calculated from duplicate ash determinations on duplicate chars. Error bars represent reproducibility at the 95% confidence level. It is apparent, particularly from Figure 30 which covers the range of particle size 41 to 201 microns, that weight loss is independent of particle size over this range. This is true for pyrolysis temperatures from 700 to 1000°C.

The fact that weight loss is independent of particle size in the isothermal furnace has interesting implications. Firstly, it eliminates internal heat or mass transfer as the rate controlling mechanism except possibly for mass transfer in the micropores. The microporous structure may not be altered significantly by grinding.

Table 8. Weight Loss in the Isothermal Furnace

Reaction Distance, cm	Weight Loss, % daf coal					
	60x80	70x100	100x140	140x200	200x270	270x400
700°C						
7.62		0		0		0
15.24		4.0		3.6		4.3
22.86		7.5		13.0		12.0
30.48		11.2		20.4		17.5
38.10		15.2		26.2		22.5
45.72		23.1		-		26.3
800°C						
7.62		0	0	0.1		0
15.24		5.9	4.5	5.3		9.7
22.86		14.8	12.1	15.9		19.6
30.48		20.4	24.2	28.9		27.2
38.10		25.6	-	32.3		32.9
45.72		30.3	-	-		35.7
900°C						
7.62		0	0	1.0	1.7	0
15.24		5.5	-	8.5	9.0	13.3
22.86		16.3	20.2	19.2	21.1	22.5
30.48	-	23.2	27.5	31.8	30.2	31.5
38.10	22.7	29.5	35.7	37.6	38.5	38.2
45.72	28.1	33.5	-	40.1	-	42.5

Table 8. (Continued)

	1000°C			
7.62	0.3	1.3	2.3	3.0
15.24	12.1	18.0	23.0	27.3
22.86	20.0	33.7	32.0	39.6
30.48	28.0	40.0	43.0	47.1
38.10	36.0	42.7	45.1	49.5
45.72	41.1	46.7	-	53.4

Figure 28. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME AT 700°C

Figure 29. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME AT 800°C

Figure 30. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME AT 900°C

Figure 31. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME AT 1000°C

The violent nature of pyrolysis reactions, however, diminishes the likelihood of mass transfer control in micropores. Secondly, it eliminates external heat or mass transfer, that is boundary layer transfer, as a controlling process. This derives from the fact that changing the particle size from 41 to 201 microns increases the relative particle/gas velocity by a factor of 1.7, thereby significantly reducing the boundary layer thickness. The foundation is firm, therefore, to infer chemical rate control for pyrolysis in the isothermal furnace.

The present data disagree with previous reports of particle size dependency for similar operating conditions (2,50). In the previous analyses however, particle residence times were based on the gas plug-flow velocity, a procedure which introduces considerable error. When the data are replotted using the velocity curves of Figure 13, particle size dependency essentially disappears as shown in Figure 32. Both the previously studied coal, North Dakota lignite PSOC-246, and the present lignite have approximately the same density, justifying the use of Figure 13 in the former case.

Figures 28 to 31 are incorporated into a single plot, Figure 33, which illustrates the effect of temperature over the range 700 to 1000°C on weight loss. It is apparent that for residence times less than 0.4 s, weight loss for a specified residence time increases as the pyrolysis temperature rises. Bands are used to encompass the scatter of the data.

5.8 Maximum Potential Weight Loss for Isothermal Furnace Conditions

It is important for at least two reasons to know the maximum potential weight loss under isothermal furnace conditions. Firstly,

Figure 32. WEIGHT LOSS FROM REFERENCE 50 AS A FUNCTION OF RESIDENCE TIME FOR PSOC-246 LIGNITE AT 808°C

Figure 33. EFFECT OF TEMPERATURE ON WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME

it is an important parameter required to model the kinetics of the overall pyrolysis reaction process. Secondly, it has practical significance to pulverized coal combustors and gasifiers in which it is advantageous to maximize the yield of volatiles. Unfortunately, this parameter is not measurable directly by a single pass of coal through the isothermal furnace because of limited residence times. Recycling of the char is potentially a viable technique for achieving maximum weight loss but pyrolysis in the latter stages is extremely slow (2) forcing numerous recycles with minimal weight loss per pass.

