

CATALYTIC EFFECTS OF PYRITE AND  
HYDROGEN SULFIDE ON HYDROGENATION OF COAL

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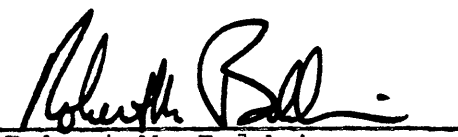
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## ABSTRACT

Coal hydrogenation employing a hydrogen donor solvent (tetrahydronaphthalene) was studied in a 300 cc batch reactor at 380°C and 2000 psig. The catalytic effect of coal-derived pyrite in the presence and absence of added gas phase hydrogen sulfide was investigated at residence times of ten and sixty minutes.

Pyrite was found to be an effective coal hydrogenation catalyst. The addition of hydrogen sulfide, when pyrite was present, had no effect at the ten minute residence time but had a significant effect at the sixty minute residence time by increasing the conversion. Hydrogen sulfide appeared to be responsible for maintaining a catalytically active form of pyrite (metal sulfide). A minimum amount of hydrogen sulfide was necessary to maintain the active catalytic form which, if exceeded, had no effect on coal conversion.

Hydrogen sulfide was also shown to be an effective catalytic agent for coal liquefaction reactions. Homogeneous and heterogeneous catalytic mechanisms have been proposed to explain the catalytic effect of hydrogen sulfide.

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## INTRODUCTION

Conversion of coal to liquid products occurs by the addition of hydrogen to the coal structure. At high temperatures (greater than 350°C) and high pressures (greater than 1000 psi), the coal fragments forming free radicals. In the presence of a hydrogen donor solvent, hydrogen is abstracted from the donor solvent stabilizing the free radical and adding hydrogen to the coal. The donor solvent, now in an hydrogen-poor state, must be replenished in order to maintain hydrogen transfer activity.

Hydrogen transfer reactions can be catalyzed. The ability of a hydrogenation catalyst to aid in converting coal to liquid products has led some investigators to look at the catalytic effect of coal mineral matter. The inherent mineral matter in coal is potentially an abundant and inexpensive source of catalysts for coal liquefaction and hydrodesulfurization reactions. If minerals which are inherent in "as mined" coal do act as hydrogenation catalysts at liquefaction conditions, coal liquefaction processing schemes may be able to be optimized by addition or removal of certain coal mineral matter constituents. It is also important to discover whether or not coal mineral matter is beneficial catalytically since the cost of mining

and transporting coals with a high mineral matter content is expensive. Coals with a high mineral matter content also increase abrasive wear on machinery, involve higher material throughputs, poison added hydroprocessing catalysts, and pose ash filtration and disposal problems.

Hydrogenation catalysts have been, traditionally, metals. Due to the high sulfur levels encountered in coal liquefaction processes, the active catalyst is usually not the metal but the metal sulfide.

The objective of this study was to determine the catalytic effect of coal-derived pyrite in the presence and absence of added gas phase hydrogen sulfide. The ability of hydrogen sulfide to maintain a catalytically active form of pyrite (metal sulfide) was investigated in this study, as was the catalytic effect of hydrogen sulfide acting in the absence of pyrite.

### Historical Background

Three fundamental developments were necessary to make direct hydrogenation of coal a commercial reality (Donath and Hoering, 1977):

- 1) In 1910, ammonia synthesis introduced high pressure and high temperature to the chemical industry.
- 2) In 1913, F. Bergius showed that coal could be liquefied by adding hydrogen at high pressure and high temperature.
- 3) In 1923, M. Pier found selective hydrogenation hydrocracking catalysts that were resistant to sulfur.

In 1920's, the I. G. Farben Company developed the two-stage Bergius process. The first stage (liquid-phase) hydrogenated a coal/oil slurry to a middle oil (approximately 325°C end point) in the presence of a disposable catalyst. The middle oil was then hydrogenated over a fixed bed catalyst in the second stage (vapor-phase) to produce gasoline.

Liquid phase hydrogenation of lignites was performed at 475-485°C and 3500-4300 psi. The hydrogenation catalyst was iron oxide. Iron oxide commonly referred to as red mud, luxmasse, or bayermasse was mixed into the coal slurry

in amounts of 2 to 5% based on the coal and discarded after one pass through the reactor.

Liquid phase hydrogenation of bituminous coals was conducted in a similar manner but with pressures in the range of 5000-10000 psi. Depending on the pressure either  $\text{NH}_4\text{Cl}$ -promoted tin oxalate or iron oxide was used as catalyst. Table 1 shows typical yields of products produced in liquid-phase Bergius hydrogenation (Berkowitz, 1979).

The first commercial plant using the two-stage Bergius process was built in 1927 at the Leuna works in Central Germany. Throughput was 100,000 metric tons per year producing 2500 barrels per day of gasoline (Lowry, 1945).

The Pott-Broche process yielded an ash-free extract by mild hydrogenation of coal. The process was commercially exploited in a 125 ton per day plant at Welheim, Germany, between 1938 and 1944 (Berkowitz, 1979). The Pott-Broche process was not important with respect to catalysis but laid the foundation for the development of the Solvent Refined Coal (SRC) process.

The SRC I process was designed to produce a substantially sulfur and mineral matter free boiler fuel from coal by mild hydrogenation. The SRC II process grew out of SRC I technology but produced liquid products not solid fuels. The SRC II process uses a portion of the product

Table 1

Liquid-phase hydrogenation of coal<sup>a</sup>

	<u>Lignite</u> <sup>b</sup>	<u>Bituminous coal</u> <sup>c</sup>
Feedstock		
Raw coal	100.0	100.0
Slurrying oil	51.4	132.5
Products		
Middle oils (b.p. less than 325°C)	21.5	52.4
Heavy distillate oils	33.6	66.7
Heavy centrifuge oils	42.9	96.6
Heavy coker oils	10.9	12.8
Hydrocarbon gasses	10.5	20.5

a ; all quantities in tons

b with 52% moisture; hydrogenated at 30 MPa

c with 8.5% moisture; hydrogenated at 70 MPa

slurry for slurring fresh coal. Mineral matter in the product slurry is thus recycled. The use of this recycle stream increases conversion of coal to lower molecular weight products. Vacuum bottoms (typically about 30% mineral matter) are gasified with oxygen to produce hydrogen.

Early studies of the SRC II process indicated that coal mineral matter displayed significant catalytic activity towards the dissolution of coal (Wright and Severson, 1972). This, coupled with the German experience of iron addition provides the general background for the studies described in this thesis.

## LITERATURE SURVEY

Conversion of coal to liquid products (benzene solubles) occurs either by addition of hydrogen to the coal structure, or by carbon rejection. Pyrolysis of coal results in the rupture of chemical bonds and the formation of highly reactive free radicals. According to Neavel (1975), in the absence of a hydrogen donor species, these free radicals combine with surrounding molecules to form high molecular weight substances which are not benzene soluble. Alternatively, in the presence of a hydrogen donating vehicle, hydrogen is abstracted from the vehicle and stabilizes these primary free radicals. The products obtained are then relatively low in molecular weight and benzene soluble.

