

Title: FUNDAMENTAL STUDIES OF WATER PRETREATMENT OF COAL

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Objective: The goals of this project are to gain an understanding of the chemistry of water or steam coal pretreatments and to assess the importance of such pretreatments on subsequent coal liquefaction.

ABSTRACT

A series of water pretreatment experiments has been done on four coals (Zap, lignite, Wyodak subbituminous, Illinois No. 6 bituminous and Pittsburgh bituminous) obtained from the Argonne Premium sample bank. Most of the experiments were done in subcritical water at 4000 psig and 350°C with pretreatment times varying from 5 minutes to 1200 minutes in a batch reactor. Selected experiments have been done with a continuous flow version of the reactor and with variations in the heating profile and water injection procedure. For each experiment, the yields of gases, water soluble material and residue are determined. The residues are subjected to analysis by a variety of techniques (TG-FTIR, solvent extraction, solvent swelling, FT-IR, oxygen reactivity index, and donor solvent liquefaction). The preliminary conclusions of this work are that the effects of water pretreatment occur in two different regimes:

- At short pretreatment times, the process loosens up the coal structure (extractable and tar yields increase) and oxygen is removed as if the coal was subjected to an accelerated aging process. However, liquefaction yields appear to decline relative to the raw coal.
- At longer pretreatment times, the process partly recombines the structure (extractable and tar yields decline). Oxygen continues to be removed, although ether groups go through a maximum. However, liquefaction yields are closer to values for the raw coal.
- The apparent decline in liquefaction yields at short pretreatment times may be explained by solvent adduction.
- Unusual liquefaction behavior is exhibited by the Illinois coal. Yields are very sensitive to the amount of oxygen exposure. The participation of an oxidized form of pyrite in the liquefaction pretreatment chemistry is thought to be likely.

INTRODUCTION

Water pretreatment of coal has been studied previously as a means to increase the yields of liquid products from pyrolysis or liquefaction 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. Blenkowski et al. (1,2) have studied the effect of steam pretreatment on

coal liquefaction. They used a Wyodak coal which had been carefully stored (under water) to avoid weathering. The experimental conditions were adjusted to provide 750 psig steam for 30 minutes in either a pretreatment (-200°C) stage and/or liquefaction stage. Pretreatment of the suction dried coal at 200°C increased the conversion to extractable products at 400°C from 30.5 to 38.5%. If the pretreatment was carried out at 240°C , the conversion was increased to 40.3%. However, increasing the pretreatment temperature even further to 320°C led to a smaller conversion (33.8%). In a later paper, Bienkowski et al. (2) tried ammonia addition to both reaction stages and obtained even better results than with steam alone.

The explanation offered by Bienkowski et al. (1,2) for the effect of steam pretreatment was that it allows breaking of hydrogen bonds, loosening of the coal matrix and stabilization of some of the reactive components of the coal. This effect appears to be enhanced by the presence of ammonia which can also provide hydrogen bonding and which may undergo chemical reactions with oxygen functional groups.

Graff and Brandes (3-5) have observed higher yields of liquid products from pyrolysis or solvent extractions of steam pretreated Illinois No. 6 coal. The steam pretreatment was done in a stainless steel microreactor at 50 atm (~ 750 psig) and $320-360^{\circ}\text{C}$. A similar pretreatment of coal in a helium atmosphere had no effect. If the steam-pretreated coal was exposed to air, both the improvements obtained in the pyrolysis and extraction yields were lost. The mechanism for the pretreatment was explained as partial depolymerization of the coal due to disruptions of hydrogen bonds. Recent evidence has suggested that the treatment increases the number of hydroxyl groups in the coal (5). It was postulated that the steam reacts with the ether linkages in coal, forming hydroxyl groups and reducing the number of covalent crosslinks in the coal (5).

Recent work by Khan et al. (6) involved the steam pretreatment of a set of five coals which covered a wide range of coal rank. The pretreatments were done at $300-320^{\circ}\text{C}$ and 1100-1300 psig steam. The steam pretreatment was found to reduce the concentration of oxygen functional groups for the low rank coals, but did not have much effect on higher rank coals (or increased the amount of oxygen). Under pyrolysis conditions, the low rank coals showed increases in tar yields, when pyrolyzed at a rapid rate. When the steam-treated coals were pyrolyzed at a slow heating rate, the tar yields did not increase significantly for any of the coals tested.