The alternative is to calculate the maximum potential weight loss based on a standard property which changes regularly with weight loss. Change in proximate volatile matter between the original daf coal and char is one property which correlates well with weight loss (20). Changes in proximate volatile matter are given in Table 9 as a function of isothermal pyrolysis temperature, reaction distance and particle size. The derived relationship for the range of data is linear and is represented by

$$\Delta W = 1.30 \Delta V \quad 6$$

where ΔW = weight loss, % daf coal

ΔV = change in proximate volatile matter, % daf coal.

The relationship is relatively independent of particle size over the range 41 to 201 microns for isothermal pyrolysis at 1000°C as shown in Figure 34. It is also independent of pyrolysis temperature for 140 x 200 mesh coal as shown in Figure 35. These plots are illustrative of the general temperature and particle size independency of the relationship over the range of experimental conditions.

Figure 34. VARIATION OF WEIGHT LOSS AT 1000°C WITH CHANGE IN PROXIMATE VOLATILE MATTER

Figure 35. VARIATION OF WEIGHT LOSS WITH CHANGE IN PROXIMATE VOLATILE MATTER FOR 140 x 200 MESH

Table 9. Change in Proximate Volatile Matter
in the Isothermal Furnace

Reaction Distance, cm	Change in Proximate Volatile Matter % daf coal				
	70 x 100	100 x 140	140 x 200	200 x 270	270 x 400
700°C					
7.62	0		0		0
15.24	0.9		3.3		3.1
22.86	4.1		11.9		7.4
30.48	8.2		20.0		14.5
38.10	14.0		22.5		21.4
45.72	20.2		-		24.0
800°C					
7.62	0	0	0.2		0
15.24	4.7	2.9	4.9		8.9
22.86	13.6	9.1	13.9		13.3
30.48	19.0	17.4	22.1		24.6
38.10	23.2	-	25.2		27.6
45.72	26.2	-	-		30.2
900°C					
7.62	0	0	1.8	1.9	0
15.24	4.4	-	6.0	8.2	11.6
22.86	14.8	17.2	15.6	19.0	19.5
30.48	21.0	22.5	21.9	27.1	25.3
38.10	26.7	28.6	27.9	32.4	31.2
45.72	29.6	-	30.4	-	35.1

Table 9. (Continued)

1000°C				
7.62	0.6	1.6	1.3	3.1
15.24	12.3	11.8	17.2	22.9
22.86	25.0	27.2	27.9	30.8
30.48	31.2	30.3	31.2	36.9
30.10	35.5	36.9	-	40.5
45.72	-	-	-	-

The maximum potential weight loss, ΔW_{∞} as % daf coal, is obtained from the linear relationship when there is no proximate volatile matter remaining in the char, that is when the change in proximate volatile matter is maximized. For PSOC-412 lignite ΔW_{∞} is 66.6% of the daf coal. The validity of this procedure for this lignite derives from the fact that the proximate volatile matter is relatively temperature independent over the range 700 to 1000°C. For other coals this is not necessarily the case and the proximate volatile matter test should be conducted at the isothermal furnace temperature. This may give ΔW_{∞} temperature dependency. The fractional yield enhancement of volatiles, $\Delta W/\Delta V$ is termed the Q factor (20).

Equation 6 can be expressed alternatively as

$$\Delta W + R = 0.23 \Delta W + VM_0 \quad 7$$

where R = proximate volatile matter of the char, % daf coal

VM_0 = proximate volatile matter of coal, % daf coal.

$\Delta W + R$ is plotted against ΔW for 70 x 100 mesh lignite pyrolyzed isothermally at 1000°C in Figure 36. The slope of the straight line is 0.21 which is in good agreement with equation 6.

5.9 Enhancement of Yield of Volatiles in the Isothermal Furnace

It is possible that the apparent yield enhancement in the isothermal furnace is a consequence of the experimental technique which involves two-stage heating of the lignite; firstly in the isothermal furnace and then in the proximate volatile matter furnace. This possibility is tested by two-stage pyrolysis experiments in proximate volatile matter furnaces. The preset furnace temperature ranges from 250 to 800°C for stage I evolution and is always 950°C for stage II

Figure 36. ENHANCEMENT OF POTENTIAL YIELD OF VOLATILES AS A FUNCTION OF WEIGHT LOSS IN THE ISOTHERMAL FURNACE FOR 70 x 100 MESH

evolution. Loss of weight by the solid is designated VM_I as % daf coal for stage I and VM_{II} as % daf coal for stage II.