Guin et al. (1978) have suggested that the rate limiting step in the liquefaction of coal is the transfer of hydrogen to an appropriate donor solvent (re-hydrogenation). Experimental evidence in support of this hypothesis is presented in table 2 where prehydrogenated creosote oil was shown to increase conversion significantly over that of untreated solvent. This trend was found to occur both in nitrogen and hydrogen atmospheres while conversion was greater in a hydrogen atmosphere.

Ruether (1977) examined the effect of catalyst

Table 2

Comparison of hydrogenation and hydroesulfurization activity of coal in prehydrogenated solvent and that in untreated solvent (Guin et al., 1978).

Pretreatment of solvent	Temp, °C	Atmosphere	Reaction Time, min	Solvent-to-coal ratio	Conversion (based on cresol solubles)	Total sulfur, %	Organic sulfur, %
None	410	2000 psi of N <sub>2</sub>	15	3/1	42.13	0.904 ± 0.023	0.34
Hydrogenation	410	2000 psi of N <sub>2</sub>	15	3/1	83.10	0.487 ± 0.030	0.39
None	410	2000 psi of H <sub>2</sub>	15	3/1	61.03	0.912 ± 0.054	0.35
Hydrogenation	410	2000 psi of H <sub>2</sub>	15	3/1	90.70	0.506 ± 0.026	0.41

concentration on coal liquefaction, measured as a function of organic benzene solubles, on a Bruceton mine coal in hydrogen and nitrogen atmospheres. The catalyst used was silica promoted cobalt-molybdenum on alumina support. In a nitrogen atmosphere the catalyst did not aid in the conversion of the coal whereas conversion was increased with the use of catalyst in a hydrogen atmosphere. In addition, molecular hydrogen consumption in the absence of catalyst was undetectable, while molecular hydrogen consumption in the presence of catalyst was significant. He concluded that two types of reactions were occurring. The first class of reaction involved molecular hydrogen and was heterogeneously catalyzed. The second class of reaction involved the conversion of coal to asphaltenes and was uncatalyzed.

A rough reaction scheme for the hydrogenation of coal was presented by Gates (1979) and is shown in figure 1. Free radical fragments from coal formed by pyrolysis abstract hydrogen from a hydrogen donor species represented in this scheme by tetralin. The hydrogen donor, now in a hydrogen-poor state is rapidly transported to the catalyst surface. The active form of the catalyst is a metal sulfide. The hydrogen donor solvent is replenished on the catalyst surface with dissociatively adsorbed hydrogen. The donor solvent, now in a hydrogen-rich state, shuttles back to

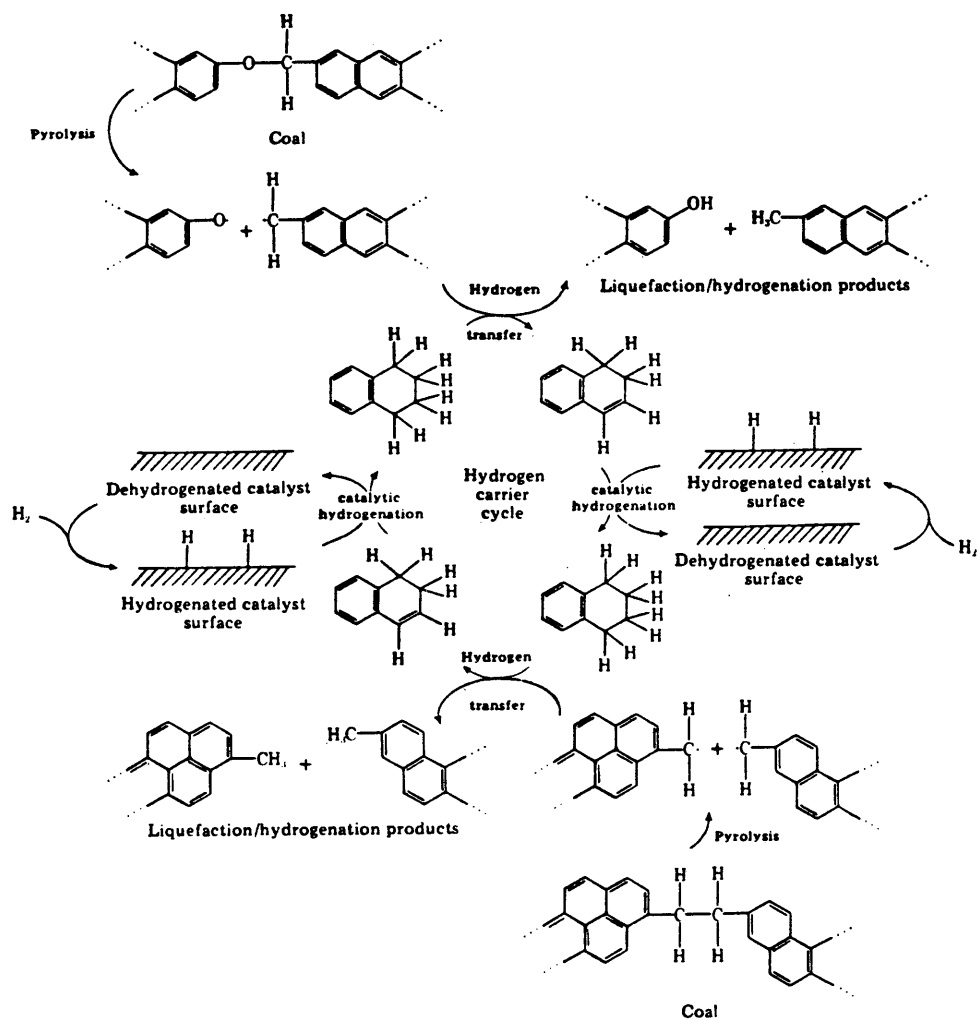


Figure 1. Schematic representation of the reaction cycles of coal liquefaction/hydrogenation (Gates, 1979).

the coal.

Guin et al. (1978) studied the transfer of hydrogen from naphthalene to tetralin using coal minerals as catalysts. Pyrite, reduced pyrite, and SRC residue were found to catalyze hydrogen transfer as shown in table 3. A Co-Mo-Al catalyst was the most effective catalyst followed by pyrite.

Since certain components of coal mineral matter have been found to catalyze hydrogen transfer reactions, their possible use as catalysts in coal liquefaction reactions is worth consideration.

The term "mineral matter" refers to all forms of inorganic material associated with coal. The major constituents of coal mineral matter are given in table 4.

Experience shows that over 95% of the mineral matter found in coal is comprised of clay minerals, carbonates, sulfides, and silica (Berkowitz, 1979). The remainder of the mineral matter is generally accounted for by oxides of K, Na, Ti, and by chlorides, sulfates, and phosphates.

Evidence that coal minerals catalyze coal liquefaction reactions has been demonstrated by Mukherjee and Chowdhury (1976). They fractionated a North Assam coal by gravity separation and chemical de-ashing. The parent coal, gravity fractions, and the chemically de-ashed sample were

Table 3

Catalytic hydrogenation of naphthalene  
by coal minerals (Guin, 1978).

