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EXPLORATORY RESEARCH ON SOLVENT REFINED COAL LIQUEFACTION

Quarterly Technical Progress Report for Period July 1—September 30, 1980

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Pittsburg & Midway Coal Mining Company
Shawnee Mission, Kansas

U. S. DEPARTMENT OF ENERGY

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EXPLORATORY RESEARCH
ON
SOLVENT-REFINED COAL LIQUEFACTION

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
JULY 1, 1980 THROUGH SEPTEMBER 30, 1980

THE PITTSBURG & MIDWAY COAL MINING CO.
P. O. BOX 2970
SHAWNEE MISSION, KANSAS 66201

February 1981

PREPARED FOR THE
U. S. DEPARTMENT OF ENERGY

UNDER CONTRACT DE-AC22-79ET14800

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ABSTRACT

This report summarizes the progress of the "Exploratory Research on Solvent Refined Coal Liquefaction" project by The Pittsburg & Midway Coal Mining Co.'s Merriam Laboratory for the period July 1, 1980 through September 30, 1980. Work continued on the study of disposable catalysts and the effect of specific additives in both the SRC I and SRC II processing modes. At 450°C, 2250 psig and 1.0 hour residence time with Loveridge coal in the SRC II mode, yields and hydrogen consumptions were essentially the same for runs with 5 wt % added pyrite or 3.3 wt % added ferric oxide. When Loveridge coal was impregnated with 0.7 wt % molybdenum, slightly higher oil yields and slightly lower hydrocarbon gas, SRC and IOM yields were obtained than with the iron compounds above. When Loveridge coal was processed in the SRC I mode at 450°C, 1900 psig and 26 minutes residence time, there was a 3.7% increase in total oil yield with a corresponding decrease in SRC yield when pyrite was added to the feed slurry. There was a smaller effect with a $\text{FeS}_2/\text{Fe}_2\text{O}_3$ combination and little or no effect when ferric oxide alone was added.

I. SUMMARY

Coal from the Loveridge Mine (Pittsburgh seam bituminous) was processed in both the SRC I and SRC II modes to study disposable catalysts and the effect of specific additives.

A. Disposable Catalysts

At 450°C, 2250 psig and 1.0 hour residence time in the SRC II mode with Loveridge Mine coal, yields and hydrogen consumptions were essentially the same for runs with added pyrite (FeS_2) or ferric oxide (Fe_2O_3). The yields obtained with Loveridge coal and 5 wt % added pyrite were similar to those obtained with the other Pittsburgh seam coals (Georgetown and an Ireland/Blacksville blend) studied recently under these conditions without added catalyst.

When Loveridge coal was processed in the SRC I mode at 450°C, 1900 psig and 26 minutes residence time, there was a significant increase in total oil yield (3.7% based on MF coal) with a corresponding decrease in SRC yield when pyrite was added to the feed slurry. There was a smaller effect with a $\text{FeS}_2/\text{Fe}_2\text{O}_3$ combination and little or no effect when ferric oxide alone was added.

B. Specific Additives

Two runs were conducted in the SRC II mode at 450°C, 2250 psig and 1.0 hour residence time with Loveridge coal containing 0.7 and 0.4 wt % molybdenum by aqueous impregnation, to compare this catalyst with pyrite and ferric oxide.

Slightly higher oil yields and slightly lower hydrocarbon gas, SRC and IOM yields were obtained with 0.7 wt % molybdenum than with 5 wt % added pyrite or 3.3 wt % added ferric oxide. The lot of pyrite used in this comparison appears to be relatively low in activity, however, compared to some other pyrite samples. Higher oil yields and lower SRC and IOM yields were achieved with 0.7 wt % molybdenum on coal than with 0.4 wt %, although the differences were slight. The sulfur levels in the heavy distillate and distillation residue from the Mo catalyzed runs were much lower than in the runs catalyzed by iron compounds. Other analyses were roughly the same for the two catalyst types.

II. INTRODUCTION

This report covers work at The Pittsburgh & Midway Coal Mining Co.'s Merriam Laboratory on the Solvent Refined Coal (SRC) process during the period July 1, 1980 through September 30, 1980.

A. Reports of Previous Work

Previous work at this laboratory has been described in interim, final, monthly, quarterly and annual reports to the Office of Coal Research, the Energy Research and Development Administration and the Department of Energy. A summary of these documents appears in

the second quarter 1979 report* along with a description of the current contract objectives and a history of the Merriam Laboratory in solvent refining of coal.

B. Currently Reported Work

Work carried out this quarter was in three main areas: "Disposable Catalysts," "Specific Additives" and "Short Residence Time Studies." The first two areas are part of Task IV, "Reaction Paths and Catalysis," of the current contract. The last area is part of Task I, "New Process Approaches."

1. Disposable Catalysts

These runs were part of subtask 4.1, the objective of which is to evaluate the effect of low-cost (disposable) catalysts in the SRC I and SRC II processes. Six experiments were conducted with bituminous coal from the Loveridge Mine and two experiments with subbituminous coal from the Belle Ayr Mine.

a. Loveridge Coal Experiments

Two runs were conducted in the SRC II mode and four runs in the SRC I mode to compare the catalytic activity of ferric oxide (Fe_2O_3) with pyrite (FeS_2).

Previous work in this area includes experiments reported last quarter** in which the catalytic activity of pyrite and ferric oxide were compared in the SRC II processing of Loveridge coal at 455°C, 1800 psig and 1.0 hour residence time. Total oil yield with pyrite was about 3% higher than with ferric oxide which was, in turn, about 1% higher than for a control run without additive. There were correspondingly lower SRC and IOM yields. Yields and hydrogen consumptions were essentially the same for runs catalyzed with pyrite or an equal iron blend of FeS_2 and Fe_2O_3 .

b. Belle Ayr Coal Experiments

Two runs were made in the SRC II mode with coal from the Amax Belle Ayr Mine and addition of two different pyrite samples. Discussion of these runs will be deferred until a later report.

* "Exploratory Research on Solvent Refined Coal Liquefaction," Technical Progress Report for the Period April 1, 1979 through June 30, 1979; July 1980; FE/14800-10

** "Exploratory Research on Solvent Refined Coal Liquefaction," Technical Progress Report for the Period April 1, 1980 through June 30, 1980; FE/14800-21.

2. Specific Additives

Two runs were conducted with Pittsburgh seam coal from the Loveridge Mine coated with molybdenum by aqueous impregnation with ammonium molybdate. These runs were part of subtask 4.3 which will evaluate addition of several specific additives and chemicals in the SRC process.

No recent work has been done at Merriam with molybdenum as an added catalyst. The effect of this catalyst on the SRC II processing of Loveridge coal is compared to that achieved with added iron compounds.

3. Short Residence Time Studies

Twenty short residence time SRC I experiments were conducted with Kentucky 9/14 and Indiana V coals. Discussion of these runs will be deferred until a later report.

III. DISPOSABLE CATALYSTS

A. Experimental

1. Run Conditions

The run conditions for all experiments reported this quarter are summarized in Table 1.

a. SRC II Mode

Runs DOE 371R and 376R were made at conditions previously established for our Task III* SRC II runs: 450°C, 2250 psig, 1.0 hour residence time, 30% Loveridge coal in the slurry and 4% hydrogen based on slurry. As in previous work under that task, the solids level in the feed slurry was held as close as possible to 45% by adjusting the separator temperatures (varying the solids content of the recycled unfiltered coal solution) and amount of recycled solvent in the formulation. Run DOE 371R was made with pyrite (FeS_2) added at a level of 1.84%, based on slurry (5% pure FeS_2 on coal). This matched the iron addition level in previous work with Loveridge coal. In run DOE 376R, the same amount of iron was added as ferric oxide (3.3 wt % on coal).

b. SRC I Mode

Runs DOE 372-375 were made at the conditions used in previous additives work with Loveridge coal in the SRC I mode: 450°C, 1900 psig, 26 minute residence time with

* A study of the relationship between coal properties and liquefaction behavior.

