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DOE/PC/89878--T5

DE92 003090

FUNDAMENTAL STUDIES OF WATER PRETREATMENT OF COAL

Second Quarterly Report

#523070-06

For the Period

January 1, 1990 - March 31, 1990

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Work Performed Under Contract No. DE-AC22-89PC89878

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ABSTRACT

The construction of the nitrogen glove box system for the sample preparation was completed. This includes air locks for sample introduction and a thermoelectric heating/cooling system for preparing vacuum-dried samples. This glove box will allow us to study water pretreatment without the complicating effects of sample weathering. The reactor for doing the preliquefaction experiments in either water or steam was also completed during the past quarter. The water feed system and pressure control systems still need to be connected in order to start the experimental work.

Samples of ion-exchanged coals (Zap, Wyodak, Illinois No. 6) have been prepared using an apparatus that permits this procedure to be done in the absence of air. The method used is that of Hengel and Walker (1984) where the coal is treated with ammonium acetate. In this case, the alkali cations are exchanged with ammonium ions (NH_4^+). Since the effect of cations is being studied under the current program, it was decided to further investigate how the methods of ion-exchange will affect the preliquefaction chemistry. Consequently, the samples of Zap lignite ion-exchanged with ammonium ion by the Hengel and Walker technique have been subjected to further treatment by a mild acid wash, and then changed back to the ion-exchanged form with ammonium ion. Similarly, a second sample of ion-exchanged Zap was exchanged with calcium and then changed back to the ion-exchanged form with ammonium ion. The samples from these various treatments were characterized by TG-FTIR and SEM/x-ray analysis.

For the modified Zap lignites in this series, the general trend is that the tar yield is positively correlated with the early H_2O yield and negatively correlated with the early CO_2 yield and the calcium content. There are notable exceptions, such as the methylated Zap which has a very low early H_2O yield. In the case of the early H_2O yields, the correlation is most apparent by considering only the results for the raw Zap and the ion-exchanged series.

"FUNDAMENTAL STUDIES OF WATER PRETREATMENT OF COAL"
SECOND QUARTERLY REPORT FOR 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 Second Quarter

The construction of the nitrogen glove box system for the sample preparation was completed. This includes air locks for sample introduction and a thermoelectric heating/cooling system for preparing vacuum-dried samples. This glove box will allow us to study water pretreatment without the complicating effects of sample weathering. The reactor for doing the preliquefaction experiments in either water or steam was also completed during the past quarter. The water feed system and pressure control systems still need to be connected in order to start the experimental work.

Samples of ion-exchanged coals (Zap, Wyodak, Illinois No. 6) have been prepared using an apparatus that permits this procedure to be done in the absence of air. The method used is that of Hengel and Walker (1984) where the coal is treated with ammonium acetate. In this

case, the alkali cations are exchanged with ammonium ions (NH_4^+). Since the effect of cations is being studied under the current program, it was decided to further investigate how the methods of ion-exchange will affect the preliquefaction chemistry. Consequently, the samples of Zap lignite ion-exchanged with ammonium ion by the Hengel and Walker technique have been subjected to further treatment by a mild acid wash, and then changed back to the ion-exchanged form with ammonium ion. Similarly, a second sample of ion-exchanged Zap was exchanged with calcium and then changed back to the ion-exchanged form with ammonium ion. The samples from these various treatments were characterized by TG-FTIR and SEM/x-ray analysis.

For the modified Zap lignites in this series, the general trend is that the tar yield is positively correlated with the early H_2O yield and negatively correlated with the early CO_2 yield and the calcium content. There are notable exceptions, such as the methylated Zap which has a very low early H_2O yield. In the case of the early H_2O yields, the correlation is most apparent by considering only the results for the raw Zap and the ion-exchanged series.

It also appears that the acid form is preferable to the ammonium form which is preferable to the calcium form. However, this series does not allow one to completely separate out the various effects on tar yield (which relates directly to liquefaction yields based on results of our other program). We were also not able to achieve complete reversibility of the ion-exchange procedure. During the next quarter, we plan to repeat the Zap series but will start with the demineralized Zap instead of the ion-exchanged Zap. We believe that this will make a better "standard" coal for assessing the effects of cation type.

II. TASK 1 - PROJECT PLANNING AND SAMPLE SELECTION

The construction of the nitrogen glove box system for the sample preparation was completed. This includes air locks for sample introduction and a thermoelectric heating/cooling system for preparing vacuum-dried samples. This glove box will allow us to study water pretreatment without the complicating effects of sample weathering.

The reactor for doing the preliquefaction experiments in either water or steam was completed during the past quarter. The water feed system and pressure control systems need to be connected in order to start the experimental work.

