# ROLE OF EXCHANGEABLE CATIONS ON THE RAPID PYROLYSIS OF LIGNITES

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## INTRODUCTION

Recently, research concerned with utilization of the vast reserves of American lignites has expanded greatly. Studies have shown that lignites react quite differently than coals of higher rank when subjected to utilization and conversion schemes. The behavior of lignites is believed to be greatly influenced by the inorganic constituents present. The most significant feature of the inorganic constitutents of lignites is the large concentration of exchangeable metal-cations. These cations are mainly alkali and alkaline earth metals associated with the carboxyl groups present in lignites. This research is concerned with the effect of exchangeable cations on rapid pyrolysis of a lignite.

## EXPERIMENTAL

Pyrolysis was carried out in a dilute-phase entrained-flow reactor. The system is a modified version (1) of that utilized by Scaroni et al. (2). The system allows pyrolysis to be studied under high heating and cooling rates ($10^4$ - $10^5$ K/s). Under these conditions, examination of pyrolysis over residence times from 0.03 to 0.30 s and at temperatures up to ~1300 K is possible. Pyrolysis occurs in a dilute stream in order to reduce the role of secondary reactions resulting from contact between the pyrolysis products.

A Montana lignite (Fort Union Seam) was utilized in this study. Details of the organic and inorganic analyses of this coal can be found elsewhere (3). In this study, three types of samples were utilized: raw lignite, acid-washed lignite and cation-loaded lignite. In the acid-washed lignite the carboxylate cations are in the hydrogen (acid) form. In the acid washing procedure, 50 g of raw lignite were mixed with 900 ml of 0.1 N HCl for 16-24 h, filtered, mixed with a new batch of HCl for an additional 4 h, filtered, and washed repeatedly. It was then refluxed in 1000 ml of boiling distilled water for 1 h to remove excess HCl (3,4).

Cation loading was always performed on the acid-washed samples because it facilitates the determination of the extent of cation loading and eliminate complexities caused by the presence of more than one cation. The conditions utilized for ion exchange can be seen in Table 1. Further details can be found elsewhere (5). Also shown in Table 1 are the results of the cation loading. As can be seen, there are four different loadings of calcium. Calcium was chosen as the cation to be studied most, because it is the predominant cation in American lignites (3).

A number of gauges of the effects of pyrolysis were utilized, the most informative is weight loss. Because of experimental conditions, weight loss was determined by using ash as a tracer. This technique has been used previously by a number of workers (2,6,7).

In addition, the decomposition of the carboxyl groups was studied by measuring the carboxylate concentrations in the chars after pyrolysis. The technique to determine the carboxyl group content is outlined in detail elsewhere (3), and is based on the work of Schafer (8). There are three basic steps involved: acid washing, exchange with barium acetate and determination of the extent of exchange.

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TABLE 1

ION EXCHANGE CONDITIONS AND RESULTS

| Sample | Exchange Media | Starting pH | g coal/l | Stir Period | m moles/g DICF Coal |
|---|---|---|---|---|---|
| Cal | 1 M Ca Acetate | 8.0 | 55 | 24 h | 0.84 |
| Ca2 | .25 M Ca Acetate + .25 M CaCl | 6.0 | 100 | 24 h | 0.75 |
| Ca3 | .25 M Ca Acetate | 5.5 | 160 | 24 h | 0.49 |
| Ca4 | 1 M Ca Acetate | 8.0 | 55 | 24 h + 24 h + 24 h + 24 h | 1.11 |
| Na | 1 M Na Acetate | 8.0 | 55 | 24 h | 0.94 |
| Mg | 1 M Mg Acetate | 8.0 | 55 | 24 h | 0.71 |
| Raw | ---------- | --- | --- | ------ | 0.94 |

## RESULTS AND DISCUSSION

Total Weight Loss -- In Figure 1, the weight loss versus time behavior for the raw, acid-washed and Cal-form samples are displayed. As can be seen, the presence of metal-cations dramatically affects the weight loss behavior in the entrained flow reactor. All three samples undergo a period of rapid weight loss followed by a region of slow weight loss. In the case of the raw and Cal-form samples, weight loss lasts for about 0.15 s until a value of about 30 wt% (Dry Inorganic Content Free-DICF) is achieved. For the acid-washed sample, the rapid weight loss is completed in 0.05 s and the final weight loss value is 50 wt% (DICF). It is very interesting to note the similarity between the behavior of the raw and Cal samples. This similarity indicates the reversibility of the ion exchange treatments in terms of coal pyrolysis behavior. This strongly suggests that the difference in pyrolysis behavior between the metal cation and hydrogen-form samples is mainly due to the presence of cations, and not to the chemical treatments to which the coals were subjected.