Ross et al. (7,8) have studied the liquefaction of Illinois No.6 coal in CO/H₂O systems at high pressure (4000-5000 psig) and high temperatures (400°C), where the water is supercritical. The conversion was measured in terms of toluene solubility (TS) and the results were found to be superior to those obtained in tetralin under the same conditions. The CO/H₂O system was most effective (indicating a kinetic isotope effect) followed by CO/H₂O and H₂/H₂O. The latter treatment was not very effective for demineralized coal. The results have been explained in terms of an ionic mechanism involving the initial formation of formate ion, as explained in Ref. 7, whereby hydrogen is donated to the coal.

Recent work by Ross and coworkers has addressed the use of liquid water as a pretreatment step to liquefaction in a conventional donor solvent (9,10). Work was done on Illinois No. 6 coal and Wyodak subbituminous coal. The results did not show a significant effect of water pretreatment on increasing the conversion to toluene solubles in a donor liquefaction solvent. However, significant changes were observed in the composition and molecular weight distributions of the liquid products.

EXPERIMENTAL

Sample Selection

The selection of coal samples was made from the Argonne Premium Sample Bank. Since pretreatment is potentially most useful for lower rank coals which are subject to retrograde reactions, the coals selected were the Zap Lignite, the Wyodak subbituminous and the Illinois No. 6 bituminous, which are also being used in a complementary study (11). It is also planned to study coals which have been dried and/or aged, as there is evidence from the work of Graff and Brandes (3-5) and Bienkowski et al. (1,2) that the pretreatment is less effective on such coals, and that aging can reverse the beneficial effects of the pretreatment. The work to date has been done on the raw Zap and Wyodak coals.

Reactor for Steam/Water Pretreatment

A new reactor system was developed for this program, which is shown as a schematic in Fig. 1. This system was designed to carry out high pressure (up to 6000 psig), high temperature (up to ~ 400°C) steam or water pretreatment of coal in a closed bomb reactor, which is also interchangeable with our current liquefaction reactor and product collection system. A schematic of the reactor is shown in Fig. 2. The inner volume of the bomb (20 ml) is divided

into upper and lower parts by a stainless steel screen and glass wool. The screen is secured on the capillary tube and the glass wool is replaced after every experiment to keep the coal from being blown out on evacuation during the gas collection phase. 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.

After the reaction, the bomb is quickly quenched with water, flooded with up to 300-600 psig N₂ and depressurized with a 0.8 liter previously evacuated sampling tank. The yields of product gases, e.g., H₂, CO₂, CO, CH₄, C₂H₆, CH₂H₄, CH₂H₂, and H₂S are determined by GC. After opening the reactor, the pretreated coal is taken out of the reactor by washing it with deionized water and filtering under an N₂ atmosphere. N₂ was passed through the coal sample for about an hour to obtain a sample with approximately the same moisture content as the starting coal sample. In addition to the reactor, an N₂ purged glove box was also constructed to facilitate all the product work up in an oxygen-free environment. It is equipped with a lock which can be evacuated or filled with N₂ to transfer the reactor to the box.

RESULTS

Low Rank Coals - An extensive series of steam pretreatment experiments was done on the Zap lignite using subcritical water at a pressure of 4000 psig and temperatures of 250, 300, and 350°C. Selected experiments were done for the Wyodak coal at 350°C, 4000 psig. The pretreatment times varied from 5 minutes to 5 hours. The pretreatment experiments with the Zap lignite over a wide range of temperatures and times give a fairly consistent picture based on analysis of the evolved gases during the pretreatment step and analysis of the solid residues by a variety of techniques (TG-FTIR, solvent extraction, FT-IR, x-ray, liquefaction). The TG-FTIR technique is a programmed pyrolysis instrument which includes on-line analysis of gases by FT-IR spectroscopy and on-line measurement of weight loss with a TGA (12,13).