The results are shown in Figure 37 for 70 x 100 mesh and Figure 38 for 60 x 80 mesh. The total volatiles, $VM_{TOTAL} = VM_I + VM_{II}$ is not significantly different from $VM_{PROX.}$, the proximate volatile content of the lignite over the range of Stage I temperature. This strongly implies that any yield enhancement in the isothermal furnace is not a product of the two-stage heating associated with the experimental technique.

5.10 Particle Size Changes During Isothermal Pyrolysis

Particle size changes during pyrolysis are determined by application of the Rosin-Rammler technique to a variety of chars. The results are shown in Figure 39 for 70 x 100 mesh lignite. Some particle shrinkage does occur over the range of weight loss but not sufficient to follow the constant particle density line. The line is calculated theoretically using a particle or mercury density of 1.4 g/cm^3 .

The indication from Figure 39 is that particle shrinkage and density reduction occur simultaneously during pyrolysis. The absence of significant particle decrepitation is also consistent with Figure 39. The limited data further suggest that particle size reduction is relatively temperature independent.

5.11 Kinetics of Pyrolysis

According to the theory of Section 3.3, compliance with a model involving two overall reactions requires a plot of $\ln(1-\Delta W/\Delta W_\infty)$ versus time to produce two straight lines with different slope. The data for

Figure 37. EFFECT OF TWO-STAGE PYROLYSIS ON WEIGHT LOSS FOR 70 x 100 MESH

Figure 38. EFFECT OF TWO-STAGE PYROLYSIS ON WEIGHT LOSS FOR 60 x 80 MESH

Figure 39. EFFECT OF WEIGHT LOSS ON MEAN PARTICLE DIAMETER FOR 70 x 100 MESH

PSOC-412, however, are reasonably modelled by a single first-order reaction equation for the experimental range of temperature and weight loss as shown in Figures 40 to 43. Replotted data for PSOC-246 also display respectable first-order behavior as illustrated in Figure 44. It is important to realize that the data do not imply that a second overall reaction is unnecessary to model complete devolatilization of the lignites. It does imply, however, that the second overall reaction, if necessary in the case of PSOC-412, does not become dominant until after at least three-quarters devolatilization. This is not inconsistent with attempts to give fundamental significance to the two reaction model (81).

It is apparent from Figures 40 to 43 that there is a delay in the onset of significant pyrolysis in every case. For purely comparative purposes it is informative to assume linear temperature rise during the delay period. This produces a heating rate of about 10,000°C/s. The apparent lack of weight loss during heatup at this high heating rate, which is inferred from the shape of the graphs, is in agreement with the theoretically calculated shift of pyrolysis reactions to higher temperatures with increasing rates of heating (26).

First-order rate constants taken from the slopes of the lines in Figures 40 to 43 are given in Table 10. An Arrhenius plot, shown in Figure 45, produces an activation energy of 7.7 kcal/mole and a pre-exponential factor of $0.9 \times 10^2 \text{ s}^{-1}$. This value is consistent with literature values as outlined in Section 2.7. It is reiterated that very little physical significance can be attached to the derived activation energy. It may, in fact, be a product of the modelling technique and not represent activation energies of individual pyrolysis reactions.

Figure 40. TEST PLOT FOR FIRST-ORDER DEVOLATILIZATION AT 700°C

Figure 41. TEST PLOT FOR FIRST-ORDER DEVCLATILIZATION AT 800°C

Figure 42. TEST PLOT FOR FIRST-ORDER DEVOLATILIZATION AT 900°C

Figure 43. TEST PLOT FOR FIRST-ORDER DEVOLATILIZATION AT 1000°C

Figure 44. TEST PLOT FOR FIRST-ORDER DEVOLATILIZATION FOR PSOC-246 AT 808°C

Table 10. First-Order Rate Constants

Temperature, °C	Rate Constant, k, s^{-1}	Correlation Coefficient
700	1.8	0.962
800	2.6	0.983
900	3.1	0.922
1000	4.8	0.983

Figure 45. ARRHENIUS PLOT FOR COAL DEVOLATILIZATION TREATED AS ONE STEP, FIRST-ORDER REACTION

6. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Significant Aspects of Pyrolysis Behavior of Dispersed Particles

The isothermal furnace is suitable equipment for studying rapid pyrolysis of pulverized lignite in the disperse phase. This is demonstrated for a lignite from the Darco Seam in Texas over the range of particle size 41 to 201 microns and range of temperature 700 to 1000°C. It is important to refrain from generalizing the conclusions from this study to all coals under all conditions or even the same coal under untested conditions. At most, the conclusions presented here are applicable to a narrow range of similar lignites under essentially the same conditions.