39% Loveridge coal in the slurry and approximately 3.5% hydrogen, based on slurry. Run DOE 372 was made with pyrite added at a level of 5% pure FeS_2 , based on coal. In run DOE 373, the same level of iron was utilized with pyrite and ferric oxide each contributing half the amount. In run DOE 374, the same amount of iron was added as ferric oxide alone. Run DOE 375 was a control run without additive.

2. Coal

The coal used in these experiments was from the Consol Loveridge Mine in West Virginia (Pittsburgh seam). It is the same lot of washed coal used in previous additives studies at Merriam. The analyses are shown in Table 3.

The moisture content of this coal has been determined by both the oven drying method (ASTM D-3173) and the toluene distillation method (ASTM D-95). The latter determination is more accurate, as discussed in Appendix A.

3. Additives

a. "Pyrite III"

The pyrite used in runs DOE 371R, 372 and 373 ("Pyrite III") was obtained from the coal cleaning operation of the U. S. Steel Robena Mine, Green County, Pennsylvania. It was finely ground by The Jet Pulverizer Co., Palmyra, New Jersey. Analysis of the material, as shown in Table 4, indicates 80.1% purity as FeS_2 . A particle size distribution (Coulter Counter method) was shown in the second quarter 1980 report (FE/14800-21). The average particle size by "Fisher Subsieve Sizer" is $0.95 \mu\text{m}$ and the surface area* is $2.61 \text{ m}^2/\text{g}$.

b. Ferric Oxide

The ferric oxide used in runs DOE 373, 374 and 376R was obtained from Matheson, Coleman and Bell (technical grade). Based on the iron analysis, the material is essentially 100% pure Fe_2O_3 . Available analyses are shown in Table 4. The material appears to be very finely divided, but the particle size has not been determined. The surface area* is $8.81 \text{ m}^2/\text{g}$.

4. Operation

Numerous minor equipment problems occurred during run DOE 371R which do not appear to be directly related to the coal or conditions under study. Operability was otherwise satisfactory during this series of experiments.

* Nitrogen adsorption B.E.T. measurement by Sandia Laboratories.

5. Material Balances

The yields for the SRC I runs, DOE 372-375, shown in Table 2, are based on distillation of filtrate. These results are considered to be more accurate than those based on distillation of unfiltered coal solution (UFCS).

The ash recovery for this series of experiments was generally satisfactory.

B. Results

1. Yields and Hydrogen Consumptions

The yields and hydrogen consumptions for all runs reported this quarter are shown in Table 2.

a. SRC II Mode

(i) Comparison of Pyrite and Ferric Oxide

The yields and hydrogen consumptions for the SRC II processing of Loveridge coal with added pyrite or ferric oxide are compared below:

Conditions [†]	DOE 371R	DOE 376R
Additive	FeS ₂	Fe ₂ O ₃
<u>Yields, Wt % MF Coal</u>		
C ₁ -C ₄	12.4	12.9
Total Oil	39.5	39.5
SRC	31.7	32.3
IOM	5.5	5.5
<u>Hydrogen Consumption,</u>		
<u>Wt % MF Coal</u>	4.7	5.1

+ For both: 450°C, 2250 psig, 1.0 hour residence time.

The yields and hydrogen consumptions were essentially the same with the two additives. It is recalled that in earlier experiments at 455°C and 1800 psig*, total oil yield from Loveridge coal was increased about 11% (to 42%) by "Pyrite I" addition and only about 1 1/2% (to 32%) by magnetite (Fe₃O₄) addition. In the work reported last quarter, also at 455°C and 1800 psig, oil yield with "Pyrite III" was about 3% higher than with ferric oxide (34.8% vs 31.5%). The catalytic activity of both the pyrites

* "Exploratory Research on Solvent Refined Coal Liquefaction," Technical Progress Report for the Period July 1, 1979 through September 30, 1979; July 1980, FE/14800-11.

and iron oxides appears to correlate with their surface areas:

<u>Material</u>	<u>Surface Area, m²/g[†]</u>
Pyrite I	4.16
Pyrite III	2.61
Fe ₃ O ₄	1.97
Fe ₂ O ₃	8.81

The Pyrite I is apparently more active than the lower surface area Pyrite III and the finely divided ferric oxide is more active than the magnetite.

(ii) Comparison with Task III Coals

The yields and hydrogen consumptions, on a moisture and ash free basis, from the SRC II processing of Loveridge coal with added pyrite are compared to results with the Pittsburgh seam coals studied during the Task III study at the same conditions:

<u>Conditions*</u>	<u>DOE*** 360RA</u>	<u>DOE*** 364R</u>	<u>DOE 371R</u>
<u>Coal</u>	Georgetown	Ireland + Blacksville	Loveridge
Pyrite Addition Level, wt % coal**	--	--	4.9
Iron in feed slurry, wt %	2.30	1.89	3.25
<u>Yields, Wt % MAF Coal</u>			
C ₁ -C ₄	15.1	15.3	14.5
Total Oil	41.9	40.1	42.8
SRC	33.7	34.9	34.3
IOM	5.2	6.0	6.0
<u>H₂ Consumption, wt % MAF Coal</u>	6.2	5.2	5.1

* All at 449-450°C, 2250 psig, 1.0 hour residence time.

** As-received jet pulverized "Pyrite III."

*** Exploratory Research on Solvent Refined Coal Liquefaction,
Technical Progress Report for the Period April 1, 1980
through June 30, 1980; FE/14800-21.

The yields and hydrogen consumption with the Loveridge coal and 5 wt % added pyrite were very similar to those of the other Pittsburgh seam coals studied at these conditions without additives.

b. SRC I Mode

The yields and hydrogen consumptions for Loveridge coal processed in the SRC I mode with pyrite, ferric oxide or a FeS₂/Fe₂O₃ blend are compared below:

† Nitrogen adsorption B.E.T. measurements by Sandia Laboratory

Conditions*	DOE 375	DOE 372	DOE 373	DOE 374
Additive	--	FeS ₂	FeS ₂ / Fe ₂ O ₃	Fe ₂ O ₃
<u>Yields, Wt % MF Coal</u>				
C ₁ -C ₄	4.5	5.5	5.1	4.9
Recycle Solvent	5.7	7.2	4.4	3.5
Total Oil	16.4	20.1	18.5	15.7
SRC	61.4	57.3	59.3	61.5
IOM	6.5	6.1	6.0	6.6
<u>Hydrogen Consumption,</u> <u>wt % MF Coal</u>				
	2.0	2.4	2.4	2.0

* All at 450°C, 1900 psig, 26 minute residence time, 2.3% additive on coal as Fe where used.

There was a significant increase in total oil yield (from 16.4 to 20.1%, based on MF coal) with a corresponding decrease in SRC yield when pyrite was added to the feed slurry. There was a smaller effect with the FeS₂/Fe₂O₃ combination and little or no effect when ferric oxide alone was added.

2. Product Quality

The heavy distillate (recycle solvent) and distillation residue (SRC) analyses for all runs reported this quarter are shown in Table 2. The solubilities of the distillation residues from runs DOE 371R and 376R in hexane, toluene and pyridine are shown in Table 6 and the solubilities of the SRC products from runs DOE 372-375R in Table 7.

a. SRC II Mode

The heavy distillate from run DOE 376R with ferric oxide had a little less sulfur (0.36% vs 0.41%) than that from the run with added pyrite (DOE 371R). The other heavy distillate analyses were essentially the same.

