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INTEGRATION OF ADVANCED PREPARATION WITH COAL
LIQUEFACTION

Third Quarterly Technical Progress Report for the Period
April 1—June 30, 1984

By
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July 24, 1984

Work Performed Under Contract No. AC22-83PC60045

Battelle
Columbus, Ohio

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THIRD QUARTERLY TECHNICAL PROGRESS REPORT

on

INTEGRATION OF ADVANCED
PREPARATION WITH COAL LIQUEFACTION

to

U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER

Contract No. DE-AC22-83PC60045

Battelle No. G-8635

Period Covered:

April 1, 1984 - June 30, 1984

July 24, 1984

by

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ABSTRACT

The objective of this work is to explore the technoeconomic feasibility of a series of unit operations involving: (1) wet grinding of coal in water, (2) removal of chlorine and sodium, release of undesirable mineral matter, and chemical incorporation, if needed, of a disposable liquefaction catalyst in coal via hot water treatment (3) oil agglomeration to dewater and deash coal while retaining most of the pyrite, and (4) solvent drying of coal agglomerates to eliminate oxidation of coal, improve coal liquefaction reactivity, save energy and prepare the coal/solvent slurry for liquefaction.

Hot-water treatment does not cause a significant increase in surface area. More than 2 percent of the carbon in Illinois #6 coal can be converted to carbon dioxide gas by hot-water treatment. The addition of ferric hydroxide appears to result in a significant increase in the liquefaction conversion of Illinois #6 coal to THF solubles. The removal of sodium from Wyodak coal occurs in less than fifteen minutes at 200°C. Sodium removal levels decrease from 300 ppm sodium left in the coal at 100°C to 100 ppm sodium left in the coal at 300°C. Very large conversions apparently occur with Wyodak coal when ferric hydroxide is added as a catalyst.

Blends of product oil and recycle solvent from ITSL processing of Wyodak coal have been used in the oil agglomeration of Wyodak coal. Agglomerated Wyodak coal moisture levels of 36 percent are the best achieved so far. Moisture levels of 50 percent can be obtained by vacuum filtration of agglomerated coal. Higher agitation speed and lower solids content in the slurry both increase the rate of oil agglomeration. A higher boiling point agglomerating oil improves moisture rejection but decreases ash rejection with Illinois #6 coal.

Foam volume generated during solvent drying goes through a maximum at about 15 percent moisture in the agglomerated coal. Liquefaction conversion is improved when oil agglomerated Illinois #6 coal is partially dried in a

vacuum oven before solvent drying. Comparison of a standard sample of oil agglomerated Illinois #6 coal dried in a vacuum oven under air or nitrogen or solvent dried did not show any trend as a function of drying method.

An apparatus capable of running five microautoclaves simultaneously has been designed and constructed. The autoclaves are shaken along the long axis to insure good mixing and pressure and temperature can be monitored in each autoclave during the run. Reproducibility experiments indicate that the standard deviation on the conversion to THF solubles is about 2.5 percent. The standard deviations in conversions to preasphaltenes and asphaltenes are much higher. A five-autoclave experiment has confirmed earlier results which indicate that wet grinding and hot-water treatment have little effect on conversion to THF solubles but that oil agglomeration followed by drying in a vacuum oven causes a large increase and oil agglomeration followed by solvent drying causes a significant but smaller increase in conversion.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	i
INTRODUCTION.....	1
OBJECTIVE.....	1
TECHNICAL APPROACH.....	2
Crushing, Washing and Grinding.....	2
Chlorine and Alkali Removal.....	2
Mineral Matter Removal/Pyrite Retention.....	2
Solvent Drying.....	2
DATA RECORDS.....	3
PROGRESS.....	3
Task 3. Hot Water Treatment to Remove Chlorine/ Sodium and Add Catalysts.....	4
Effect of Hot-Water Treatment on Surface Area.....	4
Carbon Losses During Hot-Water Treatment.....	4
Attempt to Combine Chlorine Removal and Oil Agglomeration Steps.....	5
Effect of Adding Catalysts During Hot-Water Treatment.....	5
Wyodak Subbituminous Coal Studies.....	6
Effect of Time on Sodium Removal.....	6
Effect of Hot-Water Treatment Temperature on Sodium Removal.....	6
Effect of Catalyst Addition During Hot-Water Treatment on Liquefaction Reactivity of Wyodak Coal.....	6
Future Work in Hot-Water Treatment.....	9
Task 4. Oil Agglomeration.....	9
Effect of Agglomeration Oil Blend Composition on Ash Rejection.....	9
Effect of Percent Oil on Water Rejection in Wyodak Coal...	12
Effect of Agitation Speed.....	12
Effect of Cut of Agglomeration Oil.....	12
Future Work.....	14
Task 5. Solvent Drying.....	14
Objective.....	14
Development of Solvent Drying Procedure.....	14

