

HYDROUS PYROLYSIS OF FOUR ARGONNE PREMIUM COALS

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ABSTRACT

Pretreatment experiments were done under hydrous pyrolysis conditions with four Argonne Premium coals (Zap lignite, Wyodak subbituminous, Illinois bituminous, Pittsburgh bituminous) over a range of temperatures (250-350 °C) and pressures (1000 - 4000 psig). The residues from these experiments were further studied by programmed pyrolysis in a TG-FTIR system. The yields of pyrolysis tar were found to increase sharply at short pretreatment times (< 60 min at 350 °C) and decline slowly at longer times. The yields of pyrolysis methane increase monotonically with pretreatment time, while the yields of pyrolysis CO₂ decline monotonically. All of these trends are in agreement with the contention that hydrous pyrolysis is similar to an accelerated geological aging of the coal. The results for CO evolution were somewhat contrary in that there was usually an initial increase followed by a decline. It is believed that this CO results from decomposition of hydroxy and dihydroxy structures which are created by the hydrous pyrolysis process.

INTRODUCTION

Hydrous pyrolysis (hydrothermal treatment) of coal has been studied previously as a pretreatment step to increase the yields of liquid products from extraction (1-5), pyrolysis (3-7), or liquefaction (8-11) of coal. However, the mechanisms of this process and the applications to coals of a wide range of ranks are still a subject of considerable debate. The similarity between the effects of steam or water pretreatment and accelerated geological aging of coal has recently been noted by several authors (8-11). Landais, Monthieux and coworkers have also discussed the analogy between pyrolysis in confined systems and accelerated geological aging (12-16), otherwise known as "artificial" maturation.

Siskin and Katritzky (17) have recently reviewed the reactivity of organic compounds in hot water, including a consideration of the geochemical implications. Their review indicates that, under conditions where conventional wisdom suggests that water is inert, it may be acting as a catalyst, reactant, and/or solvent. Based on work with model compounds with linkages and functional groups corresponding to those found in coals and shale kerogens, it was concluded that water has important effects on the conversion of plant and animal material into organic fuels under geological conditions of time, heat, and pressure. Much of their work was done in the range of 250 to 350 °C which is the temperature range of interest for hydrothermal treatment of coal. Because of significant changes in the physical and chemical properties of water with increasing temperature, it becomes more likely to react with organic compounds. For example, in the presence of water, ether and ester crosslinks can be readily broken by hydrolysis at relatively low temperatures (17).

The principal conclusions of their work as it relates to hydrothermal treatment of coal are: 1) it

is the ionic chemistry of water that is important under the pretreatment conditions; 2) that reactions in water systems are often "autocatalyzed" by water soluble organic reaction products; 3) aqueous chemistry provides cleavage pathways for major oxygen crosslinks which are too stable to cleave thermally; 4) water can act as a highly effective acidic or basic catalyst or even as an acid-base bicatalyst 5) reactions of water with organics can be catalyzed by clays. Siskin and coworkers (17-19) have demonstrated that there are plausible pathways for water to remove or reduce oxygen functional groups (e.g., conversion of alcohols to methyl groups) under conditions which are relevant to water pretreatment of coal.

EXPERIMENTAL

Sample Selection - The selection of coal samples was made from the Argonne Premium Sample Bank (20). The coals used were the Zap Lignite, the Wyodak subbituminous and the Illinois No. 6 bituminous. Selected experiments were also done with the Pittsburgh Seam bituminous coal from the same sample bank.

Steam/Water Pretreatment Experiments - A new reactor system was designed to carry out high pressure (up to 6000 psig), high temperature (up to ~ 400°C) hydrothermal treatment of coal in a closed bomb (20 ml) reactor. After 1-3 g coal is fed into the bomb and the reactor head is screwed on to get a gas tight seal, the system is purged with N₂ or evacuated, the high temperature, high pressure valve on the reactor base is closed, and the water is injected directly into the coal through the capillary tube with a ~ 0.1-1.0 ml/min rate. Deaerated and deionized water is used throughout the reaction.

Simultaneously with the water injection, the reactor is immersed into the fluidized sand bath held at the required temperature. The pressure is measured in the water feed capillary tubing directly after the pump. The amount of water pumped in and the temperature determines whether steam and/or water pretreatment is done. The results described in the current paper are for pretreatment with subcritical water at 350°C, 4000 psig and pretreatment times from 10 to 1200 minutes. Additional details of the experiments have been provided previously (11).