The fusion point of the residue from the ferric oxide addition run (DOE 376R) was 30°C less than that from the run with pyrite addition (DOE 371R) although the ratio of its hexane/pyridine solubility was also less (a higher solubility would be expected in conjunction with a lower fusion point). The solubilities in toluene and other distillation residue analyses were essentially the same for the two runs.

b. SRC I Mode

The recycle solvent hydrogen and nitrogen analyses were about the same for all four runs (DOE 372-375). The sulfur level was a little higher in the recycle solvent from the runs with added pyrite and the FeS₂/Fe₂O₃ combination (DOE 372 and 373) than in the runs without additive and with Fe₂O₃ alone.

There was no significant change in H, S or N levels in the SRC products due to FeS_2 or Fe_2O_3 addition. The fusion point was lowered from about 150 to 135°C by adding Fe_2O_3 or the $\text{FeS}_2/\text{Fe}_2\text{O}_3$ combination to the slurry and another 10°C (to 124°C) by pyrite addition. The range in solubilities of the SRC products in hexane and toluene measured for these runs appears to be within the normal variation for the solvent extraction method.

3. Viscosity Measurements

Unfiltered coal solution (UFCS) viscosity data are listed in Table 7 and feed slurry viscosity data in Table 8.

a. SRC II Mode

(i) Unfiltered Coal Solution (UFCS) Viscosities

UFCS viscosities from runs DOE 371R and 376R are compared in Figure 1. The run with added pyrite (DOE 371R) produced a UFCS with a much lower viscosity than the run with added ferric oxide (DOE 376R). Although the net yields were nearly the same for these two runs, a difference in formulation led to a higher level of solids and SRC in the UFCS from run DOE 376R.

The UFCS viscosity from run DOE 371R is compared to those from other Pittsburgh seam coals studied during our Task III studies on coal properties and liquefaction behavior in Figure 2. The UFCS viscosities are similar as were the yields for these three experiments.

(ii) Feed Slurry Viscosities

The feed slurry viscosities for runs DOE 371R with added pyrite and DOE 376R with ferric oxide are compared in Figure 3. The total solids level was about the same in the two feed slurries, but there was a higher concentration of SRC and a lower concentration of oil in the slurry from run DOE 376R. A higher viscosity for this slurry was the result.

b. SRC I Mode

The unfiltered coal solution (UFCS) viscosities for runs DOE 372-375 are compared in Figure 4. The UFCS products from all four runs had similar levels of solids, SRC and oil, and the viscosities were close together as a result.

IV. SPECIFIC ADDITIVES

A. Experimental

1. Run Conditions

The conditions for runs DOE 377R and 378R are summarized in Table 1.

Both runs were made at 450°C average dissolver temperature (flat profile), 2250 psig and 1.0 hour residence time with 30 wt % coal in the slurry and 4 wt % hydrogen, based on feed slurry.

In run DOE 377R, Loveridge coal coated with molybdenum by aqueous impregnation with ammonium molybdate was blended with untreated coal to give a molybdenum concentration of 0.69 wt % (~1% as MoO_3) in the coal fed. In run DOE 378R, the impregnated coal was blended with untreated coal to give a Mo concentration of 0.36 wt % (~0.5% as MoO_3) in the coal.

2. Coal

The coal used in the molybdenum addition experiments was from the Consol Loveridge Mine in West Virginia (Pittsburgh seam). It is the same lot of washed coal used in previous additives studies at Merriam. The analyses are shown in Table 3.

The weights of treated and untreated coal used in runs DOE 377R and 378R are shown in Table 9.

The moisture content of the coal used in these runs was determined by both the oven drying method (ASTM D-3173) and the toluene distillation method (ASTM D-95). The latter determination is more accurate, as discussed in Appendix A.

3. Molybdenum Additive

The Loveridge coal was coated with molybdenum by aqueous impregnation with ammonium molybdate and air dried. The treated coal used in run DOE 377R was found to contain an average of 1.50% MoO_3 as determined by precipitation of lead molybdate. The treated coal used in run DOE 378R contained an average of 2.18% MoO_3 .

4. Operation

Operability was generally good during processing of the molybdenum coated Loveridge coal. There was a noticeable increase in feed slurry viscosity when the molybdenum level was cut approximately in half for run DOE 378R.

5. Material Balances

The moisture in the feed coals and feed slurries has been measured by the toluene distillation method (ASTM D-95) for these runs.[†] In runs DOE 377R and 378R the moisture associated with the coal fed was determined from the moisture determination on the feed slurry. It is thus assumed that the moisture brought into the feed slurry with the coal is that which is present in the slurry just before charging the reactor^{††} and, in general, after some evaporation has taken place.

Overall material and ash balances were satisfactory for runs DOE 377R and 378R with the low moisture Loveridge coal.

B. Results

1. Yields and Hydrogen Consumptions

The yields and hydrogen consumptions for runs DOE 377R and 378R are shown in Table 2.

The yields and hydrogen consumptions for SRC II processing of Loveridge coal with added pyrite, ferric oxide or molybdenum are compared below:

Conditions*	DOE*** 371R	DOE*** 376R	DOE 377R	DOE 378R
Additive	FeS ₂	Fe ₂ O ₃	Mo	Mo
Addition level**, wt % MF coal	4.92	3.32	0.69	0.36
Yields, wt % MF coal				
C ₁ -C ₄	13.4	12.9	12.5	12.4
Total Oil	39.5	39.5	41.6	40.6
SRC	31.7	32.3	29.8	31.8
IOM	5.5	5.5	4.9	5.0
Hydrogen Consumption, wt % MF coal				
	4.7	5.1	5.0	4.9

* For all: 450°C, 2250 psig, 1.0 hour residence time, 30% Loveridge coal in the slurry, 4% H₂ on slurry, 42-45% total solids in slurry.

** As pure FeS₂, Fe₂O₃ or Mo.

*** From section III of the current report.

The runs catalyzed with 0.4-0.7 wt % added molybdenum in general produced slightly higher oil yields and slightly lower hydrocarbon gas, SRC and IOM yields than runs with 4.9 wt % added pyrite or 3.3 wt % added ferric oxide. All differences were close to normal experimental error, however. Hydrogen

[†] See Appendix A for a comparison of the oven drying and toluene distillation methods of water determination.

^{††} This calculation has, in fact, been used since the ASTM D-95 method was initiated for measuring water in the feed slurry during run DOE 349.

consumption for all four runs was essentially the same. It should be remembered, however, that this lot of pyrite ("Robena Pyrite III") appears to be of relatively low activity compared to some other pyrite samples, as discussed in section III above.

A higher total oil yield and lower SRC yield were achieved with 0.69 wt % Mo on coal than with 0.36 wt % Mo on coal, although the differences were very small (1.0% higher total oil, 2.0% lower SRC) and are close to or within normal experimental error. This suggests that even lower levels of molybdenum could be effective while little additional benefit would be expected with higher Mo levels.

2. Product Quality

The heavy distillate and distillation residue analyses for runs DOE 377R and 378R are summarized in Table 2. The solubilities of the distillation residues in hexane, toluene and pyridine are shown in Table 10.

The heavy distillate and distillation residue analyses from processing Loveridge coal with added pyrite, ferric oxide and molybdenum are compared below:

Conditions*	DOE*** 371R	DOE*** 376R	DOE 377R	DOE 378R
Additive	FeS ₂	Fe ₂ O ₃	Mo	Mo
Addition level**, wt % MF coal	4.92	3.32	0.69	0.36
<u>Heavy Distillate Analyses</u>				
% H	8.12	8.24	8.38	8.03
% S	0.41	0.36	0.21	0.22
% N	1.16	1.22	1.20	1.22
<u>Distillation Residue Analyses</u>				
% H	4.36	4.28	4.48	4.54
% S	4.54	4.53	2.46	2.19
% N	1.38	1.47	1.39	1.42
Fusion Point, °C	132	102	129	104
Ratio of Average Solubilities				
Hexane/Pyridine	0.548	0.425	0.582	0.540
Toluene/Pyridine	0.934	0.922	0.949	0.947

* For all: 450°C, 2250 psig, 1.0 hour residence time, 30% Loveridge coal in the slurry, 4% hydrogen on slurry.