While Cal contains about the same amount of exchangeable cations as the raw coal, it is possible to load various amounts of calcium onto the acid-washed lignite. Figure 2 displays the results of a study on the effects of varying the quantity of exchanged calcium. In this figure, the weight loss at maximum residence time in the entrained flow reactor at 1173 K is plotted for samples (270x400 mesh) with five levels of calcium ranging from 0 to 4.7 wt% (DICF). As can be seen, as the calcium content of the coal is increased there is a gradual and significant decrease in the maximum weight loss. This behavior is similar to that observed by Tyler and Schafer (9).

Other exchangeable cations are found in lignites, thus, a study was made into the effects of sodium and magnesium on pyrolysis. Results of this study are summarized in Table 2 which lists weight loss values at maximum residence time for a number of different cation loaded samples pyrolyzed at 1173 K. Firstly, it can be seen that the presence of metal cations always results in a decrease in weight loss. This result is important in itself in that it reemphasizes the importance of cations in lignite pyrolysis. Secondly, information can be gained about the relative activity of the various cations studied. If one compares the two divalent cations (calcium and magnesium), it can be seen that the elements have a similar effect on a per mole basis. The samples Ca2 and Mg have almost the same number of moles of cations, and both samples lose approximately the same weight. If one tries to assess the relative activity of sodium, it can be seen that, in general, the sodium-form coal undergoes a relatively large weight loss during pyrolysis.

TABLE 2

EFFECT OF CATIONS ON MAXIMUM WEIGHT LOSS IN ENTRAINED FLOW REACTOR
1173 K, DICF BASIS

| Sample | Weight Loss |
|---|---|
| Raw | 30.8 |
| Ca1 | 28.7 |
| Ca2 | 34.9 |
| Mg | 33.4 |
| Na | 38.7 |
| Acid Washed | 49.4 |

The monovalent nature of sodium makes a comparison of the concentrations difficult. It contains the highest molar concentration of cations, but they cover the least number of carboxyl groups.

Extended Residence Time Studies -- It was just pointed out that coals undergo rapid weight loss followed by what appears to be a region of little weight loss in the entrained flow reactor. However, although samples reach this region of constant weight loss, no samples undergo complete pyrolysis in the residence times available. Rather, this "plateau" region of weight loss is a regime of relatively slow decomposition. While it takes as little as 0.05 to 0.15 s to reach this leveling off point, it can take on the order of minutes to complete pyrolysis.

In order to determine the total pyrolysis yield, another technique was used. Basically, the approach involves capturing the pyrolyzing coal particles in a crucible at the maximum residence distance in the reactor. The captured samples are then held in the reactor for 10 min to complete pyrolysis. It is thought that this technique gives a reasonable estimation of the total pyrolysis yield possible in an entrained flow reactor.

The results of this study can be seen in Table 3 in which weight loss values for extended residence time runs are listed. If one compares the weight loss of

TABLE 3

EXTENDED RESIDENCE TIME RUNS IN THE ENTRAINED FLOW REACTOR
1173 K, DICF BASIS

| Sample | Weight Loss | A.S.T.M. Volatile Matter Content |
|---|---|---|
| Raw | 54.0 | 43.7 |
| Acid Washed | 63.3 | 43.2 |
| Ca1 | 46.1 | 43.0 |

these samples, it can be seen, once again, that the presence of metal-cations greatly reduces the amount of volatile material evolved. It is interesting to compare these results with those gained by the ASTM volatile matter test. The ASTM volatile matter contents display no effect of cation-loading. It will be recalled that this test is performed in a fixed bed (crucible) which is felt to increase the amount of secondary char-forming reactions. Thus, when secondary char-forming reactions are increased, there is little difference in the weight loss values for pyrolysis. However, decreasing the likelihood of these reactions leads to large differences in total weight loss.

