COAL PYROLYSIS IN A HIGH PRESSURE ENTRAINED FLOW REACTOR

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INTRODUCTION

Many of the proposed coal gasification processes operate at elevated pressure. Since these processes also operate at elevated temperature, pyrolysis processes are important. However, there is relatively little data on pyrolysis yields at elevated pressure, particularly for continuous flow systems or on how pressure affects the reactivity of the char to subsequent gasification.

Most of the existing studies were done in batch, captive sample systems (1-3). For example, the work of Suuberg et al. (2) showed a significant effect of pressure on a bituminous coal and a modest effect for a lignite coal. The most important effect of pressure was a reduction in tar and increase in char yield at high pressure. However, one difficulty with interpreting the results from batch, captive sample systems is the pressure and residence time of the volatiles are not varied independently. As pressure is increased, the residence time of volatiles increases inside the particle as well as near the hot zone of the reactor.

In batch, semi-flow carbonization experiments, the effects of external pressure and external residence time can be varied independently. A review of the literature on semi-flow experiments by Dryden and Sparham (4) indicated that increases in inert gas pressure at constant volatile residence time did not have a significant effect on product yields. However, it should be noted that these experiments were done with very long volatile residence times (20 to 100 s). Recent work by Schobert et al. (5) examined the effect of pressure on tar yield in a semi-flow system (at constant residence times of about 1 s) and a pressure dependence of the tar yield was observed.

Entrained flow reactors are well suited to studies of pressure effects on pyrolysis and closely resemble real coal gasification systems. However, one must consider the effect of pressure on heat transfer as well. For example, Sundaram et al. (6) examined the effect of the pressure of various inert gases (He, CO, N_2 A_r) on carbon conversion and found that yields went through a maximum before declining. It is likely that, at the short residence times of their experiments (0.6 to 1.9 s at 900°C), the enhanced heat transfer due to gas pressure was more beneficial than the detrimental effects on mass transfer.

This paper will present pyrolysis data for product yields for four coals from an entrained flow reactor operated at pressures up to 300 psig. In addition, the effect of pressure on char reactivity will be discussed.

EXPERIMENTAL

A schematic of the high pressure reactor (HPR) system is given in Fig. 1. The furnace consists of a high pressure shell (capable of containing pressures up to 600 psig), a thick layer of insulation and a high temperature region heated by Kanthal Super 33 electrical heating elements. The high temperature section (capable of temperatures up to 1650°C) contains an alumina bed heat exchanger and a test section. The ambient gas enters the furnace through the heat exchanger to bring it up to furnace temperature and then turns downward into the test section. Coal is injected at a fixed point at the top of the test section using a water cooled injector. It mixes with the ambient gas and, after a fixed distance, enters a water-cooled collector. The reactor design is similar to a previously described atmosphere pressure entrained flow reactor (EFR) (7). The major differences are the smaller diameter test section in the HPR (1.27 cm vs 5.08 cm) and the absence of an optical port.

After the collector, the reaction products enter a cyclone to separate char, followed by a Balston filter to remove tar and soot. An electrostatic precipitator was tested for use after the cyclone but did not work as well as the filter. The gas stream is reduced in pressure and collected in a holding tank. The sample tank is a steel tank with glass-lined walls which is used to collect the total gaseous effluent from the reactor system during a typical run. It is initially evacuated and, during a run, the pressure gradually increases as it fills. After an experiment, a sample is taken from the tank and analyzed in an FT-IR cell and a GC. This allows the concentration of each species to be determined and the total yield of each product is calculated from a knowledge of the tank volume and pressure. The FT-IR can quantitatively determine many gas species observed in coal pyrolysis including CO, CO_2, H_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, HCN, NH_3, COS, CS_2, SO_2, and heavy paraffins and olefins. Additional characterization is performed by gas chromatograph to determine hydrogen, H_2S, O_2, N_2, C_3H_8, C_4's, and C_5's. The overall material balance is generally better than 90 to 95%.

Routine monitoring of three temperatures (top of heating elements, bottom of heating elements, and top of preheated bed) is done with permanently mounted thermocouples. Platinum alloy thermocouples are used to meet the high temperature requirements and to allow the use of oxidizing atmospheres. Power is supplied to the heating elements by using welding power supplies with continuously variable voltage adjustment. The voltage is adjusted to maintain the reference temperatures (above) constant during a run. These reference temperatures are calibrated against the furnace wall and gas temperatures by a set of profiling experiments. The furnace wall temperature and the injector-collector separation are inputs into the particle-temperature model which allows description of the coal particle time-temperature history.