The TG-FTIR analysis of residues produced at all three temperatures shows a sharp increase in tar at relatively short pretreatment times. The results for the tar yield for pretreatment at 350°C are shown in Fig. 3 for the Zap and in Fig. 4 for the Wyodak. The significant increase in tar does not persist at long pretreatment times. These changes are delayed and attenuated as the pretreatment temperature is reduced, as shown in Fig. 5 for the Zap lignite. However, there is a monotonic increase in the pyridine extractables (not shown) with increasing pretreatment time and a monotonic decrease in CO₂, as shown in Fig. 6 for the Zap lignite. The changes in the CO₂ evolution result primarily from changes in the organic CO₂, as shown by comparing Figs. 6a and 6b. The amount of CH₄ produced upon pyrolysis of the coal increased with increasing pretreatment time, as shown in Fig. 7. The results for the trends in the yields of tar, CH₄, CO₂ and pyridine extractables suggest that steam pretreatment is similar to a geological aging of the coal since these trends are nearly identical to the rank variations in these quantities. By this it is meant that the low rank Zap lignite exhibits behavior which is more characteristic of a higher rank coal after water pretreatment. This explanation is also consistent with the fact that the benefits of steam or water pretreatment on pyrolysis yields are not observed for high rank coals (6). The similarity between the effects of steam pretreatment and geological aging has also been noted by Ross and coworkers (9,10). Landais and Monthieux have discussed the analogy between pyrolysis in confined systems and geological aging (14).

When liquefaction experiments are done on the steam pretreatment residues produced at 350°C, without shaking of the liquefaction reactor, no benefit to liquefaction yields is observed and, in fact, the yields are reduced. These results are shown in Fig. 8a. The liquefaction experiments were done in dihydrophenanthrene for 30 minutes at 400°C. A limited number of liquefaction experiments, which include shaking, have been done on the steam pretreated Zap residues produced at 350°C over a range of pretreatment times. These results are shown in Fig. 8b. These indicate a modest (10-20%) benefit to liquefaction yields at long pretreatment times (~ 5 hours).

An explanation for the effect of reactor shaking may be that the steam pretreatment process makes the coal agglomerate and thus more difficult to liquify. The agglomeration of coal by steam pretreatment was reported by Graff and Brandes (3-5) and Khan et al. (6) and has been observed in our own work.

Samples of residues from pretreatment experiments done at 350°C with Zap lignite were subjected to x-ray analysis. The results are summarized in Table 1, below.

TABLE 1
Effect of Water Pretreatment Time at 350°C, 4000 psig on Mineral
Compositions for Zap Lignite

Time (min)	Na	Ca	Al	S(o)	Ash
0	0.31	1.09	0.33	0.30	6.88
10	0.00	1.30	0.45	0.20	6.70
60	0.02	0.99	0.40	0.22	5.83
180	0.02	1.38	0.55	0.22	7.60
240	0.00	1.18	1.09	0.24	9.66

The total ash content was found to go through a minimum after about one hour pretreatment time and then increase with further increases in pretreatment time. This is in agreement with results obtained independently from a TGA combustion experiment, although the reasons for this are not yet clear. One possibility is segregation of the ash. For the individual ash components, the most significant trends were elimination of Na, and increases in Al, Si, and Fe with increased pretreatment time. The increases in Al and Fe may be due to partial dissolution of the reactor system. Little change was found for Mg, Ca, Ti, and organic sulfur.

Some of the residues from the 350°C experiments have also been analyzed by FT-IR. The preliminary results suggest that there is a reduction in oxygen functional groups during water pretreatment as was found by Khan et al. (6). Hopefully, the FT-IR results will allow us to verify some aspects of the chemistry of steam pretreatment which we suspect involves the interaction of H₂O, carboxyl groups and/or cations to produce methyl and hydroxyl groups. This is based on the fact that the beneficial effects of steam pretreatment are likely a result of a reduction in retrogressive reactions. Our previous work has suggested that carboxyl groups and cations are significantly involved in retrogressive reactions (15).

Medium Rank Coals - Recent work has been done on water pretreatment of Illinois No. 6 and Pittsburgh Bituminous coals. The results for pyrolysis and extractable yields are similar for the Illinois No. 6 as for the Wyodak and Zap in that improvements are observed at short pretreatment times followed by a decline at long pretreatment times. The Pittsburgh coal has somewhat different behavior in that these values tend to increase monotonically with increasing pretreatment time. The liquefaction yields for these two coals are most interesting in that it appears that water pretreatment can improve liquefaction yields at relatively short pretreatment times. However, the data are rather scattered in the case of the Illinois coal.

