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Volume II

**Evaluation of
Coal Minerals
and
Metal Residues
as
Coal-
Liquefaction
Catalysts**

Work Performed by
**Auburn University
Coal Conversion Laboratory**

Under Contract To
Air Products and Chemicals, Inc.

February 1982

Prepared for the United States
Department of Energy
Under Contract No.
DE-AC22-79ET14806

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as Coal-Liquefaction Catalysts

MASTER

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SUMMARY

Under DOE Contract No. DE-AC22-79ET14806, Air Products and Chemicals, Inc., subcontracted Auburn University Coal Conversion Laboratory to perform exploratory studies on the use of minerals and by-product metallic wastes in coal liquefaction. Under this program Auburn University conducted an extensive screening program on numerous materials from which the more active or interesting ones were further investigated in the continuous process development units (PDU) at Air Products. In Volume 1 of the final report a number of the results from those tests are summarized for comparison with the PDU results. Because of the very extensive and detailed work performed at Auburn University, a portion of that work is not included in Volume 1. Therefore, in order to fulfill the requirements of the contract with DOE, a compilation of the work performed by Auburn University is submitted in Volume 2.

The information from the Auburn University work was compiled from a sequence of monthly reports submitted to Air Products and Chemicals, Inc., during the course of the program. Because of the very large numbers of screening runs conducted at Auburn, the overlap between these reports is minimal. This work presents in some detail the various stages of development of screening procedures and analytical methods that were developed. The reader should also find them extremely informative as to the generation of ideas that developed during this program.

The work reported in this volume went beyond simple screening runs. Extensive exploratory studies as well as basic studies on the behavior of reactants and catalysts were performed. These results from the basic and exploratory studies impacted on the overall direction of this program.

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MAIN REPORT

Establishing a Base Line

In order to assess the "reactivity" of Elkhorn #3 coal received from APCI, two experiments have been performed, specifically cresol solubility and ash content tests. Kentucky 9-14 coal which is known to be reactive was also tested for comparison and the results are summarized in Table 1. The cresol solubility tests appear to give satisfactory results. The ash content of the Elkhorn #3 coal, 13.3%, is higher than the ash content for the Kentucky #9-14, 6.4%.

In order to establish a base line, conditions were sought which would show a sizable difference in oil produced by a non-catalyzed coal-solvent system compared with the oil produced by a strongly catalyzed system. The need to do this was not anticipated but arose when comparison of the initial data indicated the difference in catalyzed and uncatalyzed data was small.

Initially a 17.5 ml tubing bomb was employed at 410°C for 30 minutes. Eight and three tenths (8.3) ml of reactants* were charged to the tubing bomb. The reactants include 6 g solvent, 3 g coal, and one g additive, if any. A typical value of oil content for an uncatalyzed reaction was 63% of the entire coal-solvent system (Table 2). Sixty-five percent (65%) oil resulted for a reaction where the strong catalyst Co-Mo-Al was employed. The difference in oil production between catalyzed and uncatalyzed reaction was not satisfactory, especially since experimental error had been observed to be as high as 1%.

We continued to search for conditions which would yield more visible results. Three variables, specifically, size of the reactor (related to the amount of hydrogen available for reaction), time for reaction, and temperature, were explored.

A large tubing bomb reactor (46.3 ml rather than the smaller 17.5 ml reactor) was employed and an optimum temperature search was made. Figure 1 shows the temperature dependency of the oil fraction in the reaction mixture. Clearly there is a maximum near 475°C. Coking was observed at 500°C. From conversations

* Figure obtained by actual measurement with additive (Robena Pyrite) included.

Table 1. Reactivity of Elkhorn #3 Coal Compared with Ky. 9-14 Coal

	Conversion to Cresol Solubles	Ash Content
Elkhorn #3	87% $\pm$ 0.6%	13.33% $\pm$ 0.18
Ky. 9-14	92% $\pm$ 0.1%	6.41% $\pm$ 0.12%

Reaction Conditions: SRC II - Fuel Oil - 6g
Coal (Elkhorn or Ky.) - 3g
T = 410°C
Time = 30 min.
Agitation - 860 rpm
P_{H2} = 1250 psig at 25°C

Table 2. Reproducibility of 17.5 ml. Autoclave₁
and Separation Procedure

Number of Experiments	3 Trials		6 Trials		3 Trials		4 Trials	
System	Solvent and Coal		Solvent and Coal		Solvent #2		Solvent #1	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Oil (%)	62.82	0.37	62.92	0.62	90.68	0.87	85.87	1.20
Asphaltene ₂ (%)	11.99	0.33	12.28	0.80	8.66	1.21	12.82	1.05
Preasphaltene ₃ (%)	9.74	0.64	9.65	0.53	0.46	0.31	1.13	0.55
Residue (%)	15.45	0.30	15.14	0.42	0.19	0.06	0.17	0.06

¹REACTION CONDITIONS: 410°C; 2:1 Solvent: Coal (where coal was used); 1250 psig H₂; 30 min; Solvent: SRC-II fuel oil as received from A.P.C.I.; Coal - Elkhorn #3. Floyd County, Kentucky

²Toluene Soluble, pentane insoluble

³Methylene Chloride-Methyl Alcohol (10%) soluble, toluene insoluble.

Reaction Conditions: 6g solvent, 3g coal, 1g Co-Mo-Al,
30 minutes reaction time,
1250 psig H₂ initially at ambient
temperature.

Figure 1: Temperature Dependency of Oil Fraction

with Dr. D. Garg of Air Products it was decided to limit the temperature to 450°C if practical, that is, if a sufficient difference in oil production could be obtained between catalyzed and uncatalyzed reactions.

The question concerning use of a 17.5 ml reaction vessel rather than a larger vessel was approached by performing identical reactions at 450°C for 30 minutes with a strong catalyst in two different size reactors. With the smaller reaction vessel 65% of the reaction mixture was oil, and G.C. analysis showed a hydrogen consumption of 0.05 g. With the larger (46.3 milliliters) reaction vessel 76% of the reaction mixture was oil and G.C. analysis showed that 0.14 g of hydrogen was consumed. It was concluded that hydrogen was possibly a limiting reagent in the smaller bomb and that the larger bomb was necessary to increase the oil production. The amount of hydrogen available in the smaller bomb was 0.0648 g which amounted to 77% of hydrogen consumption of the available hydrogen. In the larger reaction vessel the amount of hydrogen consumed (0.14 g) was more than the hydrogen available (0.0648 g) in the smaller bomb. The amount of coal and solvent in each vessel was the same; therefore, it was interesting to note that the reaction in the smaller bomb did not consume all the available hydrogen since the reaction in the larger vessel showed that all of the hydrogen could have easily been consumed. That would indicate that the hydrogen partial pressure could be an important factor in limiting or encouraging the reaction. If the hydrogen in the large bomb had also been limited only by the same phenomenon it might be expected that the reaction in the larger bomb would have proceeded to approximately the same point; that is, both reactions would have proceeded to approximately the same partial pressure of hydrogen. The final hydrogen mole fraction in the smaller and larger bombs were determined to be 0.59 and 0.83, respectively. The final hydrogen mole fraction in the larger bomb therefore did not approach the 0.59 limitation, if it was a limitation. Therefore, it was concluded that there was sufficient hydrogen in the larger bomb with a strong catalyst to give a higher oil yield.

In the larger reactors, at 450°C, for a reaction time of thirty minutes the difference in oil production between a strongly catalyzed and an uncatalyzed reaction was 50 percentage points absolute (50%). For a reaction time of one hour at 450°C, the difference in oil production was 70% absolute. The

experimental error which could be expected was approximately $\pm 5\%$. It was decided that one hour reaction time would give sufficiently more oil production to make the extra time worthwhile in the evaluation of the coal minerals and waste materials; that is, a difference of $70\% \pm 5\%$ is better than $50\% \pm 5\%$.

In summary, the baseline conditions determined to be the most satisfactory of all the conditions studied were 450°C and one hour reaction time in a reactor sufficiently large enough to contain an adequate hydrogen supply for reaction. The requirement for a sufficient reactor volume and other considerations such as the size of reactor bath (in which the reactor is heated), ease of operation (the larger the reactor, the more difficulty involved, in the present case), availability of standard parts, and equipment durability led to the choice of a reactor with an internal volume of 46.3 ml.

Subsequently the following data in Table 3 were obtained which is considered to be baseline for the solvent, coal and solvent, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and Co-Mo-Al additives. The $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and Co-Mo-Al represent what can be expected with a very good catalyst. Table 3 presents the data for individual reactions as well as averages. The duplication is good for all cases except for the four pyrite (FeS_2) catalyzed reactions where the average may or may not be representative.

The percentages in Table 3 were obtained as follows. The initial data are in the form of grams of the various fractions of the reacted coal and solvent mixture. For illustration Experiment 48 will be employed in which the material $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was the additive to the coal solvent system. The raw data after separation was as follows:

Experiment #48

<u>Item</u>	<u>Weight (g)</u>	<u>With Adjusted Oil Value</u>
sample (initial sample)	7.0972	7.0972
oil	5.4299	5.7865
asphaltene	.5161	.5161
preasphaltene	.4550	.4550
residue	.3396	.3396

Table 3. Base Line Data₁ for Elkhorn #3 Coal
(Product Distribution)

Individual Reactions₃ (see AVERAGES below)

Additive ₈		None		FeS ₈ *		Robena * Pyrite _{2,8}		Siniola * Mexico Pyrite _{2,8}		Co-Mo-Al		SnCl ₂ ·H ₂ O *	
Experiment	Number	32	34	43	44	45	47	39	41	27	36	46	48
% oil ₅		-3	2	27	26	27	39	39	24	72	67	67	70
% asphaltene ₆		59	56	49	52	59	44	48	59	17	22	11	7
% preasphaltene ₇		15	12	6	4	5	7	6	4	3	3	21	22
% residue		28	30	18	18	9	10	7	13	8	8	1	1
% conversion		72	70	82	82	91	90	93	87	92	92	99*	99*

AVERAGES₃

Additives ₈	none	FeS	Robena Pyrite	Mexico Pyrite	Co-Mo-Al	SnCl ₂ ·H ₂ O
% oil ₅	-1	27	33	31	69	68
% asphaltene ₆	58	50	51	54	20	9
% preasphaltene ₇	14	5	6	5	3	22
% residue	29	18	10	10	8	1
% conversion	71	82	90	90	92	99

1. Conditions: 6g solvent (SRC-II Fuel Oil Blend (CPDU-121)), 3g Elkhorn #3 (Floyd County) Coal, 1g additive (e.g. pyrite) if applicable, 450°C, 1 hour reaction time, initial H₂ pressure - 1250 psig, reactor volume - 46.3 cc.
2. Experiments are reported below that address the deviation in oil values for the pyrite catalyzed reactions.
3. All calculations are based on dry ash-free coal; gas production is not accounted for in these percentages.
4. Additives or catalysts formulations are addressed elsewhere.
5. Pentane soluble.
6. Toluene soluble, pentane insoluble.
7. Methylene Chloride - Methyl Alcohol (10%) soluble, toluene insoluble.
8. The values obtained here for FeS and the two pyrites are in basic agreement with the data obtained at Sandia Laboratories for similar materials.

* See next page.

Table 3 (Continued)

* In obtaining the numerical data in Table 3 the calculations include the assumption that additives (e.g. FeS_2) remain unchanged during reaction. This, of course, may not be correct. The assumption is manifested in the calculations in the following way: if 10% by weight of additive was present in the initial reaction mixture, then 10% of the reacted mixture sample weight is subtracted which is assumed to yield a sample weight more representative of the carbonaceous material and its ash. The cautions which should be noted at this point are: 1) pyrite (FeS_2) may not be finally assumed to give better results than the FeS employed in this study; 2) the conversion of coal produced by $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ will not be as high as implied by Table 3.

At this point the residue still contains the coal ash but the residue value does not include the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ additive*. As noted above the oil value is adjusted to make the weight of the fractions equal to the initial sample weight. This particular adjustment which amounts to 6.6% is little larger than usual. For example: on the previous sample (number 47 in which Robena pyrite was employed) an adjustment of 1.4% was required. For case 48 with the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ the oil production was considerably higher than with the pyrite; therefore, it might be reasonable to assume that more light molecular weight material was produced with the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and that some of the material could have been lost when the pentane was recovered from the oil. A sample of the pentane recovered from the oil fraction from an earlier experiment has been retained for G.C analysis to determine whether any C_4 , C_6 , C_7 , or C_8 material can be identified which will perhaps confirm the loss of volatile material. A sample was also collected over liquid nitrogen in an attempt to trap any lighter hydrocarbons (C_4 to C_8).

The data are then normalized to one.

<u>Item</u>	<u>Adjusted Data (g)</u>	<u>Reduced Data</u>
sample	7.0972	1.0
oil	5.7865	.8153
asphaltene	.5161	.0727
preasphaltene	.4550	.0642
residue	.3396	.0478

The normalized data include the coal and its ash and solvent. On a basis of 1.0 g of the reaction mixture 0.6667 g was solvent and 0.3333 g was coal. Based on the average of two reactions of solvent 0.6667 g of solvent would contain the following amounts of reaction with only solvent present:

* See note marked by asterick in Table 3.

oil	.6140
asphaltene	.0510
preasphaltene	.0005
residue	.0012

These values are subtracted from the normalized data.

oil	.8153	.6140	.2013
asphaltene	.0727	.0510	.0217
preaphaltene	.0642	.0005	.0637
residue	.0478	.0012	.0466

Normalized Data	Amount from Solvent	Amount from Coal
--------------------	---------------------------	------------------------

The ash content of the coal is 13.33% so the value of (.1333% ash in coal) x (.3333 g coal) = (0.0444 g ash in residue) is subtracted from the residue which yields

oil	.2013
asphaltene	.0217
preasphaltene	.0637
residue	.0022

In percentage form this is then on a basis of the dry ash free coal:

70% oil
7% asphaltene
22% preasphaltene
1% residue
99% conversion

The conversion is simply 100% less than the amount of residue.

The above is the way the calculations were performed. Another option was to use values of oil, asphaltenes, preasphaltenes and residue from the original unreacted solvent to subtract from the reaction mixture to give amounts produced from the coal rather than to subtract the amounts from the reacted solvent. If the calculations were performed in this manner the resulting percentages would represent the amounts produced from the coal, if it were possible to recover the initial solvent from the reaction mixture. For the purpose of comparing mineral additives, however, the present calculation scheme is adequate because it simply amounts to subtracting a constant vector from variable data vector.

One of the goals was to maximize the difference in oil yields between uncatalyzed and strongly catalyzed reactions. As seen in Table 3 an uncatalyzed reaction, that is, one with only coal, solvent, and H_2 present, yields approximately no oil. The -1% in column 1, Table 3 indicates that actually an adverse situation can occur in which less oil is obtained than is available before the reaction; that is, not only the coal produces no oil, the oil content of the solvent actually decreases.

The minus value for oil production can occur because the thermally induced radicals from the coal, rather than combining with a hydrogen and terminating as "smaller" oil molecules can combine with other thermally induced radicals from the coal and become "larger" molecules more characteristic of fractions other than oil. The minus value for oil production could also simply be a case of experimental error. The strongly catalyzed reactions, specifically where Co-Mo-Al and $SnCl_2 \cdot 2H_2O$ are used, show 69% and 68% conversion of the coal to the oil fraction. The possible error associated with these figures as seen by observing the individual reactions in Table 3 indicates that the oil values might conservatively be reported as $69\% \pm 5\%$ or $68\% \pm 3\%$. The point is that the difference in oil production between an uncatalyzed reaction (approximately 0% oil) and a strongly catalyzed reaction (e.g. 68% oil) with an error of only five percentage points (5%) provides a wide enough range for obtaining good comparison of the effects of various additive to the system.

It is of note that when FeS or FeS₂ is used as an additive the oil production falls comfortably between the uncatalyzed and the strongly catalyzed reactions. When various other additives are used with FeS or FeS₂ it should be eminently possible to observe either positive or negative effects. A deviation from the average FeS₂ (or FeS) oil production value of ten percentage points (10%) will be a good indication that an added substance (coal-mineral or waste material) did effect the reaction. Since there are approximately thirty percentage points in the negative direction (30% average oil for FeS₂ to 0% oil) and approximately forty percentage point in the positive direction (30% oil to 70%) there is considerable latitude for not only seeing effects but distinguishing levels of effects as well.

In short, the care and time spent in determining the base case reaction conditions had been fruitful and resulted in the production of accurate results.

The material FeS was referred to as the base case additive. One of the primary reasons for initially suggesting that FeS be employed was that FeS would not consume hydrogen as FeS₂ would in the reaction $\text{FeS}_2 + \text{H}_2 \rightarrow \text{FeS} + \text{H}_2\text{S}$. For the present work it was found expedient to employ a reactor with 46.3 cc of volume. On two sample reactions with FeS₂, Gas Chromatograph analysis showed that about 40% of the initial hydrogen still remained available after reaction indicating there was not a hydrogen deficiency in a reactor with 46.3 ml volume. An ideal gas law calculation also indicates that the hydrogen requirement for the reaction $\text{FeS}_2 + \text{H}_2 \rightarrow \text{Fe} + 2\text{H}_2\text{S}$ for 1 g of FeS₂ is about 2.3 cc of H₂ at the initial pressure 1,250 psig and ambient temperature. The volume of the reactor occupied by gas is approximately 38 ml which again indicates sufficient H₂ is available. Since the FeS₂ requires small amount of H₂ compared with the hydrogen available (about 8% of the H₂ is required for the $\text{FeS}_2 + \text{H}_2 \rightarrow \text{FeS} + \text{H}_2\text{S}$ reaction) there is no obvious reason to use FeS rather than FeS₂. A reason to use FeS₂ is that it is more available. The FeS must be specially produced and handled. There is some difference between FeS and the pyrites: the pyrites give a greater conversion of the coal* (90% compared with 82% for FeS) and there is some apparent difference in oil and asphaltene pyrite.

Mineral Catalysis

Minerals Evaluation (Presonicator)

Table 4 presents the effect of several minerals on the coal liquefaction process. The data are the result of single reactions and are arranged in order of increasing oil production. The baseline data are also included for comparison. The negative effect on oil production of Bornite and the positive effects of "Red Mud" and ZnS lie beyond the experimental error associated with the FeS_2 baseline. The Fe_2O_3 gave a higher conversion to oil than pyrite.

The baseline (FeS_2 - Robena Mine Pyrite - 325 mesh) has been triplicated with the following results: oil, 22% with standard deviation of 2.6%; asphaltenes, $55\% \pm 2.6\%$; preasphaltenes, $5\% \pm 0.6\%$; I.O.M., $18\% \pm 0.6\%$. The assumption is made that the FeS_2 reacts with hydrogen in the system to completely form FeS . The baseline for FeS_2 (-325 mesh pyrite from the Robena Mine) in Table 4 is now considered accurate with the above reported precision.

The assumptions concerning changes of mineral matter during reaction will affect the values reported for the fractions of oils, asphaltenes, preasphaltenes, insoluble organic matter, and conversion. Table 5 shows the effects of different assumptions for FeS_2 , CaCO_3 (calcite), and Fe_2O_3 . The changes in values for some of the fractions can be considerable if the change in molecular weight is large. For example, the change in oils percentage for CaCO_3 and Ca is 23% to 10% respectively. What is presently being done is to assume the most reasonable change or to assume no substantial change (i.e., no change for the purpose of calculation) and to state the assumption for future reference. If there were reasonable uncertainty as to the nature of the mineral matter after reaction, then analysis of the mineral matter after reaction would be advisable if the calculations were sensitive to the possible changes in the mineral matter.

If a correlation could be established between a model compound system and the coal-solvent system, the rate of screening of minerals and wastes could be increased if analysis of the model system required less time than the analysis of the coal-solvent system. Some minerals from this study were used to examine

Table 4. Effect₁ of Minerals₃ on Product Distribution_{2,9} and Conversion Compared with Baseline Data

Additives ₄	No Additives	Bornite +FeS ₂	Calcite +FeS ₂	Montmorillonite +FeS ₂	Baseline FeS ₂	Feldspar +FeS ₂	Red Mud +FeS ₂	Fe ₂ O ₃	ZnS +FeS ₂	Co-Mo-Al
Experiment Number	Average	61	54	60	Average	59	58	55	53	
% Oils ₅	0	15	17	19	22 ± 2.6	25	29	29	31	69
% Asphaltenes ₆	57	59	52	58	55 ± 2.6	50	50	45	45	20
% Preasphaltenes ₇	14	6	9	6	5 ± 0.6	8	6	9	9	3
% I.O.M. ₈	29	20	22	17	18 ± 0.6	17	15	17	15	8
Conversion	71	80	78	83	82	83	85	83	85	92

1. Reaction conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 coal; 1g FeS₂ if added; 1g other material added as indicated; 450°C; 1 hour reaction time; initial H₂ pressure-1250 psig; 46.3 cc reaction volume.
2. Values for oils and Asphaltenes have been observed to be subject to an error of approximately five percentage points.
3. Information on minerals is presented elsewhere.
4. In all reactions where FeS₂ (pyrite) is present it is assumed to change complete to FeS during reaction. Other minerals in Table I are assumed to remain unchanged except Calcite (CaCO₃) which is assumed to form CaS.
5. Pentane soluble.
6. Toluene soluble; pentane insoluble.
7. Methylene Chloride - Methyl Alcohol (10%) soluble, toluene insoluble.
8. I.O.M. - Insoluble organic matter.
9. Calculations do not account for gas formation; that is, calculations are based only on liquid and solid material obtained after reaction. Calculations are on the basis of dry, ash free coal.

Table 5. Effect on Calculated Product Distribution Due to Assumed Mineral Changes During Reaction

Experiment No.	45		54			55	
Mineral	1g FeS ₂		1g CaCO ₃ and 1g FeS ₂			1g Fe ₂ O ₃	
Assumption	Unchanged	FeS formed	Unchanged	Elemental Ca formed	CaS formed	Unchanged	FeS formed
Probability of Assumption	Improbable	Very Probable	Improbable	Improbable	Assumed	Improbable	At least same will form
% Oils	27	20	23	10	17	29	32
% Asphaltenes	59	57	54	50	52	45	45
% Preasphaltene	5	5	9	8	9	9	9
% I. O. M.	9	18	14	32	22	17	14
% Conversion	91	82	86	68	78	83	86

the cracking behavior of toluene to benzene in the presence of these additives. The purpose was to determine whether a correlation existed between the activity of the minerals in the production of oils from coal and in the production of benzene from toluene. Figure 2 presents the data. As seen in Figure 2, there appears to be a direct correlation. Tests with minerals which produce between 30% and 70% oil should yield information on the existence of correlations.

Table 6 presents nitrogen, carbon, and hydrogen weight percentage for several coal-solvent-additive systems. Figure 3 shows that there may be a correlation between % oil produced and the hydrogen/carbon ratio of the systems. If it is assumed that the amount of oil produced would correlate with solvent quality, then it may be further stated that for the minerals and system employed there may be a correlation between the hydrogen/carbon ratio of the systems and the solvent quality.

Sulfur analyses were performed on the oils and asphaltene fractions of reactions where pyrite and Fe_2O_3 were the additives. The sulfur content of the asphaltene fraction was essentially zero in both cases. The sulfur content of the oil fraction where Robena Mine pyrite was employed was 0.28% by weight. When the additive was Fe_2O_3 the sulfur content was 0.19% by weight.

In Table 7 it is seen that in a system where gaseous hydrogen is deficient, FeS_2 performs nearly as well as Co-Mo-Al in terms of oil production. In the hydrogen deficient system there are only five percentage points difference in oil production between the systems with FeS_2 and Co-Mo-Al, whereas the difference increases to 46% in the hydrogen sufficient system. The results with pyrite for oils and asphaltenes obtained from Sandia Laboratories, Column 5 in Table 7, experiment No. G-341--62, are similar to the results from experiment No. 50, column 3 in Table 7 obtained at Auburn. This indicates that Sandia employed a hydrogen sufficient system.

After obtaining the initial data for the grams of sample, oils, asphaltenes preasphaltenes and residue the first step performed in reducing the data to the percentages of each fraction is to eliminate the weight of additives. The weight of additive will be subtracted from the sample weight and the residue.

1. Conditions used to produce oils are stated elsewhere.
2. Conditions used to produce benzene from toluene were: 410°C, 30 minutes, 5.0 g toluene, 0.5 g additive, 17.5 ml. tubing bomb reactor

Figure 2. Benzene to Toluene Area Ratio Versus Oil Production from Coal for Three Additives

Table 6. Nitrogen, Carbon, and Hydrogen Percentages in Coal-Solvent Systems^{1,2}

Additive	None	FeS	Siniola, Mexico Pyrite	Robena Mine Pyrite	SnCl ₂ ·H ₂ O	Co-Mo-Al
Experiment No.	32	44	39	45	46	36
Weight % N	1.5	1.3	1.6	1.0	1.4	1.3
Weight % C	91.5	91.4	93.7	85.1	78.5	93.9
Weight % H	7.5	8.3	8.0	7.6	7.2	8.3
H/C Atom Ratio	0.98	1.09	1.02	1.07	1.10	1.06

1. Data were obtained from a Perkin-Elmer 240 Elemental Analyzer.

2. Data are based on dry, ash-free, additive-free coal.

Figure 3. Hydrogen/Carbon Atom Ratio Versus Oil Production

Table 7. Behavior of Additives Related to Hydrogen Deficiency and Hydrogen Sufficiency

Experiment Number	Hydrogen Deficient System		Hydrogen Sufficient System		Sandia Laboratories
	FeS ₂ 9	Co-Mo-Al 8	FeS ₂ 50	Co-Mo-Al 36	FeS ₂ G-341--62
% Oils	10	15	21	67	25 ₂
% Asphaltenes	29	29	56	22	52
% Preasphaltenes	32	32	5	3	18 ₃
% I.O.M.	29	24	18	8	5 ₃
Conversion	71	76	82	92	94 ₃

1. Granoff, B. and Baca, P. M., "Mineral Matter Effects and Catalyst Characterization in Coal Liquefaction"; Sandia Laboratories Energy Report No. SAND-79-0505, p. 47.
2. Values are calculated to include only oils, asphaltenes, preasphaltenes, and I.O.M. as 100% of the system.
3. In extracting the preasphaltenes THF was employed by Sandia Laboratories. This will produce different results for preasphaltenes, I.O.M., and conversion than obtained for the corresponding values in columns 1, 2, 3, and 4 which were obtained at Auburn University using a methylene chloride - 10% methyl alcohol solvent to extract preasphaltenes.

For example in Experiment No. 53 the original charge to the reactor was 3 g of coal, 6 g of solvent, 1 g of pyrite, and 1 g of ZnS plus 0.268 g of hydrogen. The ZnS is assumed to remain unchanged. The pyrites FeS_2 , is assumed to yield FeS as solid material and H_2S gas after reaction with hydrogen.

A sample weighing 8.1139 g was taken after reaction. One gram of FeS_2 yields 0.7333 g of FeS and the one g of ZnS is assumed to remain unchanged. The amount of additive to be subtracted from the 8.1139 sample weight is then

$$8.1139 \times \frac{1(\text{ZnS}) + 0.7333(\text{FeS})}{6\text{g (solvent)} + 3\text{g (coal)} + 1(\text{ZnS}) + 0.7333 (\text{FeS})} = 1.3103\text{g}$$

This amount of the weight of additive in the sample after reaction and is therefore subtracted from the residue which consists of the I.O.M. (insoluble organic matter), coal mineral matter, and additive.

The calculations then proceed as we discussed earlier.

