

COAL PYROLYSIS AT HIGH TEMPERATURES AND PRESSURES

S. S. Tamhankar, J. T. Sears and C. Y. Wen

Dept. of Chemical Engineering, West Virginia University, Morgantown, W.Va. 26506

INTRODUCTION

In coal conversion processes, such as combustion or high-temperature gasification, the extent of pyrolysis is an important parameter which is affected by temperature. Increasing amounts of coal converted directly to gaseous species would reduce the remaining material which must be converted by the relatively slow char-gas reactions. Studies on this aspect, particularly at pressure and high temperatures, are scarce.

ASTM standard methods obtain the amount of coal converted to volatile matter at low temperatures, slow heating rates and long exposure times. Other procedures have generally used either direct electric-resistance heating (1, 2) or a laminar-flow furnace (3, 4, 5, 6) to obtain high heating rates and high temperatures.

Menster et al. (1) and Kobayashi et al. (6) have indicated that the maximum temperature affects the extent of pyrolysis, with an apparent plateau or a peak in the weight loss curve at 900-1100°C, followed by an increase in the extent of pyrolysis. Scaroni, et al. (7) suggest that there is no direct heating rate effect on the extent of pyrolysis, but rather the preponderance of secondary char-forming reactions of the primary volatiles may yield an apparent heating rate effect as well as a sample-weight effect. There is evidence that the char formed by rapid heating at high temperatures is very reactive (3, 8). The previous work on pyrolysis at temperatures > 1000°C has been at 1 atm pressure.

To help fill in the data gaps, the present work has therefore been focused on the examination of pyrolysis at high temperatures (800-1600°C), pressures (1-15 atm) and in various reacting and nonreacting gases.

EXPERIMENTAL

A new design of a HPHT (high pressure, high temperature) TGA was utilized in this research. The details of the design and its performance have been discussed elsewhere (9). The system is depicted in Figure 1, which mainly consists of two chambers. The chambers are designed for 1200 psi, although supporting inlet lines limited the operating pressure to 450 psi. The small Grayloc flange was used as a port to introduce samples into the TGA. By raising the top chamber, attaching the sample, then lowering the chamber and securing the flange, a cumbersome, leaky port is avoided. A rugged electrobalance with a continuous weighing system, driven by an electric motor, is employed to lower the samples into the hot zone for weight-loss data. The heating system is a yttrium-stabilized ceramic "Kanthal" heating element. These elements are capable of 1800°C surface temperature, and work best in oxidizing gases. Temperatures were monitored throughout by Pt-Rh/Pt thermocouples. Steam can be introduced via a separate stainless steel flow system from gas lines, and condensation was avoided by maintaining the entire lower chamber at elevated temperatures.

This design has capability for quickly bringing the sample from a cold zone into the hot zone in less than 5 seconds, taking subsequent weight-loss data, and then removing the sample as quickly. The temperatures at various points in the system were calibrated at each reactor temperature and pressure. The temperature profile is such that the heating of the sample in the pyrolyzing-temperature region was achieved at a rate of 500-1500 K/sec depending on the reaction zone temperature. There is provision for several ports for gas input. Pyrolysis, external gas-

diffusion limitations, and char kinetic reactivity were analyzed from the weight-loss data by both varying time in the reaction zone and gas flow rate.

The coals studied included lignite (PSOC-246), bituminous (PSOC-309) and subbituminous (PSOC-240) samples. Samples of 50-100 mg were weighed, loaded and lowered in the sample holder into the heated chamber as described. Most runs used a platinum-mesh folded screen (52 mesh) as the sample holder. For some studies on particle size, the sample holder was a disked platinum foil. The results obtained on pyrolysis and gasification using the two different sample holders matched very well, indicating no effect of sample holder geometry.

The coal particle sizes used were 35-48, 48-60, 60-80, and 80-100 mesh (\bar{d} = 358, 273, 213 and 163 μm , respectively). The gaseous environments were nitrogen, carbon dioxide, nitrogen-steam. Pyrolysis and subsequent in-situ reaction with gas following pyrolysis were run at 800-1600°C, 1-15 atm.

