

## SRC II PROCESSING OF WESTERN COALS WITH ADDED PYRITE

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### I. INTRODUCTION

#### A. History of the P&M Merriam Laboratory in Coal Liquefaction

The P&M Merriam Laboratory began a bench scale investigation of solvent refining of coal in 1962. Early work was to verify design concepts and operability for a one ton per day process development unit (PDU) in Kansas City which was built during 1963 and operated during much of 1964<sup>(1)</sup>.

In 1967, bench scale studies resumed at Merriam, primarily to support the design effort for the 50 ton per day pilot plant at Ft. Lewis, Washington which operated from 1974 until 1981. Work has continued on a large variety of coal liquefaction problems since 1967 under sponsorship of the Office of Coal Research, Energy Research and Development Administration and the Department of Energy<sup>(2)</sup>.

#### B. Current Activities

The experiments described in this paper were conducted at the Merriam Laboratory during 1980 and 81. They were begun under DOE Contract 79ET14800 during a study on the relationship between coal properties and liquefaction behavior. Additional work was carried out during the current contract (81PC40005) to investigate SRC processing characteristics with disposable catalysts using alternate coals from different regions.

#### C. Previous Work

Earlier studies had shown subbituminous coals to be of low reactivity in SRC processes (3,4,5). The low reactivity of these coals was believed to be due primarily to a lack of iron to act as an in-situ catalyst. This was verified in the current work for a variety of coals from the Rocky Mountain and Great Plains Provinces where operation without added catalyst was not possible at normal SRC II conditions. Addition of moderate amounts of pyrite (4-5 wt % FeS<sub>2</sub>, based on coal) resulted in trouble free operation, however, and attractive yields of high quality oils.

#### D. Factors Affecting the Results

The specific yields and product quality obtained in these experiments depended on the coal, source and level of pyrite added and on liquefaction conditions. Each of these factors will be discussed below.

### II. EXPERIMENTAL

#### A. Bench Scale Unit

All of the experiments were conducted at Merriam using the bench scale unit depicted in Figure 1. This unit has been in operation since 1978 and allows for recycle of solid and liquid phases<sup>(6)</sup>. It has produced results which match closely those obtained in larger scale operations.

Coal was mixed with recycled solvent and recycled unfiltered coal solution and charged at 1800 or 2250 psig with a Hills-McCanna pump. Pure hydrogen was added at

the base of the preheater. The slurry passed through a 310 cm<sup>3</sup> preheater, where the temperature was raised to 400°C, and 1 liter dissolver. The dissolver was housed in a 6-zone air furnace which allowed close temperature control and either an isothermal (at 450°C and 465°C) or simulated adiabatic (457°C average) profile. The dissolver effluent was separated into five streams by a system of four equilibrium flash vessels operated at reactor pressure as well as an atmospheric flash and distillation column.

## B. Run Conditions

The conditions used in these runs are shown in Table I. This rather generous pressure of 2250 psig, used in all of the runs except one, was chosen initially to allow operation with a wide variety of coals. The runs with added pyrite were continued until steady state was achieved. The runs without added pyrite were conducted by lining out first with pyrite in the feed and then dropping pyrite out. Yields were determined at the point at which operation could no longer be sustained.

The coals used in this series of experiments are listed in Table II. Two were subbituminous, one high volatile C bituminous and two borderline between these two classifications. A low-iron Pittsburgh seam coal is included for comparison.

Four different pyrites were used with the properties shown in Table III. The Matheson, Coleman & Bell pyrites were mined in Georgia as a discrete mineral. They were ball milled and passed through a 140 mesh screen before use. The Robena pyrites were obtained from the coal cleaning operation of the U. S. Steel Robena Mine, Green County, Pennsylvania. They were finely ground by The Jet Pulverizer Company, Palmyra, New Jersey.

## III. RESULTS

### A. Effect of Coal Source

#### 1. Sensitivity of Various Coals to Pyrite Addition

The primary difference in the SRC II processing of western coals with and without pyrite is that with pyrite they can be run, without pyrite they can not! Beyond that, there are dramatic changes in the yield patterns, as shown in Table IV. The changes shown are minimum values computed at the time when operation could no longer be sustained without additive. If the runs without additive could be lined out, the differences would be even greater.