TABLE OF CONTENTS (Cont'd.)

	<u>Page</u>
Maximum Foam Volume Measurements.....	17
Water Content Measurements.....	19
Effect of Solvent Drying on Liquefaction Conversions.....	19
Effect of Drying Conditions on Liquefaction Conversions...	20
Future Work.....	22
Task 6. Liquefaction Performance	22
Objective.....	22
Design and Construction of a Five-Autoclave Liquefaction Apparatus.....	22
Results of Five-Autoclave Reproducibility Experiments.....	24
Effect of Cumulative Pretreatment Steps on Conversion of MAF Coal to THF Solubles.....	26
Future Work.....	26
REFERENCES.....	29

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Columbus Laboratories

July 24, 1984

INTRODUCTION

Coal liquids are potential future replacements for oil. However, to be competitive, liquefaction must be accomplished economically. One way of improving coal liquefaction economics is to prepare coal so that its liquefaction performance is enhanced. This requires an understanding of the effects of coal properties on liquefaction, which can lead to optimum coal specification, and how to prepare coal to meet these specifications.

OBJECTIVE

The objective of this work is to explore the technoeconomic feasibility of a series of unit operations involving: (1) wet grinding of coal in water, (2) removal of chlorine and sodium, release of undesirable mineral matter, and chemical incorporation, if needed, of a disposable liquefaction catalyst in coal via hot water treatment (3) oil agglomeration to dewater and deash coal while retaining most of the pyrite, and

(4) solvent drying of coal agglomerates to eliminate oxidation of coal, improve coal liquefaction reactivity, save energy and prepare the coal/solvent slurry for liquefaction.

TECHNICAL APPROACH

Crushing, Washing and Grinding

After cleaning in a jig, minus 2-inch coal is ground further for chlorine removal, extensive mineral matter removal, and coal liquefaction. Wet grinding in water is employed to minimize oxidation of the coal and to further process fine coal through the aqueous chlorine removal step. This will reduce the cost of grinding, minimize excessive fines generation due to better control of classification and also minimize oxidation.

Chlorine and Alkali Removal

The process employs water at elevated temperatures, 90-275°C, possibly in the presence of additives, to efficiently extract chlorine and sodium from coal. The use of elevated temperatures apparently opens up the structure of coal so that water and additives can penetrate the coal. Finely disseminated ash is released in the process. If disposable catalysts are to be used, they can be introduced into the coal structure very effectively during hot water treatment.

Mineral Matter Removal/Pyrite Retention

Oil agglomeration is used to reject as much of the mineral matter as possible while retaining pyrite. Oil agglomeration also lowers the water content of the coal. A portion of the recycle solvent or the product liquid fraction is used as the agglomerating solvent.

Solvent Drying

The coal agglomerates containing 10-20 percent external moisture and 10-40 percent oil are dried with hot solvent. Foaming in the slurry-

mix tank must be investigated. The use of hot solvent to dry coal may also increase coal-solvent contact, resulting in more rapid liquefaction. The use of hot solvent helps conserve process heat.