The coal feeder consists of a tube which passes up through a bed of coal, with feeder gas supplied above the bed. To feed coal, the gas is turned on and the feed tube is slowly lowered from a position where the entrance is above the bed. When the entrance of the tube reaches the bed level, the coal is entrained in the gas entering the feed tube. The rate of feed is controlled by the rate at which the tube is lowered. The total weight of coal fed during a run is determined by weighing the feeder system before and after the run.

At the end of a run, the water-cooled collector is removed and any tar or char which sticks to the collector is rinsed out with solvent and weighed. Most of the char is collected in the cyclone. Fine solids (e.g., soot and coal fines) and condensed tar vapor which pass through the cyclone are collected in a filter. The filter and other parts of the collection system are extracted with solvent (methylene chloride), which is subsequently evaporated to determine the tar yield.

RESULTS AND DISCUSSION

The high pressure reactor (HPR) described above was used to determine the effects of pressure on pyrolysis behavior for four coals. The reactor was designed to provide similar temperatures and residence times as are employed in our atmospheric pressure reactor (EFR). To keep the gas requirements reasonable, a 1.27 cm I.D. tube was employed for the test section. It was found that swelling coals tended to plug the test section, so the coals tested were limited to subbituminous coals or lignites. The four coals tested were Montana Rosebud subbituminous, Gillette subbituminous, Jacob's Ranch subbituminous, and Zap (North Dakota) lignite. The coal analyses are presented in Table I. The pyrolysis yields for experiments at 800°C, 0.47 s residence time and 300 psig are given in Figs. 2-5 for these coals, respectively.

The most extensive amount of data was taken with the Montana Rosebud subbituminous due to a complementary program at AFR and Morgantown Energy Technology Center (METC) using this coal. The effects of pressure on product yields are observed to be modest in all cases. In general, with increasing pressure (at constant residence time and temperature) there is a slight reduction in tar, olefin, and ethylene yields and increase in benzene, ethane and CH_4 yields. The trend for paraffin yield varies with the coal, as does the benzene yield trend. The subbituminous coals show a minimum benzene yield at intermediate pressures.

Data was obtained for the Zap, Jacob's Ranch, and Gillette coals at 685°C for the same residence time and range of pressures (not shown). The trends for tar, olefins, C_2H_4, and C_2H_6 were similar, but the CH_4 and benzene yields declined with pressure. The complex variations of volatile yields with temperature and pressure would be expected since both in the internal secondary chemistry of the coal and the external gas phase chemistry there are temperature and pressure-dependent sources and sinks for the various species. For example, Suuberg et al. (2) have shown that methane yields increase with increasing external gas pressure in batch, capture sample experiments. This was attributed to evolution of CH_4 during secondary repolymerization of tar to form char. Arendt and van Heek (8) observed similar results for CH_4 yields in both batch and semi-flow reactors. Higher yields of methane under increased external gas pressure have also been attributed to the auto-hydrogenation phenomenon, where hydrogen evolved from the coal back reacts to form CH_4 (9). A recent paper has suggested that this reaction is more affected by residence time than external gas pressure for high and low rank coals (10).

There is also experimental evidence which suggests a decline in CH_4 yield would occur with increasing pressure. Methane decomposition is catalyzed in the presence of coal char (11,12). This has been attributed both to surface area and catalysis effects. At high pressure, the enhanced residence time of CH_4 in the pores would increase decomposition. In addition, the gas phase decomposition of CH_4 is believed to involve the following pressure dependent initiation reaction:

$$CH_4 + M = CH_3 + M + H \quad (1)$$

where M is any other molecule (13). This reaction would also be favored at high pressures. Consequently, numerous processes can operate on even such simple and relatively unreactive molecules as CH_4, making apriori prediction of pressure trends for volatile yields over a wide range of temperature difficult.