Product Analyses - The residues from the water pretreatment experiments with the four coals were subjected to analysis by programmed pyrolysis (TG-FTIR), solvent extraction, FT-IR, SEM/x-ray analysis and liquefaction experiments in a donor solvent. The liquefaction and solvent extraction experiments have been discussed previously (11). The current paper focuses primarily on the results from TG-FTIR (21) and FT-IR (22,23) analysis of the residues.

RESULTS AND DISCUSSION

Experimental Results - Figure 1 compares the TG-FTIR results for raw, water pretreated and demineralized Wyodak samples. Figures 1a, 1d, and 1g show the time-temperature profile, the TGA balance (lower curve) and the sum of gases (by FT-IR). Figures 1b, 1e, and 1h show the differential and integrated evolution curves for tar, while Figures 1c, 1f, and 1i show the same curves for CO₂. In addition, Figures 1f and 1i have the differential curves for the raw coal superimposed as dashed lines for comparison. The water pretreatment was done at 350 °C, 4000 psig for 20 minutes.

The results in Fig. 1 show that both hydrothermal treatment and demineralization lend to increases in the pyrolysis tar yield and a reduction in the pyrolysis CO₂ yield. These results are consistent with previous work which has suggested that crosslinking is associated with CO₂ evolution, i.e., the increase in tar is a result of a reduction in crosslinking (24,25). In the case of demineralization, the removal of divalent cations which act as crosslinks in the structure is

believed to be responsible for the observed result (25). In the case of hydrothermal treatment, the divalent cation content is essentially unchanged (10), so a different mechanism must be important.

A variety of explanations for the effects of hydrothermal treatment have been proposed:

- Hydrothermal treatment adds hydrogen (which can stabilize reactive fragments) and removes oxygen groups (which cause retrogressive reactions).
- Hydrothermal treatment partially depolymerizes the coal structure by breaking covalent bonds and disrupting hydrogen bonds.

Evidence for the former comes primarily from spectroscopic and elemental analysis (6-11) while evidence for the latter comes primarily from data on pyridine extractability (1-5,10,11). The relative importance of each mechanism is likely a function of coal type. Both are consistent with work that has been reported in the organic geochemistry literature on the artificial and natural maturation of organic matter (12-17). Landais and coworkers (12-16) conclude that pyrolysis in confined systems, such as occurs in hydrothermal treatment, can mimic the natural maturation process for coal and other organic matter. However, they also conclude that the presence of water may not be as important as close confinement of the sample with the products of primary pyrolysis. Of course, for low rank coals one of the principal primary pyrolysis products is water. The work of Siskin and Katritzky (17) would suggest more prominent role for water as a reactant species and in providing a medium in which ionic reactions can occur (based on an extensive series of studies with model compounds). However, they also agree that the artificial maturation reactions are auto-catalyzed, i.e., the products of the initial reactions become reactants in subsequent reactions.

Figure 2 shows a comparison of evolution curves from TG-FTIR analyses of (a-d) water pretreated Zap lignite residues (350 °C, 4000 psig) and (e-h) four Argonne premium coals of a range of rank. This figure shows four sets of plots of the differential evolution rate curves for tar, CH₄, CO₂, and CO. In the case of tar, the results in Fig. 2a indicate a sharp increase in tar yield at short pretreatment times followed by a gradual decline at long pretreatment times. This trend is consistent with the observed trend in the rank series shown in Fig. 2e. It is also true that the T_{max} values for tar increase with increasing pretreatment time, which is again consistent with the observed rank variation. As discussed above, the initial increase in the tar yield could be due to loss of crosslinking agents (oxygen functional groups) and/or depolymerization of the coal structure. The decline in tar yield at long pretreatment time could be due to an increase in the aromatic cluster size of the average repeating unit which would lend to lower volatility and/or a loss of aliphatic hydrogen which can stabilize reactive fragments (26). There is also evidence from recent solvent swelling measurements done at Advanced Fuel Research that short time water pretreatment loosens up the coal structure, while long time pretreatment makes it more compact.

The results for the CH₄ evolution rate with increasing pretreatment time (Fig. 2b) also shows the same trend that is observed in the rank series (Fig. 2f). A major source of CH₄ gas evolution is believed to be methyl groups. These can be created by rupture and stabilization of CH₂ - CH₂ bridges or CH₂ - O bridges. The latter groups are known to be reactive under hydrothermal treatment conditions. Katritzky et al. (19) have also shown that benzyl alcohols can react under these conditions to form toluene as a major product.

