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"FUNDAMENTAL STUDIES OF WATER PRETREATMENT OF COAL"

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ABSTRACT

The entire reactor system was completed during the past month, including the pressure and flow control systems. The reactor 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. A glove box was also built to facilitate all the product work up in an oxygen-free environment. The box is equipped with a lock which can be evacuated or filled with nitrogen for transfer of the reactor to the glove box.

A series of water pretreatment experiments was done with raw Zap lignite at 350°C, 4000 psi for times of 10 and 20 minutes and 1, 2, 3, and 4 hours. A second series of experiments was done at 300°C, 4000 psi for the same range of times. Measurements were made of the gas evolution under these conditions and the solid residues were subjected to TG-FTIR, FT-IR, solvent extraction, and SEM/x-ray analysis, and also subjected to coal liquefaction experiments.

The results from TG-FTIR analysis of the solid residues, GC analysis of the pretreatment off gases and solvent extraction of the residues with pyridine for steam pretreatment experiments at 300 and 350°C (4000 psig) indicate that the steam pretreatment under these conditions has a rather profound effect on the structure of the coal. The TG-FTIR analysis of residues produced at both temperatures shows a sharp increase in tar yield at relatively short pretreatment times. However, the significant increase in tar yield does not persist at long pretreatment times. There is a nearly monotonic decrease in the CO₂ yield and a monotonic increase in the pyridine extractables with increasing pretreatment time. The pyridine extractability of the water pretreated coal increases by more than a factor of two. The decrease in the CO₂ evolution results primarily from a reduction in the organic CO₂. These changes are delayed and attenuated as the temperature is reduced. The results for the yield of tar, CO₂ and pyridine extractables suggest that steam pretreatment is similar to a geological aging of the coal, at least at short pretreatment times. 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.

Liquefaction experiments were done on some of the steam pretreated residues. The preliminary results suggest only modest improvements in the liquefaction yields can be achieved with the pretreated samples produced to date.

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**THIRD QUARTERLY REPORT
CONTRACT NO. DE-AC22-89PC89878**

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I. INTRODUCTION AND SUMMARY

Introduction

The goals of this project are to gain understanding of the chemistry of water or steam coal pretreatments and to assess the importance of such pretreatments on subsequent coal liquefaction. For the achievement of these goals, coals, modified coals and model-polymers will be treated with water or steam. This study will include three coals, five modifications (dried, demineralized, ion-exchanged, Ca-loaded, Ba-loaded), three polymers and two polymer modifications (e.g. acid chlorides, amides). Experiments will be performed to investigate both conventional steam pretreatment and the possibility of using the CO/H₂O system of Ross and coworkers as a pretreatment method. The main experimental variables will be sample type and temperature. Detailed characterization of the gas, liquid and solid products from the pretreatment stage will be done. This will include analysis of gases by GC or FT-IR, liquids by capillary GC, FT-IR and FIMS, and residues by solvent swelling, solvent extraction, and elemental analysis. Selected residues will also be evaluated by a standard liquefaction test. Analysis of the raw coals and pretreatment samples will be performed using the above techniques to study changes in the crosslinking, donatable hydrogen, heteroatom composition, evolved gases, functional group composition, extraction yields, molecular weight distributions, etc. Standard tubing bomb liquefaction tests will be used to determine the effect of pretreatment on coal reactivity toward coal liquefaction. A previously developed model for coal liquefaction, the FG-DVC liquefaction model, will be used (after appropriate modifications) to model the physics and chemistry of water pretreatment.

Summary of Work During the Third Quarter

The entire reactor system was completed during the past month, including the pressure and flow control systems. The reactor 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. The reactor is also interchangeable with our current liquefaction reactor and product collection system. A glove box was also built to facilitate all the product work up in an oxygen-free environment. The box is equipped with a lock which can be evacuated or filled with nitrogen for transfer of the reactor to the glove box.

Several preliminary water pretreatment experiments were done with raw Zap lignite to check out the reactor system. Once these were completed, a series of experiments was done at 350°C, 4000 psi for times of 10 and 20 minutes and 1, 2, 3, and 4 hours. This included some repeat experiments, which generally gave quite similar results. A second series of experiments

was done at 300°C, 4000 psi for the same range of times. Measurements were made of the gas evolution under these conditions, the solid residues were subjected to TG-FTIR, FT-IR, and SEM/x-ray analysis, and also subjected to coal liquefaction experiments.