Kinetics of Total Weight Loss -- The method chosen is a simple first order Arrhenius treatment in which a single overall activation energy is utilized. The technique has been applied to the kinetics of the initial weight loss, and therefore, the weight loss values were compared to the maximum weight loss in the entrained flow reactor. Values of the apparent activation energy and preexponential factor found in this study are displayed in Table 4. It is clear that there is a similarity in the behavior of the raw and calcium-form coals. The acid-washed coal exhibits the largest activation energy, almost three times larger than that found for the raw lignite and 50% greater than that of the calcium form. Again, it is obvious that the absence of metal-cations can have a profound effect on pyrolysis kinetics and mechanisms.

TABLE 4

KINETIC PARAMETRS FOR TOTAL WEIGHT LOSS

| Sample | Activation Energy (kJ/mole) | Preexponential Factor ($s^{-1}$) |
|---|---|---|
| Raw | 58 | $8 \times 10^3$ |
| Acid Washed | 147 | $2 \times 10^3$ |
| Cal | 99 | $5 \times 10^5$ |

Effect of Exchangeable Cations on Tar Release -- Table 5 lists the results of a study in which the quantity of tar, collected on a filter, in the outlet gas

TABLE 5

TARS RELEASED IN ENTRAINED FLOW REACTOR

| Residence Time (s) | mg Tar/g Coal Fed | |
|---|---|---|
| | Raw Coal | Acid Washed Coal |
| 0.042 | 3 | 10 |
| 0.078 | 9 | 30 |
| 0.112 | 3 | 48 |

stream, was measured for the raw and acid washed samples at 1173 K at three residence times. At each residence time the amount of tar released by the acid-washed coal was significantly greater than those released by the raw coals. This trend is in the same direction as the weight loss data. That is, increases in total weight loss when metal cations are removed are also accompanied by increases in tar yield.

Tar samples (1173 K, 0.078 s) were analyzed by Fourier Transform Infrared Spectroscopy, spectra were created by use of KBr pellets in the manner described by Painter et al. (10). Spectra from the raw and acid-washed coal tars were recorded as well as the "difference spectrum" from the two samples.

The spectra of these tars from the raw and acid-washed coals were similar in many ways. The same general major features were present, such as methyl, phenol and carboxyl groups. However, there is a significant difference between the two spectra in the intensities of the carbon-hydrogen aliphatic bond stretching absorbances at about 2800 - 3000 $cm^{-1}$. Integration of this band for the two samples leads to the conclusion that tars from the raw coal contain three times the quantity of aliphatic hydrogen as do the tars from the acid-washed coal.

Effect of Exchangeable Cations on Carboxyl Group Decomposition -- Decomposition of the carboxyl groups was followed by measuring the quantity of carboxyl

groups in the parent coal and in the resulting chars. It should be pointed out that data on the decomposition of carboxyl groups enables one to study the behavior of a single species during pyrolysis, thus yielding information that cannot be extracted from overall weight loss data. Also, it should be noted that since there are about 3.1 meq/g DICF of carboxyl groups on this lignite, the decomposition of this species can account for a weight loss of up to 14% of the lignite.

Results from this study can be seen in Figure 3 in which the quantities of carboxyl groups remaining on the raw lignite as a function of residence time at 1173 are shown. The loss of the carboxyl groups is very similar to the total weight-loss behavior presented in Figure 1. That is, there is a very rapid loss of carboxyl groups followed by a region of slow decomposition. It is interesting to note that both the raw and Cal-form samples appear to complete decarboxylation at about 2.6 meq/g DICF while the acid-washed sample releases all of the 3.1 meq/g DICF present.

Although previous researchers have studied the effects of cations on the pyrolysis of carboxyl groups, most of the work has been concerned with weight loss as a function of temperature and/or the evolution of oxides of carbon. Little work has been concerned with direct determination of the kinetics of decarboxylation. Table 6 lists the results of a first-order kinetic analysis of decarboxylation of the raw and acid washed forms of the lignite. The activation energies for decarboxylation are somewhat different for the two samples studied, that found for the raw lignite is about 20% greater than that calculated for the acid-washed coal. However, the values are quite similar when compared to the spread of activation energies found for the overall weight loss data (Table 4).

## CONCLUSIONS

It must be concluded that the presence of metal cations in lignites dramatically affects pyrolysis behavior under rapid heating conditions. The presence/absence of metal cations are important in terms of the rate of evolution total weight loss and nature of the pyrolysis products. It is suggested that these data have significant importance in gasification and combustion of lignites.

