

THE EFFECTS OF MOISTURE AND CATIONS ON LIQUEFACTION OF LOW RANK COALS

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INTRODUCTION

The role of calcium in reducing liquefaction yields from low rank coals has been suggested in previous work by Whitehurst et al. (1) and Mochida et al. (2). It is also consistent with work which shows an effect of calcium on reducing pyrolysis tar yields (3-7). The role of calcium may be to provide a nascent crosslink site in the coal by allowing coordination of groups like carboxyl and hydroxyl which are prone to such reactions. Otherwise, these sites would be more likely to coordinate with water (through hydrogen bonding) than with each other. There have been no studies of the effects of cation type and the associated moisture on liquefaction yields.

Studies were done on samples of Argonne Zap Lignite and Wyodak subbituminous coals which have been demineralized and then exchanged with calcium, barium or potassium cations. Two sets of samples were prepared: 1) vacuum-dried; 2) exposed to water vapor until an equilibrium moisture content was reached. The samples were characterized by FT-IR transmission analysis in KBr pellets, programmed pyrolysis in a TG-FIR system and liquefaction in donor solvent. The pyrolysis and liquefaction results are discussed in the current paper.

EXPERIMENTAL

In order to subject coals to a variety of modifications and avoid exposure to the ambient air, an apparatus for continuous-flow, controlled-atmosphere demineralization and controlled pH ion-exchange of coals was designed and constructed. A closed system is used, where instead of stirring the batch reactor contents, a continuous flow of solvent through the sample is used. By utilizing valves, it is possible to change solvents without opening the reactor. The different solvents are held in separate reservoirs which are all equipped with sparge valve systems to deoxygenate the solvents before use (with N₂ or He as needed).

Demineralization - The procedure is similar to that described in the work of Bishop and Ward (8). The coal samples used in this study are the Zap lignite and Wyodak subbituminous coals from the Argonne premium sample bank (9). The sample sizes were all -100 mesh. Before starting the acid treatment, the samples were thoroughly wetted by mixing with de-ionized water under a nitrogen environment. Demineralization involved washing the coal with a flow of 2M HCl for 45 minutes, 50% HF for 45 minutes, 2M HCl for 45 minutes, and de-ionized water for 120 minutes. The process was performed at 80 °C. After demineralization, the sample was dried in vacuum for at least 20 hours at room temperature. The vacuum dried samples were kept in a nitrogen box for subsequent analysis and liquefaction experiments.

Ion-Exchange of Carboxyl Groups with Metal Cations - The acidity constant (k_a) of carboxylic acids is around 10^{-5} , and that of phenols is around 10^{-10} . Theoretically, almost all carboxyl OH can be exchanged with cations at pH 8, whereas the phenolic-OH can remain in the acid form, according to the equation: $[A^-] / [HA] = k_a / [H^+]$, where HA is either the carboxyl or phenolic group in acid form. At pH 8, $[A^-] / [HA]$ would be a value of order 10^3 for carboxyl groups, and 10^2 for phenols. Schafer's experimental results also suggest that the carboxyl groups in coal can be completely exchanged with cations at pH around 8-8.5, along with ortho-dihydroxy groups (10). In the case of barium, a 1N barium acetate solution, which has a pH value around 8.2, was used for ion-exchange with carboxyl groups. Roughly 3 g of demineralized coal was

mixed with 300 ml of 1N barium acetate in a cell under a nitrogen environment. After 5 minutes of mixing, the pH value of the mixture dropped to less than 7.5. The mixture was filtered through a Teflon membrane by increasing the nitrogen pressure, and the mixing cell was refilled with another 300 ml of barium acetate. The pH value of the solution dropped again after mixing. The filtration and refilling procedure was repeated, usually 15-20 times, until the pH value of the mixture in the cell reached 8.0 ± 0.1 and remained constant with mixing. The drop of the pH value was probably due to the release of H^+ from carboxylic acids in the coal.