The results from TG-FTIR analysis of the solid residues, GC analysis of the pretreatment off gases and solvent extraction of the residues with pyridine for steam pretreatment experiments at 300 and 350°C (4000 psig) indicate that the steam pretreatment under these conditions has a rather profound effect on the structure of the coal. The TG-FTIR analysis of residues produced at both temperatures shows a sharp increase in tar at relatively short pretreatment times. However, the significant increase in tar does not persist at long pretreatment times. There is a nearly monotonic decrease in the CO₂ yield and a monotonic increase in the pyridine extractables with increasing pretreatment time. The pyridine extractability of the water pretreated coal increases by more than a factor of two. The decrease in the CO₂ evolution results primarily from a reduction in the organic CO₂. These changes are delayed and attenuated as the temperature is reduced. The results for the yield of tar, CO₂ and pyridine extractables suggest that steam pretreatment is similar to a geological aging of the coal, at least at short pretreatment times. 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.

Some unusual trends were seen in the amount of ash in the steam pretreated residues. At 350°C, the ash content appeared to go through a minimum with pretreatment times between 20 minutes and 1 hour, while at 300°C, the minimum is observed at times between 60 and 180 minutes. This could be due to ash segregation in the sample rather than a true reduction in ash content. This will be the subject of further investigations using SEM/x-ray analysis to track the total ash content as well as changes in individual components.

Liquefaction experiments were done on some of the steam pretreated residues. The preliminary results suggest only modest improvements in the liquefaction yields can be achieved with the pretreated samples produced to date. The results will be reported in the Topical Report.

II. TASK 1 - PROJECT PLANNING AND SAMPLE SELECTION

This task has been completed.

III. TASK 2 - EXPERIMENTS ON THE WATER PRETREATMENT STAGE

Reactor Construction

The entire reactor system was completed during the past month, including the pressure and flow control systems. The reactor 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. The reactor is also interchangeable with our current liquefaction reactor and product collection system.

A schematic of the reactor is shown in Fig. III-1. 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 upon evacuation during the gas collection phase. After 1-3 g coal is charged 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. This made it possible to simplify the reactor construction and also to avoid any dead volumes and loops. A schematic of the entire reactor system is shown in Fig. III-2. The amount of water pumped in and the temperature will determine whether steam or water pretreatment is done. The pressure drop in an already equilibrated system will indicate a reaction between coal and steam, although it may not be quantitative due to the instability of such a system as a result of temperature fluctuations. This instability seems to be most pronounced as the critical temperature (374°C) is approached.

After the reaction, the bomb is quickly quenched with water, flooded with up to 300-600 psig nitrogen and depressurized with a 0.8 liter previously evacuated sampling tank. The yields of product gases, e.g., H₂, CO₂, CO, CH₄, C₂H₆, C₂H₄, C₂H₂, 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 nitrogen atmosphere. Nitrogen is passed through the coal sample for about an hour to obtain a sample with approximately the same moisture content as the starting coal sample. To obtain a vacuum dry sample, a thermoelectric heater is used inside a nitrogen glove box constructed for this project.

Figure III-1. Steam-Water Pretreatment Bomb Reactor.

Figure III-2. Schematic Diagram of the Steam-Water Pretreatment Reactor System

The glove box was built to facilitate all the product work up in an oxygen-free environment. The box is equipped with a lock which can be evacuated or filled with nitrogen for transfer of the reactor to the glove box.

Sample Preparation

Samples of ion-exchanged (with NH_4^+) and calcium exchanged Zap lignites were prepared starting from the demineralized form. Both samples were also subsequently converted back to the acid form using a mild acid wash. The calcium-exchanged samples were characterized by SEM/x-ray analysis to verify that the calcium was put onto the coal and then removed. The results are given in Table III-1. In some cases, repeat measurements were made which are labelled "A" and "B". The repeats were generally in good agreement with the original measurements. In addition, the calcium loaded and ammonium exchanged samples were subjected to TG-FTIR analysis to see what effect the various treatments had on the tar yields. These results are shown in Table III-2. Surprisingly, the tar yield was not reduced by calcium addition to a demineralized coal. This is the opposite result to what was obtained with a calcium loaded ammonium-exchanged lignite, also shown in Table III-2. Apparently, the severe HCl/HF demineralization process changes the coal to the extent that the calcium cannot be put back in the same way. It is planned to do FT-IR analysis of the raw, demineralized, and calcium-loaded Zap lignites to see how the structure has changed.

The calcium loaded samples will be subjected to steam pretreatment experiments under the current program and liquefaction experiments under our other program (Fundamental Studies of Retrograde Reactions in Direct Liquefaction).