Catalyst	Initial atmosphere	Reaction time, min	Tetralin to dodecane peak height ratio by gas chromatography ( $\times 10^3$ )
None	14.7 psig air	30	0.0
None	1200 psig H <sub>2</sub>	60	0.0
Co-Mo-Al (5%)	1200 psig H <sub>2</sub>	30	109.0
Pyrite (50%)	1200 psig H <sub>2</sub>	60	19.0
Reduced pyrite (50%)	1200 psig H <sub>2</sub>	60	4.0
SRC residue (50%)	1200 psig H <sub>2</sub>	60	4.0

<sup>a</sup> Original sample, 10 wt % naphthalene in dodecane; temperature, 410 °C.

Table 4

Types of Minerals Found in Coal  
(Hegarty, 1978)

## I. Aluminosilicates

Kaolinite:  $((\text{OH})_8\text{Si}_4\text{Al}_2\text{O}_{10})$

A common type of clay which is an acid  
aluminum silicate

Muscovite: Alumino type silica substance

Illite:  $((\text{OH})_4\text{K}_2(\text{Si}_6\text{Al}_2)\text{Al}_4\text{O}_{20})$

Montmorillinite

## II. Sulphides

Pyrite: A cubic structure of  $\text{FeS}_2$  in which iron atoms  
are octahedrally surrounded by five sulfur atoms

Pyrrhotite: A reduced form of pyrite with stoichiometry  
of  $\text{FeS}$

## III. Carbonates

Anserite: A mixture of  $\text{CaMg}(\text{CO}_3)_2$  and  $\text{CaFe}(\text{CO}_3)_2$

Calcite: A crystalline form of  $\text{CaCO}_3$

Dolomite: A double salt with equal molar quantities of  
 $\text{CaCO}_3$  and  $\text{MgCO}_3$

Siderite: A crystalline form of  $\text{FeCO}_3$

IV. Quartz: A crystalline form of  $\text{SiO}_2$

hydrogenated in the absence of any catalyst or pasting oil. Conversion was based on coal converted to benzene soluble products. Conversion increased from 22.5% to approximately 84% with increasing mineral matter content as shown in figure 2. Maximum conversion was attained at 57.5 grams of mineral matter per 100 grams of organic matter. Further increases in mineral matter content only had a diluent effect. Conversion also increased in the presence of either iron, titanium, or kaolinite (see figure 3). Pyrite and pyrite in the presence of organic sulfur was shown to be catalytically active as shown in figure 4. There was no clear relationship between conversion and organic sulfur in the absence of pyrite. The results suggested that organic sulfur is responsible for a catalytically active form of iron sulfide. There was also evidence presented that indicated adding elemental sulfur to a fraction rich in non-pyrite iron could increase conversion levels. For this reason, they considered the total iron present to be a catalytic agent.

Wright and Severson (1972), using the middle fraction of raw anthracene oil as solvent, washed coal insolubles from a bituminous coal in a continuous flow dissolver tube at 425°C and 1000 psig of hydrogen. They found that anthracene reacted with hydrogen in an amount proportional

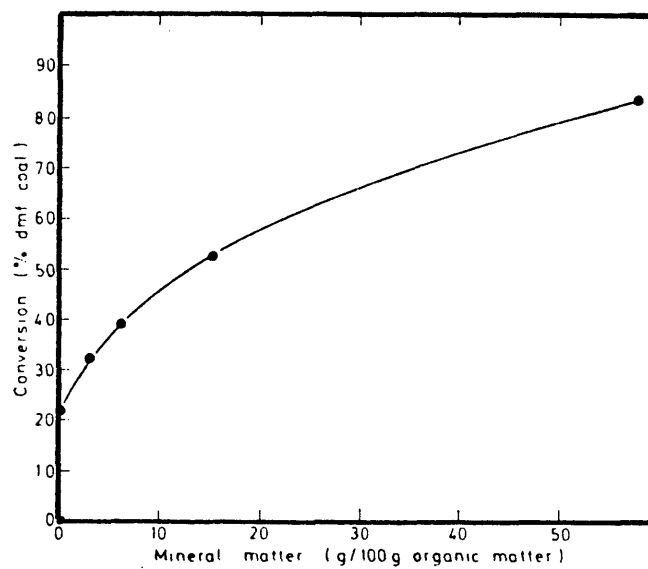
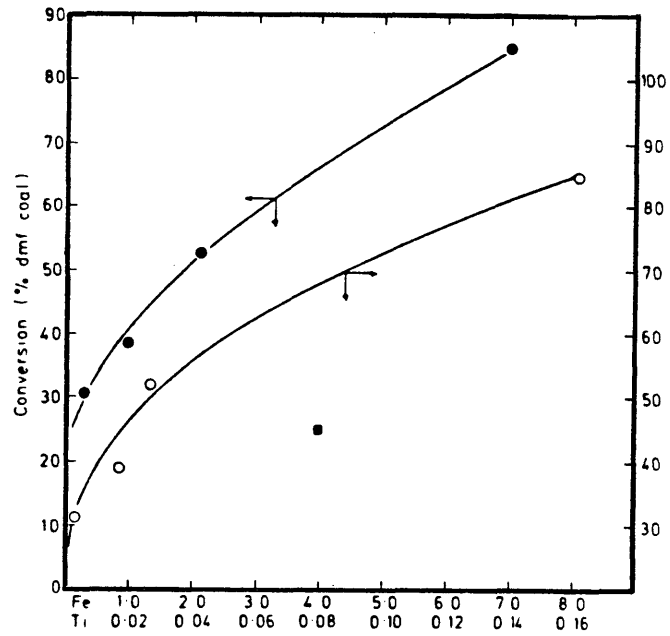


Figure 2. Relation between mineral matter content and conversion (Mukherjee and Chowdhury, 1976).

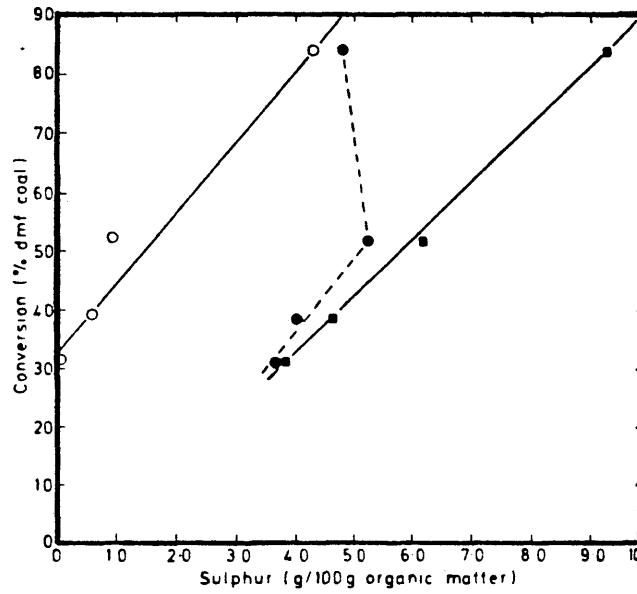


● Iron

○ Titanium

■ 1.3 sp. gr. fraction enriched with titanium

Figure 3. Relation between iron and titanium contents in ash and conversion (Mukherjee and Chowdhury, 1976).