The mixture was kept under continuous mixing conditions in a nitrogen environment for at least 20 hours before the acetate solution was purged out, and the cell was refilled with a final 300 ml charge of 1N barium acetate. After 10 minutes of mixing, the acetate solution was purged out, and the coal sample was washed with 150-200 ml of de-ionized water. The coal sample was then removed from the cell for vacuum drying, which lasted for at least 20 hours. The sample was kept in a nitrogen box after drying. A similar procedure was used for exchanging calcium and potassium cations, starting with the metal acetate.

Ion-Exchange of Phenolic and Carboxyl Groups with Metal Cations - In theory, both phenolic and carboxyl groups can be totally exchanged with cations at pH around 12.5. Schafer (10) also reported that the exchange of -OH groups was complete at pH 12.6. In this study, a solution, recommended by Schafer, of 0.8 N $BaCl_2$ and 0.2 N $Ba(OH)_2$ having a pH of 12.7, was used for ion-exchange of barium cations. A similar procedure was used for calcium and potassium cations.

Approximately 3 g of a demineralized coal sample was stirred with 300 ml of the pH 12.7 solution in a nitrogen environment. After 5 minutes of mixing, the mixture was filtered through a membrane and the cell was refilled with another 300 ml of the pH 12.7 solution. The purging and refilling procedure was repeated 3 times, and the pH value of the final mixture was around 12.6. The mixture was continuously mixed under a nitrogen environment for at least 20 hours for exchange. After this long-time exchange period, the solution was purged out, and the cell was refilled with the pH 12.7 solution.

After 10 minutes of mixing, the solution was purged out, and the coal sample was washed with a solution of 0.1 N $BaCl_2$ and 0.03 N NaOH, which has a pH around 12.7, to avoid hydrolysis of the exchanged coal. The coal sample was then removed from the cell for vacuum drying. After drying, the sample was kept in a nitrogen box for further study.

It was noticed, in the process of ion-exchange that part of the coal structure was dissolved in the high pH value solution, since the filtrate had a yellowish color. This is most likely due to hydrolysis of the ester linkage in coal. The amount of the coal structure (so called humic acids) dissolved in the high pH value solutions during complete ion-exchange was estimated to be about 6.6 wt% daf of the demineralized Zap and 17 wt% daf of the demineralized Wyodak.

Preparation of Moisturized Coal Samples - A procedure for restoring the moisture level of modified coal samples was developed. The moisturized samples were prepared by enclosing the vacuum-dried modified samples in a box with a nitrogen purge of 100% humidity. The sample exposure to moisture was performed for several days (~6 days) until no further moisture uptake was observed.

RESULTS AND DISCUSSION

The modified coal samples were characterized by FT-IR transmission analysis in KBr pellets, programmed pyrolysis in a TG-FTIR system and liquefaction in donor solvent. The results are discussed below.

Effect of Cations on Pyrolysis Tar and Liquefaction Yields - The results of sample analysis by programmed pyrolysis in the TG-FTIR are shown in Figures 1 and 2, and summarized in Table

1 for the Zap lignite. These results show that demineralization tends to increase the tar yield, whereas both the gas and char yields were reduced. Similar results were observed for the Wyodak coal (11). Table 1 also shows a decrease of the tar yield with the extent of ion-exchange with the metal cations, and a corresponding increase in the total amount of gas evolution. The liquefaction results for different samples are shown in Table 2. The data in Tables 1 and 2 show that the yields of both the pyrolysis tar and toluene solubles from liquefaction decrease with the extent of ion-exchange, i.e., in the order of (demineralized) > (ion-exchanged at pH 8) > (ion-exchanged at pH 12.5). This result indicates that having the carboxyl or phenolic groups in the salt form makes it easier to crosslink the coal structure during pyrolysis or liquefaction reactions.