In entrained flow systems, one must also contend with the effects of gas pressure on heat transfer. In our system, increasing the pressure also affects the shape of the temperature profile and, consequently, the length of the isothermal zone. In order to achieve the same nominal residence time it was necessary to reduce the gas flow rate at higher pressures. For this reason, an assessment of pressure effects for data from the reactor requires consideration of the effect of pressure on the particle time-temperature history due to: 1) changes in the experimental conditions, 2) changes in the physical properties of the entraining gas with pressure. To do this, an entrained flow reactor model was developed which is a modification of one developed recently for our atmospheric pressure reactor (EFR) (14,15). The latter model was validated by comparison to actual temperature measurements. For the HPR, direct validation is not possible because of the lack of an optical port in the reactor. Instead the model was validated by fitting CH_4 yields from low pressure HPR data (26 psig) where it was assumed that the validated kinetics from the EFR would still hold.

After the modified particle temperature model was developed and validated, the results of the HPR experiments were simulated. These simulations are shown as solid lines in Figs. 2-5. These trends, which account only for the effects of pressure on particle time-temperature history (and not on the pyrolysis chemistry) indicate that there are real pressure effects superimposed on a slight variation in the time-temperature history. The trends of the model predictions should be compared to the data trends in Figs. 2-5 to discern a pressure effect rather than the absolute values. This is because the pyrolysis model does not match all of the atmospheric pressure data (e.g., C_2H_4 yields) due to an incomplete description of gas phase cracking.

High Pressure Experiments in a Heated Tube Reactor - A set of experiments was done at 800°C with Montana Rosebud coal in an electrically heated tube reactor at 1 atm and 5 atm pressure. The results for char, tar, and gas yields are shown in Fig. 6 for the two sets of experiments, which were done at the same volumetric flow rate. The total particle residence time at 200 cm distance is about 200 ms.

Initially, product yields are reduced when compared to the one atmosphere case. This is a result of the fact that the higher gas density causes a greater heat load on the tube and hence increases the distance required to heat the gas plus coal mixture to the equilibrium temperature. It is interesting that the maximum tar yield is lower in the 60 psig case. However, it is possible that an experiment in between 50 and 100 cm would reveal a higher tar yield. The asymptotic yield of about 10% is similar for both sets of experiments. It also agrees with the 26 psig data from the HPR. The advantage of the HTR relative to the HPR is that the good time resolution allows the maximum tar yields to be better defined.

Comparison of Tar Yield Data from Three Reactors - In Table II, tar yield data are listed for all three entrained flow reactors used at AFR. In each case, the final particle temperature was about 800°C. The residence times were lower for the HTR experiments but, due to the higher heating rate, the time at final temperature was nearly the same in each case (~0.2 s) according to our calculations. The lower pressure (<5 atm) results agree well between reactors. It is also apparent from the lower temperature HPR data in Table II, and the shorter residence time HTR data in Fig. 6, that some tar cracking occurred even under these relatively mild conditions. The reductions in tar yield due to cracking of about 35% agree well with previous data on Pittsburgh Seam bituminous coal tars cracked separately (16). The approximately 25% reduction in tar yield over a pressure range of 3 to 13 atm is in good agreement with the generalized plot developed by Suuberg (17).

Char Reactivity Measurements - Some reactivity measurements of the chars produced from the HPR experiments were made using a newly developed non-isothermal technique (18). The chars are heated at a constant rate (30°K/min) in a TGA in air. A reactivity index is defined based on a critical temperature to achieve a measurable weight loss rate, which is inversely related to reactivity. These data are given for the HPR chars in Table III. There does appear to be a slight decrease in char reactivity with increasing pressure. However, a portion of this could be attributed to the slightly increased severity of the higher pressure experiments. Additional data will be required on the kinetics of thermal deactivation in order to be more conclusive.

CONCLUSIONS

1. Pyrolysis experiments in a high pressure entrained flow reactor with three subbituminous and one lignite coal revealed an effect of pressure on product yields, even after allowing for changes in heat transfer. The tar and light hydrocarbon yields were most affected.

2. The relative reduction in tar yield as the pressure was increased from 3 to 13 atm was about 25%, in agreement with literature data.

3. The maximum tar yield was not observed in the 817°C, 0.5 s experiments, even at low pressure, due to tar cracking.

4. There was a small but consistent reduction of char reactivity with increased pressure. Some of this effect may be due to the slightly increased severity of the high pressure experiments.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support of this work by the United States Department of Energy, Morgantown Energy Technology Center, under Contract No's. DE-AC21-81FE05122, DE-AC21-84MC21004, and DE-AC21-85MC22050.