Analysis Modification and Initial Data Revision

The thrust of the work at Auburn was to determine the effects of several materials on coal liquefaction. There are several "areas" which could have been chosen for examination, but it was decided that "oils" and "asphaltenes" production which is part of the product distribution analysis was of primary interest. An extraction technique employing a Soxhlet apparatus had been employed by Auburn in the past to determine product distribution of liquefaction mixtures, however, that technique was very time consuming. This caused Auburn to be interested in the extraction method refined by Frank Schweighardt. The decision was made to use Dr. Schweighardt's method. Since the sonifier was not received early in the program, experiments were performed using a careful manual extraction technique of the oils with pentane. This technique showed satisfactory reproducibility and was employed over a period. Later experiments were performed using the sonifier on reacted mixture. The results of the tests with the sonifier were that in four of six cases significantly more oils

were extracted with the sonifier aided extraction than with manual extraction. In the one case a sufficient amount of quartz, coal, and solvent were reacted so that the resultant reacted mixture could be divided into two parts: The production distribution of the second part was obtained by the sonifier-aided method.

Direct Comparison of Separation Methods

	Manual <u>Separation</u>	Sonifier Aided <u>Separation</u>
% oils	11	32
% asphaltens	42	22
% preasphaltenes	12	14
% I.O.M.	35	32

The I.O.M.'s (35 and 32) and % preasphaltenes (12, 14) are essentially the same for the two methods. However, use of Branson sonifier gave a higher oil percentage (32% compared with 11%) at the expense of the asphaltene fraction (42% from manual separation down to 22% for sonifier separation). Table 8 presents a comparison between the manual and sonifier aided extraction. The results for the Fe_2O_3 additive in Table 8 were the first data obtained using the sonifier. With Fe_2O_3 , the product distributions are very similar for both the manual and the sonifier aided extraction techniques. The last two columns of comparison to the decision to employ the sonifier for future extractions. One other observation can be made from Table 8: the value obtained in % I.O.M. and % preasphaltenes are essentially the same for a particular additive regardless of the separation procedure. The shift to a higher oil percentage with sonifier aided extraction occurs at the expense of the asphaltene fraction. The sum of the oil fraction and asphaltene fraction remain the same for both extraction procedures.

Since significant changes were indicated by employing sonifier aided method the particular solvent values to be used in calculation of product distribution were changed. The values that were employed on all earlier data above are in the

Table 8. Manual (M) Versus Sonifier (S) - Aided Extraction

Additives ₃	Fe ₂ O ₃		Solvent (Unreacted)		"Red Mud" and FeS ₂	
	M*	S**	M	S	M	S
Extraction Method						
Experiment Number	52	55	61a	72a	58	73
% Oils ₄	41	41	88.5	92.5	38	66
% Asphaltenes ₅	40	38	11.1	7.0	43	16
% Preasphaltenes ₆	10	9	.3	.4	5	5
% I.O.M. ₇	9	12	.1	.1	14	13
% Conversion	91	88	-	-	86	87

*M - Manual extraction of oils

**S - Sonifier aided extraction of oils

1. Reaction conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 coal; 1g FeS₂ if added; 1g other material added as indicated; 450°C; 1 hour reaction time; initial H₂ pressure-1250 psig; 46.3 cc reaction volume.
2. Calculations do not account for gas formation; that is, calculations are based only on liquid and solid material obtained after reaction. Calculations are on the basis of dry, ash free coal.
3. See elsewhere for information on minerals.
In all reactions where FeS₂ (pyrite) is present it is assumed to change completely to FeS during reaction. Other minerals are assumed to remain unchanged.
4. Pentane soluble.
5. Toluene soluble, pentane insoluble.
6. Methylene Chloride - Methyl Alcohol (10%) soluble, toluene insoluble.
7. I.O.M. - Insoluble organic matter.

second column of Table 9 which is the unreacted material separated by the manual method. The values in column 1, the hydrogenated solvent, were used earlier. The sonifier is able to extract more oils from the solvent. The values for a sonifier aided extraction of unreacted solvent was obtained in triplicate and will be employed in the following product distributions.

Table 10 presents data using the solvent values presented in column II of Table 9 as a basis for calculation. The data from the numbered experiments are from single experiments using the manual separation technique. Duplicate reactions will be performed, however, the sonifier aided extraction procedure will be employed.

Table 11 presents additional data for minerals and FeS_2 . The separation procedure was sonifier aided and thus not directly comparable to the data in Table 10.

Table 12 presents data showing the effect of three minerals on the liquefaction process. Reactions number 74 and 75 with rutile and quartz additives were separated by the manual method and thus not directly comparable to reaction number 76 where ZnS was employed and the separation was sonifier aided. Table 3 is presented to show the progress and direction of the work. All experiments were performed again and sonifier aided separation was employed.

Gas samples were taken for each experiment performed. The volume of gas is measured and the gas is analyzed by chromatography for mole percentages of H_2 , CH_4 , CO , CO_2 , C_2H_4 , C_2H_6 , H_2S , C_3H_6 , $i\text{-C}_4\text{H}_{10}$, and C_5H_{12} . The purpose of the analysis is to determine whether useful correlations exist between variables of interest and easily measured variables. Figure 4 is a least squares fit of oil production as a function of hydrogen consumed. For the coal-solvent-additives system in the present study, the oil production is in direct proportion to the amount of hydrogen consumed during reaction. The least squares fit in Figure 5 also shows that hydrogen consumption is directly related to conversion of the coal. Further observations can be made from Figure 4 concerning the selectivity which will be defined as the ratio of percent oil produced to the percent hydrogen consumed for each mineral additive. From Figure 4 it is

Table 9. Solvent Values for
Calculation Purposes

Treatment Separation Procedure Experiment Number	Reacted ^{1,2} Manual Average of 40 and 42	Unreacted Manual 61a	Unreacted Sonifier Aided 72a
% Oils ₃	92.1	88.5	92.5
% Asphaltenes ₄	7.6	11.1	7.0
% Preasphaltenes ₅	.1	.3	.4
% I.O.M. ₆	.1	.1	.1

1. Reaction conditions: 6g solvent (Air Products CPDU 121); 450°C; 1 hour reaction time; initial H₂ pressure-1250 psig; 46.3 cc reaction volume.
2. Calculations do not account for gas formation; that is, calculations are based only on liquid and solid material obtained after reaction. Calculations are on the basis of dry, ash free coal.
3. Pentane soluble.
4. Toluene soluble, pentane insoluble.
5. Methylene Chloride - Methyl Alcohol (10%) soluble, toluene insoluble.
6. I.O.M. - Insoluble organic matter.

Table 10. Effect₁ of Minerals and FeS₂ on Product Distribution₂ and Conversion Compared with Baseline Data - Manual Separation Procedure

Additives ₃	none	Lime and FeS ₂	La-clede fly ash (low Zn) and FeS ₂	Bor-nite and FeS ₂	Cal-cite and FeS ₂	Re-duced Robena Pyrite	Montmorillonite and FeS ₂	FeS ₂ Base-line	Feld-spar and FeS ₂	La-clede fly ash (high Zn) and FeS ₂	"Red Mud" and FeS ₂	ZnS and FeS ₂	Fe ₂ O ₃	Quartz and FeS ₂	Rutile and FeS ₂	Co-Mo-Al
Experiment Number	Aver-age	70	69	61	54	66	60	Aver-age of Three	59	67	58	53	55	63	62	Average
% Oils ₄	8	13	17	23	26	28	28	31	34	35	38	39	41	43	46	79
% Asphaltenes ₅	51	46	50	51	45	46	50	47	42	35	43	38	38	33	41	12
% Preasphaltenes ₆	13	5	15	6	8	11	6	5	8	10	5	9	9	7	7	2
% I.O.M. ₇	28	36	18	20	21	15	16	17	16	20	14	14	12	17	6	7
% Conversion	72	64	82	80	79	85	84	83	84	80	86	86	88	83	94	93

1. Reaction conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 coal; 1g FeS₂ if added; 1g other material added as indicated; 450°C; 1 hour reaction time; initial H₂ pressure-1250 psig; 46.3 cc reaction volume.
2. Calculations do not account for gas formation; that is, calculations are based only on liquid and solid material obtained after reaction. Calculations are on the basis of dry, ash free coal.
3. See Appendix 1 for information on minerals.
In all reactions where FeS₂ (pyrite) is present it is assumed to change completely to FeS during reaction. Other minerals in Table 14 are assumed to remain unchanged except Calcite (CaCO₃) which is assumed to form CaS.
4. Pentane soluble.
5. Toluene soluble, pentane insoluble
6. Methylene Chloride - Methyl Alcohol (10%) soluble, toluene insoluble.
7. I.O.M. - Insoluble organic matter.

Table 11. Effect₁ of Minerals on FeS₂ on Product Distribution₂ and Conversion - Sonifier Aided Separation

Additives ₃	Rutile and FeS ₂	Quartz and FeS ₂	Red Mud and FeS ₂
Experiment Number	71	72	73
% Oils ₄	38	54	66
% Asphaltenes ₅	41	13	16
% Preasphaltenes ₆	8	7	5
% I.O.M. ₇	13	26	13
% Conversion	87	74	87

1. Reaction conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 coal; 1g FeS₂ if added; 1g other material added as indicated; 450°C; 1 hour reaction time; initial H₂ pressure-1250 psig; 46.3 cc reaction volume.
2. Calculations do not account for gas formation; that is, calculations are based only on liquid and solid material obtained after reaction. Calculations are on the basis of dry, ash free coal.
3. See elsewhere for information on minerals.
In all reactions where FeS₂ (pyrite) is present, it is assumed to change completely to FeS during reaction. Other minerals in Table 11 are assumed to remain unchanged except Calcite (CaCO₃) which is assumed to form CaS.
4. Pentane soluble.
5. Toluene soluble, pentane insoluble.
6. Methylene Chloride - Methyl Alcohol (10%) soluble, toluene insoluble.
7. I.O.M. - Insoluble organic matter.

Table 12 Effect₁ of Minerals on Product Distribution₂

Additives ₃	Rutile (Manual Separation)	Quartz (Manual Separation)	ZnS (Sonifier Aided Separation)
Experiment Number	74	75	76
% Oils ₄	8	27	41
% Asphaltenes ₅	52	39	23
% Preasphaltenes ₆	15	15	8
% I.O.M. ₇	25	19	21
% Conversion	75	81	79

1. Reaction conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 coal; 1g FeS₂ if added; 1g other material added as indicated; 450°C; 1 hour reaction time; initial H₂ pressure-1250 psig; 46.3 cc reaction volume.
2. Calculations do not account for gas formation; that is, calculations are based only on liquid and solid material obtained after reaction. Calculations are on the basis of dry, ash free coal.
3. See Appendix 1 for information on minerals.
In all reactions where FeS₂ (pyrite) is present it is assumed to change completely to FeS during reaction. Other minerals in Table 14 are assumed to remain unchanged.
4. Pentane soluble.
5. Toluene soluble, pentane insoluble.
6. Methylene Chloride - Methyl Alcohol (10%) soluble, toluene insoluble.
7. I.O.M. - Insoluble organic matter.

1. Reaction conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 coal; 1g FeS₂ if added; 1g other material added as indicated; 450°C; 1 hour reaction time; initial H₂ pressure-1250 psig; 46.3 cc reaction volume.
2. Calculations do not account for gas formation; that is, calculations are based only on liquid and solid material obtained after reaction. Calculations are on the basis of dry, ash free coal.
3. See elsewhere for information on minerals.
In all reactions where FeS₂ (pyrite) is present it is assumed to change completely to FeS during reaction. Other minerals are assumed to remain unchanged except Calcite (CaCO₃) which is assumed to form CaS.

Figure 4. Oil Production Related to Hydrogen Consumed

1. Reaction conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 coal; 1g FeS₂ if added; 1g other material added as indicated; 450°C; 1 hour reaction time; initial H₂ pressure-1250 psig; 46.3 cc reaction volume.
2. Calculations do not account for gas formation; that is, calculations are based only on liquid and solid material obtained after reaction. Calculations are on the basis of dry, ash free coal.
3. See Appendix 1 for information on minerals.
In all reactions where FeS₂ (pyrite) is present it is assumed to change completely to FeS during reaction. Other minerals are assumed to remain unchanged except Calcite (CaCO₃) which is assumed to form CaS.

Figure 5: Percent Hydrogen Consumed Related to Conversion

noted that Co-Mo-Al and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ give approximately the same oil yields from coal but the coal/solvent slurry with Co-Mo-Al consumed less hydrogen. The Co-Mo-Al is therefore a more selective catalyst. Figure 4 shows that when Co-Mo-Al was used exclusively as an additive and when the 0.5 g Co-Mo-Al/ FeS_2 mixture was used approximately the same amount of hydrogen was consumed; however, when the Co-Mo-Al additive was used exclusively a higher selectivity resulted because more oil was produced. The additive Fe_2O_3 is more selective than the Red Mud and FeS_2 combination. The Fe_2O_3 additive is also more selective than the group of minerals clustered near to the Red Mud and FeS_2 point (0.25 Co-Mo-Al + FeS_2 , Feldspar + FeS_2 , Siniola Mexico Pyrite, Bornite + FeS_2 , Calcite + FeS_2 and montmorillonite + FeS_2) because the Fe_2O_3 additive produces the same amount or more oil than the above mentioned group of additives for less hydrogen consumption.

Figure 6 depicts the reactor and heating and agitation equipment. The tubing bomb contains the reaction mixture of coal-solvent-additive-hydrogen. The motor drives the flywheel which produces agitation (860 cycles per minute) of the tubing bomb. The tubing bomb is immersed in the fluidized bed sand bath which is maintained at 450°C.

Minerals Evaluation Results (Post Sonicator)

Tables 13, 14 and 15 present data for various mineral and waste product additives. These data are treated similarly to the calculational procedure discussed earlier. The values obtained from sonifier aided separation are solvent = (oils, asphaltenes, preasphaltenes, I.O.M.) = (95%, 4.5%, 0.4%, 0.1%) and the ash content of the coal is 14.56%.

Various mineral additives and combinations of additives were tested. These minerals are given in Table 16 and consist primarily of ferric sulfate heptahydrate, sodium carbonate and combinations thereof, and red mud, sodium sulfide and combinations thereof. The most active additives in these experiments were red mud and the combination of red mud and sodium sulfide. The other additives at the level used do not enhance the liquefaction of Elkhorn #3 over that of the no additive case.

Figure 6. Schematic of Equipment

Table 13. Effect₁ of Minerals₂ on ProductDistribution₃ and Conversion

Additive ₄ Experiment Number	None	Bornite	Rutile	ZnS Avg of AP-80,82	Quartz Avg of AP-	Robena Mine Pyrite (FeS ₂) AP-31	Fe ₂ O ₃ AP-89	Red Mud Avg of AP-84,85	Co-Mo-Al Avg of AP-88,90
% oils ₅	16	17	25	27	32	39	50	53	70
% asphaltenes ₆	48	44	41	43	35	44	41	33	15
% preasphaltenes ₇	13	12	14	14	13	7	7	7	9
% I.O.M. ₈	23	27	20	16	20	10	2	7	6
% conversion	77	73	80	84	80	90	98	93	94

1. Reaction Conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial H₂ pressure; 450°C; 1 hour reaction time; 46.3cc reactor volume.
2. Minerals have been described in previous reports.
3. Calculations do not account for gas formation which can vary from 0.5g to 1.0g.
4. For the purpose of calculations all minerals are assumed to remain unchanged except for FeS₂ and Fe₂O₃ which are assumed to form FeS. It is noted that Red Mud contains about 50% Fe₂O₃ which may be considered to yield FeS if sufficient sulfur is available however since the weights of Fe₂O₃ and 2FeS are close; no appreciable error in calculation occurs whether Fe₂O₃ is considered to remain unchanged or to form FeS.
5. Pentane Soluble.
6. Benzene soluble, pentane insoluble.
7. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble
8. I.O.M. - Insoluble Organic Matter

Table 14

Effect of Minerals on Product
Distribution and Conversion

Additive ₁	Lime	Dolomite	Na ₂ CO ₃	Laclede fly ash (high Zn)#107	ZnO	Illite	Calcite	Oil Shale	Apatite (Ca ₃ PO ₄)	Feldspar	Laclede fly ash (low Zn)#108	Zircon	Ilmenite	Phosphate Slime	Reduced Pyrite	K ₂ CO ₃
Experiment Number	95	101	108	93	100	99	98	104	106	97	94	102	105	107	96	110
% Oils ₂	-27	9	22	22	22	25	25	26	27	27	28	28	29	34	41	44
% Asphaltenes ₃	23	48	43	46	51	42	43	38	38	37	42	39	42	46	40	21
% Preasphaltenes ₄	12	17	8	12	11	14	15	16	12	14	14	15	13	12	9	6
% I. O. M. ₅	92	26	27	20	16	19	17	20	23	22	16	18	16	8	10	29
% Conversion	8	74	73	80	84	81	83	80	77	78	84	82	84	92	90	71

Reaction Conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial H₂ pressure; 450°C; 1 hour reaction time; 46.3 cc reactor volume.

1. For the purpose of calculations all minerals are assumed to remain unchanged . Calculations do not account for gas formation which can vary from 0.5g to 1.0g.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter

Table 15. Effect of Minerals on Product Distribution and Conversion

Additive ₁ Experiment Number	Silica AP-121	Montmor- illonite AP-119	Gypsum AP-123	Magnetite AP-120
% Oils ₂	25	29	34	36
% Asphaltenes ₃	37	34	36	36
% Preasphaltenes ₄	13	12	13	14
% I. O. M. ₅	25	25	17	14
% Conversion	75	75	83	86

Reaction Conditions: 6g Solvent (Air Products CPDU 121); 3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial H₂ pressure; 450°C: 1 hour reaction time; 46.3 cc reactor volume.

1. For the purpose of calculations all minerals are assumed to remain unchanged. Calculations do not account for gas formation which can vary from 0.5g to 1.0g.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter.
6. Minerals are described elsewhere.

Table 16
Product Distribution and Coal Conversion Using Various Minerals as Additives

Additive*	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{Na}_2\text{CO}_3$		Na_2CO_3	Red Mud	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{Na}_2\text{S}$		Na_2S	Red Mud	Na_2S
Amount (g)	0.3	0.3	0.06	0.06	0.2	0.3	0.06	0.06	0.2	0.06
Gases (g)	0.38	0.41		0.37	0.33	0.35		0.36	0.32	
Oils (g)	5.79	5.82		5.54	5.78	5.84		5.60	5.95	
Asphaltenes (g)	0.98	0.97		0.88	0.96	1.02		0.90	0.96	
Preasphaltenes (g)	0.37	0.37		0.41	0.37	0.43		0.43	0.33	
Residues (g)	0.95	0.98		0.84	0.90	0.95		0.85	0.85	
Total (g)	8.47	8.55		8.04	8.34	8.59		8.14	8.41	
Normalized	-	-		-	-	-		-	-	
Gases (g)	0.38	0.41		0.37	0.33	0.35		0.36	0.32	
Oils (g)	6.34	6.36		6.28	6.40	6.34		6.26	6.58	
Asphaltenes (g)	1.07	1.06		1.00	1.06	1.11		1.01	1.06	
Preasphaltenes (g)	0.41	0.40		0.46	0.41	0.47		0.48	0.36	
Residues (g)	1.04	1.07		0.95	1.00	1.03		0.95	0.94	
Total (g)	9.24	9.30		9.06	9.20	9.30		9.06	9.26	
% Gases	15	16		14	13	14		14	13	
% Oils	19	20		23	27	19		22	34	
% Asphaltenes	31	31		29	31	33		29	31	
% Preasphaltenes	15	15		17	15	17		18	13	
% I.D.M.	20	19		17	14	17		17	9	
% Conversion	80	81		83	86	83		83	91	

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Elkhorn #3 Coal; 1250 psig initial H_2 pressure at ambient temperature; 1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C.

*For the purpose of calculations, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is assumed to form FeS during reaction, and the hydrate water is subtracted from the oils fraction. The other minerals are assumed to remain unchanged during reaction.

No apparent correlation exists between hydrogen/carbon atom ratio and either the oil or asphaltene production from the reacted mixture. From Table 17 it is seen that an unreacted mixture of coal and solvent will have a H/C atom ratio of approximately 1.04. Examination of the H/C atom ratios for the mineral additives given in Table 17 shows the largest differences are observed in the ratio occurs between the results for the reaction with no additive with a H/C ratio of .99 and Montmorillonite and FeS_2 with a H/C ratio of 1.10. Calculation of the error involved in the H/C atom ratio shows an error of $\pm 0.03\%$ which is half of the largest difference in the H/C atom ratio of the liquefaction reactions. Since the change in the H/C ratio is small for substantial changes in the type of mineral additive, the H/C atom ratio is not a sensitive measure of the effect of the mineral additive on liquefaction of Elkhorn No. 3 coal.

For the present discussion selectivity is defined as the ratio of the percent oil produced from coal organic matter with the use of mineral additives less the oil produced when no additives are used to the percent hydrogen consumed during the liquefaction reaction. Table 18 presents the calculated selectivity for various mineral additives and FeS_2 reaction systems as well as the experimentally determined hydrogen consumption and oil production data. For the reactions with FeS_2 present, the hydrogen consumption remained relatively constant. The selectivity therefore, correlated with oil production for the experiments with FeS_2 . In the absence of FeS_2 , both the hydrogen consumption and oil production varied with the mineral additive. The highest selectivities was observed for Co-Mo-Al, Fe_2O_3 , and red mud and is given in the upper right hand corner of Figure 7 and 8. Figures 9 and 10 are bar graphs of selectivity for selected mineral additives.

The hydrogen distribution of hydrogen in the oil fraction obtained from coal/oil slurries was examined by nuclear magnetic resonance. The samples were run neat with TMS as a reference. In general, the proton absorption envelopes in both the aromatic regions and the aliphatic region are very similar for each oil regardless of the mineral additive. To more closely examine the effect of mineral additive on the hydrogen distribution of each oil, the hydrogen

Table 17 Hydrogen to Carbon Atom Ratio

Additives	Reaction Number	H/C Atom Ratio		Slurry
		Oils	Asphaltenes	
Unreacted solvent				1.05
Elkhorn No. 3 Coal				1.03
No additive				
Solvent only	42			1.04
No additive				
coal and solvent	32	1.09	.905	.99
Lime, FeS ₂	70	1.12		1.08
Laclede fly				
ash (low Zn)	69	1.09		1.04
and FeS ₂				
Bornite and				
FeS ₂	61	1.10		1.07
Calcite and				
FeS ₂	54			1.07
Reduced Robena				
Pyrite	66	1.13		1.06
Montmorillonite				
and FeS ₂	60	1.11		1.10
FeS	44	1.10	.941	1.06
FeS ₂	50	1.11		1.07
FeS ₂	45	1.11	.928	1.08
Feldspar and FeS ₂	59	1.10		1.03
Laclede fly ash				
(high Zn) and FeS ₂	67			1.05
Red Mud and FeS ₂	58	1.12		1.09
ZnS and FeS ₂	53			1.02
Fe ₂ O ₃	55	1.10		1.06
Quartz and				
Fe ₂ O ₃	63	1.14		1.05
Rutile and				
FeS ₂	62	1.13		1.05
Co-Mo-Al	36	1.11	.919	1.06
Quartz	75			0.999
Rutile	74			1.01
Red Mud	85			1.08

For reaction conditions see Table 17. One gram of FeS₂ is used in reactions where it is listed.

Table 18. Selectivity

Manual Separation

Additive	Experiment Number	% Oil Produced =Y	Y-Y ₀	% Hydrogen Consumed =X	Selectivity =(Y-Y ₀)/X
None		8(=Y ₀)	0		0
Bornite and FeS ₂	61	23	15	63	.24
Calcite and FeS ₂	54	26	18	60	.30
Montmorillonite and FeS ₂	60	28	20	60	.33
FeS ₂	50	31	23	61	.38
Feldspar and FeS ₂	59	34	26	63	.41
Red Mud and FeS ₂	58	38	30	62	.48
Fe ₂ O ₃	55	41	33	55	.60
Co-Mo-Al	36	79	71	72	.99

Sonifier aided separation

Additive	Experiment Number	% Oil Produced =Y	Y-Y ₀	% Hydrogen Consumed =X	Selectivity =(Y-Y ₀)/X
None		16=Y ₀	0		0
Bornite	86	17	1	39	.03
ZnS	80	25	9	48	.19
Rutile	92	25	9	46	.19
Quartz	81	28	12	45	.27
ZnS	82	30	14	45	.31
Quartz	83	32	16	45	.36
FeS ₂	87	39	23	56	.41
Fe ₂ O ₃	89	50	34	51	.67
Red Mud	84	53	37	54	.68
Red Mud	85	52	36	57	.63
Co-Mo-Al	90	67	51	76	.67
Co-Mo-Al	88	72	56	71	.78

$$1. \text{ Selectivity} = \frac{\text{Percent Oil (Produced with Additives)} - \text{Percent Oil (Produced with No Additives)}}{\text{(Per Cent Hydrogen Consumed)}}$$

$$2. \text{ Relative Oil Production} = \frac{\text{Percent Oil (Produced with Additives)}}{\text{Percent Oil (Produced with no Additives)}}$$

Figure 7: Selectivity of Reactions with Minerals and Pyrite (manual separation of oils)

$$1. \text{ Selectivity} = \frac{\left(\frac{\text{Percent Oil Produced with additives}}{\text{Percent Hydrogen Consumed}} \right) - \left(\frac{\text{Percent Oil produced with no additives}}{\text{Percent Hydrogen Consumed}} \right)}{\left(\frac{\text{Percent Oil Produced with additives}}{\text{Percent Hydrogen Consumed}} \right) - \left(\frac{\text{Percent Oil produced with no additives}}{\text{Percent Hydrogen Consumed}} \right)}$$

$$2. \text{ Relative Oil Production} = \left(\frac{\text{Percent Oil Production with Additives}}{\text{Percent Oil Produced with no Additives}} \right) - \left(\frac{\text{Percent Oil Produced with no Additives}}{\text{Percent Oil Produced with no Additives}} \right)$$

Figure 8: Selectivity of Reactions with Minerals
(Sonifier Aided Separation of Oils)

Manual separation used to obtain product distributions

Figure 9 : Selectivity, of Reactions with Minerals and Pyrite

Sonifier-aid separation used to obtain product distribution

Figure 10: Selectivity of Reactions with Minerals

absorption range from 0 to 10 ppm was subdivided into four regions: H_{AR} aromatic region, 6.0 ppm to 9.2 ppm, and the aliphatic region, H_{σ} , protons attached to σ carbons from 2.0 ppm to 3.3 ppm. H_{β} , protons attached to β carbons from 10. to 2.0 ppm, and H_{γ} , protons attached to carbons γ from the aromatic ring from 0.5 ppm to 1.0 ppm. Figures 11 through 15 present the NMR data.

The hydrogen distribution of the oil fraction from the reacted coal/solvent systems using no additive, $SnCl_2 \cdot 2H_2O$, FeS, Co-Mo-Al and Robena Pyrite are given in Table 19. When no additive is present, the percent hydrogen in the aromatic fraction is approximately 4 to 5% greater than those with an additive present. The hydrogen percentage in the H_{γ} region is essentially the same for all reaction systems examined. In the presence of the mineral additives the percent hydrogen in the H_{β} region is greater than with no additive; Co-Mo-Al additive showing the highest percentage. In the H_{γ} region, Co-Mo-Al shows the lowest percentage of hydrogen while Robena pyrite shows the highest level.

