

THE EFFECTS OF CARBON DIOXIDE AND CATION CONTENT  
ON THE RAPID PYROLYSIS OF A LIGNITE

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INTRODUCTION

With the development of newer, more advanced technologies, especially those operating at higher pressures and under rapid heating conditions, the significance of certain variables on the pyrolysis process has been raised. The potential for developing the large deposits of low rank coals in the central regions of the United States using these technologies is leading a drive to examine these variables under conditions which simulate or approximate the technologies, especially with regard to rapid heating. Two variables of potential consequence to the processing of these low rank coals are carbon dioxide atmosphere and inherent cation content.

Until recently, the effect that the cations which are associated with certain oxygen functionalities on low rank coals have on pyrolysis has been ignored. There has been considerable interest about their effects in catalytic gasification and on combustion, especially with regard to slagging and fouling. But, with the work of Schafer (1980), Tyler and Schafer (1980), Morgan (1983), and Franklin et al. (1983), information is coming to light that removal of these species has a potentially important consequence on the yield and distribution of the products of pyrolysis. Thus, this effect also has potential repercussions on conversion processes. Ignition phenomena may be affected, for instance. It may also be possible to take advantage of this effect to produce premium products such as high density liquid fuels through a commercial pyrolysis process. The pyrolysis of a lignite is carried out in both a raw and an acid-washed state in order to confirm these findings and extend them to higher pressures.

It is well known that  $\text{CO}_2$  reacts with coal via the Boudouard reaction. This reaction is considered unimportant on the time scale of rapid pyrolysis, however. On the other hand,  $\text{CO}_2$  is present as a gaseous product during gasification and combustion as well as during pyrolysis. When low rank coals are pyrolyzed, the production of  $\text{CO}_2$  can be significant through the destruction of large numbers of oxygen-containing moieties, especially carboxyl groups, present on such coals. It is hypothesized that the presence of  $\text{CO}_2$  in the pores of a devolatilizing coal may have an impact on pyrolysis through interactions with the primary pyrolysis products. The capability of the atmospheric pressure entrained-flow reactor (APR) at Penn State to provide primary and secondary flow streams of different gas composition coupled with the high pressure capabilities of the high pressure reactor (HPR), also at Penn State, allows a unique study of the effect of  $\text{CO}_2$  on rapid pyrolysis. This includes a focus on the interaction of  $\text{CO}_2$  on both raw and acid-washed coal samples.

## EXPERIMENTAL

### Coal Sample Selection and Preparation

The coal selected for this study is PSOC-412, a lignite from the Darco seam in eastern Texas. Samples of the coal were obtained from the Penn State Coal Sample Bank. The coal was ground, sieved and resieved in order to provide a narrow size distribution, and then stored in closed containers at ambient conditions. All solid particles pyrolyzed in the experiments were collected between U.S. Standard Sieve mesh sizes 140 and 200. The mean diameter of these particles as determined by the Rosin-Rammler technique is 79 microns. Portions of the sized coal sample were used to prepare acid-washed samples according to a method used by Morgan (1983). The acid-washing is performed to remove the cations which are associated with the carboxyl group functionality on low rank coals. Portions of the acid-washed samples were then used to prepare a small amount of calcium-exchanged samples, again according to a method used by Morgan (1983). This procedure replaces the hydrogen ions on the carboxyl groups with calcium ions.

### Pyrolysis Procedure

Pyrolysis experiments were conducted in the entrained-flow tube furnace systems at Penn State. The construction of these furnaces is based on a design by Badzioch and Hawksley (1970).

The APR was originally constructed by Scaroni (1979). Modifications to design and operating procedure subsequently evolved as documented by Maloney (1983) and Morgan (1983). Operation of the APR in this study follows the procedure described by Maloney (1983), except for one important difference. In these experiments, the hopper which held the solid sample prior to injection into the furnace was flushed continuously with the entraining gas. The reader is referred to Maloney (1983) for details of the operational procedure for the APR.

All the tests in the APR were conducted at atmospheric pressure and 900°C. Primary and secondary volumetric flowrates were held constant at approximately 1 and 35 standard liters per minute, respectively. Residence times were varied by placing a water-cooled collector probe coincident with the axis of the reactor at various distances from the injector tip. Residence times were determined using velocity models (see below). The solids flowrate was held constant at 1 gram per minute. The primary, or entraining, gas was He or CO<sub>2</sub>, and the secondary gas was either N<sub>2</sub> or CO<sub>2</sub>, depending on the test matrix. The Reynolds number for the total gas flow, calculated at 900°C, was in the neighborhood of 200 for N<sub>2</sub> and 350 for CO<sub>2</sub> (ignoring the small, primary gas flow of He when present).