Figure 2c indicates significant reductions in the CO₂ yield with increasing pretreatment time which also parallel the changes with increasing rank (Fig. 2g). The removal of carboxyl groups by

hydrothermal treatment has been demonstrated by FT-IR analysis of pretreated samples (7,11,14). Siskin et al. (18) have shown that hydrothermal treatment at 343 °C of 1-naphthoic acid yielded only naphthalene.

The results for the change in CO evolution with hydrothermal treatment (Fig. 2d) are interesting in that they do not directly follow the trend of decreasing CO with increasing rank (Fig. 2h), i.e., there is an initial increase in CO evolution. The evolution of CO can occur from the decomposition of hydroxy or dihydroxy functionalities. Evidence from FIMS (27) and FT-IR analysis (6,11) of water pretreated coal residues shows an initial increase in the formation of phenols and catechols during water pretreatment which is consistent with the initial increase in pyrolytic CO formation. Siskin et al. (18) have shown from model compound studies that certain diaryl ethers could be readily converted to phenols under hydrothermal treatment conditions. An examination of proposed structures for low rank coals (28) would reveal several ether and hydroxyether structures where this type of chemistry could occur.

The results in Figs. 3-5 show the integral yields of tar, CH₄, CO₂, and CO from water pretreatment of Zap, Wyodak, and Illinois No.6 coals for a range of pretreatment times. The trends for Zap, shown in Fig. 3, are consistent with the more limited set of data shown in Figs. 2a-d. The results for the Wyodak coal shown in Fig. 4, are similar to those of the Zap. The results for the Illinois coal, shown in Fig. 5, appear to depend on the "freshness" of the coal sample. The freshly opened samples (indicated by the darkened circles) appear to follow the same trends as the two lower rank coals, except for the CO₂ yield. The results for samples which were opened and stored in a nitrogen purged glove box are more scattered, but appear to follow similar trends, except for the CH₄ yields. This sensitivity of the Illinois coal to aging at ambient conditions has been reported previously (29,30) and is probably related to catalytic activity of the pyrite.

Quantitative Modeling - Work was begun on using the AFR FG-DVC pyrolysis model (26) to simulate the results of the water pretreatment experiments with Zap lignite. It was decided to use the Zap data from pretreatment at 350°C for short pretreatment times, since it appears that the behavior at long pretreatment times is more complex. The pyrolysis version of the FG-DVC model was successful at predicting the increase in pyrolysis tar yield based on the lower amounts of CO₂ and the higher amounts of extractables and CH₄, which are inputs into the model (26). A comparison of the measured (*-*) and predicted (---) pyrolysis yields is given in Fig. 6 for the raw and water pretreated coals.

In Fig. 7, a plot is shown of a van Krevelen diagram for the Argonne coals. The simulation of the standard FG-DVC model for maturation conditions is shown as a solid line. The simulation of a modified FG-DVC model for maturation in which CO and CO₂ are removed with a higher rate process is shown as a dashed line. This work is discussed in more detail by Solomon et al. (31). The results for the gas yields (discussed above) and FT-IR analysis of the water pretreated residues indicate that hydrothermal pretreatment more closely follows the dashed line than the solid line, since oxygen is removed faster than hydrogen. This is especially true for the two low rank coals (Zap, Wyodak). The total hydrogen and the sum of ether and hydroxyl oxygen amounts determined by FT-IR analysis of the water pretreated residues from four coals are shown in Table 1, below. Previous work has shown that FT-IR analysis provides a good estimate of the total hydrogen content when compared to standard elemental analysis (32). It also provides a measure of the sum of ether and hydroxyl oxygen which correlates with the total oxygen content. This will be confirmed by doing elemental analysis of the residues.