It is realized that this is a more difficult comparison for the samples exchanged at pH 12.5, since considerable amounts of humic acids were observed to dissolve in the high pH value solutions. The dissolution of coals in the aqueous alkaline solutions may be due to the breaking of ester bonds in coal, i.e., $\text{RCOOR}' + \text{OH}^- \rightarrow \text{RCOO}^- + \text{R}'\text{OH}$. This coal dissolution mechanism was also proposed by other workers (12). The solubility of coal in alkaline solutions varies with the cations contained in the solution. The color difference of the calcium and potassium solutions after ion-exchange at high pH is striking, in that the potassium solution has a much darker color, indicating much more coal dissolved in the monovalent cation (K^+ here) solution than the bivalent cation (Ca^{++} here) solution. The results also show that the barium solution extracted more coal than the calcium solution, but not as much as the potassium solution. A possible reason is the fact that Ca^{++} and Ba^{++} ions can act as cross-links between two acid groups of different coal fragments (12), whereas K^+ can only interact with one acidic site. The ability of bivalent cations to act as initial crosslinks in the structure at high pH is supported by data on the pyridine volumetric swelling ratios (VSR) and pyridine extractables, shown in Table 3. The values of the VSR are lower for the bivalent cations at high pH for both the dry and moist coals. It can be seen in Table 1, for the pyrolysis of vacuum dried samples, that the tar yield was higher for the potassium-exchanged coals than the calcium and barium-exchanged samples at high pH, suggesting that bivalent cations tighten the coal structure by cross-linking coal fragments and making it more difficult for tar molecules to form (7). At pH 8; the values of the tar yield and VSR for the monovalent and bivalent cations are more similar, though lower than the values for either the raw or demineralized coals. Consequently, it appears that the monovalent cations help to hold the structure together, although this must occur through electrostatic rather than covalent interactions. It makes sense that valency would be less important in the normal state of the coal or at pH=8 since, for steric reasons, cations are unlikely to be exchanged on more than one carboxyl or ortho-dihydroxy site.

It is likely that coal solubility in aqueous alkaline solutions increases with the size of the cations of the same valence. If this is true, the dissolution of coal in sodium solution would be expected to be less than that in the potassium solution. Preliminary results show that this is the case. However, this requires further confirmation. In summary, at similar pH values (~12.5), the amounts of Zap lignite extracted by 1 liter of the cation solutions in 20 hours increases in the order of $\text{Ca}^{++} < \text{Ba}^{++} < \text{K}^+$.

In considering the size effect of the cations on the pyrolytic tar and liquefaction yields, one should compare the data for the barium- and calcium-exchanged samples. It is interesting that the size of the cations has an opposite effect on the tar and liquefaction yields. In pyrolysis, the tar yield for the barium-exchanged samples is lower than that of the calcium-exchanged samples, while in liquefaction, the yield was higher for the barium-exchanged samples. This could be due to increased extraction of tar precursors during ion-exchange in the case of barium which subsequently makes the coal more accessible to the liquefaction solvent.

Effect of Cations on Gas Yields from Pyrolysis and Liquefaction - It is of interest to note that the gas yields from liquefaction and pyrolysis do not always follow the same trend. Table 1 shows that, in pyrolysis, the total yield of oxygen-containing gases (i.e., CO_2 , CO , and H_2O) always increases with decreasing tar yield. Table 2 shows the expected increase of the

liquefaction yields with tar yield. However, the gas yields in liquefaction show an irregular variation with pH and with cation type. For example, the CO₂ yield is high for the partially barium exchanged Zap lignite, and is significantly reduced for the completely barium exchanged sample. The Wyodak subbituminous coal shows the opposite trend. For the ion-exchanged Zap lignite, the decrease of the CO₂ yield in liquefaction can be explained by the loss of some organic components, which contain CO₂-forming functions, during the barium exchange at high pH. Some of these variations could be due to catalysis of secondary gas-phase or gas-solid reactions.