The HPR was constructed to provide information about devolatilization studies under conditions more severe than those possible with the APR. It was designed to conduct pyrolysis at pressures to 1500 psig, temperatures to 1300°C, and in reducing atmospheres, including pure hydrogen. All experiments in the HPR were conducted at a nominal temperature of 900°C and at pressures of 200 psig. Due to the design of the HPR (and unlike the APR), the composition of the primary and secondary gas was necessarily the same for a given experiment. Pyrolysis was conducted in either He or in CO<sub>2</sub> atmospheres. The gas Reynolds number for the experiments in He ranged between 50 and 250. For CO<sub>2</sub> the gas Reynolds number varied between 500 and 2500. The solids flow rate was 1 gram per minute. As with the APR, residence times were determined using velocity models (see below). The reader is referred to Reuther (1988) for details of the pyrolysis procedure in the HPR.

### Residence Time Determination

The designs of the APR and the HPR make measurement of particle velocities and residence times extremely difficult. Instead, the distances over which the particles are entrained in the hot zones of the reactors (from injector tip to collector probe entrance) are transformed into residence times using a gas velocity model coupled with a particle velocity model. The approach used is similar to that used by Morgan (1983), Maloney (1983), and Tsai and Scaroni (1984) and was originally described by Morgan (1983) for the APR. The design of the reactors and the associated pyrolysis procedures cause the gases and entrained particles to enter the reaction zone under laminar plug flow conditions with development of a parabolic flow profile following immediately. The particles are injected with a cold entraining gas (primary stream) through nozzles which are inserted down the axes of the reactors. The much larger flow of hot secondary gas flows into the reactors through the annular region created by the nozzles.

The development of the parabolic profile, created by the drag of the gas along the wall, affects the gas velocity at every point in the reactor. Also, because the gas velocity is accelerating in the region in which the particles reside, the effect this has on particle velocities must subsequently be considered. The model used for the development of the parabolic flow profile was originally described by Campbell and Slattery (1963).

The equation governing particle velocity is derived by considering the forces acting on the entrained particle (Shu, 1978). This equation is numerically solved using the fourth-order Runge-Kutta computational technique. As a consequence of the solution, one can determine the distance the particles have fallen as a function of time, thus giving a residence time for the particles in the reactor.

#### Discussion of Particle Temperatures

The particles are assumed to be heated primarily by the hot, secondary gas stream. That is, radiation from the walls is believed to be an important mode of heat transport under the experimental design. Thus, the gas temperature is an important parameter in determining particle temperatures. For particle diameters less than 100 microns, the particle temperature closely follows the surrounding (primary) gas temperature, and the primary gas temperature is most sensitive to conductive heating by the secondary gas. These assumptions are in general agreement with previous studies on heat transfer in such systems (see e.g., Sass, 1972; Freihaut et al., 1977; Tsai and Scaroni, 1984; Suuberg, 1987; Hajaligol, 1987). Flaxman and Hallett (1987) have subsequently confirmed these results for an entrained-flow reactor which is based on the same design and operating principles as the APR at Penn State.

Thus, the most effective way to enhance particle heating rate is to use a low heat capacity, high thermal conductivity gas (i.e., a gas with a high thermal diffusivity) as the primary (cold) gas. This is equivalent to external heat transfer control for particle heating. It follows that particle temperatures and heating rates are higher when a gas with a high thermal diffusivity, such as He, is used as the primary gas than when a gas with a lower thermal diffusivity, such as N<sub>2</sub>, is substituted. It is argued, based on the above statements, that when a lower thermally diffusive gas is substituted for a higher in the primary stream, the particle temperature is the same or lower for a given residence time. Thus, if the weight loss is found to be higher, such increased weight loss must be due to something other than temperature. In this work, the controversy concerning the temperature of the particles during pyrolysis in a dilute-phase, entrained-flow environment is avoided as much as possible by accepting the preceding arguments and those which follow. When drawing conclusions from comparisons among pyrolysis experiments it is assumed that (1) any two experiments run under the same conditions of gas flow and composition but with different 'kinds' of solid particles (raw versus acid-washed, etc.) have equivalent particle heating rates and final temperatures and (2) when the gases are different but the particles are the same, it is pointed out which particles may have heated up faster and/or to

a final higher temperature. The overriding assumption is that particles which heat up faster and to a higher temperature lose weight more rapidly and that higher pyrolysis temperatures result in higher weight losses. It should be noted that it is not assumed that the particles pyrolyze isothermally.