- Organic
- Pyritic
- Organic + Pyritic

Figure 4. Variation of conversion with different forms of sulfur (Mukherjee and Chowdhury, 1976).

to the concentration of coal minerals. They conjectured that FeS was the active catalyst, since it was the most abundant form of iron under their reaction conditions and the catalytic effects of iron had been well documented in the literature (Rapoport, 1955; Weller, 1956; Kawa et al., 1960; Kawa and Hiteshue, 1963).

Tarrer et al. (1976) studied the effects of coal minerals and the hydrogenation and hydrodesulfurization of creosote oil. A batch autoclave reactor with total pressure as a rough indicator of reaction rate was used. Their results are presented in figure 5. The upper and lower curves show extremes with no catalyst and a commercial Co-Mo-Al catalyst respectively. Pyrite and SRC residue were found to catalyze hydrogenation of creosote oil better than other coal minerals. It was interesting to note that -80+150 mesh pyrite exhibited lower catalytic activity than -325 mesh pyrite indicating that not only the coal mineral but its physical state is of importance (e.g. mass transfer effects may limit the effectiveness of certain coal minerals as catalysts). Hydrodesulfurization activity was in general agreement with the catalytic activity sequence witnessed by the total pressure data with two exceptions. Pyrite, which was a very good hydrogenation catalyst, was a very poor catalyst for hydrodesulfurization (see figure 6).

Reaction Conditions  
 Temperature: 425°C  
 H<sub>2</sub> Pressure: 3000 psig @ 425°C  
 Agitation Rate: 2000 rpm  
 Autoclave: 300 cc  
 Charge: 100 g Creosote Oil/15 g catalyst

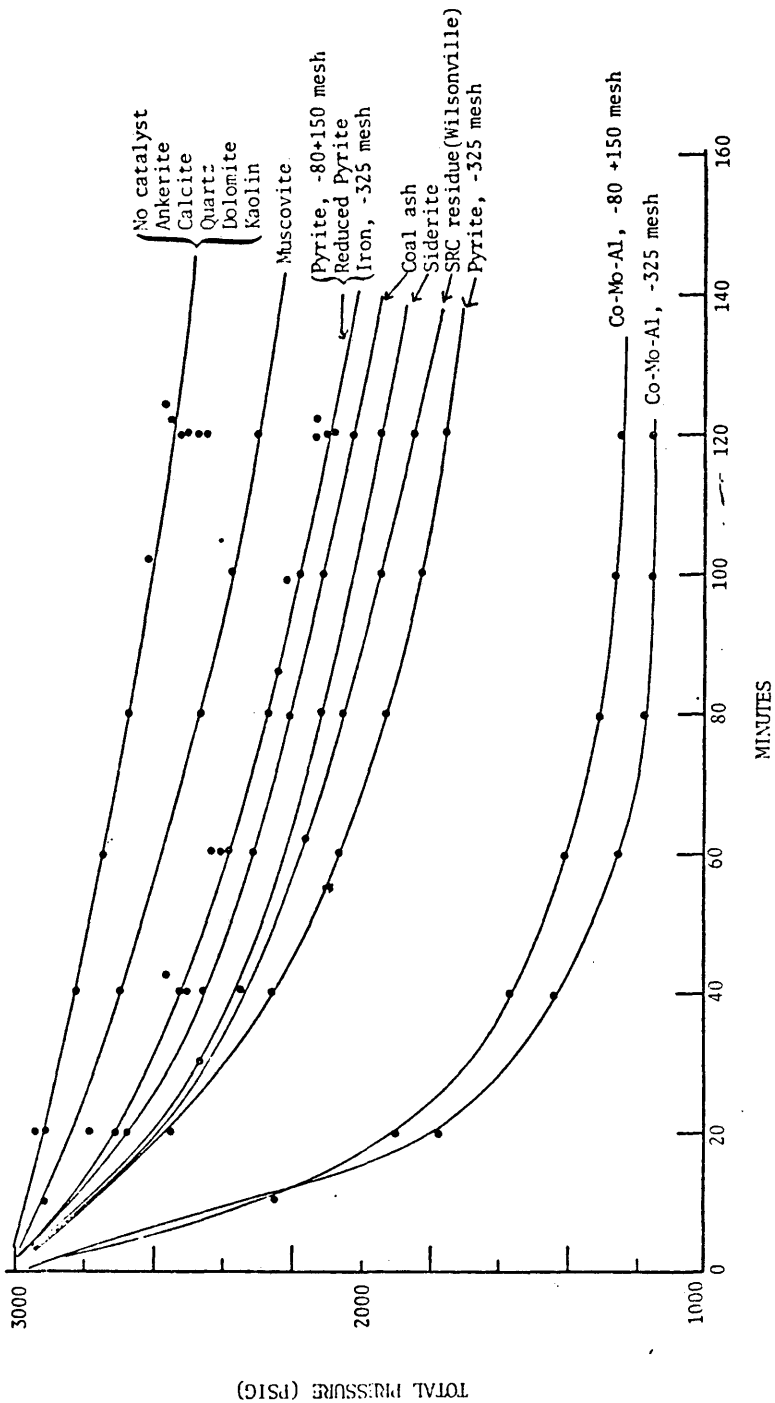


Figure 5. Catalytic effect of coal mineral matter as indicated by total pressure (Tarrer, 1976).