The pretreatment behavior for this coal is very sensitive to whether the coal has been exposed to air. The liquefaction behavior for all of the pretreated coals may be obscured by solvent adduction. In addition, in the case of the Illinois coal the pyrite may participate in the pretreatment and/or liquefaction reactions.

CONCLUSIONS

The preliminary conclusions are as follows:

1. At short pretreatment times, the process loosens up the coal structure (extractable and tar yields increase) and oxygen is removed as if the coal was subjected to an accelerated aging process. However, liquefaction yields appear to decline relative to the raw coal.
2. At longer pretreatment times, the process partly recombines the structure (extractable and tar yields decline). Oxygen continues to be removed, although ether groups go through a maximum. However, liquefaction yields are closer to values for the raw coal.
3. The apparent decline in liquefaction yields at short pretreatment times may be explained by solvent adduction.
4. Unusual liquefaction behavior is exhibited by the Illinois coal. Yields are very sensitive to the amount of oxygen exposure. The participation of an oxidized form of pyrite in the liquefaction pretreatment chemistry is thought to be likely.

PLANS

The future work will include: 1) experiments on modified coals (demineralized, ion-exchanged) and model polymers; 2) explanation of the results qualitatively in terms of chemical mechanisms and quantitatively in terms of the FG-DVC liquefaction model.

ACKNOWLEDGEMENTS

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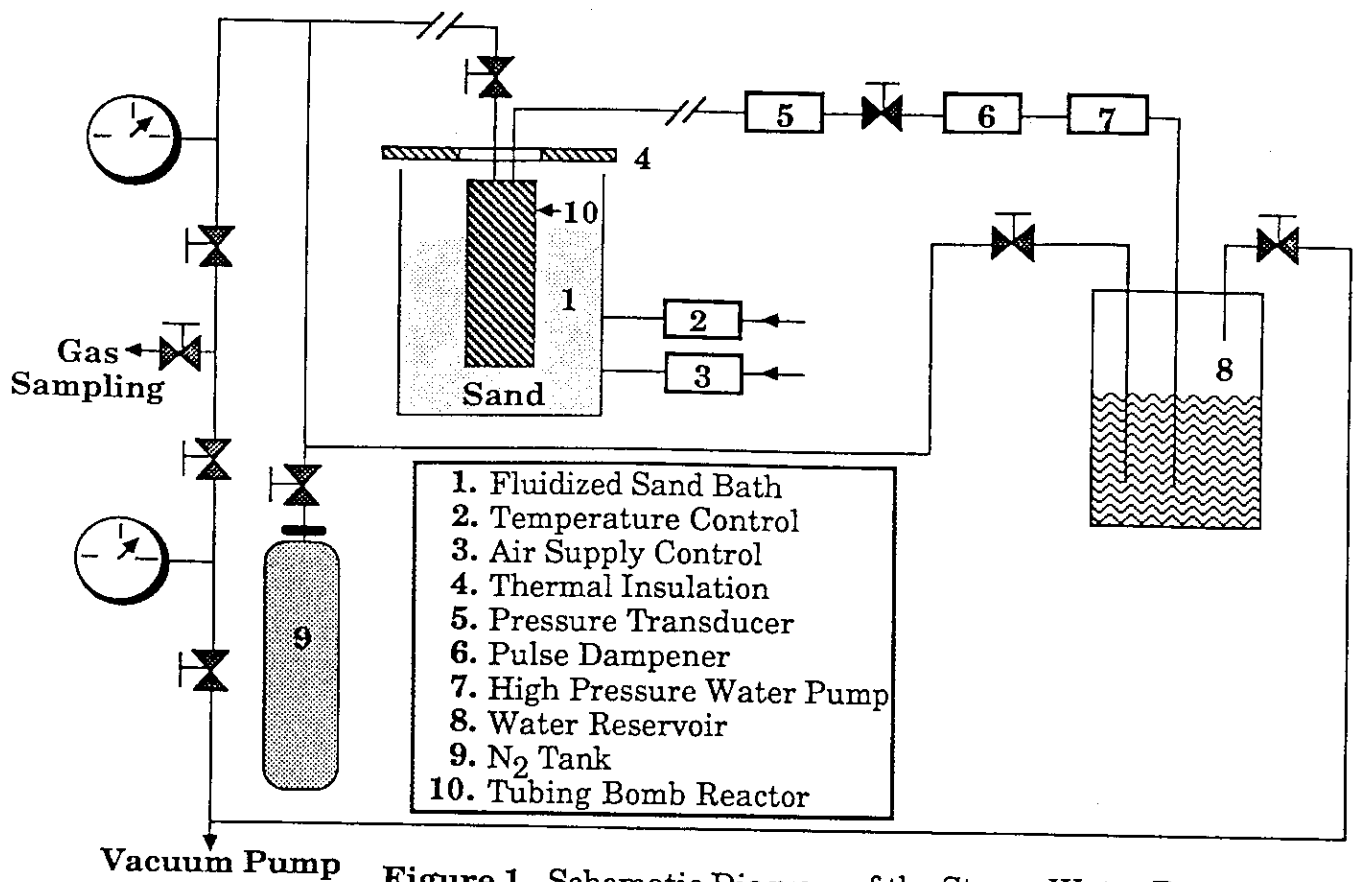