#### Weight Loss Analysis

All char samples were subjected to a moisture analysis followed by a proximate ash analysis in order to determine weight lost during a pyrolysis run. The procedures used were slight modifications of those specified by the American Society for Testing Materials (ASTM) Test D3173-73, Moisture in the Analysis Sample of Coal and Coke, and Test D3174-73, Test for Ash in the Analysis Sample of Coal and Coke. The procedural modification in each case was to substitute approximately 0.5-gram samples for the suggested 1.0-gram sample amounts in order to conserve sample. All samples were done in duplicate. If any of the duplicate values differed significantly (i.e., outside of the recommended ASTM limits of 0.5%), further samples were ashed until the discrepancy was resolved. The amount of organic material that was devolatilized in each experiment, i.e., the weight lost, was calculated from the proximate ash values of the devolatilized sample and the undevolatilized sample using the "ash tracer" technique, as described by Scaroni (1979).

### RESULTS AND DISCUSSION

#### Weight Loss Results

Weight loss results are presented below as a function of the presence of cations and CO<sub>2</sub> atmosphere.

#### Effect of Cations

The effect of the presence of cations on rapid pyrolysis was studied in both the APR and the HPR. Pyrolysis was performed on raw, acid-washed, and, to some extent, calcium-exchanged coal samples. The results of these experiments in various atmospheres are plotted in Figures 1, 2, 3, 4, and 5.

Figures 1, 2, and 3 are from experiments at atmospheric pressure (i.e., in the APR). Figure 1 shows the results of pyrolysis on raw, acid-washed, and calcium-exchanged coals in He/N<sub>2</sub>. (This nomenclature (e.g., 'He/N<sub>2</sub>') is followed throughout this discussion. The first gas listed is the primary or entraining gas, and the second gas is the secondary flow gas.) Figure 2 presents weight loss results on the same three solid samples in He/CO<sub>2</sub>. Figure 3 displays the results of pyrolysis in CO<sub>2</sub>/CO<sub>2</sub> on the raw and the acid-washed samples, only. There is a dramatic drop in weight loss for the calcium-exchanged sample in both He/N<sub>2</sub> (Figure 1) and He/CO<sub>2</sub> (Figure 2) at longer residence times. There appears to be a small drop in weight loss for the raw sample compared to the acid-washed sample in He/N<sub>2</sub>, which is most significant at intermediate residence times. The results in He/CO<sub>2</sub> are similar to those in He/N<sub>2</sub>. In CO<sub>2</sub>/CO<sub>2</sub> (Figure 3), where only raw and acid-washed samples were compared, there is again a drop in weight loss in going from acid-washed to raw sample. In this case the difference appears to be more significant than in He/N<sub>2</sub> or He/CO<sub>2</sub>, however, and occurs throughout the range of residence times examined.

The preliminary conclusions to be drawn from these three figures are:

1. Removal of cations appears to have had a small impact on weight loss with this coal, being most significant at intermediate to longer residence times.

2. Replacement of hydrogen ions on the carboxyl groups by calcium ions to a saturation level had a dramatic effect on weight loss.
3. The presence of  $\text{CO}_2$  in the pores at the onset of pyrolysis has an added effect on weight loss from the acid-washed coal sample compared to the raw sample.

Figures 4 and 5 are the results of experiments in the HPR at 200 psig. Figure 4 presents the weight loss results of raw and acid-washed samples in He/He. Figure 5 shows the pyrolysis of these same two samples in  $\text{CO}_2/\text{CO}_2$ . The weight loss of the raw sample in He/He is again reduced compared to the acid-washed sample except for the longest residence time recorded, which occurs at what appears to be an asymptotic or ultimate rapid pyrolysis yield under these conditions. When these same two samples are pyrolyzed in  $\text{CO}_2/\text{CO}_2$ , however, only at the earlier residence times considered is there a noticeable reduction in weight loss for the raw sample compared to the acid-washed sample. At the longer residence times, as with Figure 4, weight losses are virtually identical.

Thus, as with the APR results, the presence of cations appears to reduce weight losses during the earlier periods of rapid pyrolysis in an inert atmosphere (He). The weight loss reduction is more significant at this higher pressure and may be an indication that the species which are contributing to reduced weight loss are themselves affected by mass transfer considerations. If, for example, the cations are retarding weight loss by attaching themselves to potential volatile species which, in turn, makes it more difficult for them to exit the particle under mass diffusion considerations (increased molecular weight and size), then additional constraints to mass transfer, such as increased pressure, could enhance this effect. Or, if the cations reduce weight loss via cracking reactions, then mechanisms which impede mass transfer, such as increased pressure, will allow more time for this process to occur. Both of these possible roles for cations as weight loss inhibitors are discussed by Morgan (1983) and others. What is also significant, however, is that ultimate weight loss is virtually the same in both Figures 4 and 5. This indicates that most (if not all) of the mass associated with the initially formed volatiles eventually exits the particle given enough time, although it may not have the same molecular structure as when first formed because of one or more secondary reactions. ("Initially formed volatiles" is taken to mean those species which are originally solid but which exist in the vapor state, however transiently, under the conditions of the experiment upon the initial breaking of a bond which had held it to the rest of the solid matrix.)