TABLE 1

FT-IR ANALYSIS OF WATER PRETREATED RESIDUES FROM FOUR COALS

COAL	PRETREATMENT TIME (mins. at 350°C, 4000 psig)	H _{TOTAL}	O _{SUM}
ZAP	----	3.9	10.5
	20	4.9	9.7
	180	4.4	8.2
	1080	4.5	6.7
WYODAK	----	5.1	10.2
	20	5.4	8.8
	180	5.0	8.0
	1080	4.0	7.0
ILLINOIS #6	----	5.7	6.0
	20	4.4	5.4
	300	4.3	5.1
	1080	3.4	4.5
PITT	----	5.8	4.4
	20	5.9	6.3
	180	5.3	5.0
	1200	4.7	4.1

CONCLUSIONS

The conclusions can be summarized as follows:

1. The analysis of pyrolysis data from water pretreated Zap lignite and Wyodak subbituminous coal (reduction in CO₂ yield, maximum in tar yield, increase in CH₄ yield) shows a strong similarity of hydrothermal treatment to an accelerated geological aging process. The results for the Illinois and Pittsburgh bituminous coals were generally similar, though less dramatic.
2. The geological aging analogy is also consistent with results that were obtained in the literature on hydrothermal treatment, since it explains why the treatment is effective in increasing pyrolysis yields for low rank coals and is ineffective or reduces pyrolysis yields for high rank coals. However, there are certain trends, such as the fact that the CO yield appears to follow the tar yield (goes through a maximum along with the tar) which do not agree completely with this analogy.
3. The FT-IR data indicate a rapid reduction of oxygen groups during water pretreatment for low rank coals, although there is an initial increase in hydroxy functionalities, and a slower loss of hydrogen after an initial increase.

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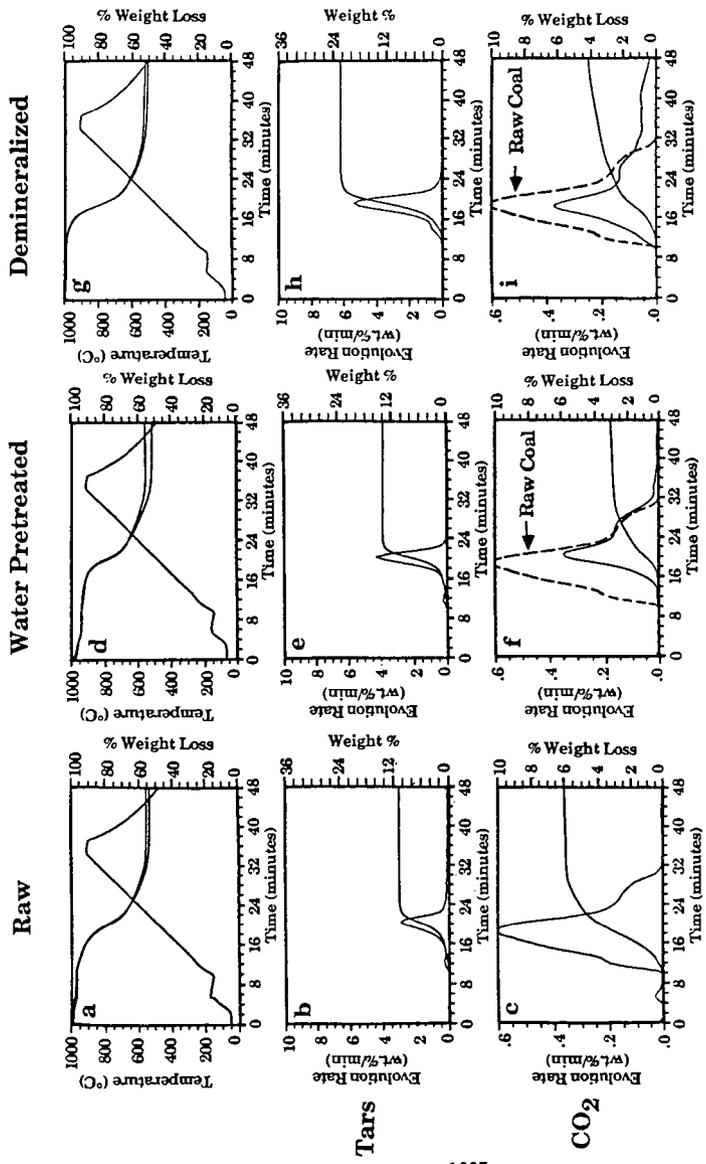


Figure 1. Product Evolution Curves for Raw, Water Pretreated and Demineralized Wyodak Subbituminous Coal. a,d,g) Weight Loss and Temperature Profile; b,e,h) Tar Evolution and Weight Loss; c,f,i) CO₂ Evolution and Weight Loss. Raw Coal Evolution Curve is Indicated in (f) and (i) as a Dashed Line for Comparison. The Water Pretreatment was done at 350°C, 4000 psig for 20 min.