For CO evolution in pyrolysis, the demineralized samples show the major evolution at temperatures between 400 and 800 °C. CO evolution also occurs in a similar temperature range for fresh and ion-exchanged samples. However, the evolution is depressed at temperatures lower than about 750 °C, but elevated above this temperature by comparing with that of the demineralized samples. It was also noted that the fraction of CO evolving before 750 °C increases with increasing tar yield, as shown in Fig. 3a for the Zap lignite. This observation is significant. The higher CO evolution at temperatures lower than 750 °C for demineralized samples could be due to more oxygen functions evolving as CO without crosslinking. For ion-exchanged samples, the depressed CO evolution at lower temperatures is probably caused by oxygen retention through crosslinking between oxygen functions, and the CO evolved at 750 °C or above, is likely from the decomposition of the metal carboxylate groups which can produce carbonates as a decomposition product. The raw and cation exchanged samples have a sharp evolution peak in the TG-FTIR analysis, as shown in Figs. 1 and 2. This occurs in the same temperature range as the decomposition of carbonates and could be the result of catalytic gasification of the CO₂ produced to CO. The correlation of the total CO evolution in coal pyrolysis with pyrolytic tar and liquefaction yields was studied, as shown in Fig. 3b for the Zap lignite. The data shows that both tar and liquefaction yields increase with decreasing total (pyrolysis) CO yield. Therefore, both the relative amount of CO evolved before 750 °C and the total CO evolution are indicators of the extent of crosslinking.

Figures 1 to 2 also show that CO₂, H₂O, and low temperature CO evolve in a similar temperature range. This might imply that these products are derived from a consecutive mechanism. The CO₂ evolution curve does not show as much shape variation with changes in cation content. However, the yield is basically a decreasing function of tar yield. In previous work, the relationship between CO₂ evolution and crosslinking events has been noted (13-15). This has been explained by the mechanism that elimination of CO₂ would create aryl radicals to enhance crosslinking. The CH₄ yield also showed a trend opposite to that of the tar yield for the ion-exchanged samples. This has been generally reported in coal pyrolysis studies. By reincorporation into the solid matrix by more stable bonds, the tar precursors can yield volatiles only by cracking off of small side groups, hence the increased CH₄ yields with decreasing tar yields.

One aspect of the H₂O evolution data revealed in Figs. 1 and 2 merits further comment. For samples which contain acidic functions in the salt form, including fresh and barium exchanged samples, there is always a water evolution peak present at around 200 °C. This 200 °C peak is obscure for demineralized samples. It is very likely that this peak is due to the evolution of moisture which is ionically bonded on the salt structure. For vacuum dried samples, it can be seen that the moisture content increases with the amount of barium in the samples, as shown in Table 3. This indicates that the acidic functions in the salt forms attract polar water molecules. These attracted water molecules cannot be removed by vacuum drying, but only by raising the temperature of the sample.

Analysis of Carboxyl and Phenolic Groups by Barium Titration - In theory, all of the carboxyl groups of demineralized samples can be exchanged with barium at pH 8. Consequently, it follows that one could determine the concentration of carboxyl groups in coal by knowing the amount of barium ion exchanged at pH 8. The chemical composition of ash formed by combustion of the barium exchanged sample is predominantly BaO. Therefore, from the ash

content of the samples ion-exchanged at pH 8, one can estimate the concentration of carboxyl groups in the coal. Similarly, the total concentration of carboxyl and phenolic groups can be determined by the ash content of the sample ion-exchanged at pH 12.6. The concentration of phenolic groups can be obtained from the difference of the above two measurements. The concentrations of carboxyl and phenolic groups determined in this manner for Zap and Wyodak are shown in Table 4. The results shown in Table 4 are similar to those determined by Schafer (10, 16) for Australian low-rank coals, using barium titration methods. However, our FT-IR results indicate that not all of these groups can be exchanged and that the cations can interact with additional sites in the coal. This will be the subject of a separate publication.