Finally, Figure 5 reinforces the impression that the presence of  $\text{CO}_2$  is having an effect on weight loss. To confirm this, the pyrolysis results were replotted to show the effect of atmosphere for each coal sample (raw and acid-washed) in each reactor (APR and HPR).

#### Effect of Atmosphere

Figure 6 shows the results of the pyrolysis of the raw coal in the APR in He/ $\text{N}_2$ , He/ $\text{CO}_2$ , and  $\text{CO}_2/\text{CO}_2$  atmospheres. The weight loss in He/ $\text{N}_2$  is less than in He/ $\text{CO}_2$  or in  $\text{CO}_2/\text{CO}_2$  over most of the residence time measured. The particle temperature in He/ $\text{N}_2$  and in He/ $\text{CO}_2$  should be very nearly the same from a thermodynamic standpoint. This is because the primary gas is the same in the two cases, and the heat content of the secondary gases are identical (the volumetric flowrates and volumetric heat capacities are the same). Thus, the increased weight loss in He/ $\text{CO}_2$  over He/ $\text{N}_2$  is clearly due to some interaction of  $\text{CO}_2$  with the devolatilizing sample. Also, heat transfer in  $\text{CO}_2/\text{CO}_2$  should be lower than in He/ $\text{CO}_2$  based on the thermal diffusion arguments. Thus, it might be expected that a higher weight loss would occur in  $\text{CO}_2/\text{CO}_2$  over He/ $\text{CO}_2$  on a temperature-adjusted basis at the earlier residence times.

Figure 7 shows the results of the pyrolysis of the acid-washed sample in He/ $\text{N}_2$ , He/ $\text{CO}_2$ , and  $\text{CO}_2/\text{CO}_2$  atmospheres. Again, there is a difference in weight loss between

He/N<sub>2</sub> and He/CO<sub>2</sub> which can only be due to the interaction of CO<sub>2</sub> and the devolatilizing sample. Weight loss in CO<sub>2</sub>/CO<sub>2</sub> exceeds even that in He/CO<sub>2</sub> at early residence times, but by the longest residence time measured the weight losses have converged. Weight lost from He/N<sub>2</sub> is still below that from the other two gas compositions for the longest residence time measured, however, which is in contrast to Figure 6.

Figures 8 and 9 show the results of experiments conducted in the HPR. Figure 8 shows pyrolysis of raw coal in He/He and CO<sub>2</sub>/CO<sub>2</sub>. Figure 9 shows pyrolysis of acid-washed coal in He/He and CO<sub>2</sub>/CO<sub>2</sub>. The pyrolysis of raw coal in He/He has significantly less weight loss than in CO<sub>2</sub>/CO<sub>2</sub> over the intermediate residence times. Again, heat transfer in CO<sub>2</sub>/CO<sub>2</sub> may be poorer than in He/He, thus reinforcing the weight loss differences. Again, at long residence times the weight losses converge.

Figure 9 shows a smaller difference in weight loss over intermediate times with ultimate weight losses again converging. Still, some effect of CO<sub>2</sub> over intermediate times even with the acid-washed sample is evident.