Treated Pilot Plant Residues - Table 20 presents product distribution data for SRC residue ash, Kerr McGee Residue Ash, and diatomaceous earth filter aid treated at different temperatures. All samples were obtained from the Wilsonville Pilot Plant.

The diatomaceous earth filter aid gives identical product distribution at the three ashing conditions. There appears to be little effect on the product distribution obtained with the SRC residue, which contains a considerable amount of filter aid, when it is ashed at 510°C or 800°C. Similarly, there is no substantial difference in the product distributions obtained when Kerr McGee residue is ashed either at 510°C or 800°C and each of the ashes is used as an additive. These when materials treated in the L.F.E. Corporation L.T.A. 504 give higher conversions to oils.

Figure 11: NMR Data for Reaction Using No Additive (AP-34)

Figure 12: NMR Data for Reaction Using Robena Pyrite (AP-47)

Figure 13: NMR Data for Reaction Using FeS Additive (AP-43)

Figure 14: NMR Data for Reaction Using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ Additive (AP-46)

Figure 15: NMR Data for Reaction Using Co-Mo-Al Additive (AP-36)

Table 19. Hydrogen Distribution in the
Oil Fractions Obtained from Coal/Solvent
Slurries with Mineral Additives
Hydrogen (%)

Mineral Additive	H _{AR}	H _α	H _β	H _γ
No Additive	41.3	20.8	25.5	12.3
Sn Cl ₂ ·2H ₂ O	37.3	20.5	28.0	14.1
FeS	37.1	20.6	28.8	13.5
CoMoAl	36.7	21.2	31.3	10.7
Robena Pyrite	35.3	19.4	27.1	18.2

H_{AR}: 6.0 ppm to 9.2 ppm

H_α: 2.0 ppm to 3.3 ppm

H_β: 1.0 ppm to 2.0 ppm

H_γ: 0.5 ppm to 1.0 ppm

Table 20. Effect of Ashing Temperature
of Residues on Product Distribution and Conversion

Experiment Number	SRC Residue Ash			Kerr McGee Ash			Diatomaceous Earth Filter Aid		
	AP-113	AP-115	AP-129	AP-111	AP-112	AP-132	AP-124	AP-127	AP-130
Ashing Temperature ₇	800°C	510°C	LTA ₈	800°C	510°C	LTA ₈	800°C	510°C	LTA ₈
% Oils ₂	35	38	46	41	42	50	36	36	37
% Asphaltenes ₃	34	36	29	36	34	31	31	31	30
% Preasphaltenes ₄	13	10	8	10	10	8	12	11	10
% I.O.M. ₅	18	16	17	13	14	11	21	22	23
% Conversion	82	84	83	87	86	89	79	78	77

Reaction Conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial H₂ pressure; 450°C; 1 hour reaction time; 46.4 cc reactor volume.

1. For the purpose of calculations ashes and diatomaceous earth are assumed to remain unchanged. Calculations do not account for gas formation which can vary from 0.5g to 1.0g.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter
6. Ashes are described elsewhere.
7. Residues are heated at "Ashing Temperature" for 1 hour; for L.T.A. see 8 below.
8. LTA - Low Temperature Ash - Ashing was accomplished using a L.F.E. Corporation L.T.A. 504. Equilibrium (stable sample weight) required approximately 60 hours with three stirrings. Approximately 50 watts were used with 1.5 to 2.0 gram samples per chamber. The oxygen flow rate was 0.05 sec/min; the oxygen pressure was 1mm Hg.

Coal Preparation Plant Waste Material - Table 21 presents the effect of several coal preparation plant waste materials on product distribution and conversion. All of the materials show effects greater than the baseline with no additive, though none of the materials are as effective as pyrite. Table 22 shows the effect of Fe_2O_3 supported on either fly ash or silica in varying amounts on the product distribution and conversion. The data seems to indicate that the "noncalcined" materials result in a greater production of oils than the calcined counter parts. For example, a calcined sample, 813x1-1x4, containing 75% Fe_2O_3 as an additive, produced 29% oils on a maf coal basis. In contrast, the noncalcined material 813 1-1 when used as an additive produced 34% oils in the reaction product on a maf coal basis.

Table 23 shows that mesh sizes of quartz has no effects on product distribution. It is noticeable that these particular quartz samples are very ineffective compared with a quartz obtained from a different source and used in experiments AP 75 (Table 12), which yielded 27% oils.

Additional Minerals and Metallic Wastes

Effect of Minerals - Table 24 shows the effect of several mineral samples on product distribution and conversion. The oil conversion result of 58% with molybdc oxide is one of the highest obtained during the study.

Table 25 shows the results of two experiments with reduced pyrite in quantities of less than the usual 1 g per 6 g of solvent and 3 g of coal. With 0.1 g of reduced pyrite, the coal conversion and oil yield are less than with the 1 g case. However, at a level of 0.25 g of reduced pyrite per 6 g of solvent and 3 g of coal both the product distribution and the conversion are comparable to that obtained with 1 g of reduced pyrite.

When molybdenite and mica are added to the liquefaction reaction, neither enhancement nor inhibition of the oils produced from the coal is observed as shown in Table 26. Previously, when $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as an additive in AP-136 (see Table 27), the one gram sample weight included the waters of

Table 21. Effect of Coal Preparation Plant Waste Materials on Product Distribution and Conversion

Additives _{1,2,7}	5429-21-1	5429-21-4	5429-21-6	5429-21-5	5429-21-8	5429-21-2	5429-21-7	5429-21-3
Experiment No.	AP-184	AP-187	AP-189	AP-188	AP-191	AP-185	AP-190	AP-186
% Oils ₃	22	27	31	34	35	35	38	38
% Asphaltenes ₄	33	31	34	32	33	33	31	31
% Preasphaltenes ₅	29	15	15	15	16	13	13	15
% I.O.M. ₆	16	27	20	19	16	19	18	16
% Conversion	84	73	80	81	84	81	82	84

1. Reference No.	Sample	Plant/Company
5429-21-1	100% Elkhorn #3	Hendrix/Beth-Elkhorn
5429-21-2	100% Elkhorn #3	Gund/Island Creek
5429-21-3	100% Elkhorn #3	Gund/Island Creek
5429-21-4	55% Hazard #4	Spurlock/Island Creek
	33% Elkhorn #2	
	12% Elkhorn #1	
5429-21-5	51% KY #11	Gilbrator/Amax
	28% KY #13	
	22% KY #12	
5429-21-6	100% KY #11	Fies/Island Creek
5429-21-7	100% KY #9	Hamilton #1/Island Creek
5429-21-8	53% KY #14	Colonial/P&M
	47% KY #17	

Reaction Conditions: 6g Solvent (Air Products CPDU 121); 3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial H₂ pressure; 450°C: 1 hour reaction time; 46.3 cc reactor volume.

- For the purpose of calculations all minerals are assumed to remain unchanged.
- Pentane Soluble.
- Benzene soluble, pentane insoluble.
- Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
- I. O. M. - Insoluble Organic Matter.
- Additives were heated at 500°C for 2 hours in air before use.

Table 22. Effect of Fe_2O_3 with Fly Ash or Silica on Product Distribution and Conversion

Additive Identification 1,2	Calcined 813x1-1x4	Calcined 705x9-3x2	Not Calcined 705x9-3	Calcined 705x16-1x6	Not Calcined 81x-1-1	Not Calcined 705x16-1	Calcined 705x8-5x1	Calcined 814x1-1x12	Calcined 814x3-2x2
Experiment No.	AP-165	AP-175	AP-169	AP-168	AP-161	AP-166	AP-167	AP-173	AP-17
% Oils ₃	29	31	34	34	34	36	37	39	40
% Asphaltenes ₄	33	32	32	32	30	31	31	31	31
% Preasphaltenes ₅	20	14	13	13	17	13	15	16	12
% I.O.M. ₆	18	23	21	21	19	20	17	14	17
% Conversion	82	77	79	79	81	80	83	86	83

1. Mineral Contents of Additives

813x1-1x4	75% Iron Oxide	25% Fly Ash
705x9-3x2	25% Iron Oxide	75% Fly Ash
Not Calcined 705x9-3	25% Iron Oxide	75% Fly Ash
705x16-1x6	25% Iron Oxide	75% Pure Silica
Not Calcined 813x1-1	75% Iron Oxide	25% Fly Ash
Not Calcined 705x16-1	25% Iron Oxide	75% Pure Silica
705x8-5x1	25% Iron Oxide	75% Fly Ash
814x1-1x12	50% Iron Oxide	50% Fly Ash
814x3-2x2	50% Iron Oxide	50% Pure Silica

Reaction Conditions: 6g Solvent (Air Products CPDU 121); 3g Elkhorn #3 Coal; 1g additive; 1250 psig H_2 initial H_2 pressure; 450°C: 1 hour reaction time; 46.3 cc reactor volume.

- For the purpose of calculations all minerals are assumed to remain unchanged. Additives were ground to -200 mesh before use.
- Pentane Soluble.
- Benzene soluble, pentane insoluble.
- Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
- I. O. M. - Insoluble Organic Matter.

Table 23. Effect of Quartz Size on Product Distribution and Conversion

Quartz. Size ₁	5 _μ	10 _μ	15	30 _μ
Experiment No.	AP-176	AP-177	AP-178	AP-179
% Oils ₂	18	19	16	16
% Asphaltenes ₃	32	31	30	32
% Preasphaltenes ₄	14	17	16	17
% I. O. M. ₅	36	33	38	35
% Conversion	64	67	62	65

Reaction Conditions: 6g Solvent (Air Products CPDU 121);
 3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial
 H₂ pressure; 450°C: 1 hour reaction time; 46.3 cc
 reactor volume.

1. For the purpose of calculations quartz samples are assumed to remain unchanged.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter.

TABLE 24

Effect of Mineral Samples on
Product Distribution and Conversion

Additive and Air Products Sample Number ₁	X-Type Molecular Sieve 5429-76-6	Mordenite 5429-76-4	Chabazite 5429-76-5	Albanian Chrome Ore Conc 5429-76-1	Red Oxide 5429-76-8	Speculite 5429-76-2	Molybdic Oxide 5429-76-3
EXPERIMENT NO.	AP-152	AP-150	AP-151	AP-148	AP-147	AP-149	AP-138
% Oils ₂	20	22	28	33	39	40	58
% Asphaltenes ₃	33	33	35	34	36	35	29
% Preasphaltenes ₄	19	14	13	13	11	11	2
% I. O. M. ₅	28	31	24	20	14	14	11
% Conversion	72	69	76	80	86	86	89

Reaction Conditions: 6 g solvent (Air Products CPDU 121);
3 g Elkhorn #3 Coal; 1 g additive; 1250 psig H₂ initial H₂
pressure; 450°C: 1 hour reaction time; 46.3 cc reactor
volume.

1. For the purpose of calculations all minerals are assumed to remain unchanged.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter.

TABLE 25

Effect of Differing Amounts of Reduced Pyrite
on Product Distribution and Conversion

Amount of Reduced Pyrite Additive	0.1g	0.25g	1.0g
Experiment No.	153	140	96
% Oils	25	42	41
% Asphaltenes	33	33	40
% Preasphaltenes	16	13	9
% I. O. M.	26	12	10
% Conversion	74	88	90

Reaction Conditions: 6g Solvent (Air Products CPDU 121);
3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ Initial H₂
pressure; 450°C: 1 hour reaction time; 46.3 cc reactor
volume

1. For the purpose of calculations additives assumed to remain unchanged.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter.

Table 26
Effect of Minerals on Product Distribution and Conversion

Additive ₁	Dolomite ₆	Molybdenite MoS ₂	Mica	FeSO ₄ ·7H ₂ O
% Oils ₂	17	27	28	50
% Asphaltenes ₃	40	31	31	30
% Preasphaltenes ₄	16	16	16	13
% I.O.M. ₅	27	26	25	7
% Conversion	73	74	75	93

Reaction Conditions: 6 g Solvent (Air Products CPDU 121); 3 g Elkhorn #3 Coal;
1 g Additive except FeSO₄·7H₂O (1.83 g); 1250 psig H₂
initial pressure at 25°C; 450°C, 1 hour reaction time;
860 RPM; 46.3 cc reactor volume.

1. For the purpose of calculations, all minerals except FeSO₄·7H₂O are assumed to remain unchanged. FeSO₄·7H₂O is assumed to lose the water of hydration during reaction. The amount of water was subtracted from the sample weight and oils fraction. Calculations do not account for gas formation which can vary from 0.2 g to 0.8 g.
2. Pentane Soluble.
3. Benzene Soluble, Pentane Insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) Soluble, Benzene Insoluble.
5. I.O.M. (Insoluble Organic Matter).
6. Average of two experiments.

TABLE 27

Effect of Waste Materials and
Chemicals on Product Distribution and Conversion

Additives 1	Kaolinite	Super Alloy Grindings	Alinco	FeSO ₄ ·7H ₂ O	APCI Flue Dust	Red Mud and Sulfur
EXPERIMENT NO.	AP-137	AP-134	AP-133	AP-136	AP-139	AP-135
% Oils ₂	32	35	39	46	48	51
% Asphaltenes ₃	33	39	40	38	37	37
% Preasphaltenes ₄	13	13	9	10	7	7
% I. O. M. ₅	22	13	12	6	8	5
% Conversion	78	87	88	96	92	95

Reaction Conditions: 6g Solvent (Air Products CPDU 121):
3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial H₂
pressure; 450°C: 1 hour reaction time; 46.3 cc reactor
volume.

1. For the purpose of calculations all minerals are assumed to remain unchanged except the sulfur and red mud combination of AP 135 - see Appendix II, and the FeSO₄·7H₂O of AP-136 which is assumed to lose the water of hydration during reaction. One gram of FeSO₄·7H₂O was the additive in AP-136, so the weight of FeSO₄ was 0.5464 gram.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter.

hydration. In a subsequent experiment, 1.83 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used providing a one gram equivalent of FeSO_4 which corresponds to the typical additive amount used in this study. In both cases, the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ additive yielded 46-50% oils. In a previous experiment (AP-101, Table 14), dolomite as an additive appeared to inhibit the oils production. When the experiment with dolomite was repeated, no significant effect on the product distribution was observed when compared to the no additive case.

Effect of Metallic Wastes - Table 28 presents the product distribution results for several reactions using different fly ashes and bottom ashes as additives. Table 29 presents the effects on product distribution and conversion when the additive used is pyrite reduced at several different conditions. The conditions for the pyrite reduction are listed in Table 29. X-ray diffraction results at Air Products indicate that all samples were essentially FeS . The samples were ground before being subjected to X-ray analyses. The first column of Table 29 is the product distribution and conversion obtained with the untreated pyrite. As seen in Table 29, all samples of reduced pyrite gave essentially identical results within experimental error. Table 27 presents product distributions and coal conversion obtained for various waste materials and chemicals.

Effect of Pyrite Source on Liquefaction - To ascertain the effect of pyrites from different sources on the product distribution and conversion of Elkhorn #3 coal, a set of experiments were performed using pyrite from Mexico, South Dakota, Robena Mine and MCB. The product distributions and conversions shown in Table 30 were essentially identical, within experimental error, regardless of the pyrite source.

Two additional sources of pyrite were examined in the study of the effect of the pyrite source on reactivity (Table 31). A concentrate containing 46.82% by weight pyrite from the deep cleaning of Ireland Mine Coal produced an oil yield of 42%. A concentrate containing 97.2 wt% pyrite from Climax Molybdenum Company yields an oil fraction of 34%. The apparent difference between the two values may be due to carbonaceous material or the presence of other minerals in the Ireland Mine Coal concentrate which lead to higher oil yields.

TABLE 28

Effect of Several Fly Ashes and Bottom Ashes on
Product Distribution and Conversion

EXPERIMENT NO.	Brown Fly Ash 5429-20-1 AP-157	Paradise Bottom Ash 5429-20-6 AP-163	Green River (Blend) Fly Ash 5429-20-3 AP-159	Green River (High) Fly Ash 5429-20-4 AP-160	Paradise Fly Ash 5429-20-2 AP-158	Brown Bottom Ash 5429-20-5 AP-162	Green River Bottom Ash 5429-20-7 AP-164
% Oils	14	21	23	24	28	29	38
% Asphaltenes	32	31	35	31	36	33	34
% Preasphaltenes	22	15	14	14	14	13	14
% I. O. M.	32	33	28	31	22	25	14
% Conversion	68	67	72	69	78	75	86

Reaction Conditions: 6g Solvent (Air Products CPDU 121);
3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial
H₂ pressure; 450°C: 1 hour reaction time; 46.3 cc reactor
volume.

1. For the purpose of calculations all minerals are assumed to remain unchanged.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter.

TABLE 29.

Effect of Pyrite Reduced at
Different Conditions on Product Distribution and Conversion

Additive _{1,2}	Pyrite (Starting Material) 5429-1-5	5429-1-5 CH001	5429-1-5 CH002	5429-1-5 CH003	5429-1-5 CH004	5429-1-5 CH005	5429-1-5 CH006
EXPERIMENT NO.	AP-131	AP-141	AP-142	AP-143	AP-144	AP-145	AP-146
% Oils ₃	46	41	41	41	42	40	42
% Asphaltenes ₄	31	35	34	31	32	34	34
% Preasphaltenes ₅	9	10	11	11	10	10	10
% I. O. M. ₆	14	14	14	17	16	16	14
% Conversion	86	86	86	83	84	84	84

Reaction Conditions: 6g solvent (Air Products CPDU 121);
3 g Elkhorn #3 Coal; 1 g additive; 1250 psig H₂ initial H₂
pressure; 450°C; 1 hour reaction time; 46.3 cc reactor
volume.

<u>I. Additive</u>	<u>Type</u>	<u>Reaction Conditions*</u>
5429-1-5	-200 Mesh Pyrite	
5429-1-5 CH001	Reduced Pyrite	T = 400°C, P = 1000 psig H ₂ , t = 10 min.
5429-1-5 CH002	Reduced Pyrite	T = 450°C, P = 1000 psig H ₂ , t = 10 min.
5429-1-5 CH003	Reduced Pyrite	T = 500°C, P = 1000 psig H ₂ , t = 10 min.
5429-1-5 CH004	Reduced Pyrite	T = 600°C, P = 1000 psig H ₂ , t = 10 min.
5429-1-5 CH005	Reduced Pyrite	T = 450°C, P = 1500 psig H ₂ , t = 10 min.
5429-1-5 CH006	Reduced Pyrite	T = 450°C, P = 500 psig H ₂ , t = 10 min.

- For the purpose of calculation the pyrite (FeS₂) is assumed to form FeS during reaction. The Reduced Pyrite samples, CH001 through CH006 are assumed to remain unchanged.
- Pentane Soluble.
- Benzene soluble, pentant insoluble.
- Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
- I. O. M. - Insoluble Organic Matter.

Table 30

Effect of Different Pyrites on Product
Distribution and Conversion

Additive ₁	Robena Pyrite	Siniola Mexico Pyrite	South Dakota Pyrite	MCB Pyrite
% Oils	46	47	48	46
% Asphaltenes	39	29	29	28
% Preasphaltenes	7	9	10	10
% I.O.M.	8	15	13	16
% Conversion	92	85	87	84

Reaction Conditions: 6 g Solvent (Air Products CPDU 121); 3 g Elkhorn #3 Coal;
1 g Additive; 1250 psig H₂ initial pressure at 250C; 1
hour reaction time; 860 RPM; 46.3 cc reactor volume.

1. For the purpose of calculations, all pyrites (FeS₂) are assumed to form FeS during reaction. Calculations do not account for gas formation which can vary from 0.2 g to 0.8 g.

Table 31

Effect of Different Pyrites on Product
Distribution and Coal Conversion

<u>Additive*</u>	<u>Ireland Mine Concentrate</u>	<u>Concentrate From Climax Molybdenum Co.</u>
Gases (g)	0.21	0.22
Oils (g)	6.19	5.64
Asphaltenes (g)	0.84	0.88
Preasphaltenes (g)	0.28	0.28
Residues (g)	1.39	1.38
Total (g)	8.91	8.40
Normalized	-	-
Gases (g)	0.21	0.22
Oils (g)	6.77	6.56
Asphaltenes (g)	0.92	1.02
Preasphaltenes (g)	0.31	0.33
Residues (g)	1.52	1.60
Total (g)	9.73	9.73
% Gases	8	9
% Oils	42	34
% Asphaltenes	26	29
% Preasphaltenes	11	12
% I.O.M.	13	16
% Conversion	87	84

Reaction Conditions: 6g Solvent (Air Products, CPDU 121);
3g Elkhorn #3 coal; 1g Additive; 1250 psig initial H₂
pressure at ambient temperature; 1 hour reaction
time; 46.3 cc reactor volume; 860 RPM; 450°C.

*For the purpose of calculations, pyrite is assumed to form
FeS during reaction.

1. Ireland Mine concentrated pyrite was received from the
Pittsburgh Energy Technology Center, P.O. Box 10940,
Pittsburgh, PA 15236. Sample contains 46.82 wt% pyrite.
2. Pyrite from Climax Molybdenum Co. was received from Air
Products and Chemicals, Inc. Sample contains 97.2 wt%
pyrite and 45.4 wt% iron.

**Average of two runs.

Six different pyrites shown in Table 32 with varying levels of purity were used. The product distributions obtained from these reactions are very similar with the oil produced varying from 31% to 43% with no obvious correlation with purity.

Cryoground Tires - Cryoground tires were also used as an additive. The product distribution of reacted tires is shown in Table 33. The product distribution of the tires gives approximately 70% oils, no asphaltenes or preasphaltenes. The oils fraction produced from the tires is considerably higher than the oils produced from coal in a liquefaction reaction. When the cryoground tires were added at the one gram level to the liquefaction reaction (see Column 4, Table 33) no enhancement of the oils fraction from the coal was observed.

Miscellaneous Studies - To determine the accuracy and reproducibility of the experimental gas measurements for many of the runs that follow, two experiments were performed at liquefaction conditions using hydrogen gas as the charge. Before and after reaction, hydrogen was collected in a sampling bag and the gas volume was measured using the water displacement method. The volume of gas charged to the reactor before and after reaction differed by only 1.3%. When the measured volume was compared to the volume calculated by the ideal gas law, the difference was 3.5%. These two experiments confirm the accuracy of the experimental gas data included in this report.

Red mud obtained from Bergbau-Forschung in Essen (Germany) was tested as an additive in the liquefaction system. When the catalytic activity of the "German" red mud is compared to that from Kaiser Aluminum, Co., Bayer Process, the activity of the German red mud in the production of oil from Elkhorn #3 appears to be less as shown in Table 34. Several other mineral additives, tungsten disulfide, molybdenite concentrate and pyrite abstracted from Kentucky #9 coal, were used in the Elkhorn #3 liquefaction system. The oil production with these additives is in the same range as that when Robena Mine pyrite is used as an additive.

Table 32

Effect of Various Pyrites from Different Coals
on Product Distribution and Coal Conversion

Additive*	West Virginia	Union Kentucky	Lower Kittanning	Western Pennsylvania	Kentucky #9 (acid extr)	Kentucky #9 (no trtment)
Gases (g)	0.33	0.31	0.32	0.36	0.32	0.27
Oils (g)	6.02	6.09	5.84	6.01	5.30	5.96
Asphaltenes (g)	0.87	0.92	0.83	0.94	0.76	0.94
Preasphaltenes (g)	0.32	0.27	0.29	0.32	0.24	0.36
Residues (g)	1.60	1.31	1.38	1.49	1.08	1.45
Total (g)	9.14	8.90	8.66	9.12	7.70	8.98
Normalized	-	-	-	-	-	-
Gases (g)	0.33	0.31	0.32	0.36	0.32	0.37
Oils (g)	6.54	6.72	6.69	6.55	6.79	6.50
Asphaltenes (g)	0.94	1.01	0.95	1.02	0.97	1.03
Preasphaltenes (g)	0.35	0.30	0.33	0.35	0.31	0.39
Residues (g)	1.74	1.45	1.58	1.62	1.38	1.58
Total (g)	9.90	9.79	9.87	9.90	9.77	9.77
% Gases	13	12	13	14	13	11
% Oils	33	40	39	33	43	31
% Asphaltenes	26	29	26	29	27	30
% Preasphaltenes	13	11	12	13	11	14
% I.O.M.	15	8	10	11	6	14
% Conversion	85	92	90	89	94	86

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Elkhorn #3 Coal; 1g Additive; 1250 psig initial H₂ pressure at ambient temperature; 1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C.

*a For the purpose of calculations, pyrite is assumed to form FeS during reaction.

b All the pyrites were received from Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105.

c The analysis of pyrite from different coals is as follows:

Additive %	Source	Pyrite, wt%	Ash, wt%	Fe, wt%
1	Pyrite from West Virginia	37.1	83.6	22.2
2	Pyrite from Union Kentucky	78.4	68.5	44.4
3	Pyrite from Lower Kittanning	50.1	73.9	27.3
4	Pyrite from Western Pennsylvania	36.9	70.3	20.9
5	Pyrite from Kentucky #9 (acid extr)	87.0	70.0	
6	Pyrite from Kentucky #9 (no trtment)	87.0	70.0	

Table 33
Product Distributions of Tires and Effect of
Tires on Product Distributions of Coal

Solvent (g) CPDU 121	6.0	6.0	6.0
Coal (g) Elkhorn #3	--	--	3.0
Cryoground Tires* (g)	1.0	3.0	1.0
% Oils	76	68	26
% Asphaltenes	0**	0**	31
% Preasphaltenes	0	0	15
% I.O.M.	24	32	28
% Conversion	76	68	72

Reaction Conditions: 1250 psig H₂ initial pressure at 25°C; 450°C, 1 hour reaction time, 860 RPM.

*The ash content of cryoground tires (4.84 + 0.21%) was subtracted from sample weight and residue. Calculations do not account for gas formation which can vary from 0.2 g to 0.8 g.

**Calculated actual value is negative; it does not make sense because we cannot actually recover or subtract the solvent. Therefore, we set asphaltenes to zero to get reasonable values, but did not account for change in solvent. Thus, the values of oils, preasphaltenes and I.O.M. were normalized to 100%.

Table 34

Catalytic Activities of
Minerals in Coal Liquefaction

Additive ^a	Red ^b Mud	Red ^c Mud	Tungsten ^d Disulfide	Molybdenite ^e Conc.	Pyrite ^f
Gases (g)	0.32	0.18	0.46	0.29	0.23
Oils (g)	6.03	5.53	6.20	6.10	5.96
Asphaltenes (g)	1.00	0.88	0.92	1.09	0.94
Preasphaltenes (g)	0.30	0.16	0.26	0.34	0.36
Residues (g)	1.61	1.29	1.63	1.41	1.45
Total (g)	9.26	8.04	9.47	9.23	8.94
Normalized	-	-	-	-	-
Gases (g)	0.32	0.18	0.46	0.29	0.23
Oils (g)	6.53	6.91	6.56	6.63	6.50
Asphaltenes (g)	1.08	1.10	0.97	1.18	1.03
Preasphaltenes (g)	0.33	0.20	0.28	0.37	0.39
Residues (g)	1.74	1.61	1.73	1.53	1.58
Total (g)	10.00	10.00	10.00	10.00	9.73
% Gases	13	7	18	11	9
% Oils	32	47	34	36	31
% Asphaltenes	32	33	27	36	30
% Preasphaltenes	12	7	10	14	14
% I.O.M.	11	6	11	3	16
% Conversion ^g	89	94	89	97	84
% Conversion ^h	86	88			

Reaction Conditions: 6 g Solvent (Air Products, CPDU 121); 3 g Elkhorn #3 Coal; 1 g Additive; 1250 psig initial H₂ pressure at ambient temperature; 1 hour reaction time; 46.3 c.c. reactor volume; 860 RPM.