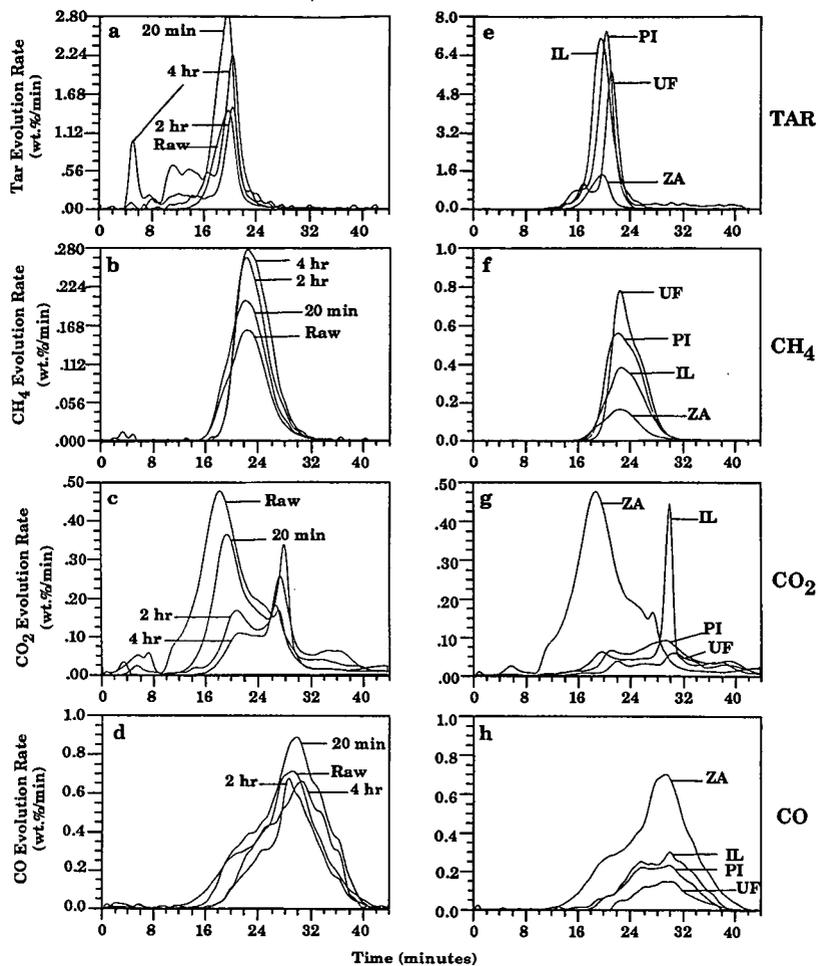


Figure 2. Comparison of Evolution Curves from TG-FTIR Analysis of a-d) Water Pretreated Zap Lignite Residues (350°C, 4000 psig) and e-h) Four Argonne Premium Coal Samples. The Evolution Rates are Given on an As-Received Basis. For the Water Pretreated Samples, the Rates are Normalized to the Moisture Content of the Raw Coal. The Samples are Heated to 150°C for Drying and then at 30°C/min to 900°C (starting at about 10 minutes).

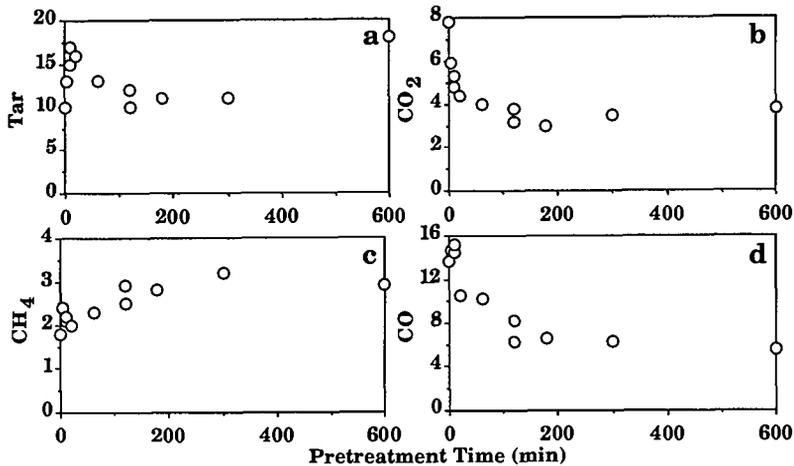


Figure 3. Results from TG-FTIR Analysis of Zap Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. All Results are Given on a DAF Basis.