It is instructive to first go back to Figure 8 to explain the role of CO<sub>2</sub> in rapid pyrolysis. Even at the earliest recorded residence time (~76 milliseconds), weight lost in the CO<sub>2</sub> atmosphere exceeds weight lost in He by nearly a factor of two. By 135-140 milliseconds residence time, weight loss in CO<sub>2</sub> is more than twice that in He. Eventually, however, the weight losses converge at the longest residence times. Since it has been shown that the cations inhibit weight loss over this same time interval and at this pressure, the CO<sub>2</sub> must somehow be counteracting this effect. It is hypothesized that CO<sub>2</sub> could be tying up the calcium, perhaps converting CaO (calcium oxide, a known tar cracker) to CaCO<sub>3</sub> (calcium carbonate, inert to cracking reactions?). (The increase in char weight due to the carbonate formation is only on the order of 1% assuming all the calcium in the raw coal were carbonated. Thus, it should not significantly affect the weight loss analysis). Alternatively, the CO<sub>2</sub> could be enhancing weight loss by affecting active sites on the char directly. For example, active carbon sites on the pyrolysing char (created by initial bond breaking to form volatiles) could have CO<sub>2</sub> adsorb onto them. This would make the sites unavailable for reattachment or cracking of previously formed volatiles. Finally, CO<sub>2</sub> could be stabilizing reactive volatiles through the formation of carboxyl groups at the reactive sites in a Kolbe-type reaction (Morrison and Boyd, 1973, p. 804). This would allow the volatiles to more readily escape the devolatilizing char matrix. Again, it is instructive that the weight losses converge, strongly implying that all (or nearly all) of the potential volatiles exit the devolatilizing lignite given enough time, although not necessarily in the same molecular form. Also, the weight loss increase due to CO<sub>2</sub> is probably not due to the Boudouard reaction. More needs to be said about the second point. If the Boudouard reaction were important, it is likely that increased ultimate volatile matter would appear in CO<sub>2</sub> atmospheres. This is not evident. Also, most measures of the Boudouard reaction show it to be much slower than the weight loss rates considered here.

A further indication that the Boudouard reaction is not important is illustrated in Figure 9. The effect of CO<sub>2</sub> on acid-washed coal is not as strong as it is with raw coal. An increase in weight loss over intermediate times is apparent, however. If increased weight loss were due primarily to the Boudouard reaction, one would expect to see the differences in weight losses evident in Figure 8 as well as increased weight loss at the longest residence time. On the other hand, a comparison between Figures 8 and 9 does show that much of the effect of CO<sub>2</sub> in the HPR experiments is probably due to the direct effect of CO<sub>2</sub> on the cations.

The results of Figures 6 and 7 can thus be explained as follows. Figure 7 shows the effect of the presence of CO<sub>2</sub> in the absence of the complication from cations. Initial weight loss in He/CO<sub>2</sub> exceeds that in He/N<sub>2</sub> because of a stabilizing effect of CO<sub>2</sub> on developing active sites on the char and/or stabilization of volatiles. An additional increase in weight loss is seen in CO<sub>2</sub>/CO<sub>2</sub> because of the presence of CO<sub>2</sub> in the pores at the onset of pyrolysis.

Figure 6 also shows that  $\text{CO}_2$  has a strong stabilizing effect on initially formed volatiles. Additional weight loss due to the initial presence of  $\text{CO}_2$  in the pores is masked by the inhibitory effect of cations and by (again) the somewhat scattered nature of the  $\text{He}/\text{CO}_2$  data from the raw coal sample.

It has been hypothesized that  $\text{CO}_2$  may be blocking the effect of calcium to retard weight loss through formation of  $\text{CaCO}_3$ . In the HPR the partial pressure of  $\text{CO}_2$  is sufficient to tie up calcium as the carbonate. In the APR the equilibrium condition is not as well-defined because of the proximity of the operating condition to the calcination condition. In  $\text{He}/\text{CO}_2$  atmospheres there would not be enough concentration of  $\text{CO}_2$  in the pores initially to block the effect of the cations. The indication that a  $\text{CO}_2$  atmosphere does enhance weight loss under these conditions thus supports an argument that  $\text{CO}_2$  must diffuse to the surface of the coal particle rather quickly and then penetrate at least part way into the macropore space where it accelerates weight loss by blocking the effect of cations and/or by stabilizing tar/char. In the  $\text{CO}_2/\text{CO}_2$  experiments in the APR, there is probably a high enough pressure of  $\text{CO}_2$  in the pores initially to tie up the cations, thus accelerating weight loss. In addition, there is  $\text{CO}_2$  present for stabilization as the first bonds in the coal matrix break, thus leading to the even greater weight loss at early residence times in this atmosphere compared to  $\text{He}/\text{CO}_2$ , which is most clearly seen in Figure 7.

#### Gas Analyses

Most experiments in the HPR had gas analyses of the product gas performed using a dedicated gas chromatograph (Carle 158S Automated Gas Chromatograph). The only peaks to appear which were large enough to measure quantitatively were those associated with  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_2\text{H}_4$ . It was somewhat surprising that little measurable hydrogen appeared. In addition, the  $\text{C}_2\text{H}_4$  peak was unresolvable during pyrolysis experiments in  $\text{CO}_2$  atmospheres due to its proximity to the  $\text{CO}_2$  peak.

The following items are noteworthy. First, the  $\text{C}_2\text{H}_4$  content of the product gas generally increased with increased weight loss or residence time during pyrolysis of both the raw and acid-washed samples in He. There was significantly more  $\text{C}_2\text{H}_4$  produced at similar weight losses from the raw sample than from the acid-washed sample. This is consistent with the observation that there appears to be more cracking-type reactions occurring in the presence of the cations, since  $\text{C}_2\text{H}_4$  is often a by-product of the cracking of larger species.