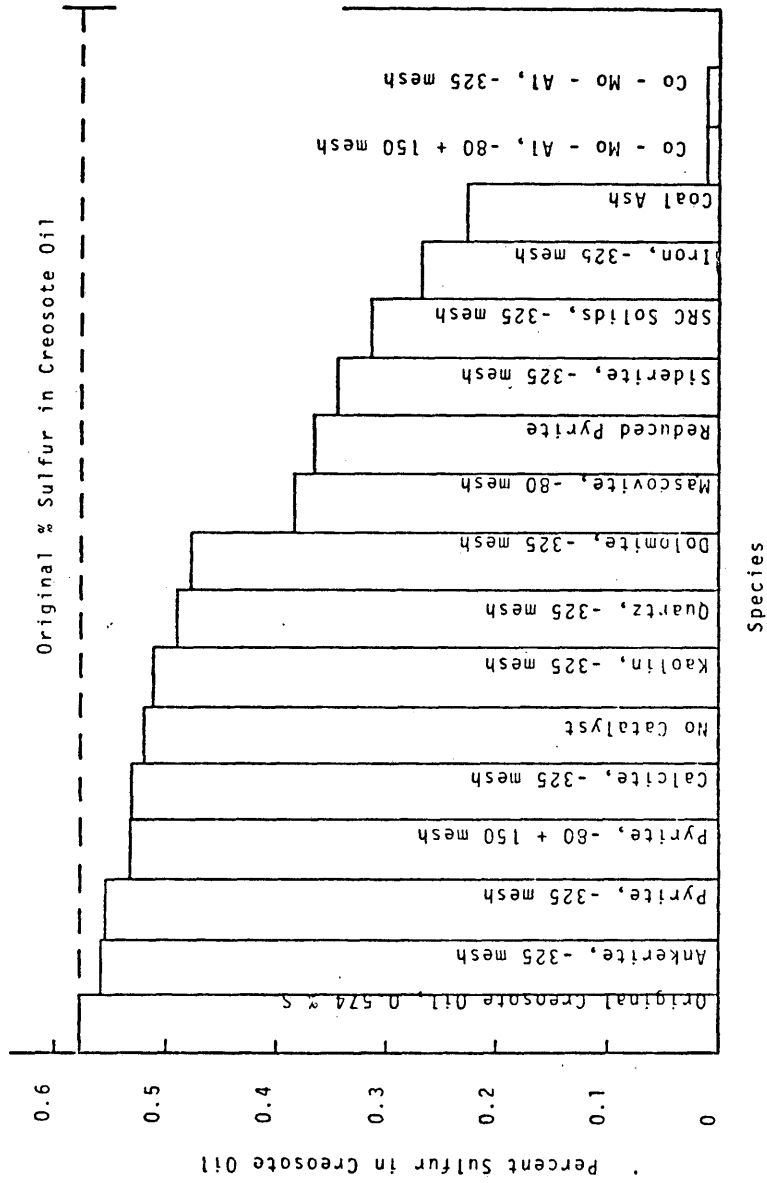


Figure 6. Comparison of desulfurization activity of catalyst (Tarrer, 1976).

Iron which showed little hydrogenation activity was an excellent catalyst for sulfur removal. Iron appears to react with any  $H_2S$  produced to form sulfides. The poor hydrodesulfurization activity of pyrite appears to be related to its reaction with hydrogen to form  $H_2S$  and its reduction to  $Fe_7S_8$  during hydrogenation.

The work of Guin et al. (1978) supports the work of Tarrer et al. (1976). Iron was found to be a scavenger of  $H_2S$  and certain coal minerals, particularly iron compounds, were found to have hydrogenation activity.

Guin et al. (1980) studied benzothiophene hydrogenolysis using pyrite as a catalyst. This system was considered to be representative of a coal mineral/coal liquids component reaction. Benzothiophene in dodecane was reacted in a tubing bomb reactor at coal liquifaction conditions. Conversion of benzothiophene to ethylbenzene was measured by gas chromatography. Pyrite was found to be most effective in catalyzing hydrogenation of the thiophenic ring.

Granoff and Thomas (1977) worked towards the establishment of a predictive correlation between mineral matter content and liquid product composition. Creosote oil was the solvent vehicle employed. Several high rank bituminous coals with mineral matter contents varying from 5% to 21%

were examined. The coals had similar petrographic characteristics and most were vitrinite rich (greater than 85%). Coals with the highest mineral contents experienced the highest conversions and were the most active with respect to organic sulfur removal. Granoff and Traeger (1978) prepared samples with varying mineral contents by gravity separation. The study was conducted in a one liter batch autoclave at a pressure of 1000 psig hydrogen, a reaction temperature of 405°C, and a residence time of 30 minutes. Figure 7 shows that increasing mineral matter content increases conversion of coal to benzene solubles. Preasphaltene content decreased significantly with increasing mineral matter content while asphaltenes were virtually unaffected. Conversion to pentane soluble oil increased linearly with mineral matter content.

Lee et al. (1977) did a comparative study of the rates of hydrogenation and hydrodesulfurization of coal/oil slurries under different reaction conditions and in the presence of different coal minerals. Iron was discovered to be a more effective hydrodesulfurization catalyst than either pyrite or reduced pyrite.

Guin et al. (1979) reacted demineralized coals in the presence of added minerals in a tubing bomb reactor with either tetralin or light recycle oil as solvent. The

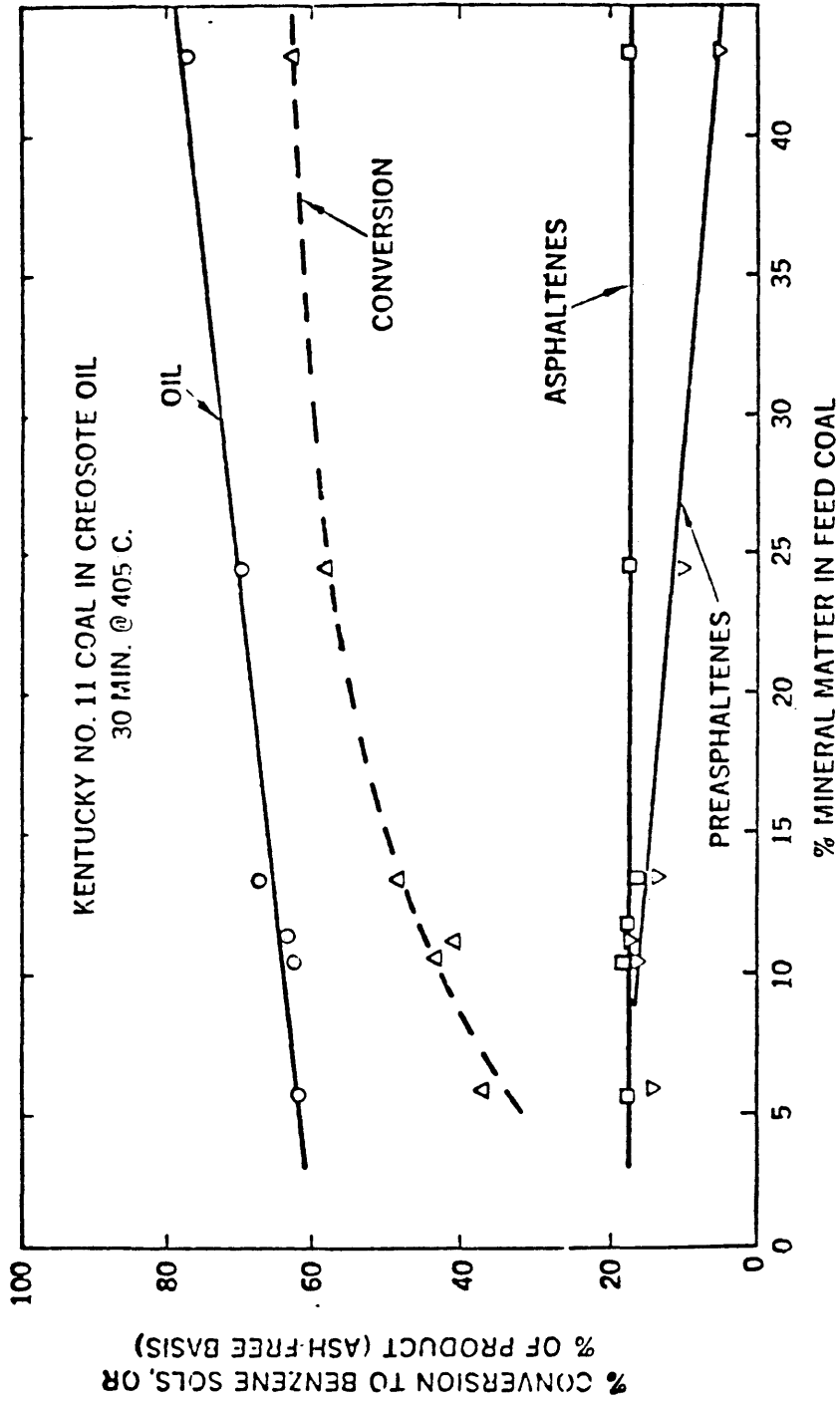


Figure 7. Mineral matter effects (Granoff and Traeger, 1978).

effect of coal minerals on the replenishment of the hydrogen donor solvent was examined. Coals containing mineral matter were more effective in solvent rehydrogenation than their demineralized counterparts. Reduced pyrite, in particular, showed significant catalytic activity for both hydrogenation and dehydrogenation of the solvent, the ultimate direction of reaction depending on the initial hydrogen partial pressure.