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TABLE I

SAMPLE PROPERTIES

WT% DAF

	Zap, North Dakota Lignite	Gillette Subbituminous	Montana Rosebud Subbituminous	Jacob's Ranch Subbituminous
Carbon	66.5	72.0	72.1	74.3
Hydrogen	4.8	4.7	4.9	5.2
Nitrogen	1.1	1.2	1.2	1.1
Sulfur (Organic)	1.1	0.5	1.2	0.6
Oxygen (Diff.)	26.5	21.6	20.3	18.8
Ash (Dry Wt%)	7.1	5.0	10.0	7.8

TABLE II

OBSERVED TAR YIELDS (DAF) FROM VARIOUS REACTORS AT 800°C, 0.1–0.5 S RESIDENCE TIME

Coal:			Zap Lignite	Gillette	Montana Rosebud	Jacob's Ranch
Reactor	Pressure (atm)	Time (s)				
HTR	1.0	0.2	10.3		10.0	
HTR	5.0	0.2			10.0	
EFR	1.0	0.4	10.0*			
HPR	2.6	0.5	6.0 (8.0)	9.4 (13.6)	9.2	7.6 (11.0)
HPR	13.0	0.5	4.5 (7.5)	7.8 (11.5)	6.0	6.5 (9.5)

NOTES: Values in parentheses are for 658°C experiments at the same residence time and pressure.

* Tar plus missing.

HTR = Heated Tube Reactor
EFR = Entrained Flow Reactor
HPR = High Pressure Reactor

TABLE III

CRITICAL TEMPERATURE FOR OXIDATION OF CHARS FORMED AT VARIOUS PRESSURES

Coal:	Zap Lignite	Gillette	Montana Rosebud	Jacob's Ranch
Pressure (atm)				
2.6	365	368	403	370
7.8	366	378	415	370
13.1	378	381	419	376
21.4	---	---	429	---

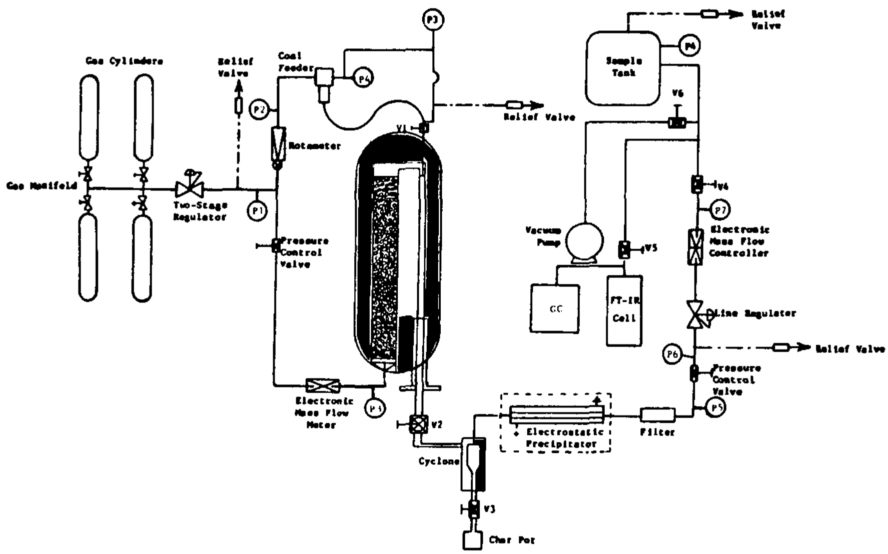

Figure 1. Schematic of High Pressure Entrained Flow Reactor System.