Second, both the  $\text{CO}$  and the  $\text{CO}_2$  content are higher for comparable weight losses when cations are present during pyrolysis in He. This is consistent with the observations of Schafer (1980) in again giving a role to the cations, primarily as calcium, in creating additional carbon oxides from reactions with oxygen-containing species other than carboxyl.

#### SUMMARY AND CONCLUSIONS

There are two likely roles that the cations could be playing to inhibit weight loss. First, they could be attaching themselves to potential volatile species, and thereby inhibiting their release by retarding mass diffusion. Second, potential volatile species could be cracked by the cations, thereby depositing at least some of the cracked material back onto the solid surface, at least temporarily. A third possibility, also suggested by Morgan (1983) in his study, is strongly discounted here. That is that the cations are inhibiting the release of volatiles by blocking pore exits. Although this could be a minor contribution, the indication that the presence of  $\text{CO}_2$  reverses the effect of the cations argues strongly against pore blockage being a major impediment to volatiles release. This same argument also applies, although somewhat more weakly, to the supposition that cations inhibit pyrolysis via mass diffusion. In addition, gas analyses were shown to substantiate

the hypothesis that the cations affect weight loss through cracking reactions. It was also hypothesized that flooding the pores of the devolatilizing coal with CO<sub>2</sub> inhibited the cracking reactions by tying up the calcium ions in a nonreactive form.

It was also shown that the presence of CO<sub>2</sub> enhances weight loss even in the absence of cations. This is most likely due to chemical interactions between CO<sub>2</sub> and the developing char surface and/or between CO<sub>2</sub> and reactive volatile species. The CO<sub>2</sub> is hypothesized to stabilize reactive sites on the surface, which in turn prevents cracking of volatiles, and/or to cap reactive volatile species such as hydrogen is believed to do during hydropyrolysis.

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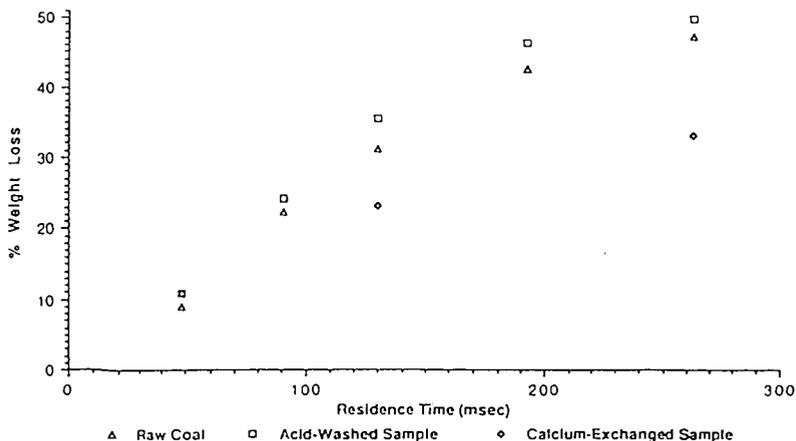


Figure 1 The Effect of Cations on Pyrolysis, P=0 psig, He/N<sub>2</sub> Atmosphere

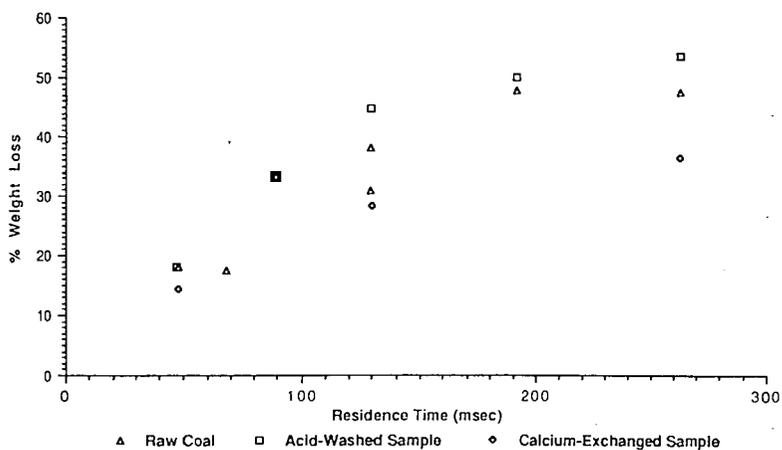


Figure 2 The Effect of Cations on Pyrolysis, P=0 psig, He/CO<sub>2</sub> Atmosphere