RESULTS AND DISCUSSION

Typical weight-loss data obtained at 1200°C in both nitrogen and nitrogen-steam for the lignite coal are shown in Figure 2. Note that the determination of percent pyrolysis in the inert nitrogen is straightforward, while in a reacting environment it is obscured by the rapid chemical reactions of the volatiles and char. If the break in the curve is identified by extrapolating the primary pyrolysis and reaction curve portions, respectively (p) and (r), this weight-loss can be called the apparent pyrolysis; and the apparent percent pyrolysis determined. The values thus obtained for the apparent percent pyrolysis as well as the pyrolysis time were found consistent and reproducible under a given set of conditions, as confirmed by repeated runs. It may be noticed from Figure 2 that the ultimate pyrolysis in nitrogen is greater than the apparent pyrolysis in the reacting gas, while in the same time period the amount pyrolyzed is more or less the same in the two cases.

In Figure 3 are presented the apparent percent pyrolysis of lignite as a function of temperature for different gases. Note that the apparent percent pyrolysis in CO_2 and $\text{N}_2\text{-H}_2\text{O}$ is less than that in nitrogen, in agreement with the above discussion.

There is a plateau in the curve of percent apparent pyrolysis (devolatilization) versus temperature in the region 1200-1400°C. This type of phenomena can be found in the data of Menster et al. (1) and Kobayashi et al. (6). Suuberg et al. (10) observed two stages (or plateaus) in coal pyrolysis up to a temperature near 1100°C, and a third stage was envisaged above that temperature. This third stage was assumed to remove primarily CO and CO_2 . The data of Kobayashi et al. (6) indicate percent weight-loss near 60 percent at temperatures above 1500°C. The present results are consistent with the results reported by these authors and confirm a third plateau stage.

Figure 4 presents devolatilization results at various temperatures for pre-dried coal and for various particle sizes in a CO_2 gas. There appear to be significant effects of the moisture content in coal and various particle sizes. Although these results are inconclusive, they can be explained by either an effect of heating rate on pyrolysis or by secondary pyrolysis reactions which are influenced by available surface area, moisture and other gases which could result in internal volatile decomposition and coke formation.

Figure 5 presents the effect of pressure on the apparent pyrolysis in a steam environment. At lower temperatures (800-1100°C) the apparent pyrolysis increases slightly with pressure, while at higher temperatures (1200-1400°C) there is a decrease in apparent pyrolysis with pressure. One possible explanation is that at lower temperatures the increased gas concentration increases the gas-volatile re-

actions, decreasing the secondary char formation reactions; at higher temperatures the increased pressure prevents some volatiles from escaping the solid and thus participating in secondary char-formation reactions. Similar results have been reported earlier (8) in a hydrogen atmosphere, wherein the amount of pyrolysis was found to increase only beyond about 20 atm pressure. Notably, in steam this effect is observed at lower pressures. The present studies also bring out the effect of temperature on this behavior. Further work in this area is necessary to confirm the anomalous results.

Table 1 presents results of subsequent reactivity of chars formed by coal devolatilization. A comparison is shown of chars formed in-situ, as in the present method with chars formed separately and then reacted. Note that in-situ-formed char is a factor two to ten times more reactive than chars formed separately. Thus, keeping the char at high temperatures for longer times before reaction apparently renders the char less reactive, and can be interpreted as a morphological rearrangement. These results are in agreement with previous results at this laboratory (11), and extend these results to higher temperature regimes. It is suggested that the char preparation method dramatically affects subsequent char reactivity. These effects must be considered in models of char reactivity and in the use of char reactivity data in coal-conversion reactor models and in the interpretation of pilot-unit data.

CONCLUSIONS

Devolatilization generally increases with temperature in a manner consistent with the proposed three-stage mechanism for the evolution of volatiles. Results here show a plateau at 1200-1400°C and a maximum devolatilization above 1500°C. Reactive gases can interact with the freshly formed volatiles and affect the secondary char-forming reactions which can cause changes in the apparent percent pyrolysis. This was evident from the effects of moisture content, particle size, pressure and gaseous environment on the extent of pyrolysis. Reactivity of char formed in-situ and immediately reacted was found to be higher than reactivity of chars formed separately and then brought into the reactive environment. It is suggested that morphological rearrangements may be important in pyrolysis and subsequent char reactions.