DATA RECORDS

The data upon which this report is based are recorded in the following Laboratory Record Books.

<u>Task</u>	<u>Record Book</u>
2	39214
3	39446
4	39443
5	39516
6	39214,39785

PROGRESS

The program is divided into seven tasks.

- Task 1. Project Work Plan
- Task 2. Material Selection, Preparation and Characterization
- Task 3. Chlorine Removal and Minor Elements Removal/Addition
- Task 4. Oil Agglomeration
- Task 5. Solvent Drying
- Task 6. Liquefaction Performance
- Task 7. Preliminary Technoeconomic Evaluation

The progress on each active task during the past reporting period is discussed in detail below.

Task 3. Hot Water Treatment to Remove Chlorine/Sodium and Add Catalysts

A variety of experiments have been done to increase our understanding of the water treatment process with Illinois #6 bituminous coal.

Effect of Hot-Water Treatment on Surface Area

Illinois #6 coal (-100 x 0 mesh) in a 3:1 water slurry with ~ 4 percent (by weight of coal) added cobalt acetate was treated in a stirred autoclave for 0.5 and 4.5 hours at 200°C. Surface areas measured before and after were < 27.1 m²/g and 25.0 and 25.1 m²/g, respectively. Thus, it does not appear that hot-water treatment increases the surface area significantly as originally hypothesized.

Carbon Losses During Hot-Water Treatment

The water treatment step seems to result in the loss of a significant amount of carbon from the coal. Two attempts were made to locate the carbon in the gas above the slurry or in the water after filtration. Analysis of gas samples taken from above the slurry at the end of hot water treatments with Illinois #6 coal for 60 minutes at 150°C and 4.5 hours at 200°C showed mostly CO₂ but this accounted for only 0.4 and 2.2 weight percent of the total carbon respectively.

Total organic carbon in the filtered water from treatment of Wyodak (Upper Seam) subbituminous coal at 250°C for 30 minutes accounted for only 0.0027 weight percent of the total carbon in the coal. A significant additional location for missing carbon may be in the water as sodium carbonate or bicarbonate, formed by trapping CO₂ with the sodium ions released from the Wyodak coal during hot water treatment. This possibility will also be studied.

Attempt to Combine Chlorine Removal and Oil Agglomeration Steps

Two attempts were made to combine chloride removal and oil agglomeration by adding +650°F Illinois #6 coal product oil from the ITSL pilot plant to the hot water treatment step. In two experiments at 3:1 water-to-coal, 200°C for 30 minutes, 20 percent and 40 percent (by weight of coal) of heavy oil was added and the autoclave stirrer was run at top speed (~ 1000 rpm). The chlorine removal was good. In both cases, chlorine levels below 200 ppm were achieved but the coal did not agglomerate. It is likely that the mixing action was not sufficient to disperse the immiscible oil in the water-coal slurry.

Effect of Adding Catalysts During Hot-Water Treatment

Illinois #6 coal (-100 x 0 mesh size) was treated at 3:1 water-to-coal, for 30 minutes at 200°C with 4.2 weight percent of cobalt acetate, 4.2 weight percent of cobalt acetate plus 1.0 weight percent sodium hydroxide, and 0.03 weight percent of ferric hydroxide. The treated coals were filtered to remove water, dried in a vacuum oven at room temperature under a nitrogen purge and tested for liquefaction reactivity using the microautoclave techniques described previously⁽¹⁾. The conversions of MAF coal to THF solubles are listed in Table 1. The use of cobalt acetate has a positive effect on the conversion. Adding sodium hydroxide does not have a significant effect. The use of ferric hydroxide on Illinois #6 coal has not been tested yet.