- ^a For the purpose of calculations, pyrite is assumed to form FeS during reaction, and the other additives are assumed to remain unchanged.
- ^b Red Mud from Bergbau-Forschung in Essen, sample Source: Arthur L. Conn & Associates, Ltd., 1469 East Park Place, Chicago, Illinois 60637, TEL: (312) 842-6388/667-1521.
- ^c Red Mud - Bayer Process red mud waste from Kaiser Aluminum Co. Average of two runs (AP-84 and AP-85).

Table 34 Cont.

^d Tungsten Disulfide (WS_2) was received from Air Products and Chemicals, Inc.

^e Molybdenite concentrate from Climax Molybdenum Co., Langeloth, Pa., was received from Air Products and Chemicals, Inc., and extracted with THF first and dried in vacuum oven ($100^{\circ}C$, 25 mm Hg) overnight.

Composition (on a dry and oil free basis)

MoS₂ 86-96 Wt%
Copper 0.20 Wt% max.
Balance Siliceous Material

^f Pyrite (FeS_2) from Kentucky #9 Coal, was received from Air Products and Chemicals, Inc.

^g Based on I.O.M.; % conversion = 100% - % I.O.M.

^h Based on ash balance

Table 35 presents the results of experiments with Kentucky #9 coal. The coal without additive appears more active than the Elkhorn #3 coal presently being used in this study. The results of Robena mine pyrites with Kentucky #9 coal are essentially the same as Robena pyrite with Elkhorn #3 coal considering experimental error.

At the request of Air Products and Chemicals, Inc. the liquefaction behavior of fusinite in the presence and absence of pyrite was examined. Table 36 shows the comparison. Pyrite shows definite catalytic activity by increasing the oil yield from fusinite from 1 to 10% and the conversion of fusinite from 8 to 26%.

Water Production in Tubing Bomb Experiments

Table 37 shows the effects of including water in the reactants in three liquefaction experiments. The water is subtracted from the sample weight during the calculations, so the product distributions in Table 37 are representative of the organic constituents. Other experiments with no water correction and diatomaceous earth (AP-124, 127, 130) as an additive (see Table 20) yielded 36% to 37% oils compared with 14% with water correction and diatomaceous earth in AP-170.

Two experiments were performed for the specific purpose of determining the amount of water produced during the reactions. The procedure used is given below. After reactions the bombs were opened and a measured volume of methanol was added to each of the tubing bombs. The bombs were shaken and a sample of the supernatant fluid was removed and analyzed by gas chromatography. The percentage of water was determined based on prepared calibration curves for water and methanol and based on a methanol blank. The total amount of water was calculated based on the total volume of methanol added.

To include the water produced in the product distributions the following observations are made. The water will be included in the sample weight since essentially the entire contents of the tubing bomb are used as a sample. In terms of the fractions the water in the sample will be included in the oils fraction because of the following considerations. First, the asphaltenes,

Table 35. Liquefaction Experiments with Kentucky No. 9 Coal

Additive ₁	None	Robena Mine Pyrite
Experiment No.	AP-182	AP-183
% Oils ₂	30	44
% Asphaltenes ₃	36	35
% Preasphaltenes ₄	15	12
% I.O.M. ₅	19	9
% Conversion	81	91

Reaction Conditions: 6 g Solvent (Air Products CPDU 121); 3 g Elkhorn #3 Coal; 1 g additive; 1250 psig H₂ initial H₂ pressure; 450°C: 1 hour reaction time; 46.3 cc reactor volume.

1. For the purpose of calculations FeS₂ is assumed to form FeS, and the KY #9 Coal is assumed to contain 13.1% ash.
2. Pentane soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I.O.M. - Insoluble Organic Matter.

Table 36
Liquefaction Behavior of Fusinite^a

<u>Additive^b</u>	<u>None</u>	<u>-325 Robena Pyrite</u>
Gases (g)	0.06	0.40
Oils (g)	4.51	5.27
Asphaltenes (g)	0.22	0.21
Preasphaltenes (g)	0.10	0.06
Residues (g)	2.21	2.72
Total (g)	7.10	8.66
Normalized	-	-
Gases (g)	0.06	0.40
Oils (g)	5.72	5.95
Asphaltenes (g)	0.28	0.24
Preasphaltenes (g)	0.13	0.07
Residues (g)	2.81	3.07
Total (g)	9.00	9.73
% Gases	2	15
% Oils	1	10
% Asphaltenes	1	(1) ^c
% Preasphaltenes	4	2
% I.O.M.	92	74
% Conversion	8	26

Reaction Conditions: 6g Solvent (Air Products, CPDU 121): 3g Elkhorn #3 Coal; 1g Additive; 1250 psig initial H₂ pressure ambient temperature; 1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C.

^aFusinite contains 13.39% ash

^bFor the purpose of calculations, pyrite is assumed to form FeS during the reaction.

^c() indicates a negative value.

Table 37. Experiments with Added Water

Additives ₁	Robena Pyrite	Robena Pyrite	Diatomaceous Earth
Water Added (g) ₆	0.3	0.31	0.25
Experiment No.	AP-180	AP-171	AP-170
% Oils ₂	44	51	14
% Asphaltenes ₃	34	26	31
% Preasphaltenes ₄	9	10	16
% I. O. M. ₅	13	13	39
% Conversion			

Reaction Conditions: 6g Solvent (Air Products CPDU 121);
 3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial
 H₂ pressure; 450°C: 1 hour reaction time; 46.3 cc reactor
 volume.

1. For the purpose of calculations FeS₂ is assumed to form FeS.
2. Pentane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter.
6. The water has been subtracted from the sample weight before calculation, so the product distributions are on a maf basis.

preasphaltenes, and insoluble organic matter (I.O.M.) matter fractions are completely dry after separation, thus containing no water. Secondly the oils fraction is calculated value which is obtained as the difference between the sample weight (which contains the water) and the asphaltenes, preasphaltenes, and I.O.M. (all of which are dry). Thus the water is included in the oils fraction.

The two reaction systems chosen for the water analysis experiments were one with no additive and one with Fe_2O_3 as an additive. These examples were chosen because they are representative of a case with little catalytic activity, no additive, and a case with fairly high activity, Fe_2O_3 . Therefore, the range of water production in the reactions performed for this contract is fairly well covered. The percentages of the water in the calculated product distributions were 2.6% for the nonadditive case and 3.3% for the Fe_2O_3 additive case. The adjusted product distribution for the two reactions given in Table 38 were taken from experiments numbered AP-192 with Fe_2O_3 and AP-193 with no additive. These values were adjusted and combined with experiments AP-89 (Table 13) with Fe_2O_3 and AP-91 (Table 13) with no additive. Preliminary experiments have been performed to determine the effect of the initial methanol wash on the total product distribution. Further experiments are necessary to conclusively state the effect.

Effect of Iron Mineral

Effect of Concentration

Table 39 presents the effect of pyrite concentration on product distribution and conversion. In general, increased pyrite loading gives more conversion of the coal to solubles and more conversion of solubles to the oils fraction.

The effect of different amounts of ferric oxide additive on the product distribution of Elkhorn #3 was also examined. At levels of 0.1, 0.2, 0.3, 0.5 and 1.0 g, the oil production varies from 25 to 32% as given in Table 40. It is apparent that under these experimental conditions, the oil yield increases slightly with the amount of catalyst added.

Table 38. Water Included in Product Distribution Data

Additive	None	Fe ₂ O ₃
% Water	3	3
% Oils	14	47
% Asphaltenes	48	41
% Preasphaltenes	12	8
% I. O. M.	23	1

Table 39. Effect of Pyrite Concentration
on Product Distribution and Conversion

Run Number	AP-122	AP-125	AP-118	AP-126	AP-128
Robena Pyrite ₁ (grams)	0.25	0.5	1.0	1.5	2.0
% Oils ₂	37	46	46	59	62
% Asphaltenes ₃	38	33	39	24	26
% Preasphaltenes ₄	9	7	7	7	6
% I.O.M. ₅	16	14	8	10	6
% Conversion	84	86	92	90	94

Reaction Conditions: 6g solvent (Air Products CPDU 121); 3g Elkhorn #3 Coal; 1g additive; 1250 psig H₂ initial H₂ pressure; 450°C; 1 hour reaction time; 46.3 cc reactor volume.

1. For the purpose of calculations FeS₂ is assumed to form FeS. Calculations do not account for gas formation.
2. Penetane Soluble.
3. Benzene soluble, pentane insoluble.
4. Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
5. I. O. M. - Insoluble Organic Matter.
6. Robena Mine Pyrite, - 325 mesh. Source: Air Products and Chemicals Co.

Table 40

Effect of Different Amounts of Fe_2O_3 on Product
Distribution and Coal Conversion

Amount of Fe_2O_3 (g)	0.1	0.2	0.3	0.5	1.0*
Gases (g)	0.41	0.39	0.31	0.37	0.32 ± 0.03
Oils (g)	5.89	5.75	5.76	5.62	5.77 ± 0.06
Asphaltenes (g)	0.95	0.92	0.95	0.93	0.95 ± 0.03
Preasphaltenes (g)	0.31	0.43	0.43	0.32	0.32 ± 0.02
Residues (g)	0.88	0.91	0.96	1.11	1.52 ± 0.04
Total (g)	8.44	8.40	8.41	8.35	8.88 ± 0.16
Normalized	-	-	-	-	-
Gases (g)	0.41	0.39	0.31	0.37	0.32 ± 0.03
Oils (g)	6.37	6.33	6.39	6.43	6.52 ± 0.05
Asphaltenes (g)	1.03	1.01	1.05	1.06	1.07 ± 0.02
Preasphaltenes (g)	0.34	0.47	0.48	0.37	0.37 ± 0.02
Residues (g)	0.95	1.00	1.07	1.27	1.72 ± 0.02
Total (g)	9.10	9.20	9.30	9.50	10.00 ± 0.14
% Gases	16	15	12	14	13 ± 1
% Oils	26	25	27	29	32 ± 2
% Asphaltenes	30	29	30	31	31 ± 1
% Preasphaltenes	12	17	18	14	14 ± 1
% I.O.M.	16	14	13	12	10 ± 1
% Conversion	84	86	87	88	90 ± 1

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Elkhorn #3 Coal;
1250 psig initial H_2 pressure at ambient temperature; 1 hour
reaction time; 46.3 cc reactor volume; 860 RPM; 450°C.

*Standard deviation of three runs (AP-348, AP-356 and AP-357)

Effect of Particle Size

Pyrite - A fairly extensive study of pyrite and its effect on the liquefaction system as a function of reaction parameters was undertaken. The initial set of experiments examined the effect of various pyrite particles sizes on liquefaction behavior. The pyrite, sized to +40 mesh, 40 x 80 mesh, 80 x 140 mesh and 140 x 200 mesh, was received from Air Products and Chemicals, Inc. The reactions using the various sized pyrite were performed under the same reaction conditions as the majority of experiments in this contract in that steel balls were used in the reactor.

The reaction conditions are:

Solvent: 6 g Air Products, CPDU 121
Coal: 3 g Elkhorn #3
Pressure: 1250 psig H₂ at 25°C
Time: 1 hour
Reactor Volume: 46.3cc
Agitation: 860 RPM with two steel balls
Temperature: 450°C

The product distributions for the different sized pyrites along with that of -325 mesh Robena Mine pyrite are given in Table 41. It is apparent from each fraction of the product distribution that each sized pyrite fraction has an equivalent effect on the reaction system under the reaction conditions used.

The reactions with the pyrite sized from +40 mesh to 140x200 mesh were performed a second time without using steel balls. The results from this study are given in Table 42. It is apparent from the product distribution that the pyrite used is effective in producing approximately 40% oils. Changes in pyrite particle size produce no apparent changes in the product distribution and conversion.

Magnetite - An extension of particle size effect experiments performed using various sized magnetite particles was performed. Magnetite particles ranging from 40x80, 80x140, 140x200 and -200 mesh were used in the Elkhorn #3 coal reaction system. (See Table 43). In the magnetite experiments no steel ball

Table 41

Effects of Different Particle Sizes of Pyrite
on Product Distribution and Conversion

Additive ^a	5429-1-1 Pyrite	5429-1-2 Pyrite	5429-1-3 Pyrite	5429-1-4 Pyrite	Robena Pyrite
Particle Size	+ 40 Mesh	40 x 80 Mesh	80 x 140 Mesh	140 x 200 Mesh	-325 Mesh
Gases (g)	0.23	0.23	0.24	0.25	0.25
Oils (g)	5.87	5.97	5.94	5.90	5.74
Asphaltenes (g)	0.89	0.91	0.87	0.87	1.06
Preasphaltenes (g)	0.29	0.28	0.30	0.29	0.17
Residues (g)	1.36	1.37	1.34	1.33	1.16
Total (g)	8.64	8.76	8.69	8.64	8.38
Normalized	-	-	-	-	-
Gases (g)	0.23	0.23	0.24	0.25	0.25
Oils (g)	6.63	6.65	6.67	6.67	6.69
Asphaltenes (g)	1.00	1.01	0.98	0.98	1.24
Preasphaltenes (g)	0.33	0.31	0.34	0.33	0.20
Residues (g)	1.54	1.53	1.50	1.50	1.35
Total (g)	9.73	9.73	9.73	9.73	9.73
% Gases	9	9	9	10	10
% Oils	36	37	38	38	39
% Asphaltenes	29	30	28	28	38
% Preasphaltenes	12	11	13	12	7
% I.O.M.	14	13	12	12	6
% Conversion	86	87	88	88	94

Table 41 Cont.

Reaction Conditions: 6 g Solvent (Air Products, CPDU 121); 3 g Elkhorn #3 coal; 1 g Additive; 1250 psig initial H₂ pressure at 25°C; 1 hour reaction time, 46.3 c.c. reactor volume; 860 RPM; 450°C.

- ^a1. For the purpose of calculations, all pyrites are assumed to form FeS during reaction.
2. Pyrite samples (5429-1-1 through 5429-1-4) were obtained from Air Products and Chemicals, Inc. X-ray diffraction showed that Sample (5429-1-1) was 95% pure pyrite and samples (5429-1-2, 5429-1-3, and 5429-1-4) were 97% pure pyrite.

Table 42

Effect of Various Particle Sizes of Pyrite on
Product Distribution and Conversion In Absence
of Two Steel Ball Agitators

Additive ^a Particle Size	Pyrite ^b +40 Mesh	Pyrite ^c +40 Mesh	Pyrite 40x80 Mesh	Pyrite 140x200 Mesh
Gases (g)	0.75	0.32	0.33	0.22
Oils (g)	5.84	6.48	5.89	5.89
Asphaltenes (g)	0.86	0.88	0.80	0.79
Preasphaltenes (g)	0.25	0.34	0.26	0.29
Residues (g)	1.27	1.36	1.25	1.37
Total (g)	8.47	9.38	8.53	8.56
Normalized	-	-	-	-
Gases (g)	0.25	0.32	0.33	0.22
Oils (g)	6.74	6.73	6.75	6.72
Asphaltenes (g)	0.99	0.92	0.92	0.90
Preasphaltenes (g)	0.29	0.35	0.29	0.33
Residues (g)	1.46	1.41	1.44	1.56
Total (g)	9.73	9.73	9.73	9.73
% Gases	10	13	13	8
% Oils	41	40	41	40
% Asphaltenes	28	25	25	25
% Preasphaltenes	10	13	11	12
% I.O.M.	11	9	10	15
% Conversion	89	91	90	85

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Elkhorn #3 Coal;
1g Additive; 1250 psig initial H₂ pressure at ambient temperature;
1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C; without
two steel balls.

^aFor the purpose of calculations, pyrite is assumed to form FeS during reaction.

^bAverage of two runs (AP-267 and AP-270).

^cAfter taking out the sample, the reactor was washed with THF. The THF washed solution was rotovaporized to remove the THF. Then the rest was combined with the sample scrapped out of the reactor.

Table 43

Effect of Different Particle
Size of Magnetite on Product
Distribution and Conversion

Additive	Magnetite	Magnetite	Magnetite	Magnetite	Magnetite ^a
Particle Size (Mesh)	40x80	80x140	140x200	-200	-200
Gases (g)	0.37	0.36	0.30	0.40	0.27
Oils (g)	5.71	5.88	5.69	5.77	5.76
Asphaltenes (g)	0.95	0.98	1.02	1.06	1.04
Preasphaltenes (g)	0.44	0.35	0.37	0.40	0.34
Residues (g)	1.80	1.64	1.62	1.68	1.57
Total (g)	9.27	9.21	9.00	9.31	8.98
Normalized	-	-	-	-	-
Gases (g)	0.37	0.35	0.30	0.40	0.27
Oils (g)	6.18	6.40	6.34	6.22	6.44
Asphaltenes (g)	1.03	1.07	1.14	1.14	1.16
Preasphaltenes (g)	0.47	0.38	0.41	0.43	0.38
Residues (g)	1.95	1.79	1.81	1.81	1.75
Total (g)	10.00	10.00	10.00	10.00	10.00
% Gases	14	14	12	16	11
% Oils	19	28	25	20	29
% Asphaltenes	30	31	34	34	35
% Preasphaltenes	18	14	15	16	14
% I.O.M.	19	13	14	14	11
% Conversion ^b	81	87	86	86	89
% Conversion ^c	79	81	82	81	83

Reaction Conditions: 6 g Solvent (Air Products, CPDU 121); 3 g Elkhorn #3 Coal; 1 g Additive; 1250 psig initial H₂ pressure at ambient temperature; 1 hour reaction time; 46.3 c.c. reactor volume; 860 RPM; Without two steel balls.

^aWith two 3/16" O.D. steel balls.

^bBased on I.O.M.

^cBased on ash balance

agitators were used. To determine if the steel ball agitators had any effect on the product distribution, an experiment was performed using -200 mesh magnetite and steel balls. In all the experiments with the various sized magnetite with and without steel balls the oil production appeared to fluctuate around a mean of 24% with a deviation of $\pm 5\%$. The observed small differences in the oil production between the various sized magnetite particles will have to be verified before significance could be placed on the differences.

Table 43 also shows conversions based on two different calculation methods. The first is based on the amount of I.O.M. in reaction product. By definition,

$$\% \text{ Conversion} = \frac{\text{maf coal-I.O.M.}}{\text{maf coal}} \times 100\% = 100\% \text{ I.O.M.}$$

The second calculation is based on an ash balance. By definition,

$$\% \text{ Conversion ash} = \frac{100(F-A_o)}{F(1-M)}$$

The terms and the derivation of the above equation are given below. The primary difference between the two methods is in the experimental method. For calculation of method I, the reaction product is scrapped out of the bomb and put through the solvent separation procedure. The amount scrapped out is normalized to the total input quantity. It is assumed that the residual remaining in the bomb is distributed in the same manner as the recovered product. In the ash method, the bomb is washed out with a solvent such as THF after the reaction products have been recovered. The I.O.M. from the reaction separation is combined with the solids washed from the bomb and are ashed. As shown in Table 43, the results from both methods are identical within experimental error.

The product distribution calculations that follow were used for all calculations used in Table 43.

Case I : No Additive

C_o = Weight of the Dry Coal charged to the reactor

C = Weight of the Unreacted Dry Coal after reaction (including insoluble organic matter, I.O.M., and ash)

A_o = Weight Fraction of Ash in the Original Dry Coal

M = Weight Fraction of Mineral Matter in the Coal after Reaction
(Weight fraction of mineral matter in the original dry coal)

F = Weight Fraction of Ash in the Cresol Insoluble Residues (including unreacted coal and mineral matter)

Y = Yield of Moisture-Ash-Free (MAF) Coal (weight fraction of MAF coal)

A = Weight Percent Conversion of MAF Coal

Ash Balance

Total Ash before Reaction = Total Ash after Reaction

$$A_o C_o = (C + M(C_o - C))F$$

$$\frac{C}{C_o} = \frac{A_o - M F}{F(1-M)}$$

$$Y \equiv \frac{\text{MAF Coal} - \text{I.O.M.}}{\text{MAF Coal}} = \frac{(C_o - C A_o) - (C - C A_o)}{(C_o - C A_o)} = \frac{C_o - C}{C_o} = 1 - \frac{C}{C_o}$$

$$Y = 1 - \frac{C}{C_o} = 1 - \frac{A_o - M F}{F(1-M)} = \frac{F - F M - A_o + M F}{F(1-M)}$$

$$Y = \frac{F-A_o}{F(1-M)}$$

$$A = Y \times 100\% = \frac{100(F-A_o)}{F(1-M)} \quad (\text{eqn. 1})$$

An approximation is to use equation (1) with $R = 1$.

$$\text{Approx.} = \frac{100 (F-A_o)}{F(1-A_o)} \quad (\text{eqn. 2})$$

Equation (2) will never give 100% conversion even if I.O.M. is pure mineral matter.

The difference in A and Aapprox is normally small but it can be appreciable if a catalyst is used and factored into the calculation as additional ash in the coal. Generally, Aapprox. is always less than A.

Case II : With Additive

C_o, C, A_o, M, F, Y, A same as case I.

m_c = Weight of the Additive charged to the reactor

A_c = Weight Fraction of Ash in the Original Additive

M_c = Weight Fraction of Mineral Matter in the Additive after Reaction

Ash Balance

Total Ash before Reaction = Total Ash after Reaction

$$A_o C_o + A_c m_c = (C + M(C_o - C) + M_c m_c) F$$

$$(1-M)CF = (A_o - MF)C_o + (A_c - M_c F)m_c$$

$$\frac{C}{C_o}(1-M)F = (A_o-MF) + (A_c-McF) \frac{m_c}{C_o}$$

$$\frac{C}{C_o} = \frac{(A_o-MF) + (A_c-McF) \frac{m_c}{C_o}}{F(1-M)}$$

$$Y \equiv \frac{MAF \text{ Coal} - \text{I.O.M.}}{MAF \text{ Coal}} = \frac{(C_o-C_o-A_o)-(C-C_Ao)}{(C_o-C_o-A_o)} = \frac{C_o-C}{C_o} = 1 - \frac{C}{C_o}$$

$$Y = 1 - \frac{C}{C_o} = 1 - \frac{(A_o-MF) + (A_c-McF) \frac{m_c}{C_o}}{F(1-M)}$$

$$= \frac{F - FM - A_o + MF - (A_c-McF) \frac{m_c}{C_o}}{F(1-M)}$$

$$= \frac{F - A_o - (A_c-McF) \frac{m_c}{C_o}}{F(1-M)} \quad (\text{eqn. 3})$$

If no catalyst is added to the system, then $m_c = 0$, and equation (3) can be reduced to equation (1). Therefore, the general form of coal conversion based on ash balance is

$$A = 100 \times \frac{F - A_o - (A_c-McF) \frac{m_c}{C_o}}{F(1-M)}$$

Effect of Reaction Temperature

An examination of reaction temperature on product distribution and conversion using 140 x 200 mesh pyrite was also undertaken. The temperatures studied ranged from 400°C to 500°C at 25°C intervals. The distribution of the products obtained at each reaction temperature is given in Table 44 and shown in Figure 16. A maximum in oil production is observed near 450°C.

Table 44

Effect of Reaction Temperature On
Product Distribution and Conversion

Temp ($^{\circ}\text{C}$)	400	425	450	475	500
Gases (g)	0.12	0.14	0.25	0.59	1.40
Oils (g)	5.17	6.00	5.90	5.33	4.81
Asphaltenes (g)	1.27	1.18	0.87	0.76	0.72
Preasphaltenes (g)	0.63	0.38	0.29	0.18	0.17
Residues (g)	1.48	1.43	1.33	1.36	1.70
Total (g)	8.67	9.13	8.64	8.42	8.80
Normalized	-	-	-	-	-
Gases (g)	0.12	0.14	0.25	0.59	1.40
Oils (g)	5.81	6.40	6.67	6.45	5.42
Asphaltenes (g)	1.43	1.26	0.98	0.89	0.81
Preasphaltenes (g)	0.71	0.40	0.33	0.21	0.19
Residues (g)	1.66	1.53	1.50	1.59	1.91
Total (g)	9.73	9.73	9.73	9.73	9.73
% Gases	5	5	10	23	55
% Oils	4	27	38	29	(11) ^a
% Asphaltenes	45	39	28	24	21
% Preasphaltenes	27	15	12	8	7
% I.O.M.	19	14	12	16	28
% Conversion ^b	81	86	88	84	72

Table 44 Cont.

Reaction Conditions: 6 g Solvent (Air Products, CPDU 121); 3 g Elkhorn #3 coal; 1 g (140 x 200 Mesh) Pyrite^b; 1250 psig initial H₂ pressure at 25°C; 1 hour reaction time; 46.3 c.c. reactor² volume; 860 RPM.

a() indicates a negative value.

^bFor the purpose of calculations, pyrite is assumed to form FeS during reaction.

Reaction conditions: 6g solvent
(Air Products, CPDU 121); 3g
Elkhorn #3 coal; 1g (140 x 200 Mesh)
pyrite; 1250 psig initial H₂
pressure at 250°C; 1 hour reaction
time; 860 RPM; 46.3c.c. reactor
volume

Figure 16. Effect of reaction temperature on coal liquefaction

Both the asphaltenes and preasphaltenes decreased with increasing temperature. The I.O.M. fraction is essentially level up to 475°C and appears to increase slightly at 500°C. The most dramatic change due to temperature in the product distribution is seen in the gas fraction produced from the coal which increases from 5% at the lower temperature range, 400 and 425°C, to 55% at 500°C. Concurrently, the oil fraction at 500°C declined to -11% from a high of 38% at 450°C. At 500°C the liquefaction system does not make a sufficient quantity of oil from the coal to maintain solvent balance; therefore, a net deficiency oil from coal is observed at 500°C. Coal conversion at 500°C is also lower than that at lower reaction temperatures. Since coal conversion is defined as 1-I.O.M., the decrease in conversion may be due to coke formation which is insoluble in methylene chloride and methyl alcohol.

Effect of Agitation Rate

To determine the effect of agitation rate on the product distribution using 140 x 200 mesh pyrite, reactions were performed at agitation rates ranging from 0 to 1000 RPM. The effect of agitation rate on product distribution is given in Table 45 and shown in Figure 17. When steel balls are used as agitators in the tubing bombs, the oil production increases from -39% at 0 RPM and -26 at 200 RPM to ~39% at 400 RPM and above. Both the asphaltene and preasphaltene levels remain essentially constant for all agitation rates when steel balls are used. Coal conversion increases radically from less than 33% to 200 RPM to greater than 85% at 300 RPM and above. One experiment was performed at 400 RPM without the steel ball agitators. Comparison of the product distribution at 400 RPM with and without steel balls shows a substantial decrease in oil production and coal conversion and an increase in I.O.M., preasphaltenes and asphaltenes without the steel balls. Considering the results of the above experiments it is apparent that agitation rate has a strong influence on product distribution and that the agitation rate must be maintained at a sufficiently high level so that mass transfer is not limiting.