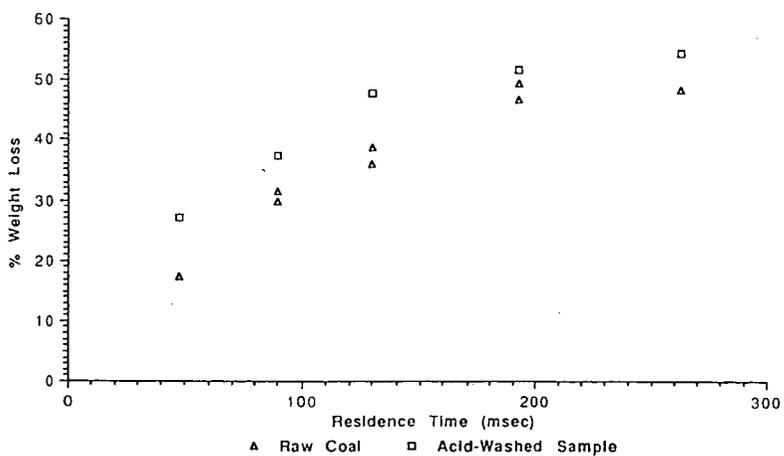


Figure 3 The Effect of Cations on Pyrolysis, P=0 psig, CO<sub>2</sub>/CO<sub>2</sub> Atmosphere

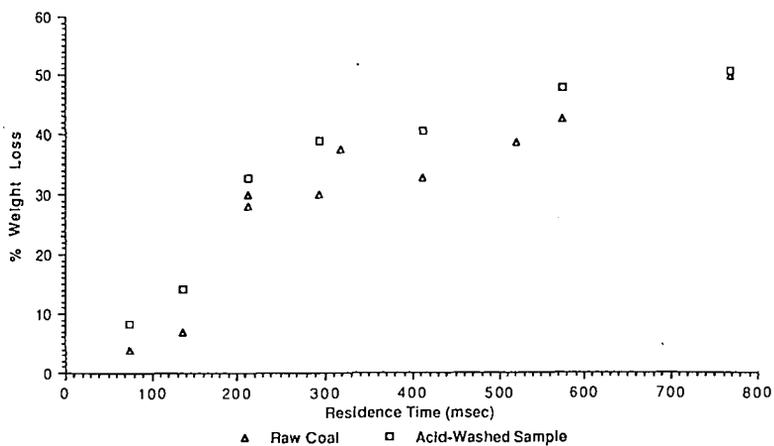


Figure 4 The Effect of Cations on Pyrolysis, P=200 psig, He/He Atmosphere

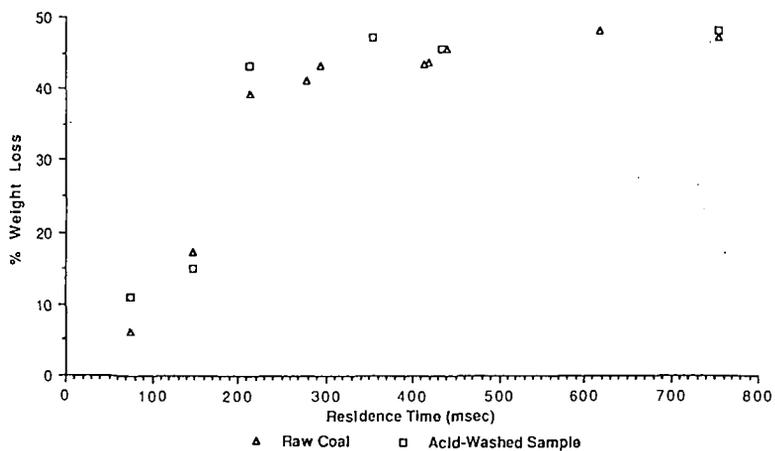


Figure 5 The Effect of Cations on Pyrolysis, P=200 psig, CO<sub>2</sub>/CO<sub>2</sub> Atmosphere