The invariance of char sampling efficiency indicates that coal particles flow approximately down a vertical streamline in the isothermal furnace. Particle velocities, although dependent to some extent on particle density and diameter variations, are reasonably predicted by summing initial free-fall velocities and the gas plug-flow velocity. During pyrolysis, particle shrinkage and density increases occur but there is no evidence of particle decrepitation. Using proximate ash as a tracer accurately determines weight loss in the isothermal furnace if devolatilization of inorganics, mainly sulfur, during pyrolysis are accounted for.

Pyrolysis rate in the isothermal furnace, in which heating rates are of the order of 10,000°C/s, is independent of particle size over the experimental range. This is interpreted to mean the absence of physical rate control. No significant weight loss occurs during particle heat-up. Pyrolysis is modelled by a single overall first-order

reaction equation for weight losses up to 80% of the maximum which occurs under isothermal conditions. A second overall reaction equation may be necessary to describe the completion of pyrolysis. Despite probable chemical rate control little physical significance can be attached to the absolute value of the activation energy derived assuming the Arrhenius expression. The relatively low value of 7.7 kcal/mole is not necessarily inconsistent with chemical rate control.

The maximum potential weight loss in the isothermal furnace, 66% of the daf coal, is predicted from the linear change in proximate volatile matter with weight loss. Maximum potential weight loss is particle size independent implying an absence of secondary char deposition inside particle pores. The maximum weight loss under the conditions of the isothermal furnace is significantly greater than the proximate volatile matter of 51% of the daf coal and represents the true volatile matter associated with the lignite.

6.2 Significant Aspects of Pyrolysis Behavior in Packed Beds

As lignite pyrolysis changes from the disperse phase where particle interaction is minimal to a porous bed of packed particles as for the proximate volatile matter test, important associated parameters change. Heating rate, for example, is controlled predominantly by conductive heat transfer in packed beds and decreases as sample weight or bed depth increases and as the particle size increases. Pyrolysis rate is sample weight and particle size dependent, therefore heating rate dependent. Experiments involving inert additives suggest that secondary char formation occurs on the external surface of particles, the total area of which increases as

bed depth increases or as the particle size diminishes. The result of secondary char formation is to reduce the yield of volatiles. The yield is also dependent on pyrolysis rate which controls residence time of the volatiles in the packed bed.

6.3 Future Work

Two basic limitations of the present study are that it does not cover a range of coals nor does it establish an upper limit of particle size independency of pyrolysis rate. There is also a need to expand the study to atmospheres of hydrogen and oxygen and to pressures above atmospheric. Coal research in general suffers from lack of an adequate model of coal constitution. The consequence is endless repeat of experiments on all coals of interest under all conditions of interest. There is urgent need, therefore, for such a model.

APPENDIX A. Calculation of Free-Fall Velocities

The procedure is outlined in Reference 79. A sample calculation is presented for 201 micron particles of PSOC-412 lignite in nitrogen at 20°C.

Data: particle diameter, $d = 2.01 \times 10^{-2}$ cm
 particle density, $\rho_s = 1.4$ g/cm³
 nitrogen density, $\rho = 11.14 \times 10^{-4}$ g/cm³
 nitrogen viscosity, $\mu = 175 \times 10^{-6}$ g/s cm

$$R'/\rho u^2 \times Re'^2 = [2d^3 \rho g(\rho_s - \rho)]/[3\mu^2]$$

where R' = the force exerted on unit projected area of the particle in a plane at right angles to its direction of motion.

u = the velocity of the particle

Re' = a modified Reynolds number

g = the acceleration due to gravity.

$$\begin{aligned} R'/\rho u^2 \times Re'^2 &= [(2) \times (2.01 \times 10^{-2})^3 \times (981) \times (1.4 - 11.4 \times 10^{-4}) \\ &\quad \times (11.14 \times 10^{-4})]/[(3) \times (175 \times 10^{-6})^2] \\ &= 270 \end{aligned}$$

From Figure 46, $Re' = 13.0$

$$\begin{aligned} u &= Re' \mu / \rho d \\ &= (13.0) (175 \times 10^{-6}) / (11.14 \times 10^{-4}) (2.01 \times 10^{-2}) \\ &= 102 \text{ cm/s} \end{aligned}$$

Figure 46. PLOT TO ALLOW CONVENIENT ESTIMATION OF FREE-FALL VELOCITIES FOR SPHERICAL PARTICLES

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