Table 45

Effect of Agitation Rate on Product
Distribution and Conversion

Agitation Rate (RPM)	0	200	300	400	400 ^c	600	860	1000
Gases (g)	0.28	0.26	0.36	0.24	0.44	0.27	0.25	0.20
Oils (g)	4.44	4.53	5.98	5.88	5.45	6.17	5.90	6.32
Asphaltenes (g)	1.09	1.01	1.00	0.91	1.07	0.99	0.87	0.93
Preasphaltenes (g)	0.42	0.39	0.33	0.29	0.44	0.27	0.29	0.33
Residues (g)	2.96	2.61	1.44	1.25	1.67	1.37	1.33	1.33
Total (g)	9.19	8.80	9.11	8.57	9.07	9.07	8.64	9.11
Normalized	-	-	-	-	-	-	-	-
Gases (g)	0.28	0.26	0.36	0.24	0.44	0.27	0.25	0.20
Oils (g)	4.71	5.02	6.41	6.70	5.87	6.63	6.67	6.76
Asphaltenes (g)	1.16	1.12	1.07	1.04	1.15	1.07	0.98	1.00
Preasphaltenes (g)	0.44	0.43	0.35	0.33	0.47	0.29	0.33	0.35
Residues (g)	3.14	2.90	1.54	1.42	1.80	1.47	1.50	1.42
Total (g)	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73
% Gases	11	10	14	10	17	11	10	8
% Oils	(39) ^a	(26) ^a	28	39	7	36	38	41
% Asphaltenes	35	33	31	30	34	31	28	29
% Preasphaltenes	16	16	13	12	18	11	12	13
% I.O.M.	77	67	15	9	24	11	12	9
% Conversion ^b	23	33	86	91	76	89	88	91

Table 45 Cont.

Reaction Conditions: 6 g Solvent (Air Products, CPDU 121); 3 g Elkhorn #3 coal; 1 g (140 x 200 Mesh) pyrite^b; 1250 psig initial H₂ pressure at 25°C; 1 hour reaction time, 46.3 c.c. reactor volume; 450°C.

^a() indicates a negative value.

^bFor the purpose of calculations, pyrite is assumed to form FeS during reaction.

^cNo steel balls.

Reaction Conditions: 6g Solvent
(Air Products, CPDU 121); 3g
Elkhorn #3 coal; 1g (140 x 200 Mesh)
pyrite; 1250 psig initial H₂
pressure at 25°C; 1 hour reaction
time; 450°C; 46.3 reactor volume.

Effect of Heat-up Rate

During the initial stages of this work, the effect of reaction temperature on oil production from Elkhorn #3 coal in the presence and absence of an active commercial catalyst Co-Mo-Al was determined. The reaction temperature of 450°C was chosen after consultation with Air Products and Chemicals, Inc. mainly because of the large differential between oil production with and without catalyst. However, when hydrogen consumption is compared between coal liquefaction at lower reaction temperatures (390° - 410°C) to those at higher reaction temperatures (440° to 460°C), the hydrogen consumption at the higher temperatures is always more than at lower temperatures when all other reaction conditions are held constant. It is believed that at the high reaction temperature range, many bonds in the coal structure are broken very rapidly. A considerable amount of cracking of small fragments also occurs at high temperature causing an increase in the net gas production. During this condition of rapid bond breakage, it is possible that localized instantaneous hydrogen starvation may occur. In other words, the hydrogen although present in sufficient quantity for the overall reaction may not be replenished quickly enough at the reaction site to supply sufficient hydrogen to the reacting coal fragments to prevent retrogressive or repolymerization reactions. If, however, the initial breaking of the coal molecules were to progress more slowly, there would be sufficient time to allow replenishment of hydrogen at the reaction site.

To test these ideas, a reaction was performed using Elkhorn #3 coal in the presence -325 mesh Robena Mine pyrite with temperature programming of 250° to 450°C at 2.22°C/min. The total reaction time was 90 minutes. When the reaction temperature reached 450°C, the reaction was quenched immediately. Comparison of the long heat-up reaction to the standard quick heat-up reaction at 450°C is given in Table 46. The most obvious differences between the two experiments are 1) no gas was produced in the long heat-up experiment and 10% gas was produced in the quick heat-up experiment and 2) coal conversion is less during the long heat-up versus the quick heat-up. The difference in oil production between the two experiments bordered on experimental error with the quick heat-up having 6% more oil than the slow heat-up. The effect of hydrogen starvation at the reaction site further and its effect on product slate includes minimizing gas production and maximizing oil production and coal conversion.

Table 46
Effect of Heat-Up Time Period on Product Distribution

<u>Additive</u>	<u>Slow Heat-Up Robena Mine Pyrite -325 Mesh</u>	<u>450°C Reaction Robena Mine Pyrite -325 Mesh</u>
% Gases	0	10
% Oils	33	39
% Asphaltenes	38	38
% Preasphaltenes	12	7
% I.O.M.	17	6
% Conversion	83	94

Several different heat-up rates and temperature programs were studied. Results are shown in Table 47. In all cases, the TPR mode decreased the amount of gases produced when compared to a reaction at 450°C for 60 to 120 minutes. When TPR is combined with a reaction maintained at 450°C for 20 to 30 minutes, the oil yield increases to ~50%. A number of combinations of temperature programs and final reaction times were tried. The best product slate was achieved with heat-up times of 90 to 100 minutes with an initial temperature of 250°C and a final temperature of 450° and a final reaction time of 20 to 30 minutes at 450°C. The attainment of the ~50% oil yield and 2 or 3% gas production by TPR with Robena Mine pyrite is a noteworthy achievement and may have important process implications with regard to hydrogen utilization and product quality.

The effect of reaction time on the product distribution with no additive present was determined (Table 48) after one and two hours of reaction. Comparison of the product slate produced after two hours when compared to the one hour reaction demonstrates a decrease in asphaltenes from $39 \pm 5\%$ to 27%. In these experiments the conversion was calculated based on the two above mentioned methods. The conversion was again identical by both methods.

Analysis of Mineral Reaction Products

Eleven disposable catalysts were analyzed by X-ray powder diffraction methods to determine if changes occurred in the catalysts during a coal liquefaction reaction. The disposable catalysts used were:

1. Laclede fly ash (a mixture of zincite and franklinite)
2. Laclede fly ash with FeS_2 and ZnS added
3. Robena pyrite (FeS_2)
4. reduced Robena pyrite (Fe_{1-x}S)
5. sphalerite (ZnS)

Table 47
Temperature Programmed Reactions
Performed in the Presence of Robena Mine Pyrite*

Reaction Temp (°C)	450	250- 450	250- 450 450	250- 450 450	250- 450 450	250- 450 450	380- 450 450	250- 450 450	250- 450 450	450	250- 450 450 ^a
Reaction Time (min)	60	90	90 30	100 20	100 30	90 60	60 30	105 90	200 30	120	120 30
Gases (g)	0.25	0.00	0.04	0.09	0.02	0.10	0.02	0.16	0.03	0.32	0.00
Oils (g)	5.74	5.90	6.37	5.83	6.26	6.04	5.27	6.08	5.96	5.97	6.07
Asphaltenes (g)	1.06	1.13	0.92	0.85	0.90	0.99	0.80	0.90	0.85	0.80	0.54
Preasphaltenes (g)	0.17	0.30	0.28	0.23	0.36	0.35	0.29	0.20	0.25	0.22	0.20
Residues (g)	1.16	1.45	1.21	1.09	1.27	1.23	1.05	1.33	1.34	1.12	1.03
Total (g)	8.38	8.78	8.82	8.09	8.81	8.71	7.43	8.71	8.40	8.43	7.84
Normalized	-	-	-	-	-	-	-	-	-	-	-
Gases (g)	0.25	0.00	0.04	0.09	0.02	0.10	0.02	0.16	0.03	0.32	0.00
Oils (g)	6.69	6.54	7.03	7.02	6.92	6.76	6.91	6.84	6.88	6.93	7.53
Asphaltenes (g)	1.24	1.25	1.01	1.03	0.99	1.11	1.05	1.01	0.98	0.93	0.67
Preasphaltenes (g)	0.20	0.33	0.31	0.28	0.40	0.39	0.38	0.22	0.29	0.25	0.25
Residues (g)	1.35	1.61	1.34	1.31	1.40	1.37	1.37	1.50	1.55	1.30	1.28
Total (g)	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73
% Gases	10	0	2	3	1	4	1	6	1	12	0
% Oils	39	33	52	52	48	41	47	45	46	48	71
% Asphaltenes	38	38	29	30	28	33	31	29	28	26	16
% Preasphaltenes	7	12	11	10	15	15	14	8	11	9	9
% I.O.M.	6	17	6	5	8	7	7	12	14	5	4
% Conversion	94	83	94	95	92	93	93	88	86	95	96

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Elkhorn #3 Coal; 1g Additive; 1250 psig initial H₂ pressure at ambient temperature; 46.3 cc reactor volume; 860 RPM.

*For the purpose of calculations, pyrite is assumed to form FeS during reaction.

^aSolvent is tetralin.

Table 48

Effect of Reaction Time
On Product Distribution and
Conversion in Absence of Additive

Reaction Time (hr)	1	2
Gases (g)	0.27 ± 0.04^a	0.58
Oils (g)	5.35 ± 0.17	4.83
Asphaltenes (g)	1.11 ± 0.12	0.75
Preasphaltenes (g)	0.32 ± 0.02	0.30
Residues (g)	0.85 ± 0.09	0.71
Total (g)	7.90 ± 0.28	7.17
Normalized	-	-
Gases (g)	0.27 ± 0.04	0.58
Oils (g)	6.12 ± 0.05	6.17
Asphaltenes (g)	1.27 ± 0.14	0.96
Preasphaltenes (g)	0.37 ± 0.02	0.38
Residues (g)	0.97 ± 0.10	0.91
Total (g)	9.00 ± 0.32	9.00
% Gases	11 ± 2	23
% Oils	16 ± 2	18
% Asphaltenes	39 ± 5	27
% Preasphaltenes	14 ± 0.5	14
% I.O.M.	20 ± 4	18
% Conversion ^b	80 ± 4	82
% Conversion ^c	85 ± 2	83

Reaction Conditions: 6 g Solvent (Air Products, CPDU 121);
3 g Elkhorn #3 Coal; 1250 psig initial
H₂ pressure at ambient temperature;
46.3 c.c. reactor volume; 860 RPM

^aStandard deviation of four runs (AP-91, AP-109, AP-114, AP-117)

^bBased on I.O.M.

^cBased on Ash Balance

6. red mud is a mixture of goethite (FeO(OH)) and boehmite (AlO(OH)) plus amorphous iron and aluminum oxides
7. hematite (Fe_2O_3)
8. Elkhorn #3 coal LTA
9. rutile (TiO_2)
10. calcite (CaCO_3)
11. quartz (SiO_2).

Analyses of these materials are found in Table 49.

Major mineral alterations observed as being caused by the liquefaction process were:

1. pyrite (FeS_2) converted to pyrrhotite (Fe_{1-x}S)
2. hematite ($\alpha\text{Fe}_2\text{O}_3$) converted to maghemite ($\gamma\text{Fe}_2\text{O}_3$)
3. goethite ($\alpha\text{FeO(OH)}$) and boehmite (AlO(OH)) decomposed into an amorphous product, and
4. fly ash containing zincite (ZnO) and franklinite ($\text{Zn, Mn}^{2+}, \text{Fe}^{2+} \text{Fe}^{3+}, \text{Mn}^{3+})_2\text{O}_4$ converted to an as yet unidentified product.

Sphalerite (ZnS), quartz, calcite, rutile, and reduced Robena pyrite were essentially unaffected by the liquefaction reaction. Coal LTA from an Elkhorn #3 coal showed conversion of pyrite to pyrrhotite and an apparent loss of some ash components, as yet unidentified.

The objective of this work is to analyze minerals in disposable catalysts sampled before and after a coal liquefaction reaction. X-ray powder diffraction analysis (XRD) is used to determine the type and amount of mineral alteration caused by the liquefaction reaction. The mineral alteration should be of three types: 1) recrystallization, 2) decrystallization, and 3) dehydration.

Table 49

Analysis of the Additive Before Reaction

Catalyst	Composition
ZnS	62.6% Zn, 31.2% S, 2.45% SiO ₂ , 1.00% Fe
Rutile	95.9% TiO ₂
Quartz	99.5% SiO ₂
Laclede Zinc Fly Ash	33.6% Zn, 22.5% Fe, 3.00% Mn, 4.80% Ca
Robena Pyrite	75% Pyrite, 5% Quartz, 20% Carbonates, Sulfates and Clays
Fe ₂ O ₃	Fisher reagent grade
Calcite	Composition unknown
Red Mud	15% Al ₂ O ₃ , 51.5% Fe ₂ O ₃ , 6.7% TiO ₂ , 7.0% CaO

Recrystallization is a rearrangement of the internal structure of the mineral usually caused by either heat or pressure or both. Recrystallization may involve loss of an ion as in the case of pyrite going to pyrrhotite, or it may be only a rearrangement as in hematite to maghemite. Amorphous material may also crystallize to form a material that can be detected by XRD, but normally this requires conditions not found in the liquefaction reaction. Recrystallization is an easily detectable reaction and can be expected in many sulfide and easily reducible oxide minerals.

Decrystallization is the disruption of a structure to produce an X-ray amorphous state. An example of this is goethite which decomposes below 400°C into an amorphous iron oxide. Decrystallization is difficult to detect by XRD since the reaction product is amorphous and can be identified only as a reduced intensity of the diffraction peaks after the liquefaction reaction.

Dehydration is the loss of water without a disruption of the crystal structure. The effect is most often observed in clay minerals and zeolites. The amount of water contributed to the system may be negligible compared to that produced by the liquefaction reaction. Minerals that are easily rehydrated, for example the iron sulfates, may be affected by this water, i.e. dissolved.

Within the limits of XRD, this investigation will determine 1) the mineral composition of the original catalyst 2) the type and amount of recrystallization, and 3) the amount of decrystallization of the eleven disposable catalysts to be studied.

Experimental Method - The reacted and unreacted disposable catalysts were analysed using X-ray powder diffraction methods conducted on a Phillips X-ray diffractometer. The samples were ground to -200 mesh and mounted as an acetone slurry on glass slides. 100 mg of sample was used for both the unreacted and reacted samples and then the pattern of the reacted sample was corrected for dilution by organic residue and residual coal ash. Reaction products were identified using the ASTM powder diffraction index for inorganic substances. Some reaction products could not be identified by this method and were classified as unknowns.

Alteration of Minerals during Coal Liquefaction - The Elkhorn #3 coal used in this study has an ash composition of approximately

35% kaolinite
15% mica
15% quartz
12% pyrite
9% calcite
9% gypsum
1-5% smectite

1-5% chlorite, and 1-5% mica-smectite and a total low temperature ash content of 17.8%. At a ratio of 3 g coal to 1 g catalyst this gives a dilution of 1 part catalyst residue to 0.534 parts ash residue. Because of this dilution, the calcite, gypsum, smectite, chlorite, and mica-smectite peaks were obscured and could not be detected after reaction; however, kaolinite, mica, and quartz had quite intense peaks and the reaction product of the pyrite, pyrrhotite, was also detectable. The reaction products of the disposable catalysts studied represent actual coal liquefaction runs in which the catalyst was added to the Elkhorn coal and then reacted. Before determining the amount and type of alteration the patterns were corrected for this ash dilution.

The mineral alterations detected in the disposable catalysts were of two types: 1) recrystallization in the Robena pyrite, hematite, and Laclede fly ash, and 2) decrystallization in the red mud, rutile and sphalerite. Refer to Table 50 for the quantities of minerals formed. The amount of decrystallization in the rutile and sphalerite was very small and barely within the limits of detection. Minerals unaffected by the liquefaction reaction were calcite, quartz, and reduced Robena pyrite. The calcite and quartz were simply unreactive. The reduced Robena pyrite was already converted to pyrrhotite so that it was not changed by the liquefaction reaction.

Further studies of these disposable catalysts should include tests run without an added coal to determine the pure reaction products so that a comparison of the systems can be made. Nothing is known of the synergistic or antagonistic effects coal ash may have on these types of catalysts nor is anything known

Table 50
Alteration of Minerals After Coal Liquefaction

Disposable Catalyst	Original Minerals Present	Reaction Products	% Change	Theoretical Original Weight	Theoretical Final Weight
Robena Pyrite	Pyrite FeS_2	Pyrrhotite Fe_{1-x}S	100	$\text{FeS}_2 = 1 \text{ g}$	$\text{FeS} = 0.73$
Reduced Robena Pyrite	Pyrrhotite FeS_x	-	0	1 g	1 g
Fe_2O_3	Hematite $\alpha\text{Fe}_2\text{O}_3$	Magnetite Fe_3O_4	100	1 g	1 g
Red Mud	Goethite FeOOH , Boehmite AlOOH	Amorphous	100	1 g	0.91*
Laclede Fly Ash	Zincite ZnO , Franklinite (Zn, Mn) $(\text{Fe})_2\text{O}_4$	Unidentified	50	1 g	Unknown*
Rutile	Rutile TiO_2	Amorphous, Anatase	10	1 g	1 g
ZnS	Sphalerite ZnS	Amorphous, Wurtzite ZnS	10	1 g	1 g
Quartz	Quartz SiO_2	-	0	1 g	1 g
Calcite	Calcite CaCO_3	-	0	1 g	1 g
Elkhorn #3 Coal LTA	Kaolinite, mica, pyrite Gypsum, <20% calcite and others	Pyrrhotite, Anhydrite	-	1 g	0.95 g

*Materials became amorphous and thus cannot be identified by x-ray diffraction.

about mixtures of catalysts and their interactions. A knowledge of the thermal stability of catalytic minerals would be an aid in predicting reaction products. While much is known about the endotherms and exotherms of minerals determined from DTA, DSC, and TGA little is known about what corresponding alterations have taken place in the minerals.

Summary of Results - Disposable catalysts show a wide response to liquefaction reactions ranging from no effect at all on the catalyst to complete conversion to another mineral. Easily reducible and thermally unstable minerals will recrystallize or decrystallize depending on conditions. Hydrated minerals will dehydrate and add some water to the system.

Recalculation of Conversion Based on X-Ray Diffraction Results - The Elkhorn #3 coal has an LTA ash content of 17.8%. X-ray diffraction shows that the pyrite (FeS_2) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) present in the coal mineral (ash) change during reaction to FeS and CaSO_4 , and the other minerals remain unchanged. Based on these changes one gram of original coal minerals would become 0.95 gram after reaction. The 17.8% coal ash would become 16.9%. This value could be used in calculations rather than the 14.6% high temperature ash content now used. This particular change would effect all product analyses equally and thus would not change the comparisons between additives. Because of this no recalculations will be done.

The change in red mud is not visible by X-ray diffraction because the reaction product is amorphous and cannot be analyzed by X-ray diffraction. However, X-ray diffraction analysis of the unreacted material shows significant amounts of goethite ($\text{FeO}(\text{OH})$) and boehmite ($\text{AlO}(\text{OH})$). At reaction conditions (450°C) it is known that some water will be lost, and is noted as the "loss-upon-ignition" value (9.3%) discussed above on water loss. Noting the loss-upon-ignition value and recalculating the data from experiment number AP-85 with the additive red mud gives 50% oils, 32% asphaltenes, 6% preasphaltenes, and 12% insoluble organic material. These values compare with previously calculated values for AP-85 of 52% oils, 33% asphaltenes, 6% preasphaltenes, and 9% insoluble organic materials. As seen the data changes little, and red mud still qualifies as one of the very good additives in terms of conversion of coal to oils.

Transition Metal Catalysis

In the screening studies using bulk catalysts, a series of metal sulfides were used as additives. These metal sulfides include the sulfides of molybdenum, vanadium, tin, cobalt and chromium. Also used were zinc oxide and zinc sulfide, each mixed with quartz, and Kerr McGee ash concentrate received from Air Products and Chemicals, Inc. The ZnO and ZnS mixed with quartz showed very poor liquefaction activity as given in Table 51. The Kerr McGee ash concentrate additive is essentially inactive producing a product distribution very similar to the no additive case. The bulk transition metal sulfides produced an oil yield to the same range as that of pyrite. The nickel, vanadium, and stannous sulfides appear to be the most active with an activity somewhat greater than pyrite. The molybdenum, cobalt and chromium sulfides are slightly less active in oil production than pyrite. Several replicates of these experiments would be necessary to effectively rank the activity of the bulk transition metal sulfides. The same statement is true concerning comparisons of activity between the bulk transition metal sulfides and the impregnated transition metals that are reported below.

Table 52 shows the effect of impregnating Elkhorn #3 coal with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ or $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ on the product distribution. The actual metal concentration is given for each additive. Comparison of the activities shows that molybdenum impregnated at a concentration of 10^{-4}gMo/g coal gives a product distribution very similar to iron impregnated at 10^{-2}gFe/g coal . Iron impregnated at a lower concentration, 10^{-3}gFe/g coal , shows less oil production and coal conversion than the higher impregnated iron concentration or the lower molybdenum concentration.

Table 53 shows the effect of impregnating coal with compounds containing Co, Ni, and Mo. The liquefaction reaction, with the impregnated molybdenum compound, ammonium paramolybdate, showed one of the highest oil conversions, 64%, observed in the study, the highest conversion being obtained by use of the active Co-Mo-Al catalyst or $\text{Sn Cl}_2 \cdot 2\text{H}_2\text{O}$, as additives.

Table 51

Catalytic Effect of Minerals on Coal Liquefaction Using Zinc Oxide and Metal Sulfides

Additive*	ZnO/SiO ₂	ZnS/SiO ₂	MoS ₂	Ni ₂ S ₃	VS ₂	SnS	CoS	Cr ₂ S ₃	Kerr-McGee Ash FSKM-20
Gases (g)	0.38	0.25	0.36	0.43	0.46	0.33	0.46	0.36	0.38
Oils (g)	4.66	3.53	5.92	5.70	6.22	6.03	6.05	6.14	5.42
Asphaltenes (g)	0.93	0.90	0.93	0.78	0.78	0.76	0.92	0.92	0.97
Preasphaltenes (g)	0.38	0.31	0.39	0.28	0.21	0.29	0.30	0.36	0.46
Residues (g)	1.63	1.73	1.56	1.26	1.31	1.38	1.54	1.52	1.64
Total (g)	7.98	6.72	9.16	8.45	8.98	8.79	9.27	9.30	8.87
Normalized	-	-	-	-	-	-	-	-	-
Gases (g)	0.38	0.25	0.36	0.43	0.46	0.33	0.46	0.36	0.38
Oils (g)	5.90	5.32	6.48	6.80	6.96	6.89	6.55	6.62	6.14
Asphaltenes (g)	1.18	1.35	1.02	0.93	0.87	0.87	1.00	0.99	1.10
Preasphaltenes (g)	0.48	0.47	0.43	0.33	0.24	0.33	0.32	0.39	0.52
Residues (g)	2.06	2.61	1.71	1.51	1.47	1.58	0.67	1.64	1.86
Total (g)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
% Gases	15	10	14	17	18	13	18	14	15
% Oils	8	(15) ^a	31	43	49	47	33	36	17
% Asphaltenes	35	42	29	26	23	23	28	28	32
% Preasphaltenes	18	18	16	12	9	12	12	15	20
% I.O.M.	24	45	10	2	1	5	9	7	16
% Conversion	76	55	90	98	99	95	91	93	84

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Elkhorn #3 coal; 1g Additive; 1250 psig initial H₂ pressure at ambient temperature; 1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C.

^a() indicates a negative value

*For the purpose of calculations, all minerals are assumed to remain unchanged during reaction.

1. ZnO/SiO₂, Zinc Oxide supported on silica (4% Zinc Oxide by weight on silica), prepared and supplied by Air Products and Chemicals, Inc., Allentown, PA 18105.
2. ZnO/SiO₂, presulfided Zinc Oxide supported on silica. The sulfiding technique developed by Chemical Engineering Department, Auburn University was used.
3. MoS₂, Molybdenum Disulfide, received from Air Products and Chemicals, Inc.
4. Ni₂S₃, Nickel Sulfide, received from Air Products and Chemicals, Inc.
5. VS₂, Vanadium Sulfide, received from Air Products and Chemicals, Inc. Source: ICN Pharmaceuticals, Inc., Plainview, NY.

Table 51 Cont.

6. SnS, Stannous Sulfide, received from Air Products and Chemicals, Inc., and ground to -115 mesh.
7. CoS, Cobalt Sulfide, received from Air Products and Chemicals, Inc., and ground to -115.
8. Cr₂S₃, Chromium Sulfide, received from Air Products and Chemicals, Inc., and ground to -115 mesh.
Source: ICN Pharmaceuticals, Inc., Plainview, NY.
9. FSKM-20, Kerr-McGee ash concentrate, received from Air Products and Chemicals, Inc.

Table 52.

Effect of Impregnating Coal with
Fe or Mo Compounds on Product
Distribution and Conversion

Coal Impregnated with Additive*	$\frac{3.6 \times 10^{-4} \text{ g Mo}}{\text{g coal}}$	$\frac{2.2 \times 10^{-4} \text{ g Mo}}{\text{g coal}}$	$\frac{2.4 \times 10^{-2} \text{ g Fe}}{\text{g coal}}$	$\frac{1.1 \times 10^{-2} \text{ g Fe}}{\text{g coal}}$	$\frac{2.2 \times 10^{-3} \text{ g Fe}}{\text{g coal}}$	$\frac{8.8 \times 10^{-3} \text{ g Fe}}{\text{g coal}}$
Gases (g)	0.39	0.36	0.37	0.27	0.36	0.37
Oils (g)	6.16	6.13	6.15	5.27	5.75	5.19
Asphaltenes (g)	0.94	0.87	0.97	0.72	0.87	0.86
Preasphaltenes (g)	0.34	0.37	0.38	0.35	0.43	0.38
Residues (g)	0.72	0.75	0.95	0.73	0.89	0.83
Total (g)	8.55	8.48	8.82	7.34	8.3	7.63
Normalized	-	-	-	-	-	-
Gases (g)	0.39	0.36	0.37	0.27	0.36	0.37
Oils (g)	6.50	6.52	6.47	6.60	6.27	6.18
Asphaltenes (g)	0.99	0.93	1.02	0.90	0.95	1.02
Preasphaltenes (g)	0.36	0.39	0.40	0.44	0.47	0.45
Residues (g)	0.76	0.80	1.00	0.91	0.97	0.99
Total (g)	9.00	9.00	9.26	9.12	9.02	9.01
ases	15	14	15	11	14	15
Oils	31	32	24	32	22	18
% Asphaltenes	28	26	29	25	26	29
% Preasphaltenes	14	14	15	16	18	17
% I.O.M.	12	14	17	16	20	21
% Conversion	88	86	83	84	80	79

Reaction Conditions: 6 g Solvent (Air Products, CPDU 121); 1250 psig initial H_2 pressure at ambient temperature; 1 hour reaction time; 46.3 c.c. reactor volume; 860 RPM. Plus (1) 3.00 g Elkhorn #3 coal impregnated with 0.066% $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (2) 3.00 g Elkhorn #3 coal impregnated with 0.04% $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, (3) 3.3343 g Elkhorn #3 impregnated with 10% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, (4) 3.1580 g Elkhorn #3 impregnated with 5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, (5) 3.0303 g Elkhorn #3 impregnated with 1% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, (6) 3.0123 g Elkhorn #3 impregnated with 0.4% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

*For the purpose of calculations the following assumptions are made:

- (a) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ yields MoS_2 during reaction
- (b) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ yields FeS during reaction, and the weight of the hydrate water was subtracted from the oils fraction

Table 53

Effect of Impregnating Coal with Co, Ni, and
Mo Compounds on Product Distribution and Conversion

Coal Impregnated with Additive 1,6	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
AP-Sample No.	5543-20-1	5543-20-2	5543-20-3
Experiment No.	AP-154	AP-155	AP-156
% Oils ₂	40	42	64
% Asphaltene ₃	37	35	23
% Preasphaltenes ₄	9	13	5
% I.O.M. ₅	14	10	8
% Conversion	86	90	92

Reaction Conditions: 6 g solvent; 1250 psig H_2 ; 450°C, 1 hour reaction time, plus (AP-154) -3.139 g Elkhorn #3 coal impregnated with 4.57% $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, (cobalt II nitrate), (AP-155) -3.140 g Elkhorn #3 coal impregnated with 4.57% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (nickle nitrate, hexahydrate), (AP-156) -3.149 g Elkhorn #3 coal impregnated with 4.98% $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, (ammonium paramolybdate).