ACKNOWLEDGMENT

This work was made possible by a grant from the Department of Energy, Contract No. ET-78-S-01-3253.

REFERENCES

1. Menster, M., O'Donnell, H. J. and Ergun, S., "Rapid Thermal Decomposition of Bituminous Coals," Am. Chem. Soc., Div. of Fuel Chem. Preprints 14 (5) 94 (1970).
2. Menster, M., O'Donnell, J. J., Ergun, S. and Friedel, R. A., "Devolatilization of Coal by Rapid Heating," in Coal Gasification, p. 1, Advances in Chemistry Series No. 131, Am. Chem. Soc., Washington, D.C. (1974).
3. Nsakala, N.Y., Essenhigh, R. H. and Walker, P. L., Jr., Fuel 57 605 (1978).
4. Nsakala, N.Y., Essenhigh, R. H. and Walker, P. L., Jr., Comb. Sci. & Technol. 16 153 (1977).
5. Badzioch, S. and Hawksley, P. G. W., Ind. Eng. Chem. Process Des. & Dev. 9 (4) 521 (1970).

6. Kobayashi, H., Howard, J. B. and Sarofim, A. F., "Coal Devolatilization at High Temperatures," 16th Intern. Symp. on Combustion, p. 411, The Combustion Institute, Pittsburgh, Pa. (1977).
7. Scaroni, A. W., Walker, P. L., Jr. and Essenhigh, R. H., Fuel 60 71 (1981).
8. Anthony, D. B., Howard, J. B., Hottel, H. C. and Meissner, H. P., Fuel 55 121 (1976).
9. Sears, J. T., Maxfield, E. A. and Tamhankar, S. S., "A Pressurized Thermo-balance Apparatus for Use in Oxidizing Atmospheres at High Temperatures," Ind. Eng. Chem. Fundamentals (submitted 1981).
10. Suibert, E. M., Peters, W. A. and Howard, J. B., Ind. Eng. Chem. Process Des. & Dev. 17 37 (1978).
11. Agarwal, A. K. and Sears, J. T., Ind. Eng. Chem. Process Des. & Dev. 19 364 (1980).
12. Linares-Solano, A., Mahajan, O. P. and Walker, P. L., Jr., Fuel 58 327 (1979).

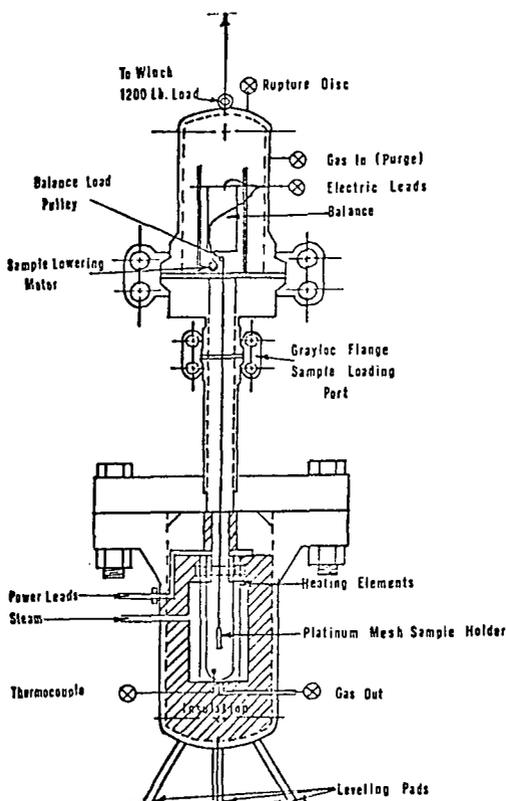


FIG. 1. SCHEMATIC OF HIGH PRESSURE/TEMPERATURE THERMOBALANCE APPARATUS.