Pyrolysis and Liquefaction of Moisturized Coal Samples - Remoisturization of vacuum dried Zap and Wyodak was done in the attempt to understand if moisture uptake for low rank coals is a reversible process and to see if moisture influences the role of the cations. The remoisturized samples were analyzed by programmed pyrolysis with TG-FTIR. Preliminary results show that the moisture content can reach that of the raw samples by remoisturization for Zap, but not for Wyodak. The results for the Zap lignite are shown in Table 3. Furthermore, the chemical structure of the coal samples seems to have been changed by remoisturization, since different CO₂ evolution behaviors were observed. A comparison of the CO₂ evolution behavior for raw and remoisturized coal samples is given in Fig. 4. The detailed liquefaction and pyrolysis results are presented in Ref. 11.

In almost every case, the asphaltene yield was increased with moisturization except for the pH 8 Zap, in which case the asphaltene yield was slightly reduced. Interestingly enough, the oil yield was reduced for most of the modified samples with moisturization, except for the demineralized Zap and the pH 12.6 Wyodak. The indication from the above results is that moisturization favors the formation of the larger molecular weight asphaltenes in liquefaction, while the formation of the smaller molecular weight oils is less favored.

It is usually shown that the trends for improved liquefaction yields parallel those for improved tar yields in pyrolysis. However, it was found in this study that the influences of moisturization on the yields of pyrolytic tars and liquefaction toluene soluble yields are different in that moisturization does not appear to have a significant effect on pyrolysis tar yields. This indicates that moisture plays different roles for the formation of tars in pyrolysis and coal liquids in liquefaction. A possible explanation for the difference is that most of the moisture is depleted early in the pyrolysis process, whereas the moisture is retained in the reactor during liquefaction and can exist in a liquid phase. This aspect requires further investigation.

The results also show that the moist samples have higher gas yields in liquefaction than the vacuum dried samples. The increase in gas yield is mainly from CO₂ and CO (especially CO₂), whereas the yields of hydrocarbon gases decrease with moisturization. One possible explanation for this result is that moisture may react with side chain structures in coal, which are the sources for the formation of oils and hydrocarbon gases during liquefaction, to form oxygen functions. The subsequent reaction of these oxygen functions produces more CO₂, CO and asphaltenes in the liquefaction of moist coals.

CONCLUSIONS

The conclusions from this study are as follows:

- The tar yields and liquefaction yields are reduced for all three cations tested (K⁺, Ca⁺⁺, Ba⁺⁺) and are lower for the fully exchanged coals. The ability of cations to act as initial crosslinks is an important aspect of their role in retrogressive reactions.
- The previously observed correlation between pyrolysis tar and liquefaction yields for coals and modified coals appears to hold for the vacuum-dried cation-exchanged coals, but not always for the re-moisturized coals.

always for the re-moisturized coals.

- The total evolution of CO₂ and CO from pyrolysis is changed significantly by cation-exchange. However, only in the case of CO does the evolution profile change significantly.
- After careful demineralization, a calcium form Zap or Wyodak coal can be prepared at pH = 8, which is similar to the raw coal with regard to pyrolysis and liquefaction behavior.
- At pH=8, cations are most likely to be coordinating multiple oxygen functionalities around themselves through electrostatic type interactions, which diminishes the importance of valency.
- Some of the moisture in a coal is associated with the cations. The moisture content has a larger role in liquefaction than in pyrolysis because it is present for a longer period of time.

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Table 1. Pyrolysis Results of Vacuum Dried Modified Zap Samples.