- For the purpose of calculations, the following assumptions are made:
 - $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ yields Co_9S_8 during reaction.
 - $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ yields Ni_2S_3 during reaction.
 - $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ yields MoS_2 during reaction.
- Pentane Soluble.
- Benzene soluble, pentane insoluble.
- Methylene Chloride - Methyl Alcohol (10%) soluble, benzene insoluble.
- I.O.M. - Insoluble Organic Matter.
- The amount of water in the quantities of additives is small enough such that it affects the values of the product distribution and conversion by less than one percentage point.

Experiments were also performed using other metal complexes impregnated on coal such as iron acetate, zinc sulfate and ammonia paramolybdate. Essentially the same order of magnitude concentrations were used for iron, zinc and molybdenum with the impregnated molybdenum yielding the highest oil production (Table 54). When the concentration of molybdenum is varied over an order of magnitude $1.4 \times 10^{-2} \text{g}$ to 2.9×10^{-3} , the product distribution remains constant. Likewise, a series of metal organoacids were added to the reaction level at quite low levels. Again, molybdenum showed the largest effect. Data are shown in Table 55.

Effect of Hydrogen Gas on Solvent Performance

CPDU-121 solvent, tetralin and creosote oil were all reacted at liquefaction conditions in the presence of Robena Mine pyrite and hydrogen gas. Under these conditions, the AP CPDU-121 solvent and creosote oil showed equivalent oil yields ~39% (Table 56). Tetralin was more effective than either of these yielding 54% oils. In general, the creosote oil produced a heavier product slate overall than did tetralin or the AP solvent. Under TPR conditions, creosote oil produced 40% oils which is less than either tetralin or AP solvent under equivalent conditions. TPR improved the product slate of the creosote oil/coal reaction to an overall lighter liquid product with no gas make.

A set of experiments was also performed utilizing the three solvent systems with hydrogen but without Robena Mine pyrite. Those data are shown in Table 57. Tetralin is unequivocally better than the CPDU 121 solvent. Surprisingly the creosote oil was comparable to the tetralin.

In another set of experiments, no additives and no hydrogen were used; in the other, hydrogen but no additives were used. The effect of the three solvents on the liquefaction of Elkhorn #3 coal with no hydrogen or additives is given in Table 58. Neither the Air Products CPDU-121 nor the creosote solvent produced any oils from Elkhorn #3 coal; in fact, the negative values of oil indicate that the solvent was incorporated into heavier products yielding high values of I.O.M. In contrast, tetralin with its known hydrogen donating ability promoted a 22% oil yield from Elkhorn #3 coal. The effect of hydrogen on the coal/solvent reaction systems is apparent in Table 58.

Table 54

Product Distribution and Conversion of Coal Impregnated with Fe, Zn and Mo Complexes

Coal Impregnated With Additive*	Fe $6.6 \times 10^{-3} \text{g Fe}$ g coal	Zn $9.7 \times 10^{-3} \text{g Zn}$ g coal	Mo $1.4 \times 10^{-2} \text{g Mo}$ g coal	Mo $7.0 \times 10^{-3} \text{g Mo}$ g coal	Mo $2.9 \times 10^{-3} \text{g Mo}$ g coal
Gases (g)	0.40	0.43	0.37	0.29	0.30
Oils (g)	5.74	5.51	6.12	5.70	6.13
Asphaltenes (g)	0.92	0.94	0.84	0.73	0.80
Preasphaltenes (g)	0.46	0.41	0.21	0.24	0.26
Residues (g)	0.66	0.93	0.74	0.73	0.70
Total (g)	7.78	8.22	8.28	7.69	8.19
Normalized	-	-	-	-	-
Gases (g)	0.40	0.43	0.37	0.29	0.30
Oils (g)	6.41	6.13	6.73	6.74	6.77
Asphaltenes (g)	1.03	1.05	0.92	0.86	0.88
Preasphaltenes (g)	0.51	0.46	0.23	0.29	0.29
Residues (g)	0.74	1.03	0.82	0.86	0.77
Total (g)	9.09	9.10	9.07	9.04	9.01
% Gases	15	17	15	11	12
% Oils	28	14	40	41	42
% Asphaltenes	30	31	25	23	24
% Preasphaltenes	19	17	8	11	10
% I.O.M.	8	21	12	14	12
% Conversion	92	79	88	86	88

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 1250 psig initial H₂ pressure at ambient temperature; 1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C; plus 3.093 g Elkhorn #3 coal impregnated with 3.1% Iron Acetate (Fe(OOCH₃)₂); 3.132 g Elkhorn #3 coal impregnated with 4.4% Zinc Sulfate (ZnSO₄·7H₂O); 3.078 g Elkhorn #3 coal impregnated with 2.6% (NH₄)₆Mo₇O₂₄·4H₂O; 3.039 g Elkhorn #3 coal impregnated with 1.3% (NH₄)₆Mo₇O₂₄·4H₂O; 3.016 g Elkhorn #3 coal impregnated with 0.45% (NH₄)₆Mo₇O₂₄·4H₂O respectively.

*For the purpose of calculations, the following assumptions are made:

- (1) Fe(OOCH₃)₂ remains unchanged during the reaction.
- (2) ZnSO₄·7H₂O yields ZnS during the reaction, and the weight of the hydrate water was subtracted from the oils fraction.
- (3) (NH₄)₆Mo₇O₂₄·4H₂O yields MoS₂.

Table 55
Effect of Organometallic Compounds on Product
Distribution and Coal Conversion

Additive* 0.1 wt% of Coal	Neo-Decanoate		Octoate				Linoleate	Naphthenate
	Co	Zn	Pb	Ni	Mo	Cr	Co	Co
Gases (g)	0.45	0.36	0.23	0.31	0.28	0.41	0.39	0.28
Oils (g)	5.33	5.51	5.43	5.22	6.14	5.44	5.74	5.72
Asphaltenes (g)	0.90	0.95	0.92	0.97	0.92	0.97	1.01	0.96
Preasphaltenes (g)	0.42	0.44	0.38	0.41	0.25	0.42	0.38	0.45
Residues (g)	0.92	0.94	0.90	1.06	0.66	0.97	0.86	0.87
Total (g)	8.02	8.20	7.86	7.97	8.25	8.21	8.38	8.28
Normalized	-	-	-	-	-	-	-	-
Gases (g)	0.45	0.36	0.23	0.31	0.28	0.41	0.39	0.28
Oils (g)	6.04	6.09	6.25	5.94	6.75	6.01	6.22	6.26
Asphaltenes (g)	1.02	1.05	1.06	1.10	1.01	1.07	1.09	1.05
Preasphaltenes (g)	0.48	0.48	0.44	0.47	0.27	0.47	0.41	0.49
Residues (g)	1.04	1.04	1.03	1.21	0.73	1.07	0.93	0.95
Total (g)	9.03	9.02	9.01	9.03	9.04	9.03	9.04	9.03
% Gases	18	14	9	12	11	16	15	11
% Oils	12	15	21	8	39	11	21	21
% Asphaltenes	29	31	31	32	29	31	32	30
% Preasphaltenes	18	18	16	18	10	18	15	18
% I.O.M.	23	22	23	30	11	24	17	20
% Conversion	77	78	77	70	89	76	83	80

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Elkhorn #3 Coal; 1250 psig initial H₂ pressure at ambient temperature; 1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C; plus 0.025 g Cobalt Neo-Decanoate (12% Co), 0.019g Zinc Neo-Decanoate (16% Zn), 0.0134g Lead Octoate (24% Pb), 0.025g Nickel Octoate (12% Ni), 0.038g Molybdenum Octoate (8% Mo), 0.029g Chromium Octoate (10.5% Cr), 0.038g Cobalt Linoleate (8.5% Co), 0.033g Cobalt Naphthenate (10.5% Co), respectively.

*^aAll organometallic compounds are received from Air Products and Chemicals, Inc. Source: The Shepherd Chemical Company, 4900 Beech Street, Cincinnati, Ohio 45212.

^bAll organometallic compounds are assumed to be completely soluble in pentane and the weight of additive is subtracted from the oils fraction.

Table 56

Solvent Effect on Coal Liquefaction in the Presence
of Robena Mine Pyrite^a and Hydrogen Gas

<u>Solvent^b</u>	<u>AP CPDU-121</u>	<u>Tetralin</u>	<u>Creosote Oil</u>	<u>Creosote^c Oil</u>
Gases (g)	0.25	0.05	0.08	0.00
Oils (g)	5.74	6.38	6.38	6.09
Asphaltenes (g)	1.06	0.65	0.75	0.76
Preasphaltenes (g)	0.17	0.18	0.30	0.25
Residues (g)	1.16	1.16	1.42	1.34
Total (g)	8.38	8.42	8.93	8.44
Normalized	-	-	-	-
Gases (g)	0.25	0.05	0.08	0.00
Oils (g)	6.69	7.38	6.96	7.02
Asphaltenes (g)	1.24	0.75	0.82	0.88
Preasphaltenes (g)	0.20	0.21	0.32	0.29
Residues (g)	1.35	1.34	1.55	1.54
Total (g)	9.73	9.73	9.73	9.73
% Gases	10	2	3	0
% Oils	39	54	38	40
% Asphaltenes	38	29	32	34
% Preasphaltenes	7	8	12	11
% I.O.M.	6	7	15	15
% Conversion	94	93	85	85

Reaction Conditions: 6g Solvent; 3g Elkhorn #3 Coal; 1g Additive; 1250 psig initial H₂ pressure at ambient temperature; 1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C

^aFor the purpose of calculations, pyrite is assumed to form FeS during reaction

^bTetralin and creosote oil are assumed to be 100% pentane soluble and are subtracted from the oils fractions.

^cTPR; programmed from 250°-450°C for 120 min and maintained at 450°C for 30 min.

Table 57

Effect of Solvent on Coal Liquefaction in the
Presence of Hydrogen and In Absence of Additives

<u>Solvent</u>	<u>AP CDPU-121</u>	<u>Tetralin</u>	<u>Creosote Oil</u>
Gases (g)	0.27	0.20	0.28
Oils (g)	5.35	5.96	6.12
Asphaltenes (g)	1.11	0.75	0.77
Preasphaltenes (g)	0.32	0.40	0.27
Residues (g)	0.85	0.66	0.65
Total (g)	7.90	7.97	7.81
Normalized	-	-	-
Gases (g)	0.27	0.20	0.28
Oils (g)	6.12	6.75	6.83
Asphaltenes (g)	1.27	0.85	0.86
Preasphaltenes (g)	0.37	0.45	0.30
Residues (g)	0.97	0.75	0.73
Total (g)	9.00	9.00	9.00
% Gases	11	8	11
% Oils	16	29	32
% Asphaltenes	39	33	34
% Preasphaltenes	14	18	12
% I.O.M.	20	12	11
% Conversion	80	88	89

Reaction Conditions: 6g Solvent; 3g Elkhorn #3 Coal; 1250 psig initial
H₂ pressure at ambient temperature; 1 hour reaction time; 46.3 cc
reactor volume; 860 RPM; 450°C.

Table 58

Solvent Effect on Coal Liquefaction in
the Absence of Additive and Hydrogen Gas

<u>Solvent</u>	<u>AP CPDU-121</u>	<u>Creosote Oil</u>	<u>Tetralin</u>
Gases (g)	0.47	0.30	0.31
Oils (g)	3.08	3.92	5.68
Asphaltenes (g)	0.95	0.83	0.53
Preasphaltenes (g)	0.33	0.24	0.29
Residues (g)	2.44	2.62	1.03
Total (g)	7.27	7.91	7.84
Normalized	-	-	-
Gases (g)	0.47	0.30	0.31
Oils (g)	3.86	4.48	6.56
Asphaltenes (g)	1.19	0.95	0.61
Preasphaltenes (g)	0.42	0.27	0.33
Residues (g)	3.06	3.00	1.19
Total (g)	9.00	9.00	9.00
% Gases	18	12	12
% Oils	(72) ^a	(59) ^a	22
% Asphaltenes	36	37	24
% Preasphaltenes	16	10	13
% I.O.M.	102	100	29
% Conversion	(2) ^a	0	71

Reaction Conditions: 6g Solvent ; 3g Elkhorn #3
Coal; Air Atmosphere; 1 hour reaction time; 46.3 cc reactor volume;
860 RPM; 450°C.

^a () indicates a negative value.

Effect of Coal Cleaning

In response to the technical redirection for this program the liquefaction behavior of Ireland mine coal cleaned at the Pittsburgh Mining Technology Center was examined. Table 59 presents the product distributions obtained from (1) Ireland Mine raw coal, (2) Ireland Mine deep cleaned coal (float 1.30), (3) Ireland Mine deep cleaned coal (float 1.30) with concentrated pyrite added, and (4) Ireland Mine coal cleaned using agglomeration. These reactions were performed in duplicate and the averaged values are given in Table 60. Examination of the product distribution suggests that the presence of pyrite either inherent or added during the liquefaction of Ireland Mine Coal aids in the production of oil from the coal. The oil yield obtained using the coal cleaned by agglomeration may be enhanced due to incorporation of the oil used in cleaning the coal.

Pyrite concentrate was added back to deep cleaned coal at a level equivalent to the pyrite concentration of the original coal. Table 61 presents the product distributions obtained. Comparison to the original activity of the raw coal indicates that back addition of pyrite to deep cleaned coal can effectively return the deep cleaned coal to the raw coal liquefaction activity level. Analysis of the pyrite concentration of the various cleaned coal fractions are given in Table 62.

FUNDAMENTAL STUDIES

Model Compound Hydrogenation

Table 63 presents the results for several minerals. The system consisted of 10% naphthalene in hexadecane (6 g) plus 0.6 g of additive. The reaction conditions were 410°C, 30 min., 1250 psig H_2 at 25°C, 860 RPM agitation of the 17.5 ml autoclave. The reaction of interest was the conversion of naphthalene to tetralin and other hydrogenated reaction products. As seen in Table 63 decalin and dihydronaphthalene were not produced in significant quantities, and the most abundant product was usually tetralin. The tetralin to naphthalene (T/N) ratio is the most definitive data. Co-Mo-Al was used as an additive in order to observe a maximum result with which other additives would be compared.

Table 59

Liquefaction Behavior of Cleaned Coal

Coal	Ireland Mine Raw Coal ^a		Ireland Mine Deep Cleaned Coal (Float 1.30) ^b		Ireland Mine Clean Coal and Pyrite ^c		Ireland Mine Clean Coal From Agglomeration ^d	
Gases (g)	0.24	0.30	0.47	0.35	0.31	0.25	0.31	0.33
Oils (g)	4.47	5.59	5.18	4.38	5.58	5.16	5.63	5.64
Asphaltenes (g)	0.88	0.95	1.35	1.33	1.15	1.06	1.13	1.13
Preasphaltenes (g)	0.22	0.31	0.52	0.54	0.38	0.42	0.35	0.39
Residues (g)	1.09	1.19	0.49	0.48	0.78	0.79	0.59	0.60
Total (g)	6.90	8.34	8.01	7.08	8.20	7.68	8.01	8.09
Normalized	-	-	-	-	-	-	-	-
Gases (g)	0.24	0.30	0.47	0.35	0.31	0.25	0.31	0.33
Oils (g)	5.88	6.05	5.86	5.63	6.14	6.08	6.35	6.30
Asphaltenes (g)	1.16	1.03	1.53	1.71	1.27	1.25	1.28	1.26
Preasphaltenes (g)	0.29	0.33	0.59	0.69	0.42	0.49	0.39	0.44
Residues (g)	1.43	1.29	0.55	0.62	0.86	0.93	0.67	0.67
Total (g)	9.00	9.00	9.00	9.00	9.00	9.00	9.00	9.00
% Gases	12	15	16	12	12	10	11	12
% Oils	9	18	6	(2) ^e	17	15	24	22
% Asphaltenes	46	39	43	49	40	39	38	37
% Preasphaltenes	14	16	19	23	16	18	14	16
% I.O.M.	19	12	16	18	15	18	13	13
% Conversion	81	88	84	82	85	82	87	87

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Coal; 1250 psig initial H₂ pressure at ambient temperature; 30 min. reaction time; 46.3 cc reactor volume; 860 RPM; 450°C.

^aIreland Mine raw coal contains 35.04% ash, and ground to 50 mesh before use.

^bIreland Mine deep cleaned coal (float 1.30) contains 2.48% ash.

^cIreland Mine deep cleaned coal (float 1.30) and concentrated pyrite mixture contains 15.47% ash.

^dIreland Mine clean coal from agglomeration contains 10.32% ash.

^e() indicates a negative value.

Table 60
Liquefaction Behavior of Cleaned Coal: Averaged Values^e

Coal	Ireland Mine Raw Coal ^a	Ireland Mine Deep Cleaned Coal (Float 1.30) ^b	Ireland Mine Clean Coal and Pyrite ^c	Ireland Mine Clean Coal From Agglomeration ^d
Gases (g)	0.27	0.41	0.28	0.32
Oils (g)	5.03	4.78	5.37	5.64
Asphaltenes (g)	0.91	1.34	1.11	1.13
Preasphaltenes (g)	0.27	0.53	0.40	0.37
Residues (g)	1.14	0.49	0.78	0.59
Total (g)	7.62	7.55	7.94	8.05
Normalized	-	-	-	-
Gases (g)	0.27	0.41	0.28	0.32
Oils (g)	5.98	5.75	6.11	6.33
Asphaltenes (g)	1.08	1.61	1.26	1.27
Preasphaltenes (g)	0.32	0.64	0.46	0.42
Residues (g)	1.35	0.59	0.89	0.66
Total (g)	9.00	9.00	9.00	9.00
% Gases	14	14	11	12
% Oils	14	2	16	23
% Asphaltenes	42	46	39	37
% Preasphaltenes	15	21	17	15
% I.O.M.	15	17	17	13
% Conversion	85	83	83	90

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Coal; 1250 psig initial H₂ pressure at ambient temperature; 30 min. reaction time; 46.3 cc reactor volume; 860 RPM; 450°C.

^aIreland Mine raw coal contains 35.04% ash, and ground to 50 mesh before use.

^bIreland Mine deep cleaned coal (float 1.30) contains 2.48% ash.

^cIreland Mine deep cleaned coal (float 1.30) and concentrated pyrite mixture contains 15.47% ash.

^dIreland Mine clean coal from agglomeration contains 10.32% ash.

^eAll experiments are duplicate.

Table 61

Liquefaction Behavior of Ireland Mine Deep Cleaned
Coal and Concentrated Pyrite Mixture*

<u>Reaction Run No.</u>	<u>1</u>	<u>2</u>	<u>Average**</u>
Gases (g)	0.27	0.29	0.28
Oils (g)	5.42	5.18	5.30
Asphaltenes (g)	1.30	1.26	1.28
Preasphaltenes (g)	0.48	0.60	0.54
Residues (g)	0.44	0.49	0.47
Total (g)	7.91	7.82	7.87
Normalized	-	-	-
Gases (g)	0.27	0.29	0.28
Oils (g)	6.19	5.99	6.09
Asphaltenes (g)	1.49	1.46	1.48
Preasphaltenes (g)	0.55	0.69	0.62
Residues (g)	0.50	0.57	0.53
Total (g)	9.00	9.00	9.00
% Gases	10	11	10
% Oils	18	11	14
% Asphaltenes	44	43	44
% Preasphaltenes	19	24	22
% I.O.M.	9	11	10
% Conversion	91	89	90

Reaction Conditions: 6g Solvent (Air Products, CPDU 121); 3g Ireland Mine Deep Cleaned Coal and Pyrite Mixture; 1250 psig initial H₂ pressure ambient temperature; 1 hour reaction time; 46.3 cc reactor volume; 860 RPM; 450°C.

* The reaction mixture of deep cleaned coal and concentrated pyrite contains 4 wt% pyrite and 8.28% ash.

** Average of 1 and 2.

Table 62

Pyrite and Sulfur Analyses of Ireland Mine Coal Samples*

<u>Sample</u>	<u>Wt % Pyrite</u>	<u>Wt% Ash</u>	<u>Sulfur Content, Wt %</u>			<u>Total</u>
			<u>Pyritic</u>	<u>Sulfate</u>	<u>Organic</u>	
Raw Coal	3.98	35.04	2.13	0.10	2.08	4.31
Deep Cleaned Coal (Float 1.30)	0.17	2.48	0.09	< 0.01	2.68	2.77
Deep Cleaned Coal (Float 1.30) and Concentrated Pyrite Mixture	3.83	15.47	2.05	0.02	2.85	4.92
Oil Agglomeration Clean Coal	5.08	10.32	2.72	0.35	2.57	5.64
Concentrated Pyrite	46.82	73.86	25.05	0.36	1.16	26.57

*Samples obtained from Dr. Richard Killmeyer of Pittsburgh Energy Technology Center

Table 63

Effect of Additives on Conversion of Naphthalene (17.5 ml Autoclave)

Catalyst	GC Peak Area Ratio x 10 ³						T/N
	Surface Area (m ² /g)	Tetralin Hexadecane	Naphthalene Hexadecane	Decalin Hexadecane	Dihydro naphthalene Hexadecane	unknown Hexadecane	
without treatment	-	-	109.9	-	-	-	-
Blank Run	-	0.80	112.28	0.50	0.94	2.96	0.007
Fe ₂ O ₃	11.27	6.49	101.95	0.46	1.37	3.38	0.063
FeS ₂ (Fisher reagent grade)	0.19	15.84	86.78	1.21	0.00	6.16	0.182
Co-Mo-Al*	200	75.02	23.36	1.00	0.00	2.73	3.210
FeS (Fe ₂ O ₃ +H ₂ S)	5.34	49.06	56.18	0.55	0.00	2.37	0.873
FeS (Fe ₂ O ₃ +H ₂ S)	3.10	23.52	75.44	0.37	0.00	1.20	0.311
FeS (FeCl ₂ +(NH ₄) ₂ S)	11.82	2.55	107.92	0.34	0.26	5.30	0.023
FeS (FeS ₂ +H ₂)	1.44	36.06	64.90	2.08	0.00	11.23	0.556
FeS (FeS ₂ +H ₂)	1.56	16.26	84.68	0.60	0.00	2.44	0.192
Robena Pyrite (as-received)	1.52	2.82	102.99	0.09	0.25	0.80	0.027
Robena Pyrite (-115 mesh)	0.98	4.60	103.35	0.11	0.20	1.22	0.044
Zircon (-325 mesh)	1.7	1.55	106.22	0.32	0.77	1.64	0.014
Zircon (-115 mesh)	0.1	1.55	105.61	0.10	0.33	1.05	0.014
Ilmenite (-115 mesh)	7.9	2.28	102.44	0.02	0.27	0.34	0.022
Rutile (-115 mesh)	0.15	0.85	105.69	0.53	0.68	2.79	0.008
FeSO ₄ (dehydrate)	13.2	1.90	105.34	0.84	0.60	5.05	0.018
FeSO ₄ ·7H ₂ O	-	1.32	109.94	0.96	1.13	12.63	0.012
Robena Pyrite (-325 mesh)	1.7	3.32	117.02	1.86	1.46	8.70	0.033
Pyrite (Siniola Mexico) (-325 mesh)	-	6.06	116.39	3.47	1.26	21.9	0.052

Reaction Conditions: 10 wt% Naphthalene in Hexadecane (6.0 g, 0.6 g of additive)

410°C, 30 min., 1250 psig H₂ at 250°C, 260 rpm (17.5 ml autoclave)

The most impressive results (other than with Co-Mo-Al catalyst) were obtained from ferrous sulfides which were produced by passing hydrogen and hydrogen sulfide over Fe_2O_3 or FeS_2 as seen in the Table 63.

The high surface area iron sulfide (FeS) was prepared at Auburn University by sulfiding ferric oxide with H_2S in the presence of H_2 . The ferric oxide used was red-anhydrous powder of over 99% purity and was obtained from Fisher Scientific Company. The hydrogen sulfide gas was of commercial purity obtained from Matheson Gas Company.

The following reaction is assumed to take place:

Figure 18 shows the schematic diagram of the apparatus used. The constant supply pressure of 2 psig was maintained on the H_2 and H_2S cylinders. The rotameters were installed to measure the individual gas flow rates. The gas flow rates were controlled by fine metering valves. A porcelain boat containing ferric oxide was placed in the center of 1" O.D. Pyrex tube. The Lindberg Electric Furnace (Type 123-12) was used to heat the Pyrex tube containing the reactant. The thermocouple attached to a digital temperature display was installed in the center of the furnace to measure and manually control the temperature. The excess H_2S in off-gas was scrubbed and other gases were vented in the hood.

Approximately 1.25 g of Fe_2O_3 was weighed in a porcelain boat. The boat was placed in the center of pyrex tube and the tube was placed in the furnace. Rubber stoppers with inlet and outlet openings for gases were installed in place.

First, the H_2 flow rate was adjusted to the desired level, usually 60 cc/min. Then the H_2S flow rate was adjusted to 6 cc/min to give an $\text{H}_2/\text{H}_2\text{S}$ flow ratio of 10/1. Once the lines and fittings were checked and corrected for leaks, the furnace was switched on and the time was entered in the log-book.

1. Fine Metering Valves
2. Rotameters
3. Rubber Stopper
4. 1" O.D. Pyrex Tube
5. Electric Furnace
6. Thermocouple wire
7. Digital Temperature Recorder
8. H₂S Scrubber

Figure 18. Apparatus for FeS Production

Usually, 50-70 minutes were required to heat the furnace from room temperature to 350°C. When the temperature reached 350°C (or desired temperature), the time was marked at zero time. The temperature was maintained within $\pm 5^\circ\text{C}$ for 150 minutes from zero time. At the end of the reaction period the furnace was switched off. The furnace was opened and the product was allowed to cool rapidly to room temperature. The product was then removed, ground, and stored under an inert atmosphere of N_2 for later use as a catalyst in hydrogenating Naphthalene to Tetralin. Surface area analysis was performed on the prepared material.

An X-ray diffraction of a sample of one of the batches showed that the material was primarily FeS (troilite and iron II sulfide).

Table 63 shows that the Fisher reagent grade pyrite is more reactive than the Robena pyrite as-received or screened to -115 mesh or -325 mesh. Table 64, which shows Granoff and Baca's work, pyrite screened to -325 mesh showed more oil production than other pyrites (FeS_2) or pyrrhotites (FeS). The source of the pyrite was a naturally occurring pyrite, 95% pure, obtained from Siniola, Mexico. A sample of this pyrite was obtained through Auburn's Geology Department.

Pyrrhotite, FeS was prepared by passing H_2S and H_2 over heated Fe_2O_3 or FeS prepared by passing H_2 over FeS_2 . Table 63, rows 6, 7, 9 and 10, show that the FeS's prepared by these methods were relatively effective additives in terms of the T/N ratio which is generally the most definitive quantity in Table 63. By contrast, the precipitated FeS (row 8 of Table 63) handled under nitrogen did not show results as favorable as the FeS prepared as previously described. Granoff and Baca's results with FeS, in Table 64, present four alternatives for sources of FeS. The most effective material was freshly precipitated material, but since Auburn's precipitated material was not as effective when compared with FeS prepared by other methods the choice for a precipitated material is not favorable unless further experimentation yielded different information. The FeS obtained by Granoff and Baca from Gallard-Schlesinger Chemical Mfg. Company was the second most effective FeS in their experiments, but it is expensive (\$125/50g).