** As pure FeS₂, Fe₂O₃ or Mo.

*** From section III of the current report.

The heavy distillate hydrogen level was a little higher in the run with 0.69% Mo (DOE 377R) than in the run catalyzed by adding iron compounds, while it was a little lower in the run with 0.36% Mo (DOE 378R). The heavy distillate sulfur levels in both runs catalyzed by Mo were significantly lower than in the runs catalyzed by iron compounds. The nitrogen levels were essentially the same in all four runs.

The nitrogen levels in the distillation residues had similar values in all four runs. The hydrogen levels were also close together although they were a little higher in the Mo catalyzed runs. The sulfur levels were significantly higher in the runs catalyzed by iron compounds (DOE 371R and 376R) than in the runs catalyzed by molybdenum (DOE 377R and 378R). This is due to a higher level of metal sulfides in the residues when the iron catalysts are used. The low fusion point measured on the residue from run DOE 378R seems out of line since less catalyst was used in this run and the hexane solubility was a little less than in run DOE 377R (which would normally correspond to a higher fusion point). The hexane/pyridine and toluene/pyridine solubility ratios of all four residues were quite high and had similar values.

3. Viscosity Measurements

Unfiltered coal solution (UFCS) viscosity data for runs DOE 377R and 378R are listed in Table 11 and feed slurry viscosity data in Table 12.

a. Unfiltered Coal Solution (UFCS) Viscosities

The unfiltered coal solution (UFCS) viscosities for Loveridge coal processed with FeS_2 , Fe_2O_3 and Mo additives are compared in Figure 5. The catalysts were in the following order in their effect on UFCS viscosities:

3.3% Fe_2O_3 > 0.4% Mo > 0.7% Mo > 4.9% FeS_2

← Increasing Viscosity

← Increasing SRC + Solids (Ash + IOM)
level in the UFCS

There was no clear relationship between the viscosities and yields.

b. Feed Slurry Viscosities

The feed slurry viscosities from the same runs are compared in Figure 6. These viscosities do not appear to correlate with yields or feed slurry compositions.

4. Elemental Balances

The elemental balances for runs DOE 377R and 378R are shown in Figures 7 and 8, respectively. These studies were carried out to elucidate the nature of the products and verify overall material balances. The yields given in Figures 7 and 8 vary slightly from those found elsewhere in the report because the analyses were performed on distillation cuts made from preliminary yield calculations. The results are summarized below:

	<u>Out/In</u>	
	<u>DOE</u> <u>377R</u>	<u>DOE</u> <u>378R</u>
Carbon	1.00	0.99
Nitrogen	0.96	1.15
Sulfur	0.96	0.84
Oxygen	1.32	1.06

The balances for carbon were excellent. The low value for sulfur in run DOE 378R was apparently due to loss of dissolved H₂S. The high value for oxygen in run DOE 377R may be due to the difficulty in calculating the oxygen (by difference) in the distillation residue.

V. COMPOSITION OF OILS MADE BY SRC II PROCESSING OF VARIOUS COALS

Elemental analyses for naphthas (IBP-193°C), middle distillates (193-288°C) and heavy distillates (288°C-EP) from a variety of coals processed in the SRC II mode with two temperature/pressure combinations and a number of different catalysts are compared in Appendix B. By and large, materials with the same boiling range are quite similar in composition, regardless of the coal feed or processing conditions.

VI. MAINTENANCE AND MODIFICATIONS

A. Maintenance

Early on the third day of run DOE 375R, the fan in zone 4 of the dissolver air furnace froze. The baffle between zones 3 and 4 in the air furnace was removed and the run was continued for another two days. After inspection of the air furnace was completed during the next shutdown, it was decided to replace the motor, shaft and bearings on the zone 4 fan and the motor and bearings on the zone 2 fan.

The unit was shut down by a power failure 2 1/2 hours after startup of run DOE 376R. On the seventh day after restarting, the Pressure Products Industries (PPI) hydrogen compressor was taken off line and the "O" rings were replaced. The compressor was plagued by a hydrogen leak which had become continuously worse during this series of runs.

B. Modification

The high pressure lines leading from the Hills McCanna slurry charge pump were modified to allow the pump heads to be changed safely while the unit is on stream. The new arrangement is shown in Figure 9. The straight sections of tubing between the pump heads and the 3/8" tees have been replaced with elbows and curved tubing. This allows the connection to be removed without bending the tubing.

TABLE 1
Conditions Summary

	DOE 371R	DOE 372	DOE 373	DOE 374	DOE 375	DOE 376R	DOE 377R	DOE 378R
Coal	Pittsburgh Seam ^a							
Operating Mode	SRC II	SRC I				SRC II		
Dissolver	DOE 3	Tubular ^b				DOE 1		
Slurry Formulation ^c , wt %								
Coal	30.0	39.0	39.0	39.0	39.0	30.0	30.0	30.0
Recycled Solvent	10.0	58.6	59.0	59.7	61.0	7.0	4.0	4.0
Recycled Coal Solution	58.2	--	--	--	--	62.0	66.0	66.0
Additive	1.8	2.4	2.0	1.3	--	1.0	--	--
Slurry Blend Composition ^c , wt %								
Coal	30.0					30.0	30.0	30.0
Middle Distillate (193-288°C, 380-550°F)	9.6					7.6	5.7	5.3
Heavy Distillate (>288°C, 550°F)	23.0					20.3		21.8
-SRC	23.1					27.3	29.2	30.5
Ash (from Recycled Coal Solution)	8.5					9.2	8.2	7.6
IOM (from Recycled Coal Solution)	4.0					4.6	4.8	4.8
Additive	1.8					1.0	--	--
Total Solids	44.3					44.8	43.0	42.4
Slurry Feed Rate								
g/hr	1217	1142	1150	1155	1158	1173	1164	1189
lb/hr/ft ³ e	71.4	164.8	166.0	166.7	167.1	70.7	70.1	71.7
Dissolver Nominal Slurry Residence Time, hr (min) ^e	1.01	(26.1)	(25.9)	(25.8)	(25.7)	1.01	1.02	1.00
Preheater Nominal Slurry Residence Time, min ^f	17.6	18.7	18.6	18.5	18.5	18.2	18.4	18.0
Coal Feed Rate ^c								
g/hr	363	442	446	446	448	350	347	354
lb/hr/ft ³	21.3	63.8	64.4	64.4	64.7	21.1	20.9	21.3
Hydrogen Feed Rate ^g								
Moles/hr	23.6	19.0	19.0	19.0	19.0	23.6	23.6	23.6
Wt % based on slurry	3.90	3.35	3.32	3.32	3.31	4.05	4.05	3.97
MSCF/ton of coal	49.3	32.6	32.3	32.3	32.1	51.1	51.5	50.5
Additive	FeS ₂	FeS ₂	FeS ₂ + Fe ₂ O ₃	Fe ₂ O ₃	--	Fe ₂ O ₃	Molybdenum	
Addition Rate, wt % based on coal ^e								
as received material	6.15	6.10	5.09	3.29	--	3.32	--	--
as pure FeS ₂ or Fe ₂ O ₃	4.92	4.89	2.44 & 2.04	3.29	--	3.32	0.69	0.36
Reactor Pressure, psig	2250	1900				2250	2250	
Average Dissolver Temperature, °C	450	450	450	450	450	450	450	450
(°F)	(842)	(842)	(842)	(842)	(842)	(842)	(842)	(842)
Actual Dissolver Temperature, °C ⁱ								
Dissolver Zone								
6 (top)	450±1	450±0	450±1	450±0	450±1	450±1	449±1	449±0
5	450±1	450±1	450±0	450±0	450±1	451±1	450±1	451±1
4	450±0	450±0	450±1	450±0	450±1	450±0	449±1	450±1
3	450±1	450±1	451±0	450±0	450±1	449±1	449±1	449±1
2	450±0	450±0	450±1	450±0	450±1	451±1	452±0	452±1
1 (bottom)	449±1	449±1	449±1	449±1	449±1	447±1	448±2	449±1
Preheater Temperature, °C ⁱ								
Top	397±1	395±1	397±1	399±1	399±1	400±2	401±1	400±1
Middle	397±3	402±1	402±2	402±1	401±1	399±2	401±1	400±1
Bottom	368±19	381±13	375±14	349±13	361±15	385±19	381±16	378±16