Figure 1. Schematic Diagram of the Steam-Water Pretreatment Reactor System.

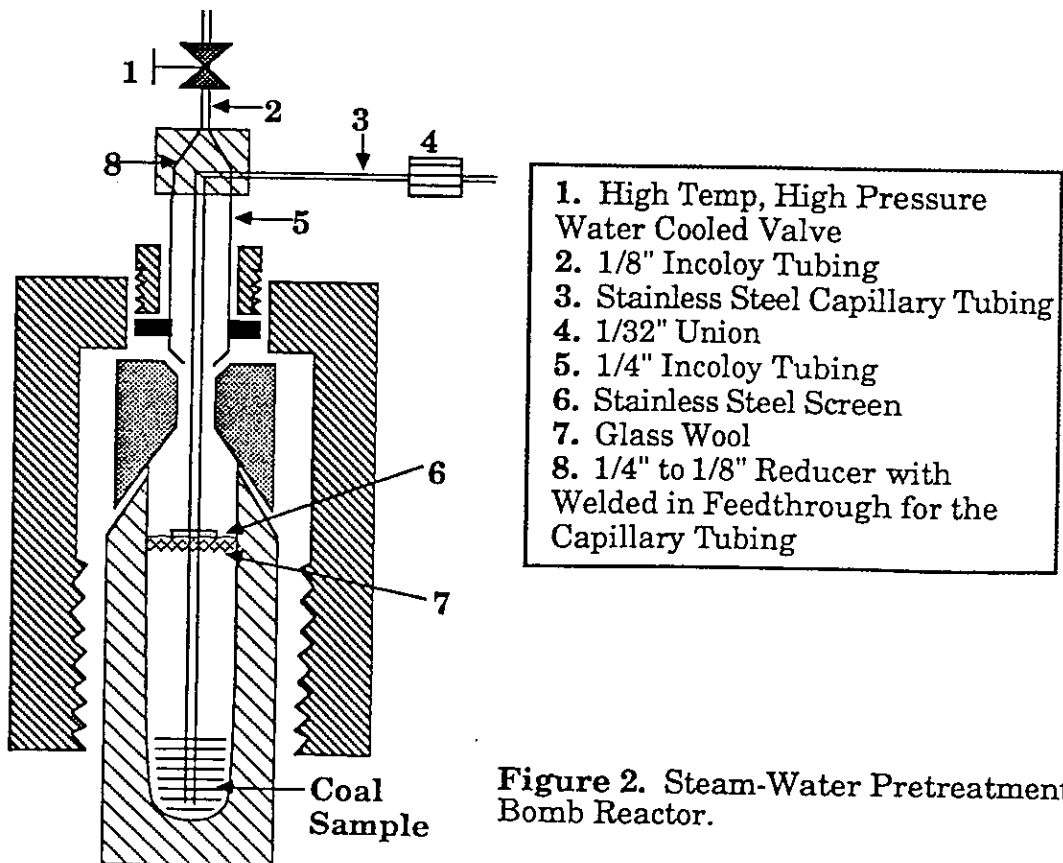


Figure 2. Steam-Water Pretreatment Bomb Reactor.