| Coal (type/preparation) | Pyrolysis Products (wt.% daf) | | | | | |
|------------------------------------|-------------------------------|-----------------|------|------------------|-----------------|------|
| | Tars | CO ₂ | CO | H ₂ O | CH ₄ | Char |
| Fresh | 7 | 8.9 | 14.7 | 14.3 | 2.2 | 57 |
| Demin. | 20 | 4.8 | 10.4 | 8.4 | 2.7 | 54 |
| Demin. + K ⁺ (pH8) | 11 | 8.6 | 9.9 | 16.0 | 1.9 | 57 |
| Demin. + Ca ⁺⁺ (pH8) | 10 | 8.6 | 13.5 | 10.3 | 2.4 | 58 |
| Demin. + Ba ⁺⁺ (pH8) | 6 | 11.7 | 15.8 | 18.6 | 2.6 | 55 |
| Demin. + K ⁺ (pH12.5) | 5 | 9.9 | 12.4 | 13.5 | 1.6 | 57 |
| Demin. + Ca ⁺⁺ (pH12.5) | 4 | 8.2 | 22.6 | 12.6 | 2.0 | 51 |
| Demin. + Ba ⁺⁺ (pH12.5) | 3 | 10.5 | 24.1 | 15.5 | 2.6 | 52 |

Table 2. Liquefaction Results of Vacuum Dried Modified Zap Samples.

| | Toluene Solubles | | | Gas | | |
|------------------------------------|------------------|------|-------------|-----------------|------|-----------------|
| | Total | Oils | Asphaltenes | CO ₂ | CO | CH ₄ |
| Fresh | 26 | 12 | 14 | 4.3 | 0.24 | 0.25 |
| Demin. | 52 | 26 | 26 | 1.1 | 0.43 | 0.27 |
| Demin. + K ⁺ (pH8) | 30 | 11 | 19 | 7.7 | 0.27 | 0.17 |
| Demin. + Ca ⁺⁺ (pH8) | 25 | 13 | 12 | 2.7 | 0.30 | 0.22 |
| Demin. + Ba ⁺⁺ (pH8) | 37 | 25 | 12 | 7.3 | 0.40 | 0.20 |
| Demin. + K ⁺ (pH12.5) | 17 | 5 | 12 | 5.0 | 0.24 | 0.27 |
| Demin. + Ca ⁺⁺ (pH12.5) | * | * | 3 | 0.7 | 0.04 | 0.08 |
| Demin. + Ba ⁺⁺ (pH12.5) | 15 | 15 | 0.5 | 0.3 | 0.27 | 0.02 |

* Yields Calculated by Difference were Negative. Solvent Incorporation is Suspected.

Table 3. Characterization of Cation-Exchanged Zap Samples.

| Coal Type | Dry | | | Moist | | |
|------------|------------------|----------------|----------|--------|----------------|----------|
| | V.S.R | P _s | Moisture | V.S.R. | P _s | Moisture |
| Zap Raw | 2.7 | 5 | NM | 1.9 | 15 | 32 |
| Zap Demin. | 3.1 | 20 | 4 | 2.6 | 22 | 16 |
| pH 8 | K ⁺ | 10 | 6 | 1.9 | 9 | 20 |
| | Ba ²⁺ | 3 | 5 | 1.5 | 4 | 22 |
| | Ca ²⁺ | 6 | 5 | 1.6 | 6 | 21 |
| pH 12 | K ⁺ | 2 | 6 | 1.4 | 2 | 29 |
| | Ba ²⁺ | 2 | 7 | 1.2 | 2 | 22 |
| | Ca ²⁺ | 1 | 9 | 1.2 | 1 | 25 |

Notes: V.S.R. = Volumetric Swelling Ratio in Pyridine; P_s = Pyridine Solubles (daf)
Moisture was Determined by TG-FTIR and is Reported on an As-received Basis.
NM = Not Measured.

Table 4. The Carbonyl and Phenolic Contents of Zap and Wyodak Coals Determined by Barium Titration. (meq g⁻¹ daf basis)

| | Carboxyl Groups | Phenolic Groups | Total Acidity |
|-------------|-----------------|-----------------|---------------|
| Zap Lignite | 2.52 | 6.74 | 9.26 |
| Wyodak Sub. | 2.40 | 5.76 | 8.16 |