a) Loveridge Mine, see Table 3 for analyses. b) Tubular dissolver made from 17.5 mm (11/16") I.D. tubing with a volume of 431.5 cm³. c) Dry coal basis. d) Included in coal weight for runs DOE 377R and 378R. e) Based on reactor volume = 1064 cm³ (.03757 ft³) for run DOE 371R, 432 cm³ (.01526 ft³) for runs DOE 372-375 and 1035 cm³ (.03655 ft³) for runs DOE 376R, 377R and 378R. f) Preheater volume = 310 cm³. g) Hydrogen feed rates do not include that added as DP cell-purge. h) One thousand cubic feet at one atmosphere and 60°F. i) Average and standard deviations.

TABLE 2

Results Summary

Yields, wt % based on MF Coal	DOE 371R	DOE 372	DOE 373	DOE 374	DOE 375	DOE 376R	DOE 377R	DOE 378R
H ₂ O	4.6	4.4	4.2	4.2	3.1	5.4	4.9	4.4
CO	0.6	0.3	0.3	0.3	0.4	0.4	0.4	0.4
CO ₂	0.7	0.9	0.9	0.9	0.8	0.6	0.5	0.5
H ₂ S ^a	2.6	2.0	1.0	0.1	1.2	0.4	1.3	1.3
NH ₃	0.5	0.2	0.1	0.1	0.1	0.4	0.7	0.6
C ₁	4.5	2.2	2.1	2.0	1.9	4.6	4.4	4.5
C ₂	3.2	1.5	1.5	1.5	1.3	3.4	3.4	3.3
C ₃	3.7	1.2	1.1	1.0	0.9	3.3	3.1	3.1
C ₄	2.0	0.6	0.4	0.4	0.4	1.6	1.6	1.5
Total C ₁ -C ₄	13.4	5.5	5.1	4.9	4.5	12.9	12.5	12.4
C ₅₊ (gas)	1.8	1.3	1.2	1.8	1.0	3.1	3.0	3.1
Naphtha, <193°C (380°F)	9.2	5.2	5.7	4.9	4.6	9.2	9.4	8.9
Middle Distillate, 193-288°C (380-550°F) ^b	13.9	6.4	7.2	5.5	5.1	12.8	13.6	13.0
Heavy Distillate, >288°C (550°F) ^c	14.6	7.2	4.4	3.5	5.7	14.4	15.6	15.6
Total Oil (C ₅ -Heavy Distillate) ^c	39.5	20.1	18.5	15.7	16.4	39.5	41.6	40.6
SRC	31.7	57.3	59.3	61.5	61.4	32.3	29.8	31.8
Insoluble Organic Matter	5.5	6.1	6.0	6.6	6.5	5.5	4.9	5.0
Ash ^d	7.7	7.7	8.1	7.7	7.6	7.7	8.4	7.9
Total	106.8	104.5	103.5	102.0	102.0	105.1	105.0	104.9
H ₂ Consumed (Gas Balance)	4.7	2.4	2.4	2.0	2.0	5.1	5.0	4.9
Additive Conversion Byproducts	2.1	2.1	1.1	0.0	--	0.0	--	--
<u>Heavy Distillate Analyses^c</u>								
% C	88.05	88.66	88.56	88.60	88.66	88.52	89.63	88.80
% H	8.12	7.81	7.74	7.76	7.72	8.24	8.38	8.03
% S	0.41	0.57	0.52	0.45	0.44	0.36	0.21	0.22
% N	1.16	0.89	0.92	0.90	0.89	1.22	1.20	1.22
% O (by difference)	2.26	2.07	2.26	2.29	2.29	1.66	0.58	1.73
Specific Gravity	1.0438	1.0608	1.0621	1.0621	1.0612	1.0509	1.0470	1.0490
<u>Distillation Residue Analyses^e</u>								
% C	68.33	87.44	87.50	87.31	87.47	69.52	71.82	72.51
% H	4.36	5.88	5.97	6.10	6.01	4.28	4.48	4.54
% S	4.54	1.03	0.94	0.94	1.04	4.53	2.46	2.19
% N	1.38	1.86	1.88	1.89	1.88	1.47	1.39	1.42
% O (by difference)	--	3.60	3.51	3.36	3.57	--	--	--
% Ash	22.37	0.19	0.20	0.40	0.03	21.85	18.77	17.95
Fusion Point, °C	132	124	138	135	152	102	129	104

a) Includes H₂S derived from added pyrite. b) Wash Solvent, 193-249°C (380-480°F), for runs DOE 372-375.

c) Recycle Solvent, >249°C (480°F), for runs DOE 372-375. d) Includes ash derived from added molybdenum.

e) SRC for runs DOE 372-375.

TABLE 3

ANALYSES OF PITTSBURGH SEAM COAL^a
LOVERIDGE MINE

Coal Identification	
Company	Consol
Mine	Loveridge
Seam	Pittsburgh
Proximate Analysis	
% Ash	7.44
% Volatile	39.13
% Fixed Carbon	53.43
	<u>100.00</u>
% Moisture	0.92
Heating Value, Btu/lb	13,958
Sulfur Forms	
% Pyrite	0.90
% Sulfate	0.00
% Organic	1.80
% Total	<u>2.70</u>
Ultimate Analyses, Wt %	
Carbon	77.25
Hydrogen	5.34
Nitrogen	1.13
Chlorine	0.10
Sulfur	2.70
Ash	7.44
Oxygen (difference)	6.04
	<u>100.00</u>
Mineral Analyses of Ash, Wt %	
Ignited basis	
% Silica, SiO ₂	42.71
% Alumina, Al ₂ O ₃	21.98
% Titania, TiO ₂	1.10
% Ferric Oxide, Fe ₂ O ₃	17.67
% Lime, CaO	5.70
% Magnesia, MgO	1.25
% Potassium Oxide, K ₂ O	1.19
% Sodium Oxide, Na ₂ O	1.12
% Sulfur Trioxide, SO ₃	6.17
% Phos. Pentoxide, P ₂ O ₅	0.17
% Strontium Peroxide, SrO ₂	--
% Barium Oxide, BaO	--
% Manganese Oxide, MnO	--
% Undetermined	0.94
	<u>100.00</u>
% Iron in Coal	0.92
Fusion Temperature of Ash, °F (Reducing)	
Initial Deformation	2080
Softening (H=W) ^b	2190
Softening (H=1/2W)	2220
Fluid	2430
% Equilibrium Moisture	--

a) Analyses performed by Commercial Testing and Engineering Company.

TABLE 4
Additives Analyses

Weight % ^a	Robena Pyrite III	Matheson, Coleman & Bell Ferric Oxide
Fe	38.72	69.93
S	41.36	--
C	5.42	--
H	0.40	--
Moisture ^b	0.22	0.73
Ash ^c	65.82	99.44
Mole Ratio S/Fe	1.86	--
Purity as FeS ₂ or Fe ₂ O ₃ , wt % (based on Fe analysis)	83.2	100.0
Average Particle Size, μm	0.95	
by Fisher Subsieve Sizer	0.95	
by Coulter Counter	3.5	
Surface Area, m ² /g ^d	2.61	8.81

a) Dry basis.
b) As volatiles at 110°C under He atmosphere.
c) Wet basis.
d) Nitrogen adsorption B.E.T. measurement by Sandia Laboratories.