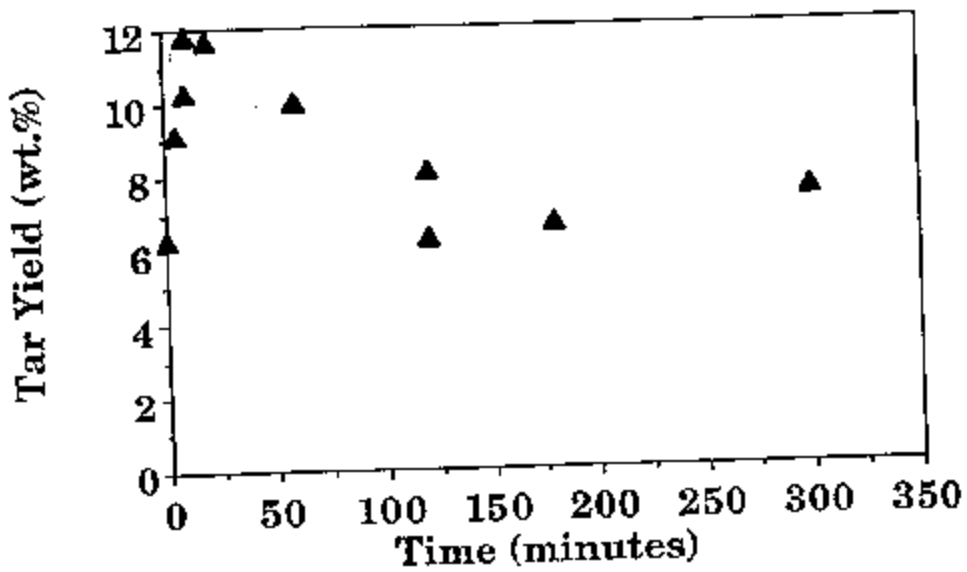


Figure 3. Tar Yield Data from Pyrolysis of Water Pretreated Zap Lignite (350°C, 4000 psig).

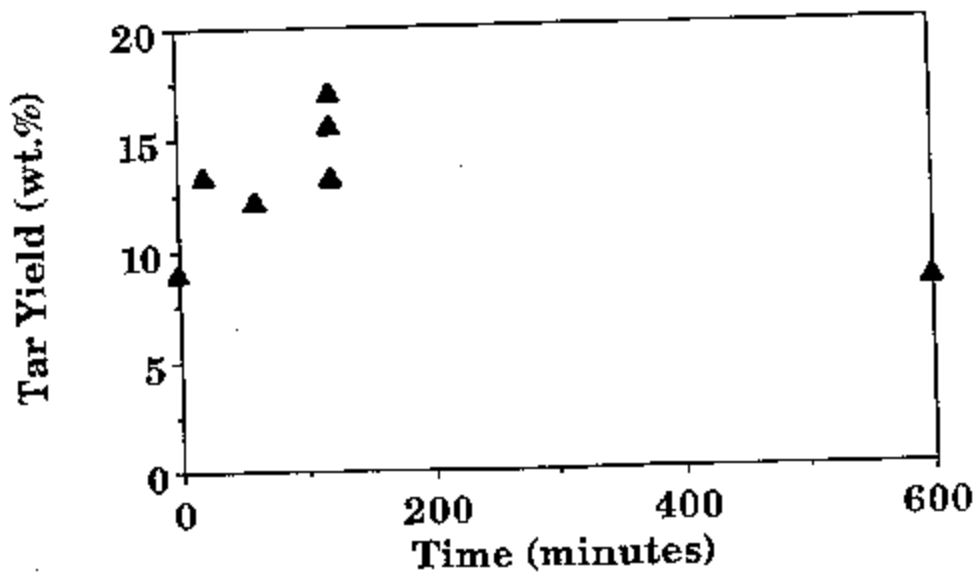


Figure 4. Tar Yield Data from Pyrolysis of Water Pretreated Wyodak Coal (350°C, 4000 psig).