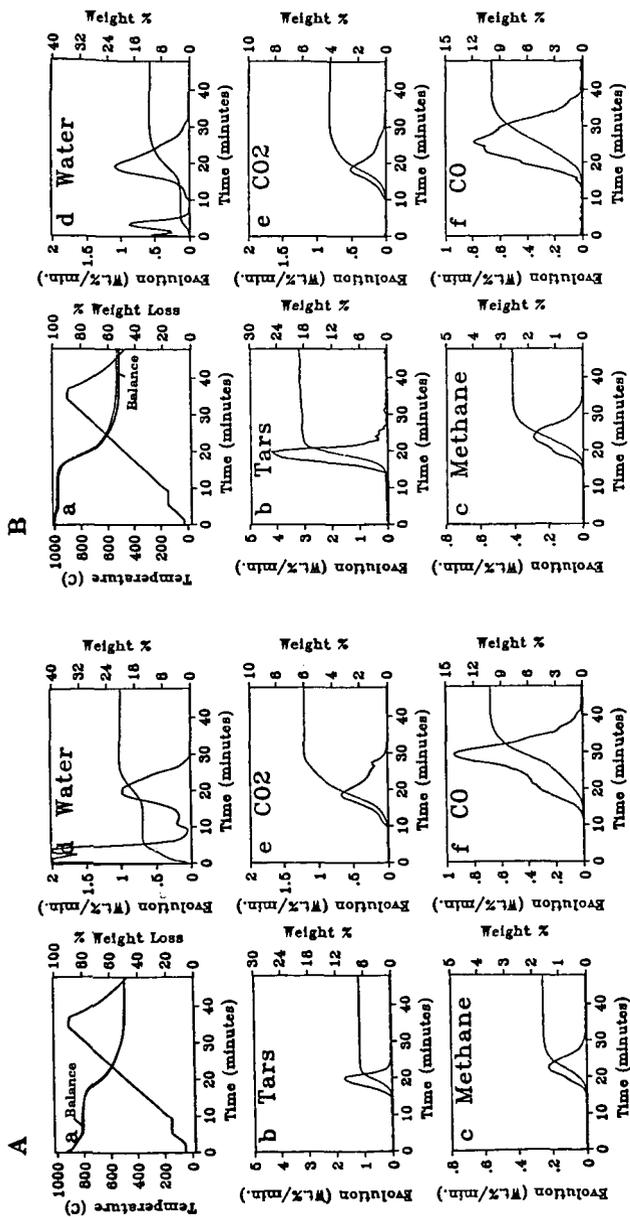


Figure 1. TG-FTIR Analysis of A) Raw and B) Demineralized Argonne Zap Lignite.