TABLE 1. RESULTS OF CATALYST ADDITION DURING HOT WATER TREATMENT ON THE MAF CONVERSION OF -100 x 0 MESH, DRIED ILLINOIS #6 COAL TO THF SOLUBLES BY LIQUEFACTION AT 427°C, 5 MINUTES, 2:1 SOLVENT/COAL UNDER 1000 psi (ROOM TEMP) HYDROGEN

Treatment Conditions	% MAF Conversion to THF Solubles
None	80.3, 79.9
Cobalt Acetate/NaOH	85.9
Cobalt Acetate	86.1

Wyodak Subbituminous Coal Studies

Upper seam Wyodak subbituminous coal has been selected as the second coal for study in this program. Several experiments with this coal, after wet grinding in a ball mill to -100 x 0 mesh and storage in a slurry under water, have been completed.

The primary objective of hot water treatment of subbituminous coal is alkali removal and catalyst addition.

Effect of Time on Sodium Removal

Wyodak coal (-100 mesh) was treated at 200°C in a 2:1 water/coal slurry and samples were taken at 5, 10, 30 and 60 minutes and analyzed for water and sodium after removal of bulk water by filtration and washing with deionized water to remove sodium in the entrained water in the cake. The results in Figure 1 show that all of the sodium which is removed is gone in 5 minutes. This presumably is not sodium which can be removed at room temperature since the Wyodak coal was wet ground prior to treatment. However, the wet ground cake which contains ~ 60 percent water was not washed prior to treatment.

Effect of Hot-Water Treatment Temperature on Sodium Removal

The effect of hot water treatment temperature when Wyodak coal is treated at 3:1 water-to-coal ratio for 30 minutes is shown in Figure 2. Sodium levels decrease by a factor of three from 100°C to 250°C. These coals were also washed after treatment with deionized water to remove any entrained sodium in the water in the filter cake.

Effect of Catalyst Addition During Hot-Water Treatment on Liquefaction Reactivity of Wyodak Coal

Initial experiments with catalyst addition to Wyodak coal were done using $\text{Fe}(\text{OH})_3$, prepared before use by mixing FeCl_3 and NaOH , filtering, and

FIGURE 1. SODIUM REMOVAL FROM WET GROUND WYODAK COAL
VS TIME BY HOT-WATER TREATMENT AT 200°C

FIGURE 2. EFFECT OF HOT-WATER TREATMENT TEMPERATURE ON SODIUM REMOVAL FROM WYODAK COAL

washing to remove NaCl. The resulting wet filter cake was weighed and added to the coal-water slurry.

Two Wyodak coals were hot-water-treated with added $\text{Fe}(\text{OH})_3$ (using 0.44 and 4.4 percent of dry coal weight) and liquified in the microautoclave. The results of conversion of MAF coal to THF solubles are compared in Figure 3 with wet ground Wyodak coal, not dried and liquified under the same conditions. There is a very impressive increase in conversion with added $\text{Fe}(\text{OH})_3$, even at low catalyst levels. However, some of the increase may be due to the lower moisture content of the dried, catalyst-treated Wyodak coals since our recent work has shown that coal conversion decreases with increasing moisture content.

Future Work in Hot-Water Treatment

The catalyst addition results will be expanded to include sodium molybdate, pyrite and H_2S . The effectiveness and efficiency of adding catalysts in this step will be examined. The effect of hot-water treatment on Ca, O and Na levels in Wyodak coal will be studied and carbon loss and CO_2 formation will be monitored. Complete mass and elemental balances will be done on this step.

Task 4. Oil Agglomeration

The work this quarter has been done with Wyodak Upper Seam coal and Wyodak -650°F product and +650°F recycle solvent or a blend of the two. Early tests showed that either Wyodak oil by itself did not agglomerate the Wyodak coal. Blends of the Wyodak oils were found to work best. Blends of product oil and recycle solvent of 25/75, 50/50 or 75/25 agglomerate Wyodak coal equally well.