With the western coals, total oil yield was 15 to 22 wt % (based on MAF coal) higher when pyrite was added and SRC yield from 9 to 12 wt % lower, with Belle Ayr Mine coal being the most responsive. For two of the coals, IOM yield decreased (total conversion increased) by 6 wt % and for Belle Ayr by 12 wt %. There were small variations in hydrocarbon gas yields, with two higher and two lower with additive. Hydrogen consumption increased by varied amounts.

The Blacksville No. 2 coal, a relatively low iron, low reactivity eastern bituminous coal, is included for comparison. The response in total oil, SRC and IOM yields to pyrite addition was about an order of magnitude less than with the western coals.

With Kaiparowits coal, a higher hydrogen level (8.6 vs 7.8 wt %) was achieved in the heavy distillate (>288°C) from the catalyzed run. With McKinley and Edna coals, however, the hydrogen levels actually decreased when catalyst was added, due to the large increase in conversion of material into the upper end of the heavy distillate boiling range. With all the western coals, the fusion point of the distillation residue was significantly lower with added pyrite and its solubilities in hexane and toluene considerably higher (lower preasphaltene content).

There were essentially no differences in elemental analyses for any of the products from the Blacksville No. 2 coal runs made with or without added pyrite.

## 2. Comparison of Coals with Added Pyrite

The yields and hydrogen consumptions resulting from the SRC II processing of five different coals at 450°C average dissolver temperature, 2250 psig and 1.0 hour residence time with added pyrite are compared in Table V.

The western coals yielded 49-57 wt % total oil (MAF coal basis) compared to approximately 44 wt % with Powhatan coals (at 457°C and 1800 psig) which are more typical of those used in development of the SRC II process. Kaiparowits and Edna Mine coals were at the high end of the range while Belle Ayr and McKinley were at the lower end.

SRC yields also varied widely, from 18-27 wt %, IOM yields from 2.8-4.6 wt %, hydrocarbon gas yields from 12-15 wt % and hydrogen consumption from 4 1/2 to 6 1/2 wt %. This compares to about 28 wt % SRC and 6 wt % IOM (MAF basis) in a conventional SRC II process with Powhatan coal. It is interesting to note that the hydrocarbon gas and hydrogen consumptions are quite low relative to oil yield compared to those for Powhatan coals. These typically yield 16 wt % hydrocarbon gas and consume a little over 5 wt % hydrogen (again, on a MAF basis).

### B. Effect of Pyrite Source and Level in the Feed Slurry

#### 1. Effect of Pyrite Source

The results of processing Belle Ayr coal with three different pyrite samples are compared in Table VI.

The Robena Pyrite II produced a much greater effect than the other two pyrite samples even though only about half as much was added and the total solids level in the feed slurry was about 5 wt % lower than in the other runs. Total oil yield was 11.3 wt % higher based on MF coal, than with Matheson, Coleman and Belle (MCB) pyrite while SRC, IOM and hydrocarbon gas yields were lower by 3.9, 5.0 and 1.3 wt %, respectively.

Addition of MCB pyrite results in a slightly higher total oil yield and slightly lower SRC yield than the Robena Pyrite III although total conversion to pyridine soluble material was less.

Hydrogen consumptions were nearly the same during these three runs.

There were no clear trends in the heavy distillate and distillation residue elemental analyses. The residue from the run with Robena Pyrite II had the lowest fusion point and highest solubilities in hexane and toluene (lowest preasphaltene content) while that from the run with MCB Pyrite II had the highest fusion point and lowest solubilities.

The conditions for these three experiments were identical except for the pyrite sample (and level) and feed slurry solids level. The Robena Pyrite II and III samples were obtained from a coal cleaning operation while the MCB pyrite was mined as a discrete mineral. The pyrite analyses differ somewhat, as shown in Table III.