Hegarty (1978) studied the effects of mineral matter addition to a high volatile A bituminous coal. The composition of the added mineral matter was 16.18% quartz, 36.25% pyrite, 3.05% gypsum, 24.28% kaolin, and 20.23% illite. Reaction was carried out in a one liter batch reactor at 400°C using a solvent mixture of tetralin, 1-methylnaphthalene, and naphthalene. Mineral matter was found to increase the rate of solvent dehydrogenation reactions and increased the overall conversion of coal both in the presence and absence of hydrogen.

Garg and Givens (1982) measured the hydrogenation of a SRC II solvent using a pyrite catalyst in the presence and absence of coal. Hydrogen content of the product oil remained constant in the presence of pyrite whereas the oil fraction lost hydrogen in the absence of pyrite. Addition of pyrite to Elkhorn no. 3 coal increased overall coal conversion and the yields of hydrocarbon gases, carbon

monoxide, carbon dioxide, hydrogen sulfide, and ammonia. Oil yield increased from 27 to 41%, asphaltenes decreased from 15 to 11%, and preasphaltenes decreased from 30 to 24%. Similar results were obtained with a Kentucky no. 9 coal.

Under coal liquefaction conditions in the presence of hydrogen, pyrite reacts to form pyrrhotite ( $\text{Fe}_{1-x}$ , where  $x$  is between 0 and 0.125) and hydrogen sulfide. Bicket et al. (1980) have measured the rate of decomposition of pyrite to hydrogen sulfide in hydrogen and nitrogen atmospheres. The rate of decomposition under nitrogen atmosphere was an order of magnitude lower than with hydrogen gas using a SRC II heavy distillate as solvent.

Richardson (1971) has studied the thermo-magnetic properties of coal char. The char was generated from a coal liquid after liquefaction in the presence of hydrogen and a donor solvent at  $400^{\circ}\text{C}$ . The coal contained approximately 14% pyrite. The results of this investigation showed that the iron present in the char was a mixture of  $\text{Fe}_7\text{S}_8$  and  $\text{FeS}_2$  with the exact composition depending on the process conditions.

Eaton (1981) conducted a disposable additive screening study in a 300 cc batch autoclave reactor at  $380^{\circ}\text{C}$  in a tetralin solvent. A low ash, low sulfur Colorado coal was

used in order to decrease any catalytic effects due to inherent mineral matter. Residence times of 10 and 60 minutes were examined. The effects of pyrite, pyrrhotite, a pyrite/ pyrrhotite mixture, technical grade FeS, and molybdenum ore on conversion are shown in figure 8 for both residence times. Overall conversion, oil, and preasphaltene yields increased with residence time. The effect of residence time on asphaltene yields was not as pronounced. Of the additives tested, FeS<sub>2</sub> and the FeS<sub>2</sub>/Fe<sub>0.9</sub>S mixture showed a significant increase in the overall conversion at a residence time of 60 minutes and only FeS<sub>2</sub> had a substantial effect on conversion at 10 minutes. The effect of the additives on product distribution is shown in figures 9 through 11. Pyrite gave the most pronounced effects. Pyrrhotite appeared not to be the active iron sulfide responsible for increasing conversion. When dibenzothiophene was present with pyrrhotite (Fe<sub>0.93</sub>S), an increase in conversion over that of Fe<sub>0.93</sub>S alone was witnessed. The results indicated that a synergistic effect exists between the total sulfur content of the reaction mixture and the catalytic activity of iron sulfide additives.

In order to attain a greater understanding of the role of pyrite in coal liquefaction, Montano and Granoff (1979) carried out a series of batch autoclave experiments with