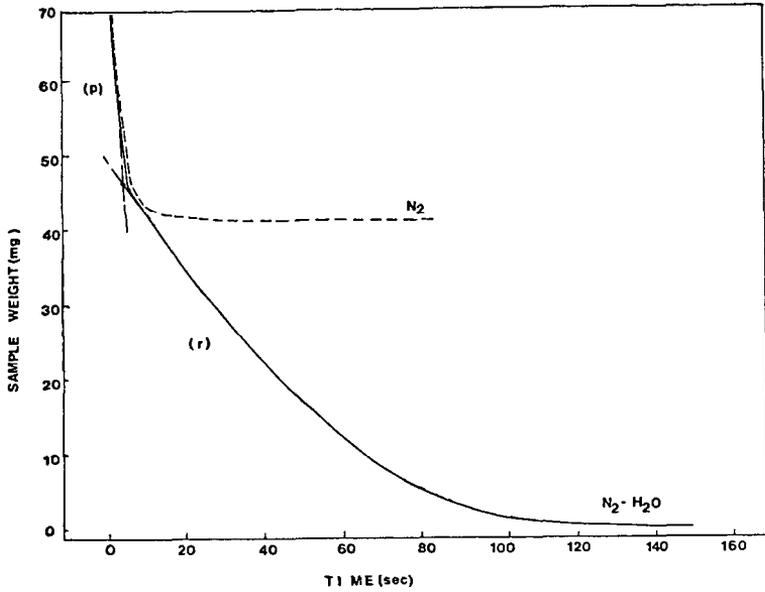


FIG. 2. REPRESENTATIVE WEIGHT LOSS CURVES OBTAINED AT 1200°C WITH PSOC-246 LIGNITE.

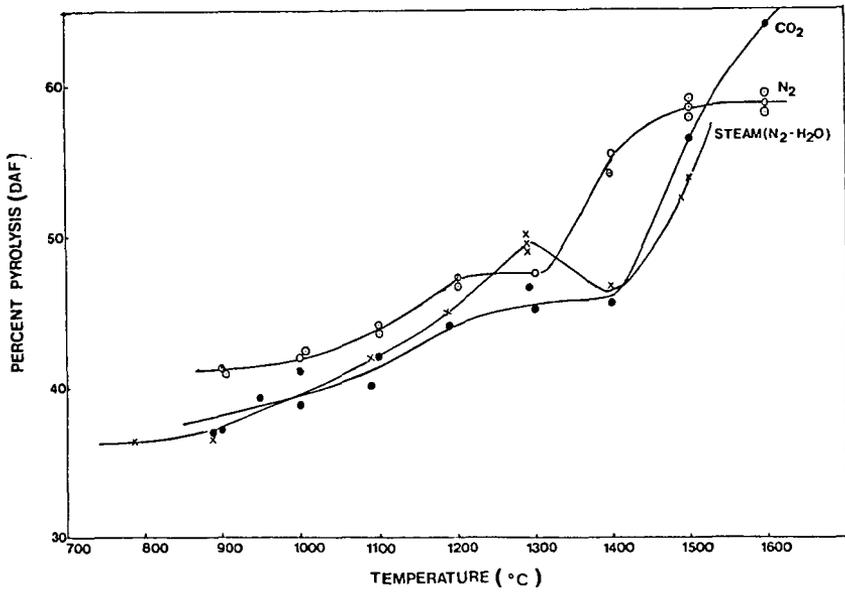


FIG. 3. EXTENT OF PYROLYSIS AS A FUNCTION OF TEMPERATURE FOR PSOC-246 LIGNITE.