As mentioned earlier, the MCB pyrite was ball milled, the Robena II was jet pulverized in air, and the Robena III was jet pulverized in a nitrogen atmosphere. The activity of the additive appears to correlate with surface area, perhaps as an indicator of differing surface structure. This conclusion is based on a small number of samples, however, and Sandia has reported that there is no correlation between surface area and pyrite activity(7).

## 2. Effect of Pyrite Level in the Feed Slurry

The effect of iron level in the feed slurry on yields was determined in run DOE 350R. The yields were calculated during steady-state operation with added pyrite and at 7 points after the additive was dropped from the formulation. It was found that yields plotted against total iron in the feed slurry on a logarithmic scale gave an essentially linear relationship, as shown in Figure 2.

The addition of 1 wt % pyrite to the feed in run DOE 350RA resulted in an iron level of about 2.5% in the equilibrated feed slurry. When pyrite addition was stopped in run DOE 350RC, the iron level in the slurry dropped to about 0.35 wt % before the run was terminated by a plug in the preheater. As iron concentration decreased over this range, total oil yield dropped from about 56 to 28 wt %, SRC yield increased from 14 to 28 wt % and IOM yield increased from 1.3 to 14 wt %. There was little effect on hydrocarbon gas yield.

The hydrogen level in the heavy distillate also dropped off significantly (from 8.5 to 7.7 wt %) as iron was worked out of the system. There was also a significant increase in distillation residue fusion point (from about 110 to 190°C).

## C. Effect of Liquefaction Conditions

### 1. Temperature Effect

The effect of increasing the average dissolver temperature from 450 to 465°C with three different coals and added pyrite is shown in Table VII. In each case there was a significant increase in hydrocarbon gas yield and hydrogen consumption at the higher temperature, as expected. There were also decreases in oil and SRC yields and increases in IOM yields. From these results it is apparent that the optimum temperature for processing these coals with added pyrite is closer to 450°C than 465°C.

In each case, there were lower hydrogen levels in the heavy distillate and distillation residue at the higher temperature. Other product analyses were generally unaffected.

### 2. Combined Temperature/Pressure Effect

The results of processing Edna Mine coal at 450°C and 2250 psig or 457°C and 1800 psig are compared in Table VIII.

The results of run DOE 427RA are qualitative since the run was ended after three days due to increasing slurry viscosity. The higher reactivity in run DOE 427RB is still apparent, however.

The total oil yield was higher and the IOM yield lower at 450°C and 2250 psig. If run DOE 427RA could have been lined out, the differences would probably be more pronounced. The gas yield was higher at the higher temperature, as expected, and not much difference was observed in SRC yields and hydrogen consumptions.

Work is planned at Merriam to find the optimum conditions for processing western coals with added pyrite, and specifically to isolate the temperature and pressure effects. It is likely, however, that at least some of the improvement was due to the increased pressure.

### 3. Effect of Slurry Recycle

The scope of this paper has been limited to SRC II mode operation. It is interesting, however, to make at least one comparison to SRC I operation to determine the effect of recycling the added pyrite. This includes the effect of the higher

resulting iron concentration in the feed slurry as well as any changes that take place in the pyrite as it passes through the system.

Pyrite addition was highly beneficial in both modes of operation with Belle Ayr coal. Even with added pyrite, however, the SRC I studies with this coal indicated an unsatisfactory level of reactivity. Under the conditions used, 31 minutes residence time, 450°C, 1500 psig, 39 wt % coal concentration and 1 wt % pyrite addition, there was a 5 wt % deficiency of recycle solvent and overall conversion was poor as indicated by a 17 wt % insoluble organic matter yield. Thus, the SRC I studies would indicate that this coal was of low reactivity even with 1 wt % added pyrite.

As mentioned previously, dramatically different results were obtained in the SRC II mode (run DOE 350). With 1 wt % added pyrite (450°C, 2250 psig and 1 hr residence time), the Belle Ayr coal was one of the most reactive coals ever investigated at the Merriam Laboratory. Oil yield was 56 wt % (MF coal basis) and total organic residue yield (SRC + IOM) was only 15 wt %.