TABLE 5

Solvent Extraction of Distillation Residues
Runs DOE 371R and 376R, Loveridge Coal

	DOE 371R		DOE 376R	
	P 62	P 63	P 63	P 75
<u>Liquefaction Conditions*</u>				
Additive	Pyrite		Ferric Oxide	
<u>Solubility of the Distillation Residue, wt % in</u>				
Hexane	33.4	38.9	25.7	31.8
	33.9	38.9	25.7	31.6
Toluene	61.4	63.2	61.4	62.9
	59.6	62.7	62.0	62.5
Pyridine	65.6	66.7	67.6	67.8
	65.6	66.7	67.0	67.7
<u>Ratio of Average Solubilities</u>				
Hexane/Pyridine	0.513	0.583	0.382	0.468
Toluene/Pyridine	0.923	0.944	0.917	0.926

* For all: 450°C, 2250 psig, 1.0 hour residence time.

TABLE 6

Solvent Extraction of SRC
Runs DOE 372-375, Loveridge Coal

	DOE 372		DOE 373		DOE 374		DOE 375	
	P 34	P 37	P 19	P 22	P 25	P 31**	P 28	P 34
<u>Liquefaction Conditions*</u>								
Additive	FeS ₂		FeS ₂ + Fe ₂ O ₃		Fe ₂ O ₃		--	--
<u>Solubility of the SRC,</u> <u>wt % in</u>								
Hexane	26.3	25.4	32.2	29.9	37.1	18.5	30.1	27.6
	28.1	28.3	33.5	33.1	36.7	19.1	30.9	28.7
Toluene	88.5	90.4	90.9	88.8	89.6	85.7	86.0	86.1
	87.3	90.5	90.5	89.7	89.3	86.3	86.0	85.9
Pyridine	99.7	99.9	99.9	99.9	100.0	99.8	99.9	99.9
	99.8	99.9	99.9	99.9	99.9	99.8	99.9	99.9
<u>Ratio of Average Solubilities</u>								
Hexane/Pyridine	0.273	0.269	0.329	0.315	0.369	0.185	0.305	0.282
Toluene/Pyridine	0.881	0.906	0.908	0.894	0.895	0.862	0.860	0.861

* All at 450°C, 1900 psig, 26 minutes residence time.

** Power failure resulted in shorter than normal extraction time.

TABLE 7

Unfiltered Coal Solution Viscosities^a
Runs DOE 371R-376R, Loveridge Coal

Run No. DOE-	Temperature °F	Shear Rate sec ⁻¹	Viscosity cP	Run No. DOE-	Temperature °F	Shear Rate sec ⁻¹	Viscosity cP
371R P 63	210	1.98	392	374 P 31	210	15.86	39.2
	210	3.96	334		210	39.64	37.6
	210	7.93	292		210	79.28	36.5
	230	1.98	256		230	39.64	24.5
	230	3.96	208		230	79.28	23.8
	230	7.93	178	375 P 34	270	39.64	14.6
	230	15.86	155		270	79.28	12.6
	270	3.96	112		210	15.86	37.2
	270	7.93	89.0		210	39.64	34.9
	270	15.86	73.5		210	79.28	34.2
372 P 37	270	39.64	60.0		230	39.64	23.4
	210	15.86	26.5		230	79.28	22.6
	210	39.64	24.9		270	39.64	12.1
	210	79.28	24.2		270	79.28	11.6
	230	39.64	17.7	376R P 75	210	0.415	2.35x10 ³
	230	79.28	16.6		210	0.830	1.93x10 ³
373 P 22	270	39.64	9.90		210	1.66	1.64x10 ³
	270	79.28	9.35		210	3.32	1.42x10 ³
	210	15.86	35.8		210	8.30	1.28x10 ³
	210	39.64	33.2		230	1.66	849
	210	79.28	32.4		230	3.32	726
	230	39.64	22.2		230	8.30	623
	230	79.28	21.2		230	16.61	564
	270	39.64	12.0		270	3.32	317
	270	79.28	11.4		270	8.30	246
					270	16.61	213

- a) Brookfield Model LV viscometer
 Spindle No. 18 for runs DOE 371R-375
 Spindle No. 28 for run DOE 376R
 Procedure: 45 minute initial warmup and equilibration;
 20-30 minute equilibration after temperature change;
 10 minute equilibration after shear rate change.

TABLE 8

Feed Slurry Viscosities^a
Runs DOE 371R and 376R, Loveridge Coal

Run No. DOE-	Temperature °F	Shear Rate sec ⁻¹	Viscosity 10 ³ cP	Run No. DOE-	Temperature °F	Shear Rate sec ⁻¹	Viscosity 10 ³ cP
371R P 63	210	0.166	11.7	376R P 75	210	0.083	48.7
	210	0.415	7.04		210	0.166	31.8
	210	0.830	4.69		210	0.415	18.0
	210	1.66	3.08		210	0.830	13.5
	210	3.32	2.29		230	0.083	35.5
	230	0.415	5.52		230	0.166	23.5
	230	0.830	3.52		230	0.415	14.3
	230	1.66	2.57		230	0.830	9.85
	230	3.32	1.91		270	0.083	50.6
	230	8.30	1.31		270	0.166	28.6
	270	0.415	6.95		270	0.415	13.7
	270	0.830	3.89		270	0.830	9.47
	270	1.66	2.20				
	270	3.32	1.28				
	270	8.30	0.758				
	270	16.61	0.511				

- a) Brookfield Model LV viscometer
 Spindle No. 28
 Procedure: 45 minute initial warmup and equilibration;
 20-30 minute equilibration after temperature change;
 10 minute equilibration after shear rate change.

TABLE 9

Coal Mixture Data^a
Runs DOE 377R and 378R, Loveridge Coal

Coal Used	% Coal in Slurry Dry Basis	Weight of Coal in Slurry	% Ash in Coal Dry Basis	Weight of Ash in Coal	% Ash in Coal Mixture	% MoO ₃ in Coal Dry Basis	Weight of MoO ₃ in Coal	% MoO ₃ in Coal Mixture
DOE 377R								
Treated Coal	20.70	239.6	8.67	20.8		1.50	3.6	
Untreated Coal	9.30	107.7	7.68	8.3		--	--	
Total	30.00	347.3		29.1	8.38		3.6	1.04
DOE 378R								
Treated Coal	7.25	85.7	9.27	7.9		2.18	1.9	
Untreated Coal	22.75	268.7	7.53	20.2		--	--	
Total	30.00	354.4		28.1	7.93		1.9	0.54

a) Average for cans used in each run.

TABLE 10

Solvent Extraction of Distillation Residues
Runs DOE 377R and 378R
Loveridge Coal

Liquefaction Conditions*	DOE 377R		DOE 378R	
	P 48	P 67	P 30	P 35
Additive	Molybdenum			
Addition Rate, wt % based on coal as pure Mo	0.69		0.36	
<u>Solubility of the Distillation Residue, wt % in</u>				
Hexane	42.0	40.1	38.8	36.5
	38.5	40.7	40.5	36.4
Toluene	66.0	66.0	66.9	66.7
	65.4	65.6	66.5	67.0
Pyridine	69.2	69.2	70.4	70.8
	69.8	69.2	70.6	70.4
<u>Ratio of Average Solubilities</u>				
Hexane/Pyridine	0.579	0.584	0.563	0.516
Toluene/Pyridine	0.946	0.951	0.946	0.947

* For all: 450°C, 2250 psig, 1.0 hour residence time.