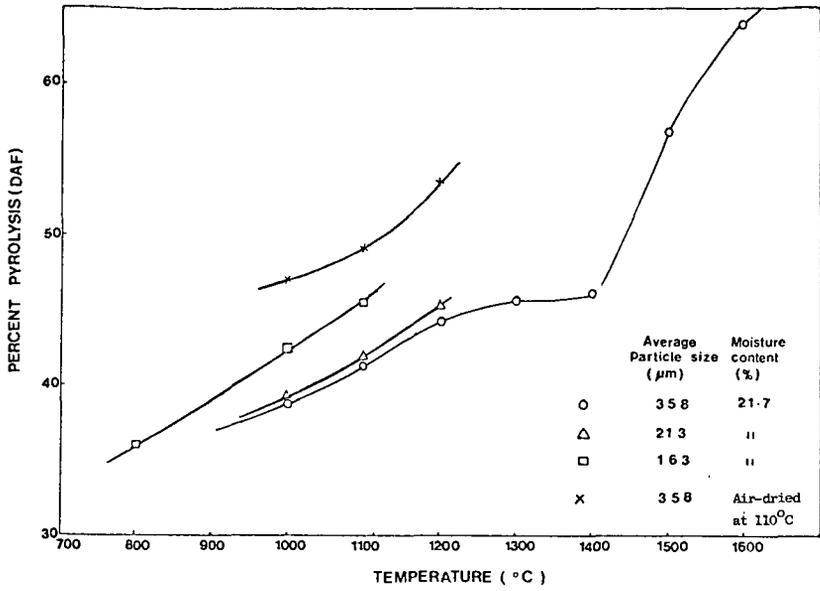


FIG. 4. EFFECTS OF PARTICLE SIZE AND MOISTURE CONTENT ON THE EXTENT OF PYROLYSIS IN CO_2 ATMOSPHERE.

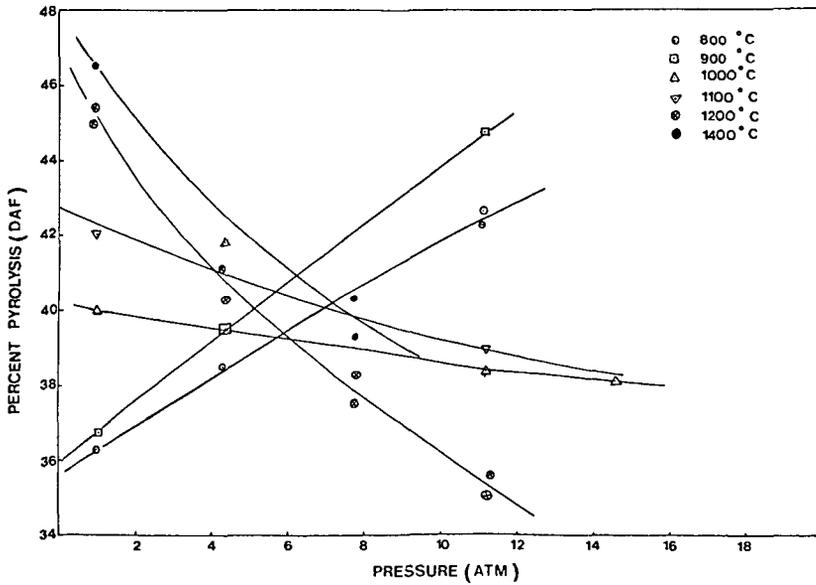


FIG. 5. VARIATION OF PERCENT PYROLYSIS WITH TEMPERATURE AND PRESSURE IN $\text{N}_2\text{-H}_2\text{O}$.

Table 1

REACTIVITY OF CHARAS AS A FUNCTION OF PREPARATION CONDITIONS

(A) Reactivity of N.D. Lignite (PSOC-246) in CO₂

Reaction Temperature °C		900	950	1000	1050	1200	1250	1300
Initial Reactivity mg/mg Min.	In-situ	0.30	0.40	0.69	0.80	2.14	2.15	2.15
	Preformed Char*	0.26	0.32	0.57	0.62	0.88	0.89	1.02

(B) Reactivity of a Subbituminous Coal (PSOC-314) in CO₂

Reaction Temperature °C		1250	1300	1350	1400
Initial Reactivity mg/mg Min.	In-situ	0.54	0.67	1.13	1.30
	Preformed Char*	0.50	0.60	0.76	0.79

(C) Comparison of In-situ Reactivities with Other Reported Results

Coal Type	Method/Treatment	Reaction Temp. °C	Gas	Maximum Reactivity mg/mg Min.	Ref.
N.D. lignite (PSOC-246)	In-situ	910	N ₂ -H ₂ O (excess H ₂ O)	0.48	Present study
N.D. lignite (PSOC-87)	Coal heated in N ₂ at 100°C/min to 1000°C, kept for 2 hrs, cooled. Reheated in N ₂ at 200°C/min to 1000°C, cooled to 910°C, held for 20 min, reacted.	910	N ₂ -H ₂ O (excess H ₂ O)	0.0467	12
HVC bituminous (PSOC-309)	In-situ at ~ 600°C/sec	920	CO ₂	0.20	Present study
HVC bituminous (PSOC-309)	In-situ at ~ 200°C/min.	920	CO ₂	0.088	11

*Char prepared by pyrolyzing coal in N₂ at 1100°C for 2 min.