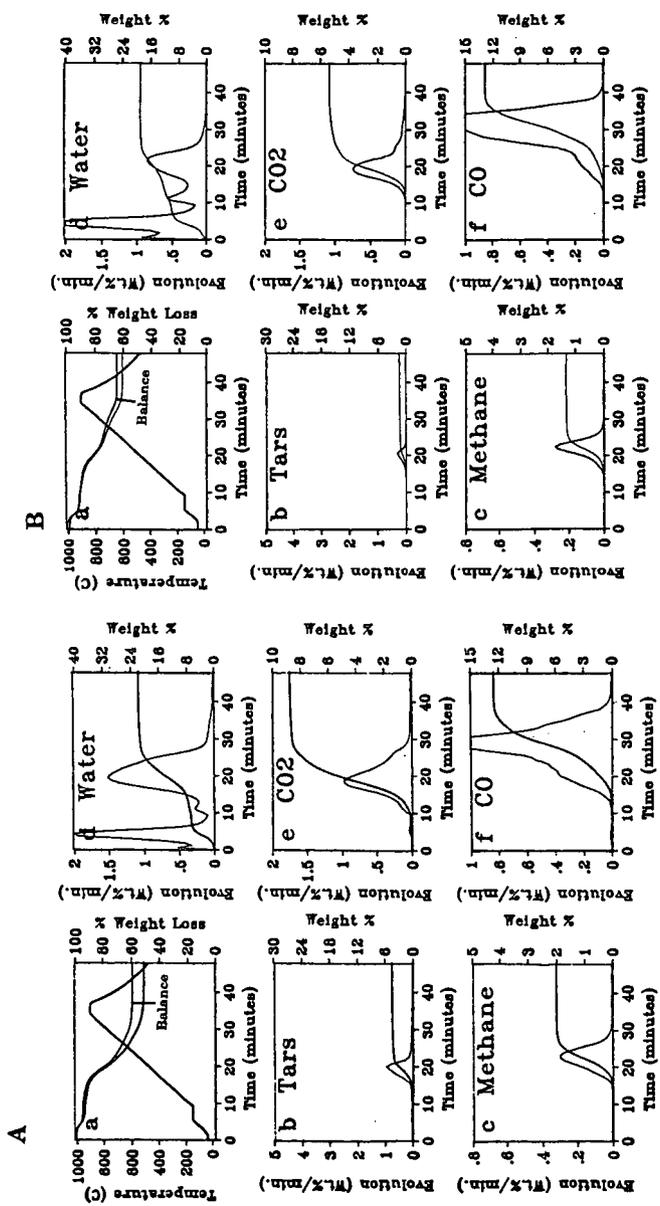


Figure 2. TG-FTIR Analysis of Zap Samples which A) have had Carboxyl Groups Exchanged with Barium; B) have had Carboxyl and Phenolic Groups Exchanged with Barium.

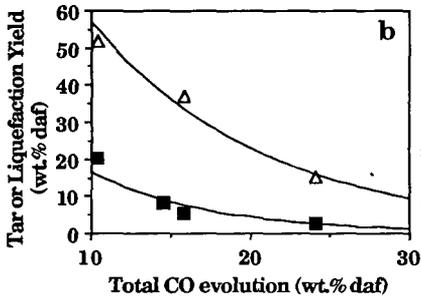
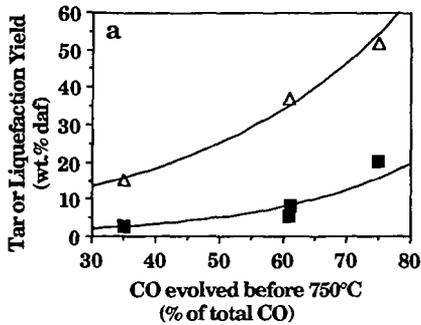


Figure 3. Correlation of Pyrolysis Tar Yield (■) and Toluene Solubles from Liquefaction (Δ) for Zap Lignite with a) Pyrolysis CO Evolution Before 750°C; b) Total Pyrolysis CO Evolution.

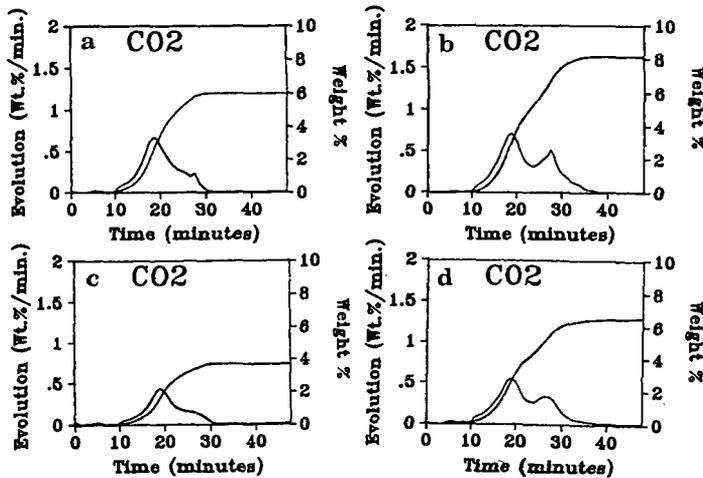


Figure 4. CO₂ Evolution During Coal Pyrolysis. a) Raw Zap; b) Remoisturized Zap; c) Raw Wyodak; d) Remoisturized Wyodak.