#### IV. CONCLUSIONS

1. Low iron, low rank coals can not be processed at normal SRC II conditions without added catalyst.
2. Addition of moderate amounts of pyrite (4-5 wt %, based on coal) results in attractive yields of high quality products and generally trouble-free operation.
3. Pyrites from different origins and those from the same origin obtained at different times may have varying activity. The factors influencing the catalytic activity of pyrite are not well understood, but in our studies activity generally increased with increasing surface area.
4. The yields from Belle Ayr coal at SRC II conditions vary with the logarithm of the iron concentration in the feed slurry over a wide range of the variables.
5. The optimum conditions for liquefaction probably vary with the coal and catalyst. The optimum temperature for the coals in this study was closer to 450°C than 465°C and yields can be expected to improve as hydrogen pressure is increased. Operating in the SRC II mode enhances the effect of added pyrite on coal reactivity.

#### REFERENCES

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- (3) "Development of a Process for Producing an Ashless, Low-Sulfur Fuel from Coal," Interim Report #6 (Vol. II-Laboratory Studies; Part 1-Autoclave Experiments); The Pittsburg & Midway Coal Mining Co., 1975, GPO #163.10:53/INT 6, NTIS #PB236-305.
- (4) "Development of a Process for Producing an Ashless, Low-Sulfur Fuel from Coal," Interim Report #7 (Vol. II-Laboratory Studies; Part 2-Continuous Reactor Experiments Using Anthracene Oil Solvent); The Pittsburg & Midway Coal Mining Co., September 1977, FE-496-T4.

- (5) "Solvent Refined Coal (SRC) Process," Quarterly Technical Report for the Period April 1, 1977 through June 30, 1977; The Pittsburg & Midway Coal Mining Co., December 1977, FE-496-141.
- (6) "Solvent Refined Coal (SRC) Process," Quarterly Technical Report for the Period April 1, 1978 through June 30, 1978; The Pittsburg & Midway Coal Mining Co., May 1979, FE-496-157.
- (7) "The Relationship Between Properties of Iron Sulfides and Their Catalytic Activity," paper presented by F. V. Stohl and B. Granoff, Sandia National Laboratories, Albuquerque, NM, at the Disposable Catalysts for Synfuel Production Symposium at the 1981 AIChE Meeting at Houston, Texas, April 5-9, 1981.

TABLE I  
RUN CONDITIONS

AVERAGE DISSOLVER	
TEMPERATURE:	450, 465°C (ISOTHERMAL) OR 457°C (SIMULATED ADIABATIC) 450°C INLET, 460°C OUTLET
PRESSURE:	1800 OR 2250 PSIG
RESIDENCE TIME:	1.0 HOUR
COAL CONCENTRATION:	30 WT % IN SLURRY
HYDROGEN FLOWRATE:	4 WT %, BASED ON SLURRY (52 MSCF/TON OF COAL)
MODE:	SRC II (RECYCLE OF UNFILTERED COAL SOLUTION)

TABLE II  
COALS

MINE	STATE	SEAM	RANK
BELLE Ayr	WY	WYODAK- ANDERSON	SUBBITUMINOUS
(KAIPAROWITS PLATEAU)	UT	RED	HVC BITUMINOUS
ENERGY	CO	WADGE	SUB A/HVC BIT.
McKINLEY	NM	*	SUBBITUMINOUS
EDNA	CO	WADGE	SUB A/HVC BIT.
BLACKSVILLE	WV	PITTSBURGH	BITUMINOUS

\* YELLOW, FUCHSIA, BLUE AND GREEN SEAMS ARE MINED.