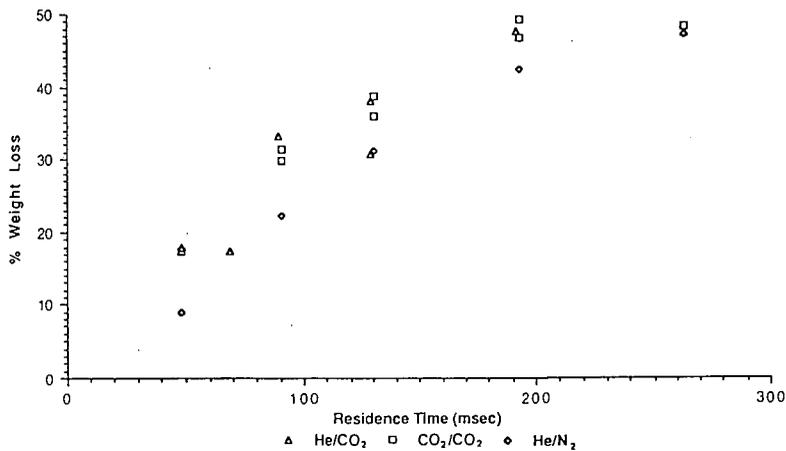


Figure 6 The Effect of Atmosphere on Pyrolysis, P=0 psig, Raw Coal

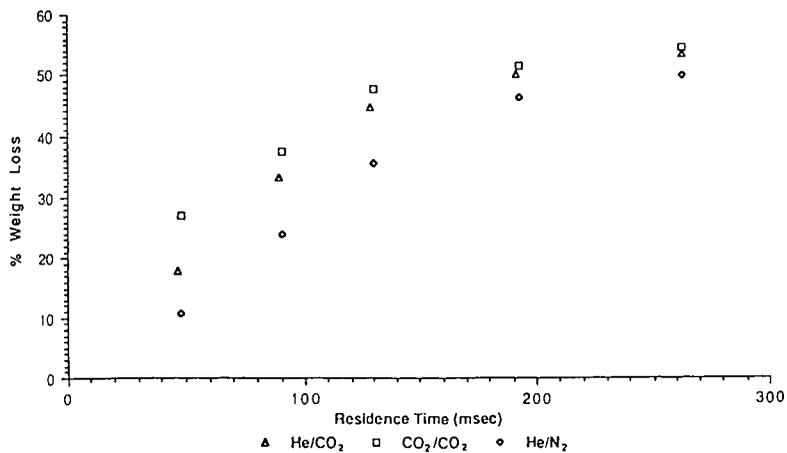


Figure 7 The Effect of Atmosphere on Pyrolysis, P=0 psig, Acid-Washed Sample

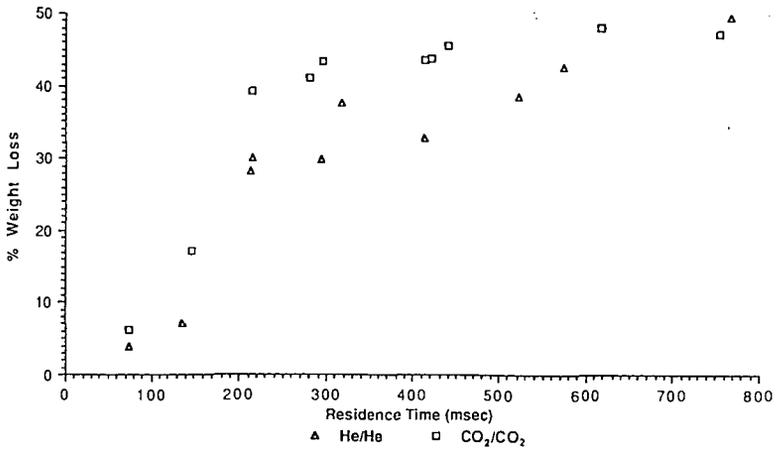


Figure 8 The Effect of Atmosphere on Pyrolysis, P=200 psig, Raw Coal

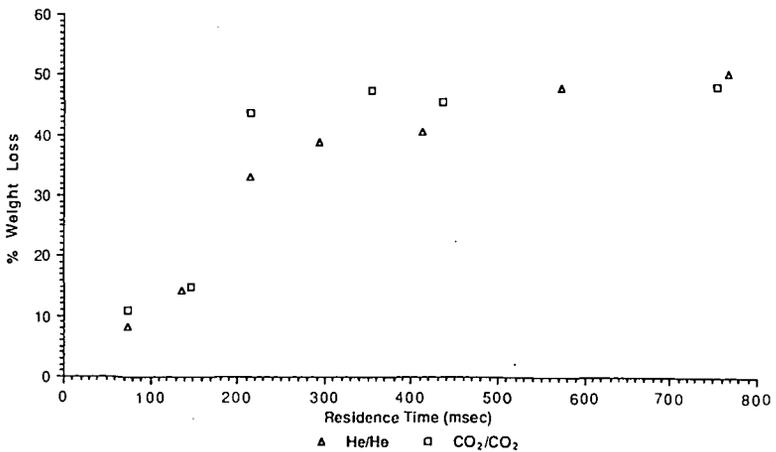


Figure 9 The Effect of Atmosphere on Pyrolysis, P=200 psig, Acid-Washed Sample