Water Pretreatment Experiments

Several preliminary water pretreatment experiments were done with raw Zap lignite to check out the reactor system. Once these were completed, a series of experiments was done at 350°C, 4000 psi for times of 10 and 20 minutes and 1, 2, 3, and 4 hours. This included some repeat experiments, which generally gave quite similar results. A second series of experiments was done at 300°C, 4000 psi for the same range of times. Measurements were made of the gas evolution under these conditions, the solid residues were subjected to TG-FTIR, FT-IR, and SEM/x-ray analysis, and also subjected to coal liquefaction experiments. The results of the analyses are described under Task 3.

TABLE III-1
MINERAL COMPONENTS OBTAINED FROM SEM X-RAY MICROANALYSIS OF RAW,
DEMINERALIZED, ION-EXCHANGED AND CALCIUM LOADED ZAP LIGNITE

	Raw	Demin.	Demin./NH ₄ ⁺		Demin./NH ₄ ⁺ /H ⁺		Demin./Ca ⁺²		Demin./Ca ⁺² /H ⁺	
			A	B	A	B	A	B	A	B
Na	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.35	0.11	0.07	0.13	0.05	0.03	0.12	0.09	0.05	0.05
Al	0.33	0.19	0.14	0.15	0.02	0.03	0.13	0.11	0.04	0.03
Si	0.38	0.02	0.07	0.02	0.08	0.08	0.15	0.16	0.14	0.13
K	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Ca	1.09	0.37	0.26	0.17	0.01	0.02	0.69	0.64	0.02	0.01
Ti	0.03	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00
S(o)	0.30	0.33	0.28	0.27	0.33	0.30	0.34	0.34	0.34	0.34
S(m)	0.39	0.12	0.17	0.56	0.63	1.93	0.17	0.13	0.16	0.11
Fe	0.17	0.07	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01
Ash	6.86	1.80	1.47	1.62	0.99	2.65	3.09	2.75	0.60	0.43

TABLE III-2
COMPARISON OF TAR YIELDS AND CALCIUM CONTENT FOR
RAW AND MODIFIED ZAP COALS

Sample	Tar Yield (Dried Basis)	Ca Content (Dried Basis)
Raw Zap	7.0	1.09
Ion-Ex Zap (NH_4^+)	11.0	ND
$\text{NH}_4^+ \rightarrow \text{H}^+$	16.0	0.02
$\text{NH}_4^+ \rightarrow \text{H}^+ \rightarrow \text{NH}_4^+$	14.0	0.01
$\text{NH}_4^+ \rightarrow \text{Ca}^{++}$	11.0	1.90
$\text{NH}_4^+ \rightarrow \text{Ca}^{++} \rightarrow \text{NH}_4^+$	11.5	0.33
Demineralized (DMN) Zap	15.0	0.37
$\text{DMN} \rightarrow \text{NH}_4^+$	12.5	0.21
$\text{DMN} \rightarrow \text{NH}_4^+ \rightarrow \text{H}^+$	14.8	0.01
$\text{DMN} \rightarrow \text{Ca}^{++}$	16.7	0.69
$\text{DMN} \rightarrow \text{Ca}^{++} \rightarrow \text{H}^+$	13.8	0.01
Methylated Zap	24.0	0.02

ND = Not Determined

IV. TASK 3 - ANALYSIS OF PRODUCTS

The results of steam pretreatment experiments at 300 and 350°C (4000 psig) are summarized in Tables IV-1 and IV-2, respectively. These tables include results from TG-FTIR analysis of the solid residues, GC analysis of the pretreatment off gases and solvent extraction of the residues with pyridine. The results to date indicate that the steam pretreatment, under these conditions, has a rather profound effect on the structure of the coal. The TG-FTIR analysis of residues produced at both 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. IV-1. However, the significant increase in tar does not persist at long pretreatment times. There is a nearly monotonic decrease in the CO₂ yield and a monotonic increase in the pyridine extractables (see Tables IV-1 and IV-2) with increasing pretreatment time. The pyridine extractability of the water pretreated coal increases by more than a factor of two. The decrease in the CO₂ evolution results primarily from a reduction in the organic CO₂. These changes are delayed and attenuated as the temperature is reduced. The results for the yield of tar, CO₂ and pyridine extractables suggest that steam pretreatment is similar to a geological aging of the coal, at least at short pretreatment times. 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.

The trend for CO production from TG-FTIR analysis was similar to that for the tar in that it goes through a maximum. The CH₄ production from TG-FTIR analysis generally increased with increasing pretreatment time, although most of the increase occurred at relatively short times. Virtually no CH₄ was produced directly by the steam pretreatment step.

One possibility is that the water hydrolyzes the carboxyl groups to form methyl and OH groups. This is consistent with the small net decrease in CO₂ production and small net increase in CH₄ production when the gas yields from TG-FTIR analysis and the subsequent pretreatment steps are combined. FT-IR analysis of the solid residues will help to confirm this.