Effect of Agglomeration Oil Blend Composition on Ash Rejection

Figure 4 shows that there is very little effect of the blend composition on the amount of ash retained in the coal. The recycle solvent is not a distillate fraction but contains ash from the ASDA step in the

FIGURE 3. LIQUEFACTION CONVERSION OF WYODAK HOT-WATER TREATED COALS WITH ADDED $\text{Fe}(\text{OH})_3$ COMPARED TO UNTREATED COAL

FIGURE 4. EFFECT OF OIL BLEND ON ASH CONTENT OF
AGGLOMERATED WYODAK COAL

ITSL process. The ash in the oil adds more ash to the coal than it rejects. We are in the process of obtaining a 650-850°F distillate cut from ITSL processing of Wyodak coal. The poor ash rejection could be the result of the ash being very finely dispersed in the Wyodak coal. A sample of the Wyodak coal has been wet ground to -100 mesh, dried and sent to R. Killmeyer at PETC for float-sink analysis to see how much ash can be removed.

Effect of Percent Oil on Water Rejection in Wyodak Coal

The moisture remaining in the Wyodak product varies from 36 and 43 percent with little or no effect due to the amount of oil used to perform the agglomeration, as shown in Figure 5. The amount of oil varied from 24 to 53 weight percent of the dry coal. The agglomeration step does reduce the moisture content of the coal from 50 percent, which it contains when it is filtered. About 24 percent oil appears to be the minimum amount that can be used and still achieve good agglomeration on untreated Wyodak coal.

Effect of Agitation Speed

The effect of agitation speed in the blender and of solids concentration on the rate of agglomeration were determined using Wyodak coal and a 50/50 blend of Wyodak oils at 25 weight percent oil. At ten percent solids content and high speed (13,000 rpm) the time to agglomerate was 3 minutes 42 seconds and at low speed (8,000 rpm) it was 5 minutes 49 seconds. At 20 percent solids the high speed time to agglomerate was 7 minutes 15 seconds and at low speed 9 minutes 40 seconds. More work is planned on these variables using different amounts of oil.

Effect of Cut of Agglomerating Oil

To determine the effect of different cuts of oil on oil agglomeration, tests were performed using Illinois #6 coal and six different distillation fractions of Illinois #6 oil. All of the runs were done at 90°C, 10 percent solids concentration and about 11 weight percent oil. Previous studies have shown that the lower boiling point oils contain more hydrocarbons and fewer heteroatoms, and that the hydrogen/carbon ratio increases with decreasing boiling point⁽³⁾. Therefore, the lower boiling

FIGURE 5. EFFECT OF CONCENTRATION OF OIL USED TO AGGLOMERATE WYODAK COAL ON WATER REJECTION

point cuts should be more hydrophilic and better agglomeration solvents. Figure 6 shows the effect of the cut of oil on the product moisture. The heavier cuts of oil give a slightly lower moisture content. Figure 7 shows the effect of the cut of oil on the ash content of the coal, on an oil and moisture free (OMF) basis. The lighter oil does a better job of rejecting ash. These results are similar to those previously reported by others.⁽⁴⁾

Future Work

Additional work will be done on the effects of variables on oil agglomeration, including the effects of agitation speed, temperature, properties of agglomerating oil and mesh size of the wet ground coal. Hot-water treated Wyodak coal will be tested to see if oil agglomeration properties are improved. The effect on liquefaction and efficiency of adding catalysts during the oil agglomeration step will also be studied. A 650-850°F distillate cut from ITSL processing of Wyodak coal will be tried as the agglomerating oil.

Task 5. Solvent Drying

Objective

The first purpose of this task is to demonstrate the process of mixing wet coal with hot solvent, thereby producing a slurry suitable as a feed for the liquefaction preheater. In the course of pursuing this objective, observations of foaming and viscosity are to be made. A second purpose is to prepare pretreatment samples for autoclave liquefaction.