TABLE III  
PYRITES

	MCB* PYRITE	MCB* PYRITE	ROBENA PYRITE	ROBENA PYRITE
WT %				
Fe	43.61	41.65	30.20	38.75
S	53.01	50.11	34.38	41.36
C	0.09	0.10	5.81	5.42
H	0.04	0.09	0.69	0.40
MOLE RATIO S/Fe	2.12	2.10	1.99	1.86
PURITY, WT % BASED ON Fe	94	89	65	83
AVERAGE PARTICLE SIZE, $\mu$ M				
BY COULTER COUNTER	--	12	1.7	3.5
BET SURFACE AREA, M <sup>2</sup> /G	2.0	1.1	5.9	2.6

\* MATHESON, COLEMAN AND BELL

TABLE IV  
SENSITIVITY OF VARIOUS COALS TO PYRITE ADDITION

CONDITIONS*	DOE 431RA/ 350RC-5	DOE 401R/ 353RC	DOE 422RA/ 422RB	DOE 424RA/ 424RB	DOE 402R/ 403R
COAL	BELLE AYR	Kaipar- OWITS	MC- KINLEY	EDNA	BLACKS- VILLE
CHANGE IN MAF YIELDS**					
C1-C4	+ 1.8	+ 0.2	- 0.9	- 2.3	- 0.1
TOTAL OIL	+22.0	+16.7	+20.3	+14.9	+ 2.6
SRC	-12.2	- 9.0	-10.5	- 9.1	- 0.7
IOM	-12.0	- 6.1	- 6.0	- 1.8	+ 0.3
CHANGE IN MAF HYDROGEN CONSUMPTION**	+ 0.1	+ 1.3	+ 2.2	+ 1.8	+ 0.7

\* ALL AT 450°C, 2250 PSIG, 1.0 HOUR RESIDENCE TIME WITH 30 WT % COAL IN THE SLURRY AND 4 WT % HYDROGEN, BASED ON SLURRY.

\*\* RUN WITH 1.86 WT % PYRITE III IN THE SLURRY COMPARED TO RUN WITHOUT ADDED PYRITE AT POINT WHERE OPERATION CEASED.

TABLE V  
PROCESSING OF VARIOUS COALS WITH ADDED PYRITE

CONDITIONS*	DOE 431RA	DOE 401R	DOE 422RA	DOE 424RA	DOE 402R
COAL	BELLE AYR	KAIPAR- OWITS	MC- KINLEY	EDNA	BLACKS- VILLE
<u>YIELDS, WT % MAF COAL</u>					
C <sub>1</sub> -C <sub>4</sub>	12.7	11.8	12.4	14.8	13.0
TOTAL OIL	49.5	56.8	49.3	53.9	42.9
SRC	21.3	17.8	26.5	21.4	36.3
IOM	2.9	2.8	4.6	4.1	6.1
<u>HYDROGEN CONSUMPTION, WT % MAF COAL</u>	4.5	5.4	5.1	6.3	4.8

- \* ALL AT 450°C, 2250 PSIG, 1.0 HR RESIDENCE TIME WITH 30 WT % COAL AND 1.86 WT % ROBENA PYRITE III IN THE SLURRY AND 4 WT % HYDROGEN, BASED ON SLURRY.

TABLE VI  
EFFECT OF PYRITE CHARACTERISTICS

CONDITIONS*	DOE 350RA	DOE 380RA	DOE 380RB
PYRITE	ROBENA II	MCB II	ROBENA III
ADDITION LEVEL, WT % COAL**	2.15	4.18	4.26
TOTAL SOLIDS IN FEED SLURRY	44.6	50.7	49.8
<u>YIELDS, WT % MF COAL</u>			
C <sub>1</sub> -C <sub>4</sub>	10.8	12.1	13.0
TOTAL OIL	55.9	44.6	41.6
SRC	13.5	17.4	19.0
IOM	1.3	6.3	5.2
<u>HYDROGEN CONSUMPTION, WT % MF COAL</u>	5.4	5.1	4.8

- \* FOR ALL: 449-450°C, 2250 PSIG AND 1 HOUR RESIDENCE TIME WITH 30 WT % BELLE AYR COAL IN THE SLURRY AND 4 WT % HYDROGEN, BASED ON SLURRY.

- \*\* AS PURE FeS<sub>2</sub>.