TABLE 11:

Unfiltered Coal Solution Viscosities^a
Runs DOE 377R and 378R, Loveridge Coal

Run No. DOE-	Temperature °F	Shear Rate sec ⁻¹	Viscosity cP
377R P 67	210	0.793	780
	210	1.98	642
	210	3.96	559
	210	7.93	487
	230	1.98	380
	230	3.96	323
	230	7.93	275
	230	15.86	242
	270	1.98	222
	270	3.96	174
	270	7.93	127
	270	15.86	104
	270	39.64	85.8
	210	0.396	1.29x10 ³
	210	0.793	1.06x10 ³
378R P 35	210	1.98	830
	210	3.96	741
	230	0.793	655
	230	1.98	514
	230	3.96	423
	230	7.93	367
	270	1.98	256
	270	3.96	193
	270	7.93	151
	270	15.86	127

a) Brookfield Model LV viscometer

Spindle No. 18

Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.

TABLE 12

Feed Slurry Viscosities^a
Runs DOE 377R and 378R, Loveridge Coal

Run No. DOE-	Temperature °F	Shear Rate sec ⁻¹	Viscosity 10 ³ cP
377R P 67	210	0.083	28.7
	210	0.166	17.6
	210	0.415	8.94
	210	0.830	7.12
	210	1.66	5.72
	230	0.415	8.31
	230	0.830	5.68
	230	1.66	3.82
	230	3.32	2.88
	270	0.166	13.2
	270	0.415	10.1
	270	0.830	7.10
	270	1.66	5.30
	210	0.083	32.5
	210	0.166	15.5
	210	0.415	13.0
	210	0.830	11.7
378R ^b P 35	230	0.083	52.3
	230	0.166	30.6
	230	0.415	16.4
	230	0.830	10.4
	270	0.083	81.7
	270	0.166	42.3
	270	0.415	20.4

Run No. DOE-	Temperature °F	Shear Rate sec ⁻¹	Viscosity 10 ³ cP
378R ^c P 35	210	0.083	42.7
	210	0.166	33.1
	210	0.415	21.9
	230	0.083	36.3
	230	0.166	22.5
	230	0.415	13.6
	230	0.830	10.2
	270	0.166	24.6
	270	0.415	12.0
	270	0.830	7.63
	270	1.66	4.65

- a) Brookfield Model LV viscometer
Spindle No. 28
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.
- b) The sample swelled significantly at 270°F.
- c) The sample was rerun using a modified procedure to eliminate the swelling. It was heated to 270°F for one hour to drive off volatiles. The sample was then cooled to 210°F and the normal procedure followed for making measurements. No boiling of volatiles or swelling was noticed during the viscosity measurements using this procedure.

46 1323

12 X 12 TO 1/4 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 1
Unfiltered Coal Solution Viscosities
Runs DOE 371R, 376R
Loveridge Coal

Figure 2
Unfiltered Coal Solution Viscosities
Runs DOE 360RA, 364R, 371R
Ireland, Blacksville, Georgetown & Loveridge Coals

46 1323

K&E 10 X 10 TO 1/4 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 3
Feed Slurry Viscosities
Runs DOE 371R, 376R
Loveridge Coal

Figure 4
Unfiltered Coal Solution Viscosities
Runs DOE 372-375
Loveridge Coal

Figure 5
Unfiltered Coal Solution Viscosities
Runs DOE 371R, 376R, 377R, 378R
Loveridge Coal

45 1323

K&E
10 X 10 TO 4 INCH 7 1/2 C INCHES
GULF P&S DESEPT CO. MADE IN U.S.A.

Figure 6
Feed Slurry Viscosities
Runs DOE 371R, 376R, 377R and 378R
Loveridge Coal

46 1323

K&M
10 X 10 TO 1/2 INCH 7 X 10 INCHES
KEU-FEL & ESSER CO. MADE IN U.S.A.

Figure 7

Run DOE 377R Elemental Balance Study

Loveridge Coal Catalyzed by Molybdenum (0.69 wt % Mo)

SUBSTANCE	YIELD	C %	H %	N %	S %	O %	C gm	H gm	N gm	S gm	O gm
Methane	4.48	74.86	25.13				3.35	1.13			
Ethane	3.41	79.89	20.11				2.72	0.69			
Propane	3.11	81.71	18.29				2.54	0.57			
Butanes	1.56	82.66	17.34				1.29	0.27			
Water	4.72		11.19			88.81		0.53			4.19
CO ₂	0.55	27.29				72.71	0.15				0.46
CO	0.39	42.89				57.11	0.17				0.22
Ammonia	0.73		17.75	82.24				0.13	0.60		
H ₂ S	1.31		5.91		94.09			0.08		1.23	
Naphtha	8.37	86.16	12.87	0.23	0.11	0.63	7.21	1.08	0.019	0.009	0.052
Middle Dist.	19.08	84.91	9.57	1.05	0.06	4.41	16.20	1.83	0.200	0.011	0.841
Heavy Dist.	12.59	88.70	8.10	1.09	0.22	1.89	11.17	1.02	0.137	0.028	0.238
Residue (ash 18.77% incl. catalyst residue)	43.96	71.82	4.48	1.39	2.46	5.56***	31.57	1.97	0.611	1.081	2.44***
TOTALS	104.26						76.37	9.30	1.567	2.359	8.381
INPUT with 100 grams of coal							76.29	4.93	1.64*	2.46	6.36

Based on analysis of
can # 118

Ash in dist. Resid. 8.25
 Ash from catalyst 1.05
 7.20
 Ash in coal ** 7.37

Hydrogen reacted by
elemental balance 4.37%Hydrogen reacted by
gas analysis data 5.06%

* Ammonium molybdate treated coal has more nitrogen than untreated coal
 (was 1.14 in untreated coal).

** The balance of ash in over ash out was 1.03 possibly due to sampling
 errors or the volatility of molybdenum trioxide. Ignitions were done
 at 550° to minimize this problem but some effect is still probable.

*** Oxygen by difference on distillation residue is a doubtful value be-
 cause of unknown composition of reduced mineral and uncertain gains
 and losses on ignition.

Figure 8

Run DOE 378R Elemental Balance Study

Loveridge Coal Catalyzed by Molybdenum (0.36 wt % Mo)

SUBSTANCE	YIELD	C %	H %	N %	S %	O %	C gm	H gm	N gm	S gm	O gm
Methane	4.55	74.86	25.13				3.41	1.14			
Ethane	3.33	79.89	20.11				2.66	0.67			
Propane	3.09	81.71	18.29				2.52	0.57			
Butanes	1.50	82.66	17.34				1.24	0.26			
Water	4.36		11.19			88.81		0.49			3.87
CO ₂	0.59	27.29				72.71	0.16				0.43
CO	0.38	42.89				57.11	0.16				0.22
Ammonia	0.65		17.75	82.24				0.12	0.53		
H ₂ S	1.25		5.91		94.09			0.07		1.18	
Naphtha	10.07	86.08	12.97	0.26	0.13	0.56	8.67	1.31	0.026	0.013	0.056
Middle Dist.	16.10	85.56	9.97	1.09	0.08	3.30	13.78	1.61	0.175	0.013	0.531
Heavy Dist.	12.56	88.74	8.34	1.15	0.20	1.57	11.15	1.05	0.144	0.025	0.197
Residue (ash 17.95% incl. cat. residue)	45.13	72.51	4.54	1.42	2.19	1.39**	32.72	2.05	0.641	0.988	0.627**
TOTAL	103.56						76.47	9.34	1.52	2.22	5.93
INPUT with 100 grams of coal* Calc. for blend can # 122 and average Loveridge							77.15	5.19	1.32	2.65	5.61
Ash in distillation residue		8.10	Hydrogen reacted by				4.15%				
Ash from catalyst		0.55	elemental balance								
		7.45									
Ash in coal		7.37	Hydrogen reacted by				4.89%				
			gas analysis data								
* Calculated for the blend of coated and uncoated coals used for this run.											
** Oxygen by difference on distillation residue is a doubtful value because of unknown composition of reduced mineral and uncertain gains and losses on ignition.											