Development of Solvent Drying Procedure

The apparatus for solvent drying was shown in the last report.⁽⁵⁾ It allows for mixing hot solvent (343 C) with cold coal under a protective atmosphere, thereby driving off most of the water from the coal. The apparatus has been used for solvent drying many samples of Illinois #6 coal.

FIGURE 6. EFFECT OF BOILING POINT OF 50°C FRACTIONS OF AGGLOMERATING OIL ON MOISTURE CONTENT OF ILLINOIS #6 COAL AGGLOMERATES

FIGURE EFFECT OF BOILING POINT OF 50 °C FRACTIONS OF AGGLOMERATING OIL ON ASH CONTENT OF ILLINOIS #6 OIL AGGLOMERATES

The expected final temperature for adiabatic mixing has been calculated and an attempt has been made to preheat the apparatus to that temperature. The final observed temperature has often been somewhat lower than this calculated temperature. The reasons are probably related to the positioning of the thermocouple on the outside of the apparatus, to the changes in heat transfer as the sample is introduced, and to the unknown temperature changes as the solvent is introduced. The sample mass is small relative to the mass of the apparatus. Nevertheless, approximately adiabatic conditions are maintained.

It has been found that many of the products of the oil agglomeration procedure have been high in moisture and oil. The enthalpy of the hot solvent has been inadequate for complete evaporative drying. Two procedural modifications have been made. Provision has been made to preheat the coal samples to about 80°C, thereby providing a little more heat for vaporizing water. In cases where there was still not enough heat, the heater wrapped on the mixing vessel has been turned up so that additional heating is provided electrically. This will be necessary routinely for the Wyodak coal.

Maximum Foam Volume Measurements

While the mixing proceeds, the volume of foam is observed. The maximum volume occurs very shortly after adding solvent. The maximum volume is shown for several experiments in Figure 8. The mixing temperature depends primarily on the water content. Therefore, the samples of low water content were mixed at the highest temperatures. The volume of foam depends on both the water content and on the temperature. It is not unexpected that there should be a maximum at about 15 percent water. At higher water levels, the temperature drops because of the heat of vaporization to a little over 100°C, where the vaporization and resultant foaming are slow. The experiments represented by circles were conducted with preheated coal samples. This procedure made it possible to dry coals with slightly higher moisture levels. The crosses represent experiments in which auxiliary electrical heat was used. It is not surprising that these should show a lot of scatter, since conditions, including especially the temperature, varied a lot.

- Dried at adiabatic temperature. Cold coal.
- Dried at adiabatic temperature. Preheated coal.
- × Dried with additional heat.

FIGURE 8. MAXIMUM FOAM VOLUME IN SOLVENT DRYING EXPERIMENTS

The solvent-dried mixtures typically retain less than 1 percent water. The amount of water varies with the temperature and the duration of the hot mixing.

Water Content Measurements

There has been some uncertainty in determining the water content of the agglomerated and solvent-dried mixtures of coal and oil or coal and solvent. The standard water analysis by weight loss at 105°C is suspect for two reasons. The oil, especially if it is a heavy oil, may block the pores of the coal and prevent the water from vaporizing. This leads to a too-low determination of water. The second problem is that oil may be lost by vaporization, leading to a too-high value. It has been found that these samples do continue to lose weight after several hours in the oven.

In order to resolve these problems, we have investigated the Karl Fischer method of water analysis. This involves a reaction of iodine and SO_2 in a pyridine solvent. The end point is detected by observing changes in electrolytic conduction. The method has been found to be satisfactory for the present samples although a small correction must be made for coal and solvent since basic functional groups and aromatic nitrogen compounds can interfere. It is possible that the Karl Fischer results may be a little low because of incomplete extraction of water from the pores of the coal.

In general, the analyses are in agreement but the oven-dried results are sometimes higher, sometimes lower than the Karl Fischer results. The latter are considered more reliable.