III. TASK 2 - EXPERIMENTS ON THE WATER PRETREATMENT STAGE

Samples of ion-exchanged coals (Zap, Wyodak, Illinois No. 6) have been prepared using an apparatus that permits this procedure to be done in the absence of air. The method used is that of Hengel and Walker (1984) where the coal is treated with ammonium acetate. In this case, the cations are exchanged with ammonium ions. In our other program (Fundamental Studies of Retrograde Reactions in Coal Liquefaction, Contract No. DE-AC22-88PC88814), samples prepared with the Hengel and Walker ion-exchange method did not show as much of a reduction in retrograde reactions when compared to demineralized or methylated samples. Since the effect of cations is being studied under the current program, it was decided to further investigate how the methods of ion-exchange will affect the preliquefaction chemistry. Consequently, the samples of Zap lignite ion-exchanged with ammonium ion by the Hengel and Walker technique have been subjected to further treatment by a mild acid wash, and then changed back to the ion-exchanged form with ammonium ion. Similarly, a second sample of ion-exchanged Zap was exchanged with calcium and then changed back to the ion-exchanged form with ammonium ion. This will allow us to determine whether the treatment or the form of the cation is most important. At each stage of preparation, the samples are being analyzed by TG-FTIR and SEM/x-ray analysis to monitor the changes. The samples will be subjected to the steam or water pretreatments under the current program. Portions of each sample are being saved to do liquefaction experiments under our other program.

The initial ion-exchange procedure has been completed on all three of the coals. Only one (Zap lignite) has been subjected to the complete sequence of other treatments so far. The samples from these various treatments were characterized by TG-FTIR and SEM/x-ray analysis. The results are given in Table III-1, along with the results for modified Zap samples generated in our other liquefaction program (Fundamental Studies of Retrograde Reactions in Coal Liquefaction, Contract No. DE-AC22-88PC88814).

For the coals in this series, the general trend is that the tar yield is positively correlated with early H_2O yield and negatively correlated with early CO_2 yield and the calcium content. There are notable exceptions, such as the methylated Zap which has a very low early H_2O yield. In the case of early H_2O yield, the correlation is most apparent by examining only the results for the raw Zap and the ion-exchanged series, which are plotted in Figures III-1 and III-2.

The positive correlation of tar with early pyrolysis water was somewhat surprising since it is opposite to the trend for the coals as a rank series, i.e., coals which produce high water generally have low tar. However, these coals also have high CO_2 and it appears that formation

TABLE III-1 - CHARACTERIZATION OF MODIFIED ZAP COALS BY TG-FTIR AND SEM/X-RAY

(As-Received Basis)

Sample	CO ₂ Yield @ 350°C	H ₂ O Yield @ 350°C*	Tar Yield (Total)	Ca Content
Raw Zap	1.66	1.30	5.5	1.09
Old Ion-Ex Zap (NH ₄ ⁺)	2.33	1.83	8.0	0.06
New Ion-Ex Zap (NH ₄ ⁺)	1.45	2.13	11.0	ND
NH ₄ ⁺ → H ⁺	1.33	2.42	16.0	0.02
NH ₄ ⁺ → H ⁺ → NH ₄ ⁺	1.30	2.23	14.0	0.01
NH ₄ ⁺ → Ca ⁺⁺	1.33	2.18	11.0	1.90
NH ₄ ⁺ → Ca ⁺⁺ → NH ₄ ⁺	1.42	2.34	11.5	0.33
Demineralized Zap	1.38	1.49	15.0	0.37
Methylated Zap	0.76	0.81	24.0	0.02

* H₂O yield at 175°C has been subtracted out to correct for moisture.

ND = Not Determined.

Figure III-1. Correlation of Pyrolysis Tar Yield with Early CO₂ Yield from TG-FTIR Analysis of Raw and Treated Zap Coals. All Yields are on an As-Received Basis.

Figure III-2. Correlation of Pyrolysis Tar Yield with Early H₂O Yield from TG-FTIR Analysis of Raw and Treated Zap Coals. All Yields are on an As-Received Basis.

of water is preferred in order to reduce crosslinking reactions. The trends of pyrolysis tar versus early H_2O and CO_2 yields for coals prepared previously are examined in more detail in the Sixth Quarterly Report for the program on Fundamental Studies of Retrograde Reactions in Coal Liquefaction.

It also appears from the results in Table III-1 that the acid form is preferable to the ammonium form which is preferable to the calcium form. However, this series does not allow one to completely separate out the various effects on tar yield (which relates directly to liquefaction yields based on results of our other program). We were also not able to achieve complete reversibility of the ion-exchange procedure. During the next quarter, we plan to repeat the Zap series but will start with the demineralized Zap instead of the ion-exchanged Zap. We believe that this will make a better "standard" coal.

IV. TASK 3 - ANALYSIS OF PRODUCTS

No work scheduled.

V. TASK 4 - RATES, MECHANISMS AND MODELING

No work scheduled.

VI. PLANS FOR THE THIRD QUARTER

- Complete preparation of experimental facilities and samples.
- Do additional variations on ion-exchange procedure.
- Begin experiments on water pretreatment of coal.

REFERENCES

Hengel, T.D. and Walker, P.L., Fuel, **63**, 1214, (1984).

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