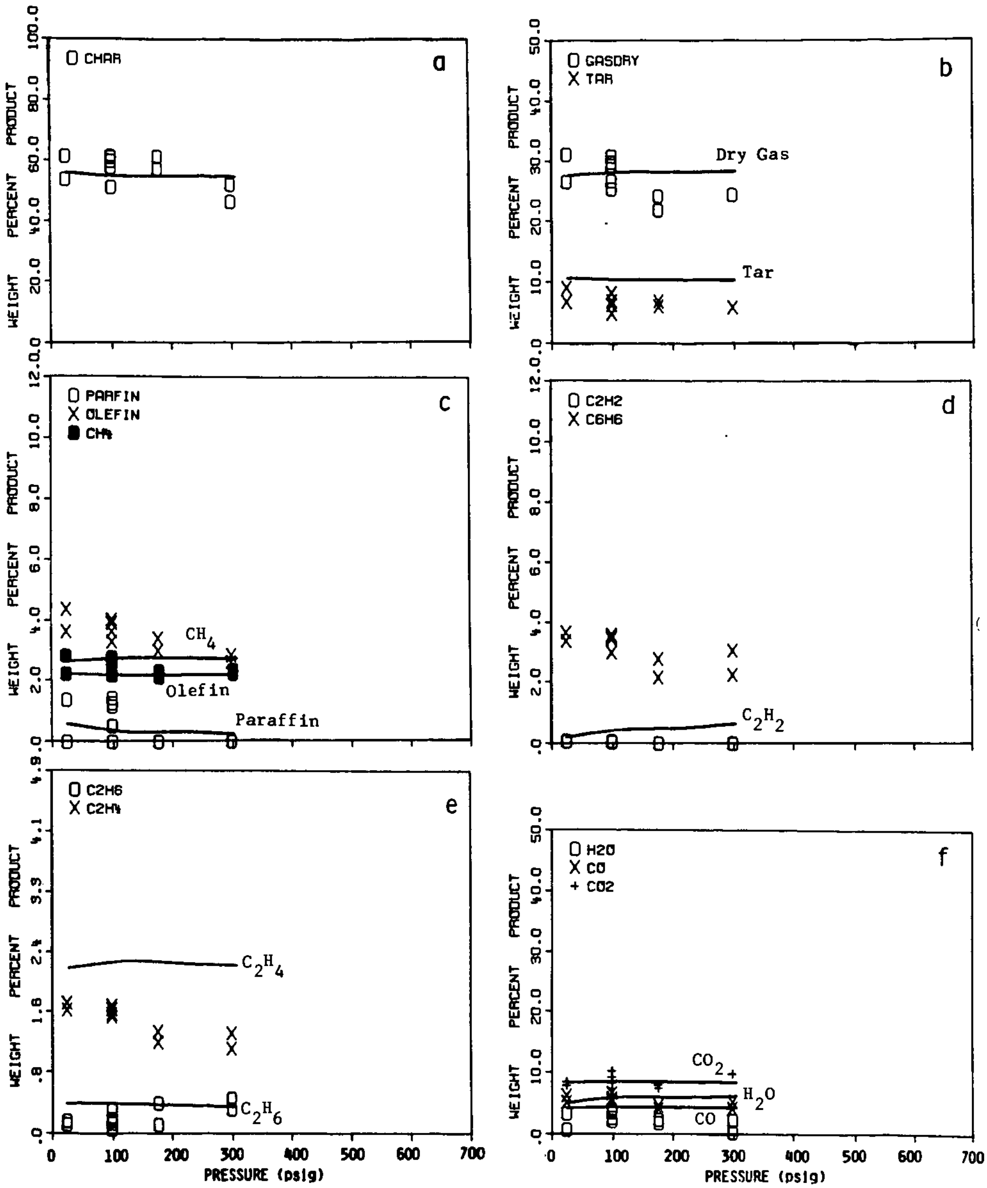

Figure 2. Pyrolysis Product Distribution for Montana Rosebud Subbituminous Coal as a Function of Pressure. Temperature = 817°C, Residence Time = 0.47 sec.