The material extracted in the water phase during pretreatment appears to have some unusual properties. After about 10 minutes, the extract has some color, but this disappears for pretreatments longer than 10 minutes. However, if the material is left standing in air, it does change color. The odor of the extracted material and the fact that it is water soluble suggests a structure similar to lignin. The ash content of this material is much higher than the original coal (- 20% vs - 10%).

Despite the - 5-10% weight loss by water extraction which is observed, at long pretreatment times there is a net weight gain of about 15% in the residue when compared to the

TABLE IV-1
RESULTS OF ANALYSES ON RESIDUES FROM STEAM PRETREATMENT
OF ZAP LIGNITE AT 350°C
(Yields Expressed using As-Received Basis)

Exp #	Time (min)	Tar ^a	CO ₂ ^a	CO ₂ ^b	CO ^a	CO ^b	CH ₄ ^a	H ₂ O ^a	Pyr Sol	H ₂ O Sol	Ash ^a
—	0	6.2	4.8	—	8.4	—	1.1	7.6	2.2	—	10.9
W10	5	9.1	4.0	0.12	9.9	0.0	1.6	8.5	2.7	1.7	8.2
W9	10	10.2	3.6	0.32	9.8	0.0	1.4	5.0	5.8	—	8.0
W5	10	11.7	3.3	0.79	10.4	1.7	1.5	5.8	16.2	2.4	9.0
W6	20	11.6	3.2	1.21	10.5	1.6	1.5	3.9	8.2	3.4	3.3
W7	60	9.9	3.0	1.12	10.2	0.7	1.7	3.0	9.1	3.3	3.0
W11	120	8.0	2.1	0.55	8.2	0.0	1.9	4.5	6.7	—	12.6
W2	120	6.2	2.4	—	6.3	—	1.6	—	7.7	—	14.3
W8	180	6.5	1.7	0.50	6.6	0.0	1.6	2.3	10.9	3.1	20.6

Notes:

- a) TG-FTIR Analysis Values
b) From GC Analysis of Steam Pretreatment Off-Gases

TABLE IV-2
RESULTS OF ANALYSES ON RESIDUES FROM STEAM PRETREATMENT
OF ZAP LIGNITE AT 300°C

(Yields Expressed using As-Received Basis)

Exp #	Time (min)	Tar ^a	CO ₂ ^a	CO ₂ ^b	CO ^a	CO ^b	CH ₄ ^a	H ₂ O ^a	Pyr Sol	H ₂ O Sol	Ash ^a
—	0	6.2	4.8	—	8.4	—	1.1	7.6	2.2	—	10.9
W13	10	9.7	4.1	0.12	9.1	0.0	1.5	7.0	1.9	1.0	7.4
W14	20	8.8	3.7	1.02	11.0	1.0	1.2	5.4	5.6	2.1	8.6
W15	60	10.3	3.3	2.38	11.6	3.7	1.6	6.8	6.7	2.5	7.6
W12	120	10.2	3.4	1.38	11.5	0.5	1.8	5.0	7.4	3.3	7.1
W16	180	9.8	1.9	0.97	7.8	0.0	0.9	5.3	—	4.5	10.6
W3	300	6.3	3.2	2.64	6.9	0.6	1.6	8.3	8.6	—	13.2

Notes:

- a) TG-FTIR Analysis Values
b) From GC Analysis of Steam Pretreatment

Figure IV-1. Tar Yield Data from TG-FTIR Analysis of Zap Lignite Coal which has been Steam Pretreated at 350°C, 4000 psig.

starting coal.

Some unusual trends were seen in the amount of ash in the steam pretreated residues. At 350°C, the ash content appeared to go through a minimum with pretreatment times between 20 minutes and 1 hour, while at 300°C, the minimum is observed at times between 60 and 180 minutes. This could be due to ash segregation in the sample rather than a true reduction in ash content. This will be the subject of further investigations using SEM/x-ray analysis to track the total ash content as well as changes in individual components.

Liquefaction experiments were done on the steam pretreated residues. The preliminary results suggest only modest improvements in the liquefaction yields can be achieved with the pretreated samples produced to date. The results will be reported in the Topical Report.

V. TASK 4 - RATES, MECHANISMS AND MODELING

No work scheduled.

VI. PLANS FOR THE FOURTH QUARTER

- Do steam pretreatment of Zap lignite at lower temperatures (250°C).
- Do steam pretreatment experiments with Wyodak coal.
- Do additional liquefaction experiments with steam pretreated residues.
- Do additional analyses (FT-IR, FIMS) of steam pretreated residues.

END

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