## ACKNOWLEDGEMENTS

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TABLE 6

KINETIC PARAMETERS FOR DECARBOXYLATION

| Sample | Activation Energy (kJ/mole) | Preexponential Factor ($s^{-1}$) |
|---|---|---|
| Raw | 106 | $4 \times 10^5$ |
| Acid Washed | 80 | $8 \times 10^4$ |

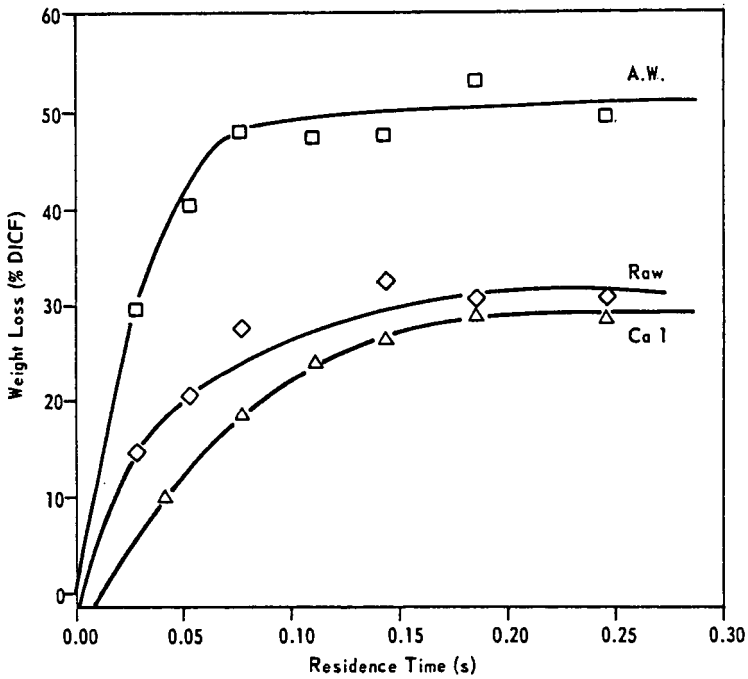


Figure 1. WEIGHT LOSS IN ENTRAINED FLOW REACTOR
270 x 400 mesh Lignite at 1173 K

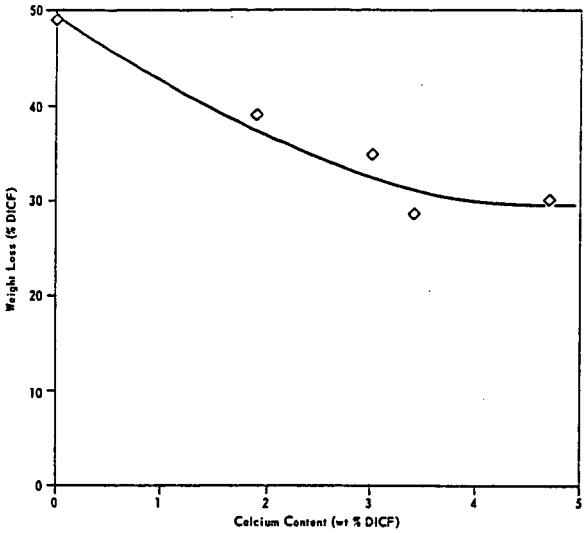


Figure 2. WEIGHT LOSS IN ENTRAINED FLOW REACTOR
Effect of Ca Loading at 1173K

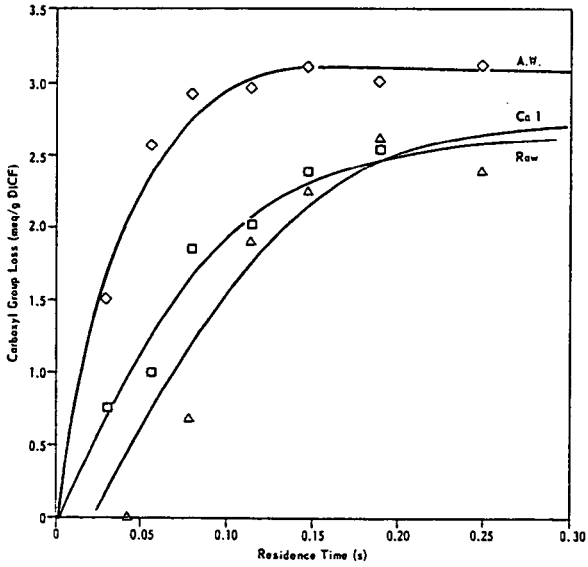


Figure 3. DECOMPOSITION OF CARBOXYL GROUPS (1173 K)