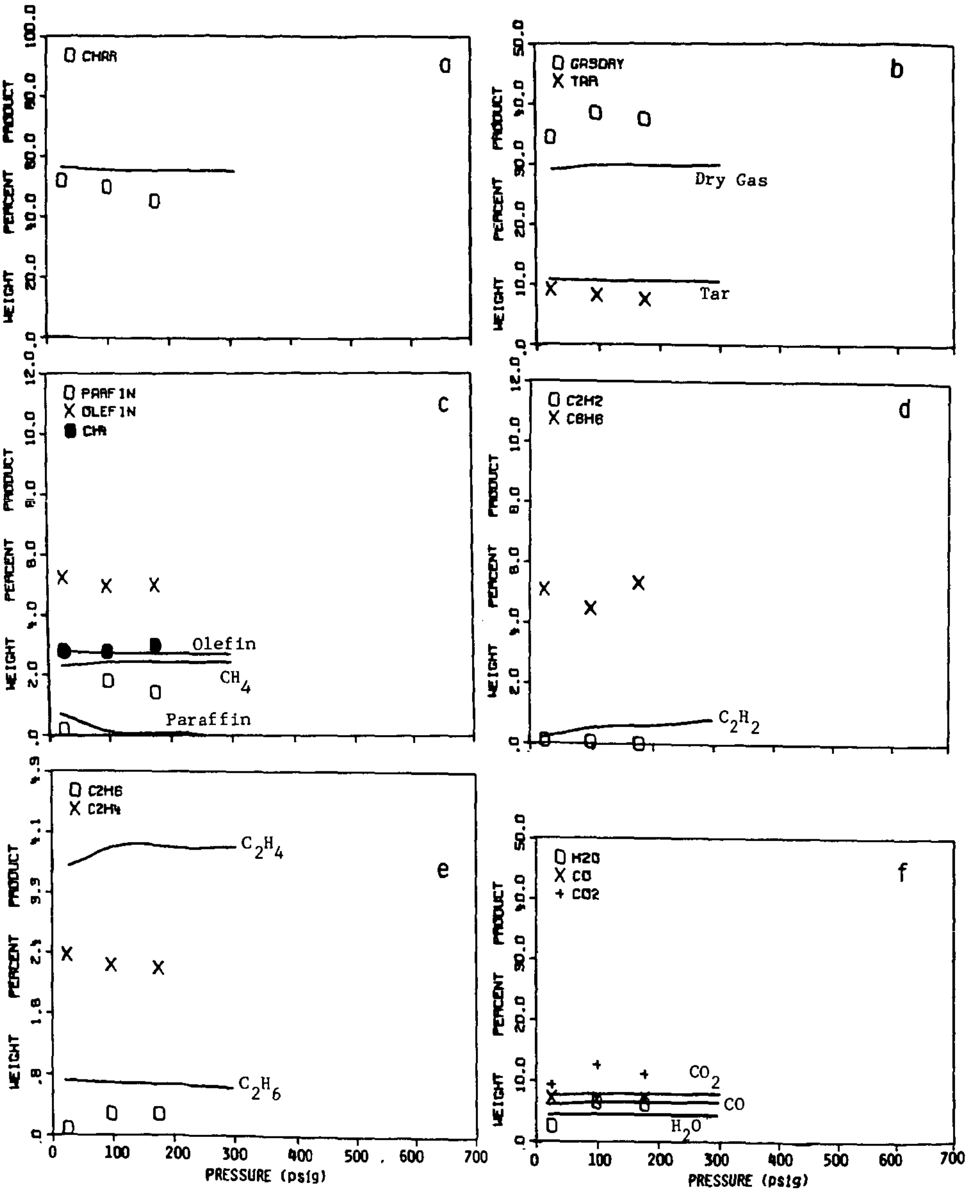

Figure 3. Pyrolysis Product Distribution for Gillette Subbituminous Coal as a Function of Pressure. Temperature = 817°C, Residence Time = 0.47 sec.