TABLE VII  
EFFECT OF TEMPERATURE ON PROCESSING  
WESTERN COALS WITH ADDED PYRITE

<u>CONDITIONS*</u>	<u>DOE</u> <u>350RA/B</u>	<u>DOE</u> <u>353RA/B</u>	<u>DOE</u> <u>355RA/B</u>
COAL	BELLE AYR	KAIPAR- OWITS	ENERGY
PYRITE	ROBENA II	MCB I	MCB I
<u>CHANGE IN MAF YIELDS**</u>			
C <sub>1</sub> -C <sub>4</sub>	+3.5	+4.4	+3.3
TOTAL OIL	-4.3	-1.7	-2.5
SRC	-2.2	-4.6	-9.5
IOM	+2.0	+0.7	+6.2
<u>CHANGE IN MAF HYDROGEN</u> <u>CONSUMPTION**</u>	+0.9	+1.0	+0.2

\* ALL AT 2250 PSIG AND 1 HOUR RESIDENCE TIME WITH 30 WT % COAL AND 1.0 WT % ADDED PYRITE IN THE SLURRY; 4 WT % HYDROGEN, BASED ON SLURRY.

\*\* RUN AT 465°C COMPARED TO ONE AT 450°C.

TABLE VIII  
COMBINED EFFECTS OF TEMPERATURE AND PRESSURE  
ON THE SRC II PROCESSING OF EDNA COAL  
WITH ADDED PYRITE

<u>CONDITIONS*</u>	<u>DOE 427RA</u>	<u>DOE 427RB</u>
AVERAGE DISSOLVER TEMP., °C	457	450
PRESSURE, PSIG	1800	2250
<u>YIELDS, WT % MF COAL</u>		
C <sub>1</sub> -C <sub>4</sub>	14.4	12.2
TOTAL OIL	43.5	46.1
SRC	20.0	21.4
IOM	6.2	4.3
<u>HYDROGEN CONSUMPTION,</u> <u>WT % MF COAL</u>	4.9	5.1

\* ALL AT 1.0 HOUR RESIDENCE TIME WITH 30 WT % EDNA MINE COAL AND 1.86 WT % PYRITE IN THE FEED SLURRY; 4 WT % HYDROGEN, BASED ON SLURRY.

FIGURE 1  
MERRIAM LABORATORY  
BENCH SCALE COAL LIQUEFACTION UNIT

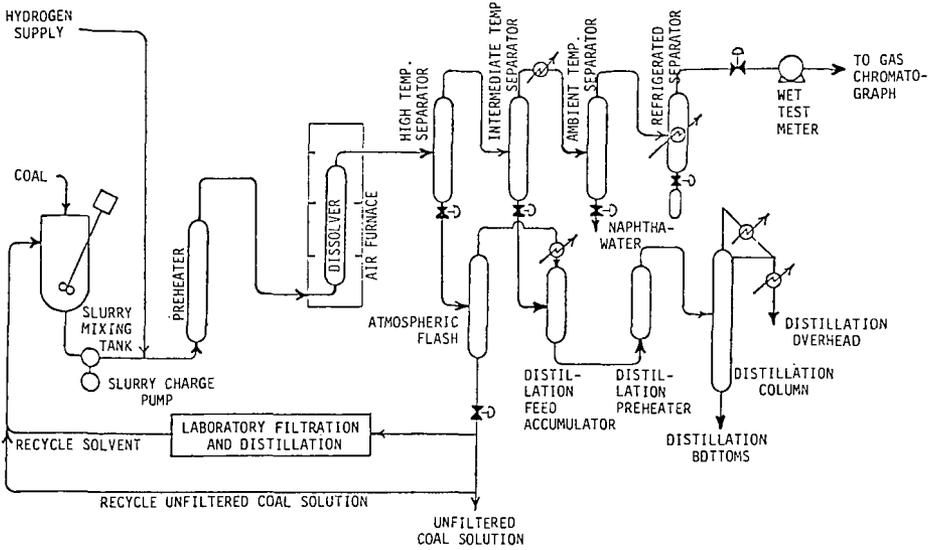


FIGURE 2  
EFFECT OF IRON LEVEL ON YIELDS  
RUN DOE 350RC