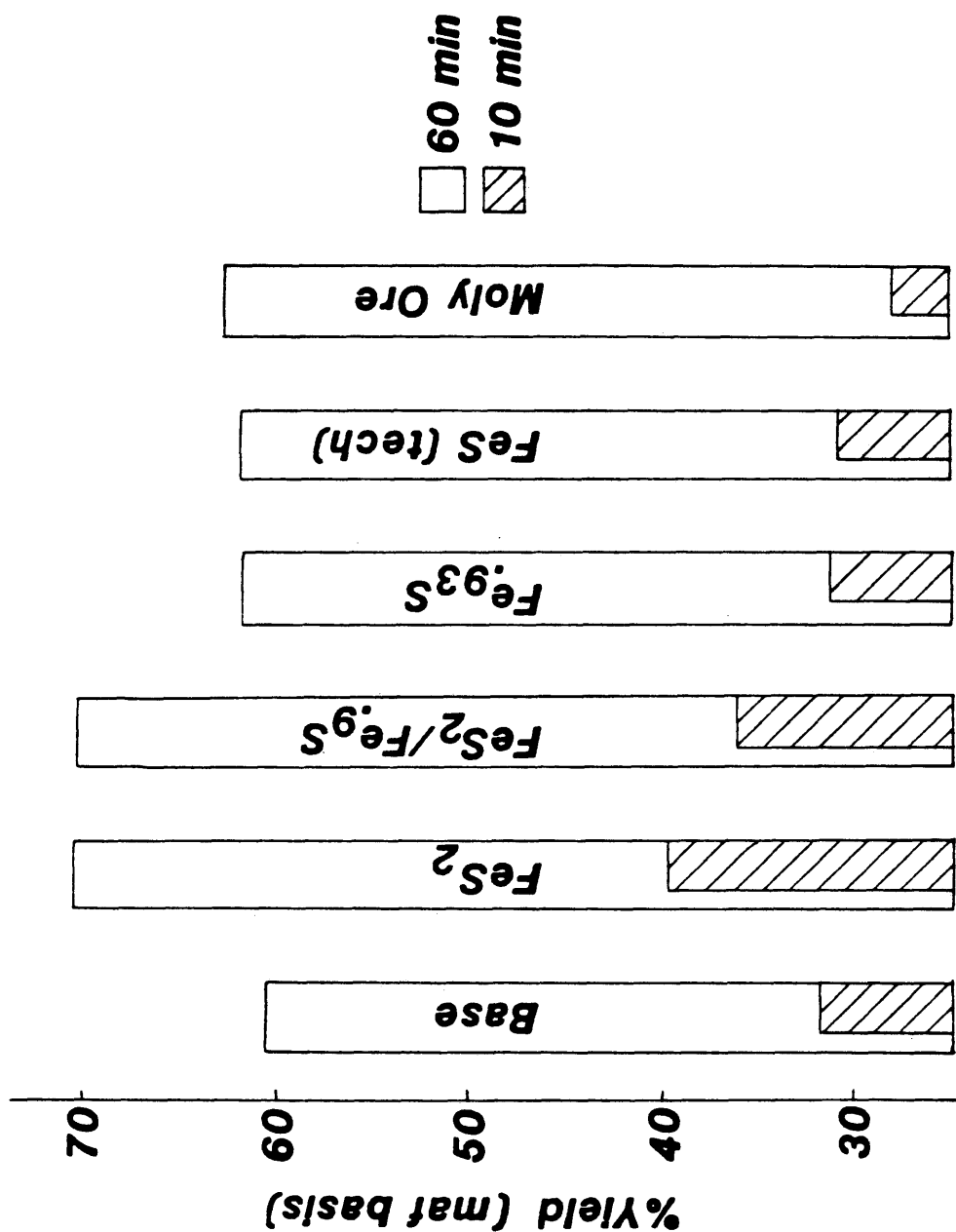


Figure 8. Effect of time and additive on conversion (Eaton, 1981).

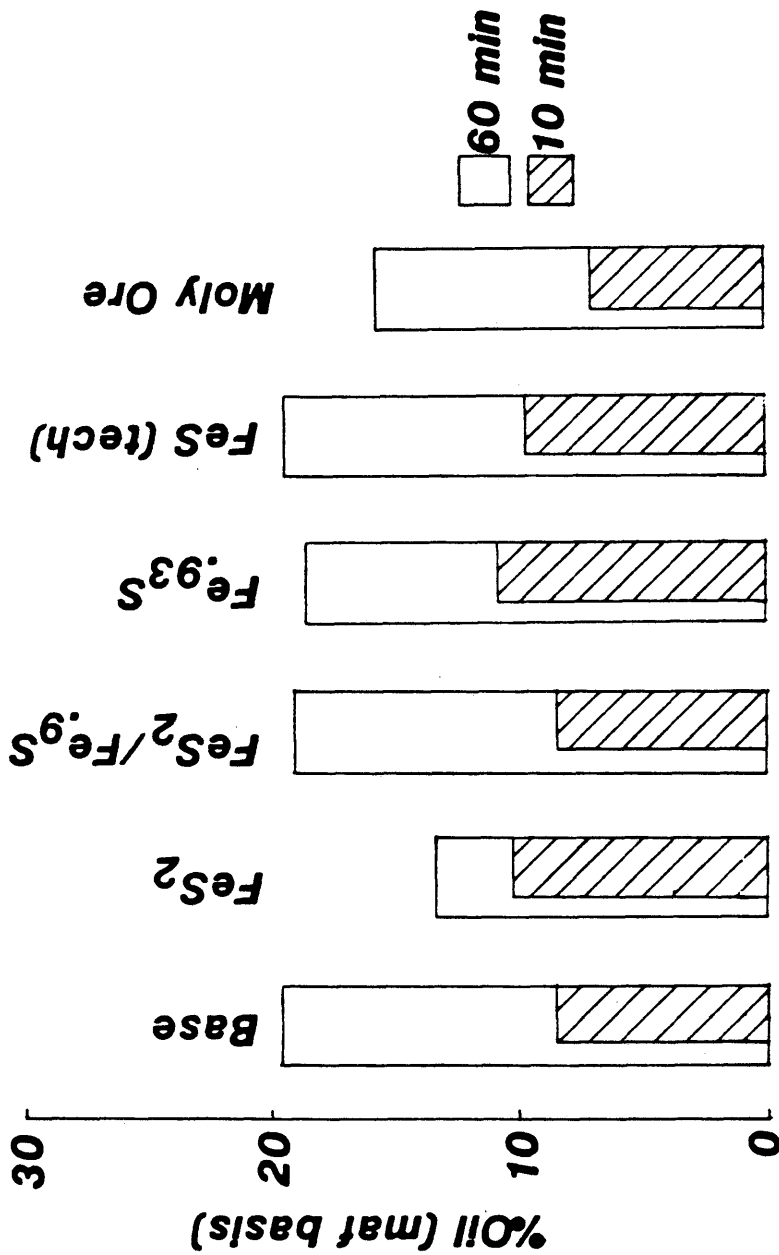


Figure 9. Effect of time and additives on oil yields (Eaton, 1981).

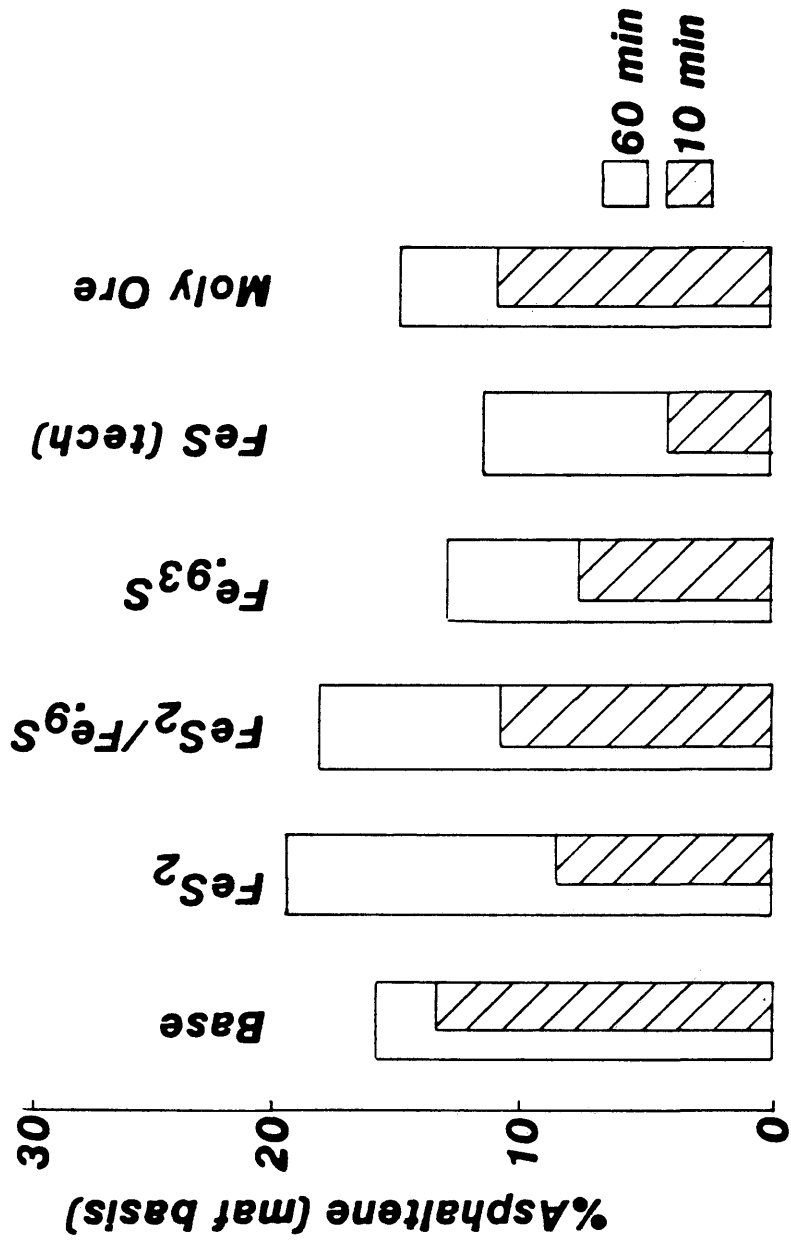


Figure 10. Effect of time and additives on asphaltene yields (Eaton, 1981).