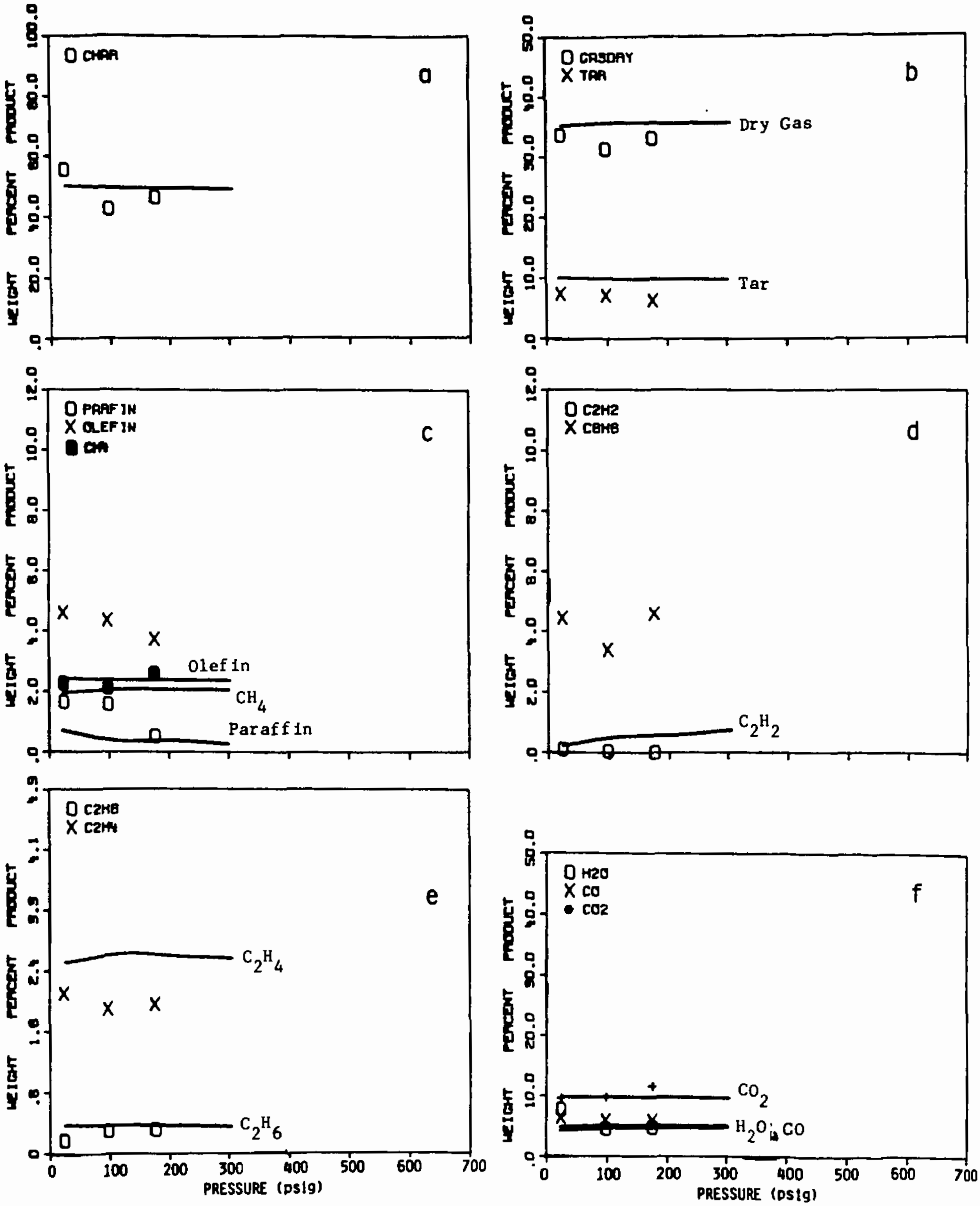

Figure 4. Pyrolysis Product Distribution for Jacob's Ranch Subbituminous Coal as a Function of Pressure. Temperature = 817°C, Residence Time = 0.47 sec.