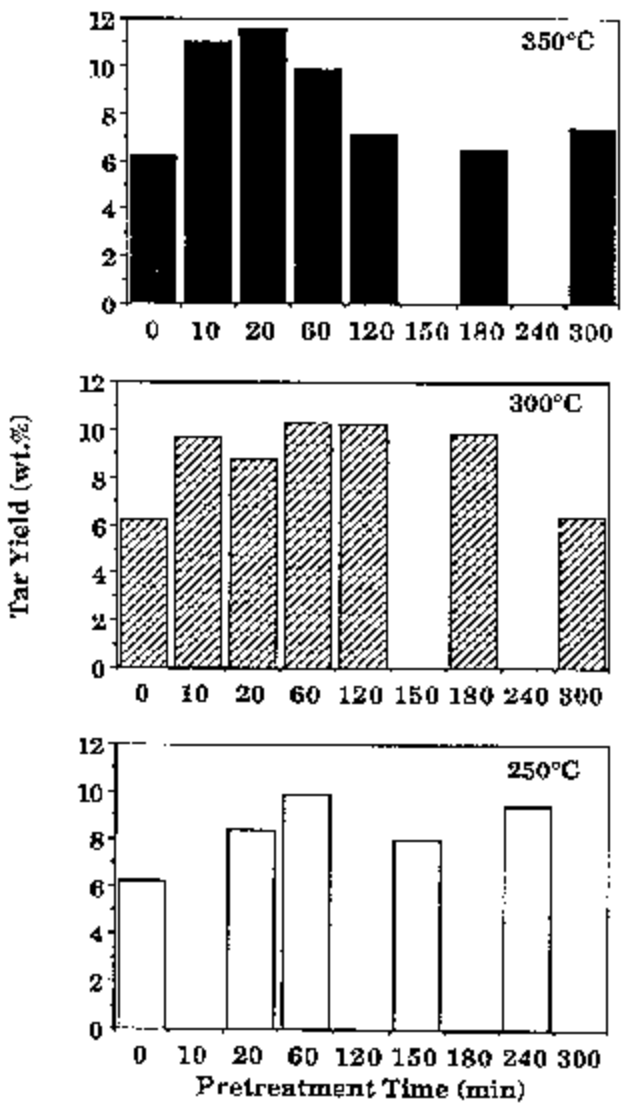


Figure 5. Tar Yield Data from Pyrolysis of Water Pretreated Zap Lignite Produced at Three Temperatures (4000 psig).

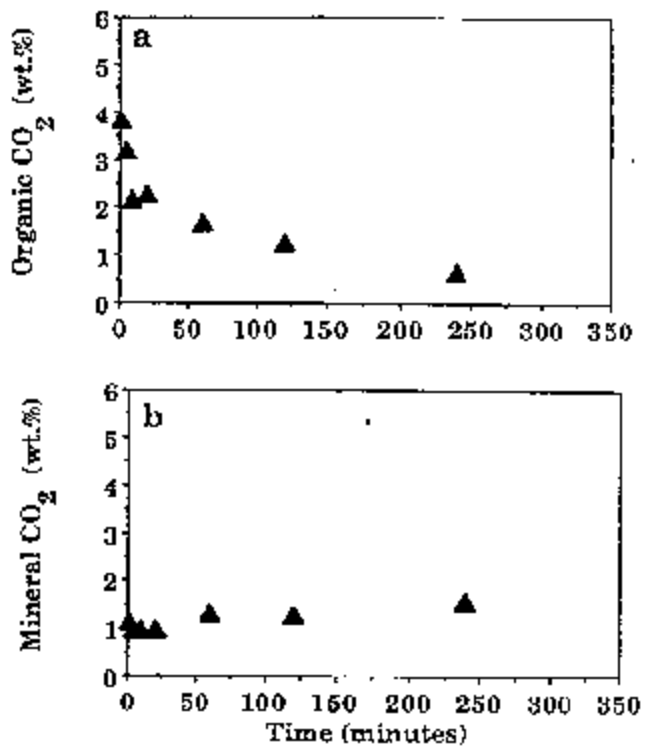


Figure 6. CO₂ Yield Data from Pyrolysis of Water Pretreated Zap Lignite (350°C, 4000 psig).