Figure 9

New Slurry Charge Pump Assembly

APPENDIX A

DETERMINATION OF MOISTURE IN FEED COALS

INTRODUCTION

Most of the work at this laboratory has involved bituminous coals which normally come to 1-3% moisture when air dried and ground to minus 150 mesh. For those feedstocks, the oven drying procedure (ASTM D-3173) was adequate to determine the moisture level in the coal. During recent work with subbituminous coals, it was decided that drying to low moisture levels was not practical and that samples should be fed wet (e.g., about 7% moisture for Belle Ayr coal). A water analysis of the feed slurry was therefore initiated to determine water loss during handling of the coal, and the method chosen was toluene distillation (ASTM D-95). The feed coals themselves were later analyzed by this procedure (because of apparent water gain by slurries, as discussed below) in addition to the oven drying method. It was found that the water recovered by toluene distillation was generally 1-2% (absolute) higher than the moisture determined by the oven drying method.

VARIABILITY OF THE OVEN DRYING METHOD

While working with Loveridge coal, it was noticed that considerable variation was present in moisture values obtained by the oven drying method. The procedure is carried out as time permits, along with other duties, so that the length of time the sample spends in the oven is variable. Normally, a 5 gram sample is placed in a platinum evaporating dish which allows the sample to be spread out in a thin layer. Particular technicians tended to reproduce work on sample sets which they ran, but significant differences between technicians occurred. To determine the reason for the variations, 5, 8 and 12 gram samples were prepared. After an hour of oven drying, the moisture determination was 0.94% on the 5 gram sample, 1.22% on the 8 gram sample and 1.30% on the 12 gram sample. The samples were then brought to "constant weight" by repeated drying and reweighing (as was normally done by one of the technicians). During this operation, all samples gained weight with the final moisture values being 0.72% on the 5 gram sample, 0.80% on the 8 gram sample and 0.95% on the 12 gram sample. The coal was then analyzed by the toluene distillation procedure to obtain 1.90% water, a value about double the oven drying moisture obtained for over 80 samples of this lot of coal. It became apparent when the data were plotted (see Figure A-1) that the initial weight loss due to water evaporation was offset by a weight gain due to oxidation of the finely divided coal powder at 105°C. Moreover, larger samples were less affected in this way than small samples. The laboratory technicians had no difficulty reproducing the toluene distillation results.

COMPARISON TO DRYING TRAIN METHOD

It is not clear why the toluene distillation method accounts for more water than is adsorbed on a reagent during the drying train procedure* (see Figure A-1). The drying train method is also temperature sensitive and different values were obtained at drying temperatures from 105 to 150°C, using helium as the sweep gas. In weighing the coal sample after drying, it was observed that the coal gained weight rapidly when exposed to the air in the balance and the weight of water collected by the reagent could not be checked against weight loss of the coal.

RATIONALIZATION OF APPARENT MOISTURE GAIN BY FEED SLURRIES

The higher coal moisture measured by toluene distillation explains the apparent increase in moisture by feed slurries sometimes observed when the coal moisture is determined by oven drying and the feed slurry moisture by toluene distillation. When both moistures are measured by toluene distillation, some evaporation of water is measured in an amount dependent on the feed coal and treatment of the feed slurry.

USE OF TOLUENE DISTILLATION AS THE MOISTURE STANDARD

Since run DOE 349, all feed slurries have had moisture determinations by toluene distillation and at least check determinations have been made on the feed coals. In all cases, the oven drying method gave a lower moisture value than the toluene distillation method. This is well known, and the literature** on moisture determination is quite explicit in recommending the use of either toluene or xylene as a distillation reagent for separating the water in coal. It is possible that toluene releases chemisorbed water (and is absorbed on the coal in its place) and the use of this kind of reagent separates the maximum amount of water from the coal.

The water fed with the coal is subtracted from the gross water yield to determine the net water yield from combination of hydrogen with oxygen in the coal. The toluene distillation method, which consistently gives the highest value for moisture, therefore most accurately reflects water derived during liquefaction.

CONCLUSION

The toluene distillation method more accurately represents the water content of feed coals than oven drying since it is not affected by oxidation of the sample and may, in addition, release chemisorbed water. This method will therefore be used at Merriam for determining water associated with feed coals and feed slurries. A more accurate determination of water yields and moisture loss by evaporation will result, particularly for high moisture coals.

* The sample is heated in a tube swept by inert gas. The vapor passes through a reagent to pickup water.

** See for example: Chemistry of Coal Utilization, ed. H. H. Lowry (New York: John Wiley & Sons, 1945), Vol. I, p. 607.

Figure A-1

Comparison of Oven Drying Behavior and
Results of Moisture Determinations by Other Common Methods
Loveridge Mine Coal

APPENDIX B

Composition of Oils Made by SRC II Processing of Various Coals

Since run DOE 363R, each SRC II experiment has been represented by a proportional blend of product oils. These blends were distilled into three standard fractions: a naphtha boiling from room temperature to 193°C, a middle distillate boiling from 193°C to 288°C and a heavy distillate boiling over 288°C. A number of coals, catalyst systems and operating conditions are included, but for the most part, the compositions of the oils in these fixed boiling range cuts are quite similar. A few exceptions are noted such as the low sulfur levels in the products from the molybdenum catalyzed runs. These data are presented on the following page.

TABLE B-1

Composition of Oils Made by SRC II Processing of Various Coals

	DOE 363R*	DOE 364R*	DOE 365R*	DOE 366R*	DOE 367R*	DOE 368R*	DOE 377R	DOE 378R
<u>Run Conditions</u>								
Coal	Ireland & Blacksville (12% ash)		Ireland (10% ash)	Ireland (14% ash)	Ireland (16% ash)		Loveridge	
Temperature	455	450		455			450	
Pressure	1800	2250		1800			2250	
Catalyst			In situ Pyrite			FeS ₂ III	Mo	Mo
Concentration in Feed Slurry wt % as Fe or Mo	2.10	1.88	2.85	2.09	2.13	3.39	1.03	0.55
<u>Naphtha Composition, wt %</u>								
C	87.26	86.01	85.64	85.83	85.70	85.84	86.16	86.08
H	13.31	13.80	12.36	12.85	12.25	12.86	12.87	12.97
N	0.21	0.26	0.24	0.21	0.23	0.24	0.23	0.26
S	0.35	0.24	0.22	0.33	0.36	0.31	0.11	0.13
O	--	--	1.54	0.78	1.46	0.75	0.63	0.56
<u>Middle Distillate Composition, wt %</u>								
C	84.26	84.95	84.78	84.27	85.31	84.99	84.91	85.56
H	9.26	8.83	9.16	8.68	9.07	9.11	9.57	9.97
N	1.02	0.99	0.98	0.98	0.92	0.98	1.05	1.09
S	0.22	0.25	0.17	0.19	0.20	0.14	0.06	0.08
O	5.24	4.98	4.91	5.88	4.50	4.78	4.41	3.30
<u>Heavy Distillate Composition, wt %</u>								
C	89.14	89.43	88.88	88.75	89.09	89.16	88.70	88.74
H	7.70	7.88	7.82	8.18	7.75	7.77	8.10	8.34
N	1.27	1.20	1.08	0.97	1.08	1.16	1.09	1.15
S	0.49	0.46	0.51	0.40	0.50	0.43	0.22	0.20
O	1.40	1.03	1.71	1.70	1.58	1.48	1.89	1.57

* From "Exploratory Research on Solvent Refined Coal Liquefaction," Technical Progress Report for the Period April 1, 1980 through June 30, 1980; FE/14800-21