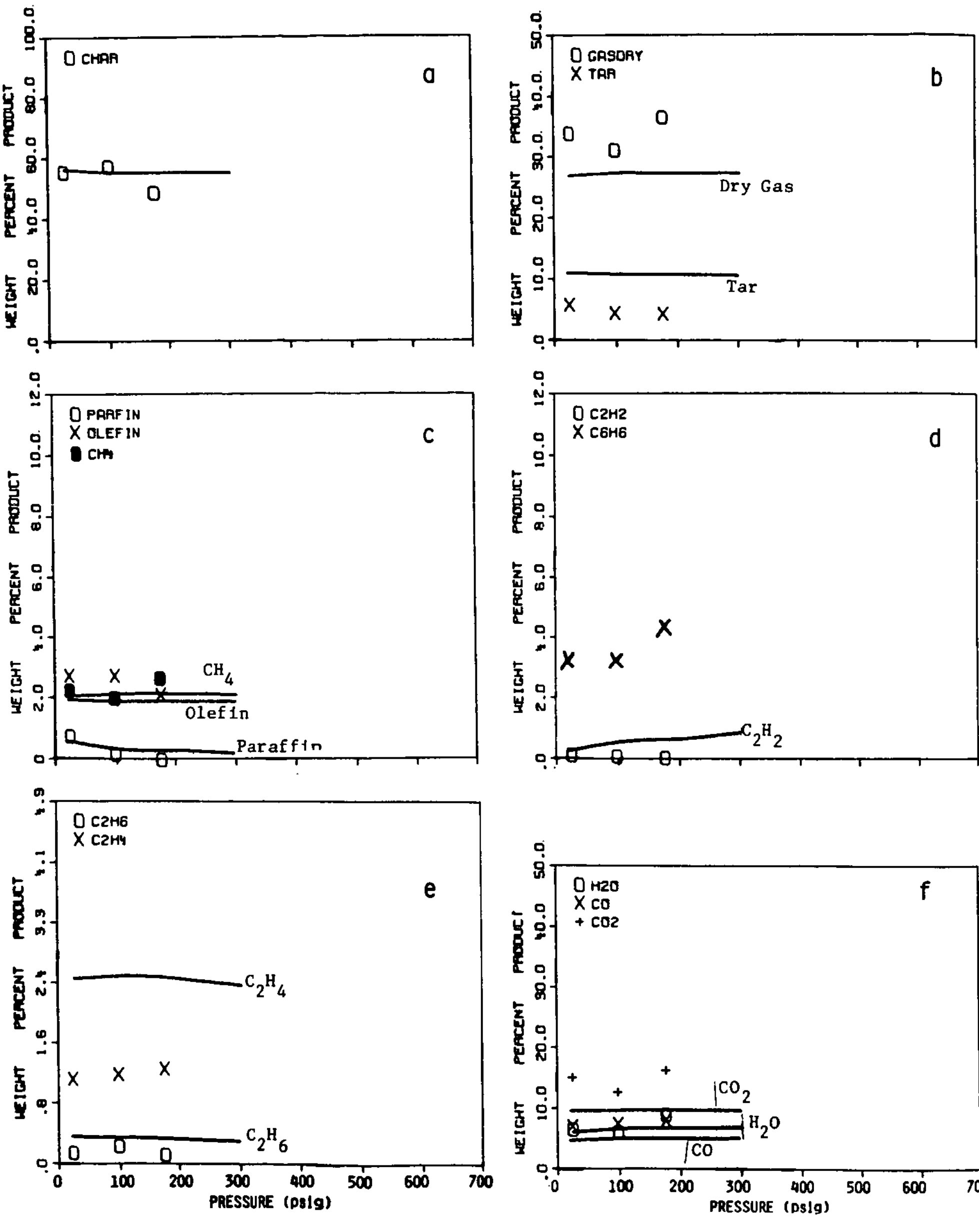

Figure 5. Pyrolysis Product Distribution for Zap, North Dakota Lignite as a Function of Pressure. Temperature = 817°C, Residence Time = 0.47 sec.

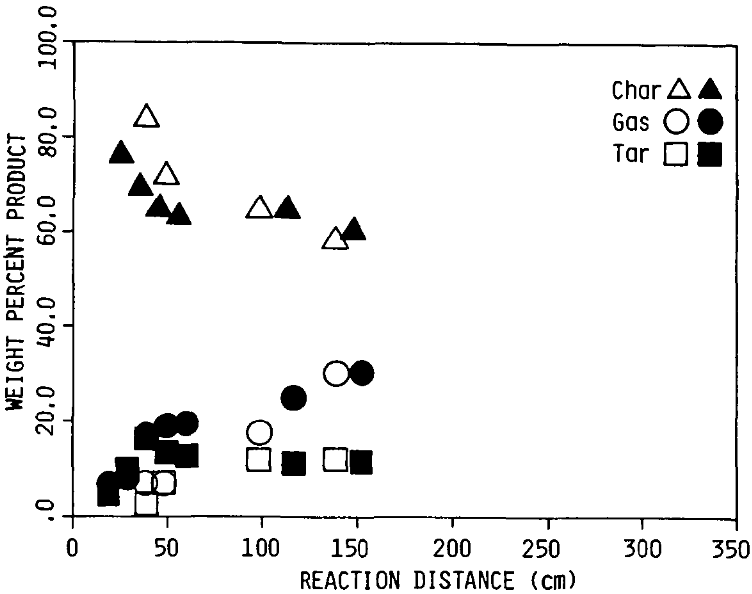

Figure 6. Comparison of Pyrolysis Data from One Atmosphere Pressure (*solid symbols*) *and* 5 *atm pressure* (*open symbols*) Experiments in the Heated Tube Reactor with Montana Rosebud Coal (200 x 270 mesh). The Equilibrium Tube Temperature was 800°C.