Table 64. FeS_2 and FeS as Additives*

Run No. G 341:	<u>72</u>	<u>62</u>	<u>77</u>	<u>67</u>	<u>76</u>	<u>64</u>	<u>80</u>
Catalyst	-	FeS_2^a	FeS_2^b	FeS^c	FeS^d	FeS^e	FeS^f
<u>Conversion (% daf coal)</u>							
Benzene Solubles	61	78	78	71	76	78	78
THF Solubles	85	96	96	92	92	95	93
<u>Product Yield (% daf coal)</u>							
$\text{C}_1\text{-C}_4$	3.1	2.7	2.9	2.9	2.9	3.0	3.3
CO, CO_2	1.5	0.8	1.3	1.4	1.3	0.8	1.2
H_2S	1.5	5.1	7.0	2.5	3.9	3.5	4.3
Oil ^g	13.9	24.6	35.7	13.1	24.1	30.5	22.2
Asphaltenes	43.9	49.9	36.7	54.3	48.0	45.0	52.0
Preasphaltenes	24.6	17.2	17.6	21.8	16.5	17.4	15.5
IOM ^h	14.8	4.4	4.1	7.7	7.7	4.6	6.7
Hydrogen Consumed ⁱ	-3.3	-4.7	-5.3	-3.7	-4.4	-4.8	-5.2

^a100 x 200 mesh. ^b-325 mesh. ^cCerac/pure. ^dGallard-Schlesinger.

^eFreshly precipitated. ^fHydrothermally synthesized.

^gPentane-soluble oil, obtained by difference.

^hIOM = insoluble organic matter.

ⁱObtained by gas balance.

*Source: Granoff, B and Baca, P.M., "Mineral Matter Effects and Catalyst Characterization in Coal Liquefaction"; Sandia Laboratories Energy Report No. SAND-79-0505, page 47.

The choice seems to be FeS prepared from Fe_2O_3 , H_2 , and H_2S or FeS prepared from FeS_2 and H_2 . A reason for using FeS_2 (pyrite) is that it simulates the actual pyrite in coal in a liquefaction reaction. However, an equally strong reason for using FeS (pyrrhotite) is that this simulates a liquefaction reaction which has been occurring for some time and has accumulated FeS resulting from the reaction of FeS_2 with hydrogen or Fe or Fe_2O_3 with H_2S .

From Table 63, FeS_2 , row 4 (T/N = 182) is intermediate in activity between the high activity FeS in row 5 (T/N = 873) and the low activity Robena pyrite as-received in row 11 (T/N = 27). It is felt that a material of intermediate activity would produce a reaction mixture sensitive to either positive or negative effects from other additives. A high or low activity FeS or FeS_2 might tend to mask the effects of additives.

Cracking Activity

To determine the hydrocracking activity limitations of different catalysts used in coal liquefaction experiments, exploratory experiments were performed with cumene and 1-methyl naphthalene (MN) as model compounds. Eventually, MN was selected as a model compound for hydrocracking instead of cumene because of relatively simple product distribution of MN reaction product. It was hoped that 1-methylnaphthalene will lose the methyl group due to HDC activity of the catalyst to produce naphthalene. Between 316 and 343°C, Patzer et al., (Patzer, J. F., Farrauto, R. J., and Montagna, A. A., Ind. Engg. Chem., Process Des. Dev., 625, 18 (1979).) did not observe the hydrogenated products, methyltetralins, when 1-methylnaphthalene was reacted over catalysts such as Ni-Co-Mo-Al. They observed that naphthalene was the major product of the reaction. Contrary to this, Brammer and Weller (Brammer, S. T., and Weller, S. W., Fuel Proc. Tech., 155, 2 (1979).) observed very little conversion of 1-methylnaphthalene to naphthalene at a temperature as high as 450°C. At these conditions, they observed a significant amount of 1-methyltetralin and 5-methyltetralin.

In the present work, two major products were observed from 1-methylnaphthalene. One of these products was identified as naphthalene by spiking with an authentic compound and comparing gas chromatographic retention times. For confirmation of naphthalene and an identification of other compounds, GC/MS data were obtained for the sample identified as KGS-275. KGS-275 is a reaction product obtained by 1-methylnaphthalene model compound experiment performed at 375°C for 15 minutes over a presulfided iron oxide catalyst. It was observed that the compound which was believed to be naphthalene was in reality 5- and/or 6-methyltetralin. The other compound was identified as 1-methyltetralin, the hydrogenation product. Here, 5-methyltetralin may have been just a hydrogenation product of 1-methylnaphthalene, or an isomerization product of 1-methyltetralin. To determine the exact reaction path of 5-methyltetralin formation will require extensive experimental work. It will be beneficial to look into some other model compound, such as cumene, for determining the hydrocracking activity of the catalyst. In brief, the present work is in good agreement with Brammer and Weller's work; but in contradiction with Patzer et al.

It is obvious from these results in Table 65 and 66 that both iron oxide and Robena mine pyrite showed very little catalytic activity, whereas presulfided iron oxide showed a significant increase in its hydrogenation activity.

It is evident from these results that the presulfided iron oxide has a behavior very similar to the Co-Mo-Al catalyst. But either the reaction conditions or the model compound should be changed to discriminate hydrocracking activities of various catalysts.

Hydrogenation Activity of Presulfided Iron Oxide Catalyst in the Presence of a Basic Nitrogen Compound

In four experiments performed in order to explore the phenomenon of catalyst poisoning, it was found that the nitrogen containing compound, quinoline retard the hydrogenation of naphthalene to tetralin. Table 67 shows that the effect of 0.06 g of quinoline on conversion of 0.5 g of naphthalene to tetralin in 4.5 g of hexadecane. The possible conclusion is that if practical it might be advisable to remove or decrease the amount of compounds which might adversely affect the activity of catalysts.

Table 65
Effect of Reaction Time and Temperature on
1-Methylnaphthalene Conversion

<u>Run No.</u>	<u>Temp. (°C)</u>	<u>Time (min)</u>	<u>%5-,6-Methyl Tetralin</u>	<u>Tetralin</u>	<u>% 1-Methyl-Naphthalene Conversion</u>
KGS-242	350	15	33.2	39.0	74.6
KGS-257	350	30	38.1	47.0	92.9
KGS-258	375	15	35.2	48.0	89.7

Reaction Conditions: 5g reaction mixture (10 wt% 1-methylnaphthalene in hexadecane); 0.25g presulfided Co-Mo-Al catalyst; 1250 psig H₂ at ambient temperature; 14.5 ml tubing-bomb reactor; 860 RPM; 2 steel ball agitators.

* * * * *

Table 66
Effect of Different Additives on 1-Methyl-Naphthalene Conversion

<u>Run No.</u>	<u>Additive</u>	<u>%5-,6-Methyl-Tetralin</u>	<u>Tetralin</u>	<u>% Methyl-Naphthalene Conversion</u>
KGS-271	None	0.3	--	0.8
KGS-258	CoMoAl ^a	35.2	48.0	89.7
KGS-273	Fe ₂ O ₃	0.3	2.0	4.0
KGS-274	Fe ₂ O ₃ ^a	16.6	17.2	34.9
KGS-275	Fe ₂ O ₃ ^a	18.2	18.5	37.4
KGS-277	Robena Pyrite (-325 Mesh)	1.0	1.0	4.2

Reaction Conditions: 5g mixture (10 wt% 1-methylnaphthalene in hexadecane); 0.25g additive; 375°C; 15 mins; 1250 psig H₂ at ambient temperature; 14.5 ml tubing-bomb reactor; 860 RPM; 2 steel ball agitators.

^aPresulfided

Table 67. Effect of Quinoline on Hydrogenation
of Naphthalene to Tetralin

Additive	Tetralin/Naphthalene Ratio	
	Without Quinoline	With 0.06 gram Quinoline
FeS	2.1	0.2
Co-Mo-Al	3.9	2.2

1. Reaction Conditions: 410°C, 30 minutes, 0.5 gram naphthalene in 4.5 grams hexadecane, 0.06 gram quinoline when used, 17.5 ml tubing bomb reactor.
2. Information on FeS and Co-Mo-Al is reported elsewhere.

A sensitivity study using different amounts of quinoline additions and reaction times was performed for hydrogenation of naphthalene over presulfided Co-Mo-Al catalyst. The hydrogenation reaction temperature employed in this study was 380°C. It was concluded that quinoline reduces the hydrogenation activity of Co-Mo-Al catalyst significantly. Two preliminary experiments were performed to determine the effect of quinoline on hydrogenation activity of presulfided iron oxide (FeS) catalyst. An order of magnitude reduction in the hydrogenation reaction rate was observed in the presence of 1 wt% quinoline per total charge versus no quinoline being present.

In addition, it was observed that the product distribution of reacted coal with Robena Mine pyrite (low hydrogenation activity) and a sulfided iron-oxide catalyst (high hydrogenation activity) were similar. Thus, the inhibition effect of basic nitrogen compounds present in a process solvent and those produced from coal may be so dominant that it masks out any improvement made in the activity of FeS.

Based on the above mentioned results, it seemed necessary to determine the inhibition effect of basic nitrogen compounds on FeS catalyst. Experiments, similar to those performed with Co-Mo-Al catalyst, were planned with the following objectives.

1. To determine the inhibition effect of basic nitrogen compounds, such as quinoline, on the naphthalene hydrogenation reaction over a presulfided iron-oxide catalyst, and
2. To compare the inhibition effect of a basic nitrogen compound on FeS catalyst with that on Co-Mo-Al catalyst.

A sensitivity study with different amounts of quinoline additions and reaction times was performed for hydrogenation of naphthalene over FeS catalyst. The hydrogenation reaction temperature of 410°C was found to allow the observation of the effect of quinoline concentration on FeS catalyst activity. The catalyst used in these experiments was prepared by sulfiding iron-oxide under controlled conditions. Table 68 includes experimental conditions and data from these experiments.

Table 68

Sensitivity Study of Quinoline Concentration On
Naphthalene Hydrogenation Over Presulfided Iron Oxide

Quinoline Concentration (Wt %)	Naphthalene Conversion, 100x (%) for Each Reaction Time, t (min)		
	5	10	15
0.00	56.2	73.6	82.0
0.25	8.0	15.2	23.4
0.52	3.3	7.4	13.0
1.02	2.0	5.8	7.0
2.04	3.0	3.7	8.5

Reaction Conditions: 5 g reaction mixture (10% naphthalene in Hexadecane + Quinoline), 0.5 g presulfided iron oxide, 410°C, 1250 psig H₂ at ambient temperature, 14.5 ml tubing-bomb reactor.

The molar concentration of H_2 was approximately 10 times higher than that of naphthalene in the reactant mixture. Thus, the hydrogen concentration can be assumed to remain virtually constant. Under these conditions, the rate of hydrogenation can be represented by:

$$r = kC_n$$

where

r = rate

k = pseudo first-order rate constant

C_n = naphthalene concentration

The integrated rate expression for the batch reactor becomes:

$$-\ln(1 - X) = k \frac{V_c}{W_s} \cdot t$$

where

X = fractional conversion

W_c = mass of catalyst, gm

W_s = mass of solvent (hexadecane), gm

t = time of reaction, min

k = pseudo first-order rate constant,
g solvent/g catal/min

Figure 19 demonstrates the application of this rate expression to the naphthalene hydrogenation. The pseudo first order rate constants determined by linear regression are presented in Table 69. A qualitative measure of inhibition can be obtained by a ratio defined as:

$$\text{Inhibition Factor (IF)} = \frac{k_i}{k_1}$$

Figure 19. Effect of Quinoline Concentration on Naphthalene Conversion over Presulfided Iron-Oxide Catalyst

Table 69

Effect of Quinoline Concentration on Naphthalene
Hydrogenation Rate Constant

Index i	Presulfided Catalyst					
	Iron-Oxide ₁			Co-Mo-Al ₂		
	Quinoline conc. (wt %)	Rate Constant, K_i $\left(\frac{\text{g Solvent}}{\text{g Catalyst} \cdot \text{min}}\right)$	Inhibition Factor, K_i/K_1	Quinoline conc. (wt %)	Rate Constant, K_i $\left(\frac{\text{g Solvent}}{\text{g Catalyst} \cdot \text{min}}\right)$	Inhibition Factor, K_i/K_1
1	0.00	1.10	1.00	0.00	2.70	1.00
2	0.25	0.16	0.14	0.26	1.26	0.47
3	0.52	0.08	0.07	0.50	1.02	0.38
4	1.02	0.05	0.04	1.03	0.71	0.26
5	2.04	0.05	0.04	1.97	0.53	0.19

Reaction Temperature: 1. 410°C 2. 380°C

where

k_i = pseudo first order hydrogenation
rate constant at i th level of
quinoline concentration.

k_1 = pseudo first order hydrogenation
rate constant without quinoline.

The inhibition factors for FeS catalyst are presented in Table 69. For comparison, the results with sulfided Co-Mo-Al catalyzed reactions are also presented in the same table. In addition, the hydrogenation experiments were performed at 410°C over presulfided Co-Mo-Al without any quinoline addition and with 1 wt% quinoline in the reaction mixture. Results of these experiments are presented in Table 70.

The effect of quinoline concentration on the inhibition factor for both catalysts are presented in Figure 20. It should be noted that the lower the value of inhibition factor, the more detrimental the basic nitrogen compound is on catalyst activity. From this figure, it can be observed that quinoline has more detrimental effect on FeS catalyst than on Co-Mo-Al catalyst. With only 1 wt% quinoline in the reaction mixture, which is equivalent to 1 wt% N based on the naphthalene charge in the naphthalene hydrogenation reaction system, the activity of the sulfided iron-oxide catalyst was reduced to 4% of its original activity; whereas reductions to 26% and 40% of the original activity of Co-Mo-Al catalyst were observed at 380°C and 410°C, respectively. At the reaction temperature of 450°C employed in the coal liquefaction experiment, the inhibition of catalytic activity by basic nitrogen compounds may be less severe for Co-Mo-Al catalyst; but the inhibition effect may continue to be severe for FeS catalyst. Also the difference in the relative inhibition of the two catalysts increases at lower quinoline concentrations. In addition, it should be noted that only 0.5 wt% quinoline in the reaction mixture reduces the sulfided iron-oxide catalyst activity to the activity level shown by mineral pyrite and Fisher reagent grade pyrite in the absence of quinoline.

Table 70
Inhibition Effect of Quinoline on Hydrogenation
Activity of Co-Mo-Al Catalyst

Index i	Quinoline Conc. (wt %)	Rate Constant, $\left(\frac{\text{g solvent}}{\text{g catal. min.}}\right)$	Inhibition Factor
1	0.00	3.48	1.00
2	1.01	1.35	0.39

Reaction Conditions: 5 g reaction mixture (10% naphthalene in hexadecane + quinoline), 0.25 g presulfided Co-Mo-Al, 410°C, 1250 psig H₂ at ambient temperature, 14.5 ml tubing bomb reactor.

Figure 20. Effect of Quinoline Concentration on Inhibition Factor

Based on this study, it can be concluded that quinoline, a basic nitrogen compound, reduces FeS catalyst activity. In general, it can be postulated that the basic nitrogen compounds may significantly limit the hydrogenation activity of the FeS catalyst. In a model compound experiment involving the hydrogenation of naphthalene to tetralin, a sample of prepared FeS produced 89% naphthalene conversion. A sample of Robena Mine Pyrite produced 5% naphthalene conversion in a similar experiment. However, when the FeS and Robena Mine Pyrite were used in coal liquefaction experiments the product distributions were identical as seen in Table 71. The improved hydrogenation activity of the FeS over the pyrite as measured by the naphthalene conversion test did not cause a different product distribution in the coal-solvent system. The presence of basic nitrogen compounds in the coal-solvent system may be the reason why the improved hydrogenation activity of the FeS catalyst did not affect the product distribution in the coal-solvent system.

Some of the causes for the severe inhibition of FeS catalyst activity can be postulated as follows:

1. Sulfided iron-oxide and Co-Mo-Al catalysts have major differences in surface areas, $5.5 \text{ m}^2/\text{g}$ and $200 \text{ m}^2/\text{g}$, respectively. The same amount of inhibitor may affect the lower surface area catalyst more severely because a greater proportion of the surface area will be covered with the nitrogen inhibitor. This coverage may not allow the main reactants, such as naphthalene and hydrogen, to adsorb on catalytically active centers.
2. The physical and chemical properties, such as surface acidity, may be greatly different for these catalysts. If the surface acidity of Fe-S catalyst is higher than sulfided Co-Mo-Al, a stronger acid-base interaction and absorption by basic nitrogen compound can be expected, which may be a significant factor in limiting the catalyst activity. Surface acidity of Fe-S and Co-Mo-Al catalysts.
3. Hydrodenitrogenation (HDN) reactions are observed to occur on Co-Mo-Al catalyst (Gupta, 1978; Goudriaan, 1973; Shih, 1978; Shih, S., Rieff, E., Zawadzki, R., and Katzer, J. R., ACS, Div. Fuel Che., Preprints, 23 (1),

Table 71

Comparison of High Activity Pyrite and
Mineral Pyrite on Product Distribution,
and Conversion

Weight % Yield	Additive	
	High Activity Pyrite (Three Expts.)	Robena Mine Pyrite (-325 Mesh) (Two Expts.)
Oil	42 $\pm$ 1.4*	42 $\pm$ 3.5**
Asphaltene	42 $\pm$ 1.9	42 $\pm$ 2.5
Preasphaltene	6 $\pm$ 0.7	7 $\pm$ 0.0
I.O.M. ₃	10 $\pm$ 2.0	9 $\pm$ 1.00
% Conversion	90 $\pm$ 2.0	91 $\pm$ 1.00

*Standard Deviation

**Deviation from the Mean

1. Calculations do not account for gas formation which can vary from 0.5 g to 1.0 g depending upon catalyst used.
2. Reaction Conditions: 6 g solvent (AP-CPDU-121); 3 g Elkhorn #3 coal; 1 g additive; 1250 psig initial H₂ pressure at ambient temperature; 450°C, 60 minutes² reaction time; 46.3 ml reactor volume.
3. In determining insoluble organic matter (I.O.M.) pyrite has been assumed to form FeS at reaction conditions.

99 (1978)). This process will remove or change the form of the inhibitor in the reaction mixture. HDN may not occur to the same degree over FeS catalyst.

One final point, which should be noted, is that the quinoline concentration should be reduced below about 0.25 wt% (0.1 wt% or less is more likely) to provide any significant improvement in the activity of Fe-S catalyst. To examine this effect, a model compound study is planned to determine the effect of an acid extraction procedure on removal of basic nitrogen compounds from reaction mixture. Also "high" surface area FeS catalyst preparation will be attempted and the inhibition effect of quinoline on this catalyst will be determined.

It was postulated during the study of quinoline inhibition on the hydrogenation activity of the catalyst that Co-Mo-Al catalyst is active for hydrodenitrogenation (HDN) reaction, whereas presulfided iron oxide may not be as active for HDN reaction. If the HDN reaction occurs, the product of the reaction may not be as detrimental as quinoline on the catalyst activity for the hydrogenation. This may be the reason why the observed inhibition by quinoline on Co-Mo-Al catalyst was less severe in comparison to that on presulfided iron oxide catalyst.

To investigate the above postulation, the GC/MS analyses were made on two product samples obtained from the naphthalene hydrogenation experiments performed in the presence of quinoline over Co-Mo-Al and presulfided iron oxide catalysts under identical reaction conditions. Propyl cyclohexane, a denitrogenation product, was the major product identified from quinoline when Co-Mo-Al was employed as a catalyst. But when presulfided iron oxide was used as a catalyst, 1,2,3,4-tetrahydroquinoline, the hydrogenation product, was the major compound identified. This gives evidence to support the above postulation. Also, it shows the necessity of determining the hydrocracking activity of different catalysts.

The inhibition effect of quinoline on presulfided iron-oxide catalyst for the hydrogenation of naphthalene was determined at 0.1 wt% quinoline per total charge. The percentage conversion of naphthalene for different reaction times

are presented in Table 72. The hydrogenation reaction rate constant for naphthalene hydrogenation was determined by linear regression for pseudo-first-order reaction and was found to be 0.34 g solvent/g catal./min. Hence, the inhibition factor, which is defined as the ratio of the hydrogenation rate constant as some quinoline addition to that at no quinoline addition, was found to be 0.31 for 0.1 wt% quinoline addition in the total reaction mixture. Figure 19 shows that the results with 0.1 wt% quinoline addition in the reaction mixture have less inhibition effect on the hydrogenation reaction rate than the higher concentrations of quinoline in the reaction mixture. Moreover, this result within experimental error, falls on the curve previously predicted. In addition, the results of these experiments give further evidence that quinoline, a basic nitrogen compound, plays a significant role in inhibiting hydrogenation activity of FeS catalyst.

To determine whether pyrrhotite (Fe_{1-x}S) prepared in-situ has any synergetic effect on the hydrogenation reaction rate, the following additives were used in the naphthalene hydrogenation reactions:

- (a) 0.3 g Robena Pyrite (-325) + 0.2 g Fe_2O_3
- (b) 0.3 g Presulfided Iron-Oxide + 0.2 g Fe_2O_3
- (c) 0.5 g Iron Oxide to + 0.5 g Thiophene

These additives were selected based on stoichiometric calculations assuming 100% completion of the following reaction:

The results of these experiments and the results obtained in previously performed experiments are presented in Table 73. These results indicate that the in-situ sulfiding of iron-oxide and hence in situ production of pyrrhotite does not have any advantage on the hydrogenation reaction rate. It should be observed that the percentage naphthalene conversion dropped significantly in all three cases.

TABLE 72

Naphthalene Conversion vs. Reaction Time

Reaction Time, t (min)	Naphthalene Conversion, 100 x (%)
5	13.7
10	28.9
15	40.1

Reaction Conditions: 5 g reaction mixture (10% Naphthalene in Hexadecane and Quinoline), 0.5 g Pre-sulfided Iron Oxide, 410°C, 1250 psig H₂ at ambient temp; 14.5 ml tubing-bomb reactor, 860 rpm.

Table 73
Effect of In-Situ Sulfiding of Iron-Oxide
on Hydrogenation Reaction Rate

Index	Additive	% Naphthalene Conversion	T/N*
1	0.3 g Robena Pyrite + 0.2 g Fe_2O_3 (1)	2.8	0.014
2.	0.5 g Robena Pyrite (1)	4.5	0.033
3.	0.3 g Presulfided Fe_2O_3 + 0.2 g Fe_2O_3 (2)	20.1	0.289
4.	0.5 g Presulfided Fe_2O_3 (2)	78.2	3.300
5.	0.5 g Fe_2O_3 + 0.5 g Thiophene (1)	5.16	0.042
6.	0.5 g Magnetite (1)	2.10	0.018

Reaction Conditions: 5 g reaction mixture (10 wt % naphthalene in hexadecane), 410°C , 1250 psig H_2 at ambient temperature, 860 rpm.

Reaction Time: (1) 30 minutes (2) 15 minutes

*Tetralin was the major product accounting for more than 90% of naphthalene converted.

Magnetite was also screened for its hydrogenation activity. Table X includes the results of this experiment. Magnetite with a T/N of 0.018 has lower hydrogenation activity than Fe_2O_3 whose T/N is 0.06.

To clearly distinguish hydrocracking activity of various catalysts, experiments are being performed using cumene as a model compound. Initial experiments were performed using 10 wt% cumene and 90 wt% hexadecane as reaction mixture. Numerous products were identified including benzene, n-alkanes ranging from C_5 to C_{10} , and some isoalkanes. Toluene and ethyl-benzene were not produced. Some of the peaks visible on the gas chromatogram were not identified. The system complicated by the apparent hydrocracking of the hexadecane did not seem suitable for distinguishing hydrocracking activities of various catalysts. Hence a simpler reaction system such as cumene alone or milder reaction conditions to avoid cracking of hexadecane will be evaluated.

A 20 wt% loading of Carbowax 20M on Chromosorb W, AW-DMCS (60-80) was prepared for packing a G.C. column to analyze the products from quinoline during inhibition study of hydrogenation activity. It is believed that analysis of these products will provide more information about the inhibition mechanism of quinoline on Co-Mo-Al and presulfided iron-oxide catalysts.

Hydrogenation Activity of Presulfided Iron Oxide Catalyst in the Presence of Various Nitrogen Compounds

Quinoline, a basic nitrogen compound, has been shown to severely inhibit the catalysis of a model hydrogenation reaction. Little has been reported regarding the role of nonbasic nitrogen compounds in inhibiting hydrogenation catalysis. Nonbasic nitrogen compounds can form basic nitrogen compounds with hydrogenation. For example, pyrrole is a nonbasic nitrogen compound. Katzer, J. R., and Sivasubramanian, R., Catal. Rev. - Sci. Eng., 20 (2), 155 (1979). But, pyrrolidine, the hydrogenated pyrrole, is a basic nitrogen compound. Morrison, R. T., and Boyd, R. C., "Organic Chemistry", Allyn and Bacon, Inc., Second Edition, Dec. 1971, Ref. pp. 1077-1081. A series of experiments with three different nitrogen compounds were performed to determine their effect on the inhibition of catalyst activity relative to that of quinoline. The experimental

conditions used were the same as in the quinoline experiment. These experiments are necessary to signify the effect of nonbasic nitrogen compounds, which may be still remaining in the acid extracted (AE) solvent, on the hydrogenation catalysis of presulfided iron oxide.

A fresh batch of presulfided iron oxide catalyst was prepared. The naphthalene hydrogenation experiments without any nitrogen compound additions were performed for different reaction times to determine the hydrogenation activity of presulfided iron oxide catalyst. The percentage naphthalene conversions for these experiments are presented in Table 74. A good agreement was observed between these results and results from other catalyst batches. Also included in Table 74 are the results on naphthalene hydrogenation activity in the presence of 0.5 wt% additions of various nitrogen compounds. The pseudo first order hydrogenation rate constants determined by linear regression are presented in Table 75. The inhibition factors (IF), which is defined as the ratio of the hydrogenation rate constant with nitrogen compound addition to that with no nitrogen compound addition, were determined for aniline, indole, and carbazole. Also presented in Table 75 are the inhibition factors for different nitrogen compounds.

Figure 21 presents the ratio of naphthalene conversion at 0.5 wt% addition of nitrogen compounds to that at no nitrogen compound addition for different reaction time. Depending upon the nitrogen compounds used, all lines follow the same pattern and show a positive slope. The inhibition factors for different nitrogen compounds are presented in Figure 22. It is obvious from these figures that different nitrogen compounds have different inhibition effect on the hydrogenation activity of presulfided iron oxide catalyst. Among the nitrogen compounds tested, quinoline was found to be the most detrimental; whereas aniline was the least detrimental to the hydrogenation activity of presulfided iron oxide catalyst.