Effect of Solvent Drying on Liquefaction Conversions

Solvent drying had been expected to cause a significant increase in liquefaction reactivity as a result of improved contact between solvent and coal when water was displaced from the pores of the coal during drying and the solvent, in close proximity, could then enter the pores of the coal. However, previously reported work from this program⁽⁵⁾ has generally shown a decrease in reactivity when an oil agglomerated sample is solvent dried versus samples dried in a vacuum oven near room temperature with a nitrogen

purge to avoid oxidation. It is known from work on an earlier program⁽²⁾ that the lighter process derived oil used for agglomeration is a better liquefaction solvent than the heavier recycle solvent used in solvent drying. Apparently, this solvent is able to enter the coal pores when oil agglomeration is followed by vacuum drying in the absence of the heavier recycle solvent.

Further, when the oil agglomerated samples were dried to various moisture contents before solvent drying, the resulting liquefaction performance again increased with extent of drying in the presence of agglomerating oil. A minimum at about 15 percent water was observed, as shown in Figure 9. Beyond 15 percent water, the conversion increased with increasing water content. These samples were solvent dried under non-adiabatic conditions in order to remove all of the moisture. The results may suggest the optimum method for utilizing solvent drying in the overall coal preparation process.

Effect of Drying Conditions on Liquefaction Conversions

A series of experiments was done to investigate the effect of different levels of drying, drying conditions (in air or nitrogen) and drying techniques (in a vacuum oven or solvent drying) on liquefaction conversions.

A single large batch of oil agglomerated Illinois #6 -100 x 0 mesh coal was prepared using the +650°F fraction of the Illinois #6 product oil, a -650°F distillate from the ITSL process. It contained 19.8 percent water, 6.1 percent ash, 15.2 percent oil and 58.9 percent MAF coal.

A series of solvent drying experiments was done using +650°F Illinois #6 recycle solvent from the ITSL pilot plant at 150-180°C initial temperature and 10-30 minute drying times. In addition, a series of drying experiments were done using a vacuum oven at 21-150°C and 20 minute to 16 hour drying times under nitrogen or air purge. All of the samples contained less than two percent moisture after drying, as measured by Karl Fischer titration.

FIGURE 9. LIQUEFACTION CONVERSION OF SOLVENT DRIED AGGLOMERATES
VERSUS WATER CONTENT BEFORE SOLVENT DRYING

The results of liquefaction of the solvent dried coals, shown in Figure 10, do not show a trend with drying conditions.

Future Work

The work on this task will concentrate on the timing of heating and solvent exposure to the coal to try to maximize liquefaction reactivity.

Task 6. Liquefaction Performance

Objective

The objective of this task is to measure the effect of the various pretreatment reactions on liquefaction reactivity and product distributions by doing small scale liquefaction experiments in microautoclaves.

Design and Construction of a Five-Autoclave Liquefaction Apparatus

Microautoclave experiments have been done singly or in pairs occasionally when a direct comparison of two charge compositions under identical reaction conditions was needed. Reproducibility studies on this and a previous program suggested that the workup procedure was quite reproducible but some variation in reaction conditions, i.e. time-temperature profile, was responsible for most of the variation between runs. Duplicate experiments were normally run for each charge under the standard reaction conditions.

Since the differences in reactivity between the coals prepared with the various pretreatment steps has been small it seemed desirable to run them under identical reaction conditions, making it necessary to design and construct a multiple autoclave reactor. Much of our effort during the past quarter has been directed to improving our overall capability for direct comparisons of microautoclave results.