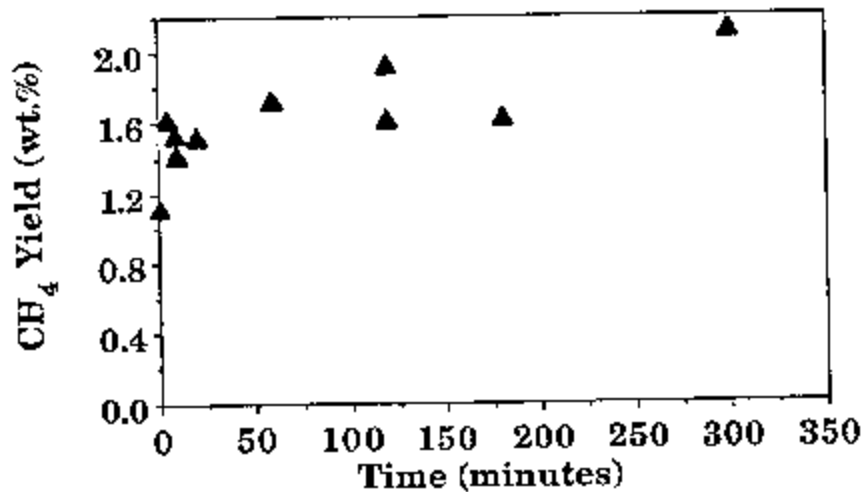


Figure 7. CH₄ Yield Data from Pyrolysis of Water Pretreated Zap Lignite (350°C, 4000 psig).

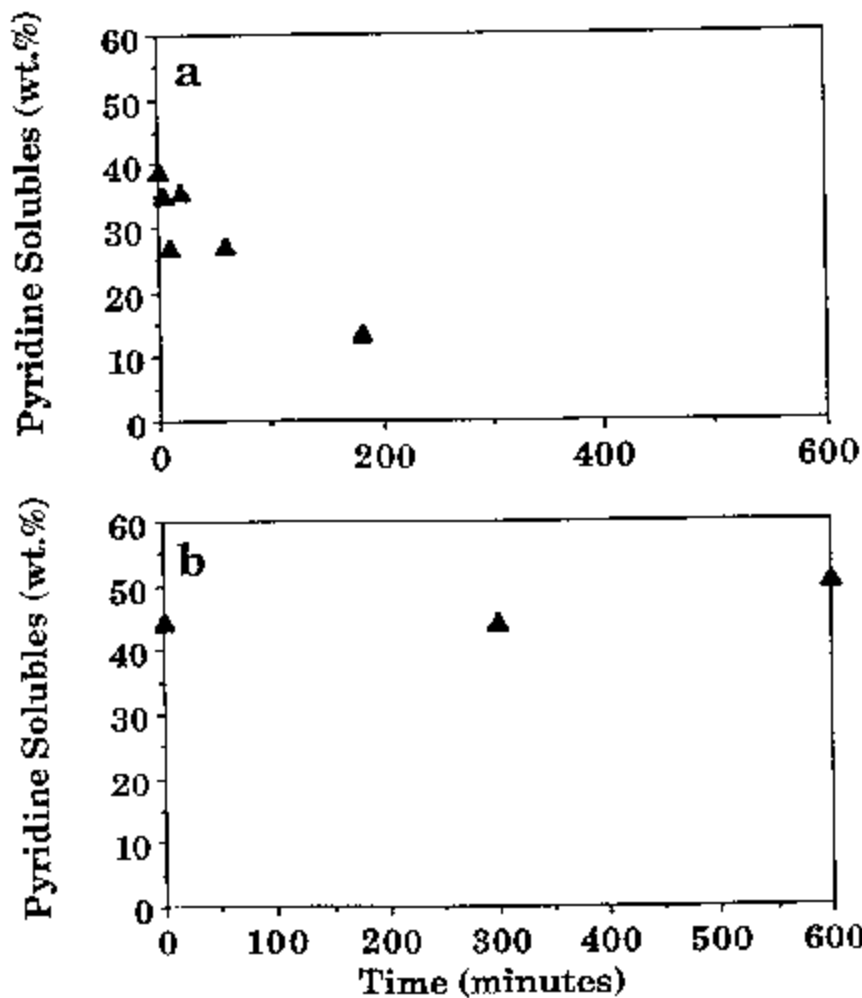


Figure 8. Pyridine Solubles Yields from Liquefaction Experiments with Water Pretreated Zap Lignite (350°C, 4000 psig).