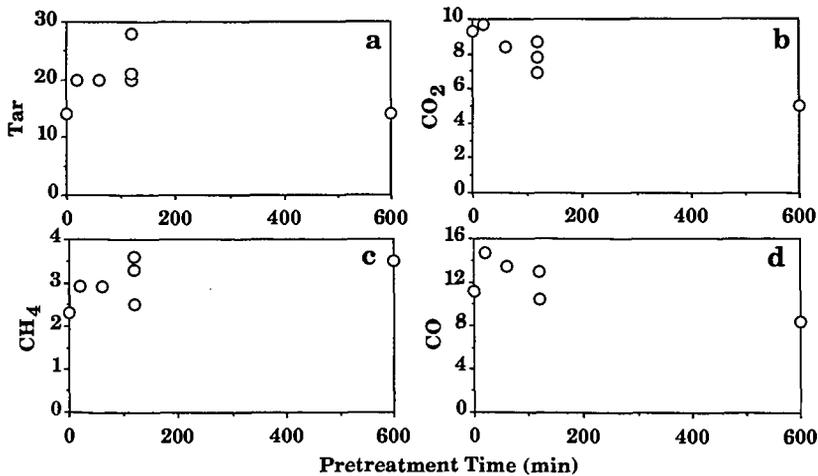


Figure 4. Results from TG-FTIR Analysis of Wyodak Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. All Results are Given on a DAF Basis.

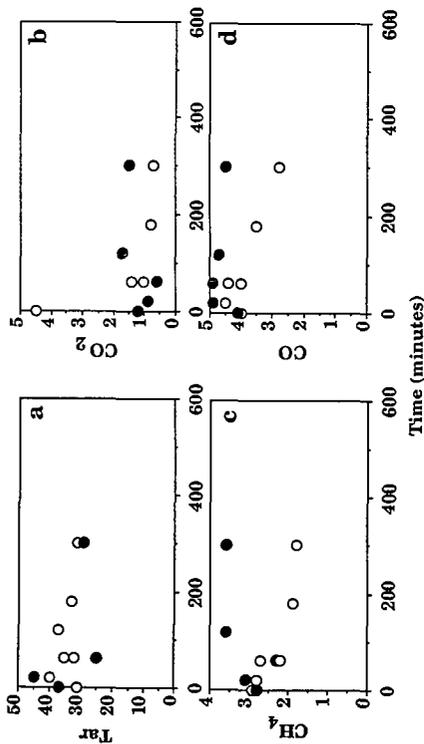


Figure 5. Results from TG-FTIR Analysis of Illinois Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. All Results are Given on a DAF Basis. Solid Circles are for Freshly Opened Samples. Open Circles are for Samples which had been Previously Opened.

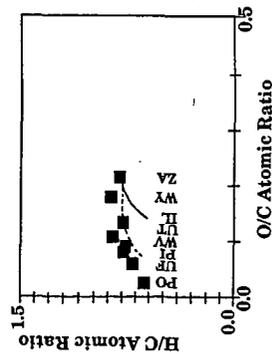


Figure 7. Maturation of Coal. Comparison of Predictions for FG-DVC Pyrolysis Model (solid line), FG-DVC Maturation Model (dashed line) and the Data for the Argonne Coals (symbols).

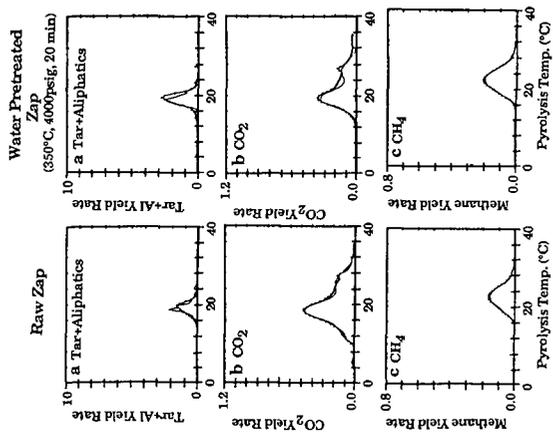


Figure 6. Comparison of Measured and Predicted Yields from Pyrolysis of Raw Zap and Water Pretreated Zap Lignites.