Two clamps were produced from 1/2" thick aluminum sheet so that five standard microautoclaves can be held equidistant from a center point

FIGURE 10. LIQUEFACTION CONVERSIONS OF OIL AGGLOMERATED ILLINOIS #6 COAL VERSUS FINAL MOISTURE CONTENT AND DRYING METHOD,

in a pentagon. One clamp holds the five valves and can be attached to the wrist-action shaker and the other holds the five autoclaves. The lower clamp was later dropped because it was not needed. The microautoclaves are still shaken on the long axis to get good mixing, aided by the ball bearing in each. Each microautoclave has a thermocouple and a pressure gauge. The pressure gauge has been used to detect leaks during the charging-reaction-quench sequence. One autoclave is equipped with a pressure transducer. The pressure and temperature are still recorded continuously during each run. A picture of the apparatus is shown in Figure 11.

The length of tube between the autoclave and the valve was shortened to cut down the torque on the shaker. This has caused the lowest autoclave to be within five inches of the sand in the sand bath and the heat has distorted the teflon valve seat causing it to leak. The minimum practical length of the tube appears to be about 10 inches.

A glass face plate must also be used on the lowest pressure gauge since the plastic face plates melt.

Other changes were necessary. The sand bath was put on wheels so that it could be moved horizontally along the axis of the shaker so that the larger apparatus could be put into the bath and fastened to the shaker. Also, the Swagelok fittings on the lower end of the tube were welded when the lower clamp was used because the extra torque caused them to leak.

Results of Five-Autoclave Reproducibility Experiments

Three experiments were done in which each of the five autoclaves was charged with 3 g of dry-ground Illinois #6 coal and 6 g of 650°F Illinois #6 solvent under 1000 psi (room temp) hydrogen and krypton. These were each run at 427°C for 5 minutes. The heatup time is longer, about 2.9 minutes average, and the temperature control is more difficult because the response is slower. The preheat must be quite accurate so that the point at which the bath levels off is very close to the desired temperature because adjustments take a significant part of the five minute run time.

The 15 run average conversion of MAF coal to THF solubles was 81.9 percent with a standard deviation of 2.5 percent. The range was from 76.4 percent to 84.9 percent, but the 76.4 percent point was significantly out of line. The next lowest point was 80.2 percent. Efforts to improve the precision are continuing.

FIGURE 10. FIVE-MICROAUTOCLAVE COAL LIQUEFACTION APPARATUS

The workup procedure has also been examined. Variations in the humidity were found to make the biggest difference in the results due to changes in the weights of the Soxhlet extraction thimbles which occur as a result. The average yields of preasphaltenes, asphaltenes and oils, on a weight percent of total charge basis, are 16.8, 18.0 and 53.4 weight percent, respectively. The standard deviations are 14.7, 16.3 and 3.7, respectively. Thus, it is clear that the problem in the workup, shown schematically in Figure 12, is in the toluene extraction step. Efforts are continuing to improve the procedure.

Effect of Cumulative Pretreatment Steps on Conversion of MAF Coal to THF Solubles

Another experiment has been done to measure the effects of the cumulative pretreatment steps on the conversion of MAF coal to THF solubles, using the five-autoclave apparatus. In this experiment, the MAF coal-to-total solvent ratio was adjusted to 2:1 for each feedstock and all but the solvent dried material were dried in a vacuum oven at room temperature under a nitrogen flow.

As shown in Figure 13, wet grinding and chloride removal have little effect on conversion but oil agglomeration followed by drying in the vacuum oven causes a large increase in conversion. When the Illinois #6 coal is treated by oil agglomeration and then solvent dried, the conversion is also increased significantly.

Future Work

Work will continue to improve the precision of the microautoclave reaction and workup procedures. The experiment on effects of cumulative pretreatment steps will be repeated to confirm the overall conclusions and the same experiment will be performed with Wyodak coal.

FIGURE 12. MICROAUTOCLAVE SAMPLE WORKUP PROCEDURE

FIGURE 13. EFFECT OF CUMULATIVE PRETREATMENT STEPS ON CONVERSION OF MAF ILLINOIS #6 COAL TO THF SOLUBLES AT 2:1 SOLVENT/COAL, 427°C , 5 MIN, 1000 PSI (ROOM TEMP) HYDROGEN

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