Aniline - Although quinoline ($K_b = 3 \times 10^{-10}$) is a weaker base than aniline ($K_b = 4.2 \times 10^{-10}$), quinoline was found to have significantly higher inhibition effect than aniline. A significant amount of aniline was converted during the reaction. Some of the products from aniline were identified as benzene, cyclohexene and cyclohexane. The identification was done by spiking with known compounds and comparing to the authentic gas chromatogram. Table 76

Table 74

Effect of Different Nitrogen Compounds
on Naphthalene Conversion

Nitrogen Compounds	Naphthalene Conversion, 100X(%) for Each Reaction Time, t(min)		
	5	10	15
None	49.2	69.1	80.5
Aniline	30.3	44.4	54.0
Carbazole	18.5	29.1	40.4
Indole	12.0	22.8	25.7

Reaction Conditions: 5g reaction mixture (10% Naphthalene in Hexadecane, 0.5g Presulfided Iron Oxide, 410°C, 1250 psig H₂ at ambient temperature, 14.5 ml tubing-bomb reactor, 0.025g nitrogen compound.

Table 75

Effect of Different Nitrogen Compounds
on the Naphthalene Hydrogenation
Rate Constant

Index	Nitrogen Compound	Rate Constant, k_i ($\frac{\text{g solvent}}{\text{gcat: min}}$)	Inhibition Factor, k_i/k_1
1	None	1.01	1.00
2	Aniline	0.50	0.50
3	Carbazole	0.31	0.31
4	Indole	0.19	0.19
5	Quinoline	-	0.07

Figure 21. Effect of Different Nitrogen Compounds on Naphthalene Conversion

Figure 22. Comparison of Inhibition Factors for Different Nitrogen Compounds

Table 76

Effect of Reaction Time on Aniline Conversion

Reaction Time (min)	GC Peak Area Ratio of Products from Aniline to Aniline
5	0.270
10	0.726
15	1.328

presents the GC peak area ratios of identified aniline products to that of aniline for different reaction times. Based on these results, it can be stated that significant denitrogenation of aniline occurs. This may be the reason why aniline does not show as detrimental effect as quinoline on the hydrogenation activity of presulfided iron oxide catalyst.

Carbazole - Carbazole is a nonbasic nitrogen compound. As shown in Figure 21, carbazole has less inhibition effect than quinoline and indole; but has more inhibition effect than aniline. No distinct product peak from carbazole was observed on a gas chromatogram. Some carbazole may have hydrogenated and product peak(s) may have overlapped.

Indole - Indole is a nonbasic nitrogen containing compound. Indole showed about 3 times less inhibition than quinoline. By comparison, only one product from indole was observed on a gas chromatogram. This peak is not identified since the spiking compounds were not readily available. But the unidentified compound is suspected to be indoline, the hydrogenated indole. Indoline is a basic nitrogen compound. Indoline may be as detrimental as quinoline.

In summary, different nitrogen compounds were found to have different inhibition effects. Based on the limited data available, it can be stated that a basic heterocyclic nitrogen compound (quinoline) is highly detrimental to the hydrogenation activity of presulfided iron oxide catalyst in comparison to a basic non-heterocyclic nitrogen compound (aniline). Nonbasic heterocyclic nitrogen compounds (indole and carbazole) were found to have less inhibition effect than basic heterocyclic nitrogen compound.

Tailored Solvent

We found that the nitrogen compounds are instrumental in limiting the hydrogenation activity of a presulfided iron oxide catalyst. It was postulated that if the nitrogen compounds were removed from the process solvent, then it may be possible to improve the catalysis for coal liquefaction over a presulfided iron oxide catalyst. Thus, the objective of this part of the work was to determine the effect of the heteroatom (N,O) content of a process solvent on the coal liquefaction catalysis.

Product Recovery

As a preliminary part of this work, it seemed essential to refine the product recovery procedure for coal liquefaction experiments. Previously, it was assumed that the composition of the product recovered by scraping the reactor walls was the same as the product which was left behind in the reactor. At this time, the percentage recovery of the products was in the range of 75 to 90% of the initial charge to the reactor. Due to low recovery, the confidence level on the experimental results will naturally be low. Thus, the main objective of this task was to increase the product recovery.

To determine the homogeneity of the products, two coal liquefaction experiments were performed. The liquid products in each experiment were divided into two parts: (1) Products which were recovered by scraping the walls with a spatula (Scraped Products), and (2) Products which were recovered by simultaneous washing and scraping the reactor walls with tetrahydrofuran (THF) and a soft nylon brush. The product distributions of the coal (based on MAF coal) for these two experiments are presented in Table 77.

The coal liquefaction Experiment 1 was performed at 400°C; whereas, Experiment 2 was performed at 425°C. The liquid products from Experiment 1 had apparently higher viscosity than the products from Experiment 2. It is obvious from the results presented in Table 77 that there are distinct differences in the product distributions of the two parts of the products recovered from the same experiment. For example, in Experiment 1, the I.O.M. yield in the THF wash product is approximately 20% higher than that in the scraped products. Also, in Experiment 2, differences in oils and preasphaltene values in two parts of the products can be observed. Based on these results, it was decided to recover as much product as possible to avoid the experimental error due to the nonhomogeneity of the sample.

Product Distributions of Solvents

Four different solvents were used in this study; i.e., the parent solvent (AP-CPDU 200), and three other solvents which were derived from the parent solvent. Three derived solvents are designated as: (1) Nitrogen Bases Free (NBF) solvent, (2) Phenol Free (PF) solvent, and (3) Nitrogen Bases and Phenol Free (NBPF) solvent.

Table 77

Effect of Product Recovery Procedure
on Product Distribution of Coal

	Experiment 1*		Experiment 2**	
	Scraped Products	THF Wash Products	Scraped Products	THF Wash Products
Oils	14.1	16.2	30.9	23.7
Asphaltenes	48.1	36.7	43.4	39.3
Preasphaltenes	30.0	19.0	11.9	21.6
I.O.M.	7.8	28.0	13.8	15.6

Reaction Conditions: 6g Solvent (AP CPDU 200), 3g Elkhorn #3 Coal,
1g Presulfided Iron Oxide, 1250 psig H₂ at ambient conditions,
860 RPM, 2 SB agitators, 60 minutes, 46.3 ml reactor

* Reaction temperature = 400°C

**Reaction temperature = 425°C

* * * * *

Table 78

Elemental Analysis of Solvents Used in Coal
Liquefaction Experiments

Element	Parent Solvent (wt%)	N-Base Free Solvent (wt%)	Phenol Free Solvent (wt%)	N-Base and Phenol Free Solvent (wt%)
C	89.44	89.66	89.80	90.36
H	7.21	7.53	7.36	8.48
O	1.70	1.45	1.07	0.42
N	1.10	0.64	1.06	0.01
S	0.55	0.72	0.71	0.73

The heteroatomic content of the parent solvent and other solvents which were derived from the parent solvent are presented in Table 78. In comparison to other solvents, the NBPF solvent shows a distinct difference in its nitrogen and oxygen content. The nitrogen content for this solvent has been reduced to almost zero, and the oxygen content is reduced by about 75% of the original oxygen content. The heteroatomic content of the parent solvent, PF solvent and NBF solvent are not greatly different.

Presented in Table 79 are the product distributions of the above mentioned solvents. These values are used in determining the product yields. The product distribution values for the NBPF solvent are somewhat questionable. This solvent is derived from the pentane soluble fraction of the parent solvent. As a result, we should expect 100 wt% oils; instead, only 95.8 wt% oils were determined by product distribution. Some heteroatomic compounds (e.g., phenols) and polyaromatic compounds are considered to be good physical solvents. Whitehurst, D. D., Mitchell, T. O., Farcasiu, M., and Dickert, J. J., EPRI Report, EPRI AF-1298 (1979). Removal of these compounds from the solvent may decrease the overall solubility in pentane. This may be the reason for the decrease in the oils value determined. Because of the limited amount of the NBPF solvent, further product distribution of this solvent was not performed. The PF and NBF solvents were derived from the benzene soluble fraction of the parent solvent. Hence, the product distributions of these two solvents are consistent with the experimental procedure.

Preparation of Solvents

The process solvent (SRC-II Fuel Oil Blend, AP-CPDU-121) was diluted with benzene and then treated with HCl gas to remove or neutralize basic organic nitrogen compounds. A precipitate did form. The benzene and process solvent mixture was then purged with dry N₂ gas to remove excess HCl. The precipitates were then removed by filtration and benzene was distilled off. The process solvent, thus obtained, is called acid extracted (AE) solvent. Several attempts were made to determine the product distribution of the AE solvent. The results of these attempts are presented in Table 80. Several modifications in the separation procedure normally employed at Auburn University were tried in an attempt to

Table 79

Product Distributions of Solvents

	Parent Solvent (wt %)	N-Base Free Solvent (wt %)	Phenol Free Solvent (wt %)	N-Base and Phenol Free Solvent (wt %)
Oils	92.8 ± 0.9	95.2	94.3	95.8
Asphaltenes	5.8 ± 0.8	4.5	5.3	2.2
Preasphaltene	0.7 ± 0.05	0.2	0.4	2.0
I.O.M.	0.7 ± 0.05	0.1	0.0	0.0

Table 80
Product Distribution of AE Solvent

	1	2	3	4	5
Oils %	84.8	80.2	78.5	81.7	81.4
Asphaltenes %	12.7	15.6	20.8	16.2	16.6
Preasphaltenes %	2.4	3.0	0.6	2.0	1.9
Residue %	0.1	1.1	0.1	0.1	0.1

- (1) Manual separation
- (2) Manual method
- (3) Freezing once under liquid N₂ and sonifier aided separation
- (4) Freezing twice under liquid N₂ and sonifier aided separation
- (5) Freezing three times under liquid N₂ and sonifier aided separation

extract maximum amount of oils with pentane. The modifications used are outlined in the same table. In each of these attempts, the asphaltenes were observed to be wet even after freeze drying, i.e., it seemed that all the oils were not extracted with pentane and the asphaltenes contained some of the unextracted oils. Similarly preasphaltenes were observed to be wet. The reason for the difficulty in extracting oils with pentane is not known.

Previously when AE solvent and coal were used in tubing bomb coal liquefaction experiments, severe corrosion of the tubing bomb was observed. The acidity of the solvent was measured and the pH was determined to be about 1.8. The lower pH of the AE solvent may be due to the excess HCl remaining in the solvent.

To reduce the acidity of the solvent, and hence to reduce the corrosion of the tubing bomb reactor, neutralization of the AE solvent was attempted. In this case, before distilling off benzene to obtain AE solvent, ammonia was bubbled through the HCl treated process solvent and benzene mixture for a few seconds. Precipitates formed instantaneously which were removed by filtration and then N_2 was bubbled through the solution to remove excess ammonia. Benzene was then distilled off to obtain acid extracted and base neutralized (AEBN) solvent. There was no difficulty encountered in determining the distribution of AEBN solvent and asphaltenes and preasphaltenes were observed to be dry. Moreover, the distribution of AEBN solvent is essentially the same as the original solvent as shown in Table 81. Hence, it seems that the excess HCl remaining in the AE solvent interferes in the separation of oils from the asphaltenes. Tubing-bomb experiments are planned using AE and AEBN solvents in near future and the product distribution of coal using these solvents will be determined.

Catalyst

Approximately 30 g of iron oxide were sulfided at 275°C and 10 cc/min of H_2S flow in three separate batches to ensure that enough catalyst of the same composition will be available for the planned study. Presulfided iron oxide catalyst from three separate batches was thoroughly mixed and carefully handled. This catalyst showed 95% naphthalene conversion in 15 minutes when tested in a model compound experiment. This result showed that the catalyst was a good hydrogenation catalyst.

Table 81
Product Distribution of AEBN Solvent

	AEBN Solvent	AP-CPDU-121
Oils %	93.6	95.0
Asphaltenes %	6.0	4.5
Preasphaltenes %	0.3	0.4
I.O.M. %	0.1	0.1

Baseline

A series of coal liquefaction experiments using the parent solvent (AP-CPDU 200) were performed between 400 and 475°C to establish a baseline. Utmost care was taken in recovering the products from the reactor. Gases produced during the reaction were collected in a gas sampling bag at the end of the reaction period, and then analyzed on a gas chromatograph for their composition. After scraping the reactor walls with a spatula, the reactor was washed with THF and the products were collected in a separate flask. THF was then evaporated at room temperature under continuous flow of nitrogen. The percentage recovery was greater than 98% for all the experiments except one.

Table 82 includes the results of these experiments. It should be observed that a drastic change in the gas production occurred when the reaction temperature was increased from 425 to 450°C; but the oil production did not change significantly. In addition, there is no significant difference in conversion at 425 to 450°C. The major differences in the yields of asphaltenes and preasphaltenes were also observed. Since the primary interest of all coal liquefaction processes is to selectively produce more oil from coal without excessive hydrogen consumption, i.e., without excessive gas production, the reaction temperature of 425°C was selected as a baseline condition for all other experiments. Also, it seems necessary to perform another experiment at 450°C to confirm the observation of excessive gas production.

Effect of Solvents

The coal liquefaction experiments were performed at 425°C in the presence of different solvents described before. In one set of experiments, 1 g of pre-sulfided iron oxide was added; whereas no addition of presulfided iron oxide established a baseline condition for that particular solvent.

Presented in Table 83 are the results of these experiments. It is interesting to note that the differential oil yields (oils) between the catalytic and non-catalytic reactions with the N-bases free (NBF) solvent and the phenols free (PF) solvent is approximately 10% higher than that for the other two

Table 82

Effect of Reaction Temperature on
Product Distribution of Coal (1)

<u>Product</u>	Yield (wt%) for each Reaction Temperature ($^{\circ}\text{C}$)			
	<u>400</u>	<u>425</u>	<u>450</u>	<u>475</u>
Gases	2	8	26	37
Oils	13	25	22	6
Asphaltenes	43	41	33	37
Preasphaltenes	25	13	8	4
I.O.M. (2)	17	13	11	16
% Recovery	99.7	98.9	101.0	94.5

Reaction Conditions: 6 g Parent Solvent (AP CPDU-200); 3 g Elkhorn #3 coal, 1 g Presulfided Iron Oxide Catalyst; 1250 psig H_2 at ambient temperature; 850 RPM; 2 Steel Ball Agitators; 60 minutes; 46.3 ml reactor

(1) Calculations are based on MAF coal and H_2 free basis.

(2) For calculation purposes, presulfided iron oxide is assumed to form FeS and H_2S during reaction.

Table 83

Effect of Solvent Composition on Product Distribution of Coal⁽¹⁾

Products	Parent Solvent		N-Bases Free Solvent		Phenols Free Solvent		N-Bases and Phenols Free Solvent	
	None	Presulfided Iron Oxide	None	Presulfided Iron Oxide	None	Presulfided Iron Oxide	None	Presulfided Iron Oxide
Gases	9	8	9	6	7	7	10	8
Oils	(2)*	24	(3)	31	(6)	30	23	48
Asphaltenes	44	42	42	39	47	35	28	26
Preasphaltenes	22	13	23	13	23	16	13	7
I.O.M. ⁽²⁾	27	13	29	11	29	12	25	11
% Recovery	100.5	98.9	98.4	100.5	98.9	101.0	99.2	101.0
Δ Oils ⁽³⁾		26		34		36		25

Reaction Conditions: 6 g Solvent; 3 g Elkhorn #3 Coal; 1 g Presulfided Iron Oxide if added; 1250 psig H₂ at ambient conditions, 425°C; 860 RPM; 2 Steel Ball Agitators; 60 minutes; 46.3 ml reactor.

(1) Calculations are based on MAF and H₂ free basis.

(2) For calculation purposes, presulfided iron oxide is assumed to form FeS and H₂S during reaction.

(3) Δ Oils - % Oils yield when catalyst was added - % Oils yield without any additive

*() indicates negative yield.

solvents. Moreover, it should be noted that the differential oils yields with the N-base and phenol free (NBPF) solvent is only 25% in comparison to 35% when NBF or PF solvent was used in coal liquefaction reaction. This is rather surprising because it seems that the removal of either N-bases or phenols increases the catalytic activity for oil production; but the removal of both the phenols and N-bases does not aid catalysis. At this point, no positive conclusion can be made about the 10% difference in Δ oils. As expected, NBF and PF solvents did not show much improvement over the parent solvent as there are no appreciable differences in the heteroatomic contents of these three solvents (see Table 78).

When NBPF solvent was used in coal liquefaction experiments, the oils yield was determined to be significantly higher with or without the addition of the presulfided iron oxide catalyst (see Table 83). As discussed earlier, the product distribution of NBPF solvent may be questionable due to the solubility factor. But, even if we assume the NBPF solvent is 100% oils, the yield of oils decreases to only 13% for the baseline; and 38% for the experiment where 1 g of presulfided iron oxide was added as catalyst. Hence, in comparison to other solvents, at least 15% higher oil yield is observed when NBPF solvent is used in coal liquefaction experiments in the absence of any additive. Thus, the higher oil yield with NBPF solvent is not mainly due to the probable error in determining the product distribution of NBPF solvent, but it is highly probable that the reactivity of the NBPF solvent may be higher in comparison to other solvents. It is not clear at this time whether the heteroatom removal increased the reactivity of the solvent or the reactivity of the solvent may have increased due to some other factors such as higher hydrogen content, and hence higher hydrogen transfer and/or donation capability of the solvent. An increase in the reactivity of the solvent should be confirmed, and then further investigated if it is indeed an increase. This may provide an insight into the coal liquefaction mechanism.

In conclusion, it can be stated that the removal of heteroatomic compounds from the process solvent appears to be a promising approach; but still needs in depth investigations to make any definitive statement.

APPENDIX I

Sources and Analyses of Additives Suppliers of Various Minerals and Metal Containing By-Product Samples

Note: All minerals are ground to -150 to -325 mesh as indicated below unless already in powder form. After grinding if necessary the minerals are dried at 100°C for 12 hours and allowed to cool in a desiccator before use.

Pyrite	U. S. Steel Corporation Robena Mine Angelica, PA
Magnetic	U. S. Steel Corporation
Zinc Flue Dusts	Laclede Flue Dust Courtesy Dave Taschler Air Products and Chemicals, Inc. Greenville, PA
Copperas ($\text{FeSO}_4, 7\text{H}_2\text{O}$)	Textile Chemical Company Reading, PA
Albanaian Chrome Ore Concentrates	Interlake, Inc. Beverly, Ohio
Brown Fly and Bottom Ashes*	Kentucky Utilities
Green River Fly and Bottom Ashes*	Kentucky Utilities
Paradise Fly and Bottom Ashes*	TVA
Kaolinite+ $\text{Al}_4\text{Si}_4\text{O}_{11}(\text{OH})_8$	Burgess Pigment Company P. O. Box 349 Sandersville, GA
Molybdc Oxide	Climax Molybdenum Company Greenwich, Connecticut

*Samples were supplied by Dr. Alan E. Bland of the Institute of Mining and Minerals, University of Kentucky, Lexington, Kentucky.

Flue Dust	Air Products and Chemicals, Inc. Greenville, Pennsylvania
Syber Alloy Grindings (Howmet)	Air Products and Chemicals, Inc. Greenville, Pennsylvania
Alnico Grindings (Hitachi)	Air Products and Chemicals, Inc. Greenville, Pennsylvania
X-Type Molecular Sieve	W. R. Grace and Company Upper Darby, Pennsylvania
Mordenite	W. R. Grace and Company Upper Darby, Pennsylvania
Chabazite	W. R. Grace and Company Upper Darby, Pennsylvania
Speculite (Fe_2O_3)	Chemalloy Company, Inc. Bryn Mawr, Pennsylvania
Red Oxide	Ferro, Ottawa Chemical Division Toledo, Ohio

Bornite - Cu_5FeS_4 (copper ore); -115 mesh.

Source: Mr. Rich Ramseier, Chief Geologist; The Anaconda Company;
Geological Dept.; 520 Hennessy Bldg.; P. O. Box 621; Butte, Montana 59701.
Phone (406) 723-4311.

Calcite - CaCO_3 ; Gird Creek; Ravalli, Montana; -115 mesh.

Source: David New-Minerals; Providence, Utah.

Co-Mo-Al - CoMox 451; presulfided at Auburn to 2.76% sulfur.

Source: Laporte Industries, Inc.

Feldspar - KAlSi_3O_8 ; Type NC-4; see November, 1979 Report for typical analysis; received in powder form.

Source: Feldspar Corporation; Box 99; Spruce Pine, North Carolina 28777.
Phone (704) 765 9051.

FeS - Prepared at Auburn University, Dept. of Chem. Engr.; See Jan., 1980 Report.

Fe_2O_3 - Type I - 116; certified; received in powder form.

Source: Fisher Scientific Co.; Fairlawn, New Jersey 07410.

Montmorillonite - $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$; type - Hydrite PX; see November, 1979 for typical analysis; received in powder form.

Source: Georgia Kaolin Co.; 433 N. Broad St.; Elizabeth, New Jersey
Phone (201) 352-9800.

FeS_2 - Pyrite from Robena Mine; -325 Mesh.

Source: Air Products and Chemicals, Co.; Box 538
Allentown, PA 18105. Phone (215) 398-4911.

Red Mud - Bayer Process red mud waste from Kaiser Aluminum Co.; - 150 mesh

Ash - see SRC Residue, Kerr McGee Residue.

Diatomaceous Earth Filter Aid - Filter Cel; 5-20-80; sample number 56678
Source: Catalytic, Inc. Wilsonville, Alabama.

Gypsum - #105 Terra Alba received in powder form. Source: C. A. Wagner,
Philadelphia, PA (215) 457-0600.

Kaolinite, Burgess #10, received in powder form. Source: Burgess Pigment
Co. (Dan Adrian), P. O. Box 349, Sandersville, GA (912) 552-2544.

Kerr McGee Residue - KM-ME 103/V107 Ash Conc.; Run 150-247; 10-19-78
S.N. 40478 #2. Source: Catalytic, Inc. Wilsonville, Alabama.

Magnetite Source: Received from Air Products and Chemicals, Inc.;
Box 538; Allentown, PA 18105 Sample number CPDU-75.

Montmorillonite - Mineral Colloid B.P. - received in Powder form. Source:
Georgia Kaolin Co. (John Callahan) 433 N. Broad St.; Elizabeth, N.J. (201)
352-9800.

Silica. -240 mesh - received from Air Products.

SRC Residue - D102 Mineral Residue; 140-B-MB, 7-9-78, S.N. -39198. Source:
Catalytic, Inc. Wilsonville, Alabama.

Molybdenite, MoS_2 . Source: Received from Air Products and Chemicals, Inc.

Mica, $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$. Source: Wards Natural Science, Ontario, Canada.
Sample were obtained from the Department of Agronomy and Soils, Auburn University,
Alabama 36849, and ground to -60 mesh.

Siniola Mexico Pyrite, FeS_2 . Source: D1 pyrite, Siniola, Mexico. Sample
was obtained from Dr. David H. Garske, Mineralogist; P. O. Box 83 (3 OK Street),
Bishee, Arizona 85603; Phone (602) 432-3362; and ground to -325 mesh.

South Dakota Pyrite, FeS_2 . Source: Received from Air Products and Chemicals,
Inc.

MCB Pyrite, FeS_2 . Source: Matheson Coleman & Bell Manufacturing Chemists, Norwood, Ohio 45212; Sample was ground to -325 mesh.

Apatite, Ca_3PO_4 . Source: Stauffer Chemical Company; Westport CT. (203) 222-3000. Received in powder form.

Dolomite, $\text{CaMg}(\text{CO}_3)$. Source: David New Minerals; Providence, Utah. Sample from Snarum, Norway. Ground to -115 mesh.

Illite $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$. Source: Source Clay Minerals Repository (W. D. Johns); Dept. of Geology; University of Missouri; Columbia, MO 65211, (314) 822-3785. Screened to -115 mesh.

Ilmenite, FeTiO_3 . Source: Pesses Co. (J. H. Johnson); 29605 Hall St. and Cockran; Salon, Ohio (216) 248-0145. Screened to -115 mesh.

K_2CO_3 . Source: Fisher Scientific Co., Number P-208 A. C. S. grade. In powder form.

Na_2CO_3 . Source: Fisher Scientific Co., Number S-263.

Oil Shale. Source: John Ward Smith, Div. Manager; Div. of Resource Characterization; U. S. Department of Energy; Laramie Energy Technology Center; P. O. Box 3395; University Station; Laramie, Wyoming 82071. Preparation. The oil shale was received in a single piece. The oil shale was broken into 1/8 inch or smaller pieces, heated in air at 400°C for six hours to release the oil. The remaining solid residue was ground to -115 mesh.

Phosphate Slime. Source: Mr. I. L. Feld, Assistant to the Research Director;
U. S. Dept. of the Interior; Bureau of Mines;
Tuscaloosa Research Center; P. O. Box L; University,
Alabama 35486. Typical Analysis follows:

CaO	16.2%
P ₂ O ₅	12.0
Equiv.	
BPL	26.2
MgO	2.9
Al ₂ O ₃	11.9
Fe ₂ O ₃	3.4
SiO ₂	36.5
Na ₂ O	0.3
K ₂ O	0.8
F	1.5
C	1.0
CO ₂	2.3
S	0.2
Loss on	
Ignition 500°C	10.3

Preparation: The phosphate slime was filtered in order to obtain the filter cake. The filter cake was subsequently oven dried (100°C) and ground to -115 mesh.

ZnO. Source: J. T. Baker Chemical Company. No. 4358 99% ZnO. Powder form.

Assumptions for Red Mud and Sulfur Combination and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

1. Red Mud and Sulfur

For the 1.0 gram of Red Mud and 1.0 gram of sulfur additives the following assumptions are made:

- a. The 0.087 g of sulfur in the original coal and solvent is neglected.
- b. 0.305 g of the sulfur additive formed 0.324 g H_2S which was obtained from the ideal gas law, measurement of the gas volume over the reacted mixture, and the % H_2S in the gas mixture as determined by G. C.
- c. 0.207 g. sulfur additive combines with the approximately 0.515 g of Fe_2O_3 in the Red Mud to form 0.567 g of FeS .
- d. 0.488 of sulfur is unchanged.
- e. The above assumptions imply that the 1 g of Red Mud and the 1 g of sulfur leaves a solid residue of 0.485 Red Mud, 0.567 FeS from the Fe_2O_3 of Red Mud, and 0.488 g sulfur totaling 1.440 g.

2. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

The one gram of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is assumed to yield 0.5464 g FeSO_4 which remains unchanged and appears in the residue and 0.4536 g H_2O which is physically included in the sample. The water is mathematically removed from both the sample weight and the oils fraction. The removing of the water mathematically from the sample weight and the oils fraction is a result of recent observations. It was observed upon adding water to some reaction mixtures both before and after reaction that the water physically became part of the sample and appeared as discrete droplets on top of or in the sample and was an addition to the sample weight. If the amount of water was known or could be estimated, it could reasonably be accounted for in the calculation of the sample weight. It was further observed

upon splitting a sample into two parts and adding to one an amount of water which would be the maximum amount of water which could theoretically be produced given the oxygen content of the coal and solvent that the added water did not physically appear in any of the fractions of the solvent separation, but did mathematically appear in the oils fraction. Further experiments concerning the solubility of water in pentane showed that the maximum amount of water which could be produced in the coal-solvent system was easily dissolved in the pentane and thus physically removed from the oils fractions during the rotovaping of the pentane; that is, it was shown that pentane with some dissolved water would evaporate at the conditions used such that the pentane and dissolved water evaporated completely with no residual water remaining.

The weight of water in the vapor phase is assumed to be negligible at room temperature. This is based on the measured 0.568 grams of hydrocarbon gas in the tubing bomb combined with the fact that at 100% humidity in an air-water system at 77°F there would be 0.011 g of water associated with 0.568 grams of air. The assumption is that there would be an order of magnitude similarity in the amount of water vapor in a given amount of air or of mixed hydrocarbon gases.