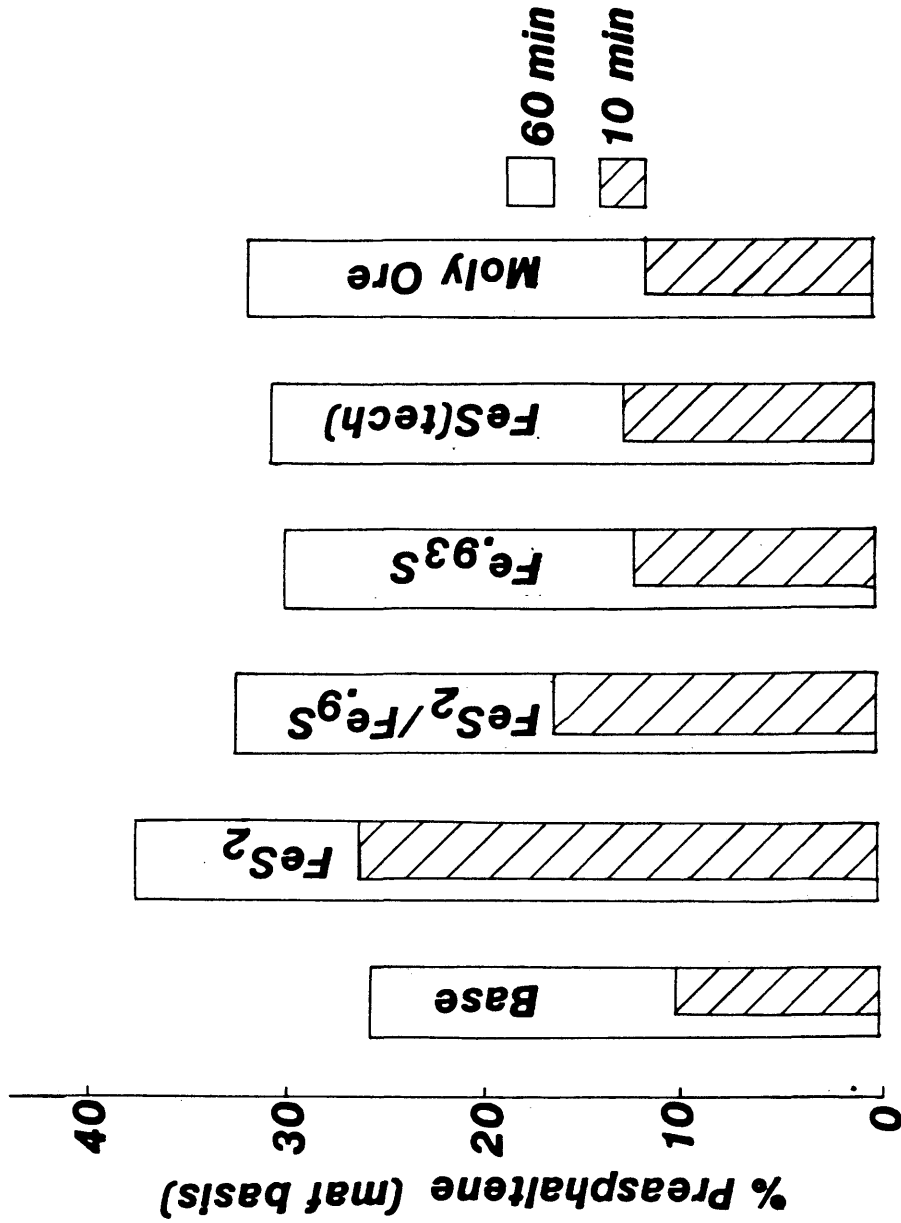


Figure 11. Effect of time and additives on preasphaltene yields (Eaton, 1981).

several coals (Illinois no. 6, Kentucky no. 9/14, and West Virginia) at 425°C. The solvent used was a SRC II heavy distillate. They discovered a rectilinear correlation between the extent of coal conversion to either benzene or tetrahydrofuran (THF) solubles and the atomic percent iron in the liquefaction residues (see figure 12). The highest conversion to liquid products was associated with a pyrrhotite having a lower atomic percent iron. When the West Virginia coal was doped with five weight percent pyrite (based on coal), the conversion to benzene and THF solubles increased. The resulting liquefaction residue contained a pyrrhotite with a lower atomic percent iron than the residue from West Virginia coal without added pyrite. A rectilinear correlation between sulfur content of the feed coal and the extent of conversion was also observed. They speculated that the sulfur of the feed coal significantly effected the composition of the pyrrhotite found in the liquefaction residues and thus the conversion.

A systematic study of the transformation of pyrite during coal liquefaction was made by Montano et al. (1981). Mossbauer measurements were taken in a reactor designed specifically for in-situ measurements. SRC II heavy distillate was the solvent used. Factors controlling the

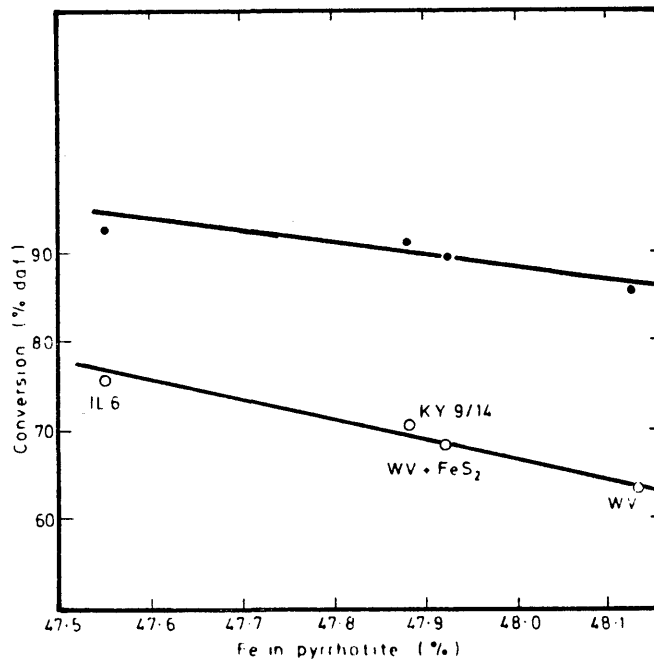


Figure 12. Conversion to • THF and ○ benzene solubles as a function of the atomic percent iron in the pyrrhotite (Montano and Granoff, 1980).

stoichiometry of the pyrrhotite produced from the decomposition of  $\text{FeS}_2$  were temperature and the  $\text{H}_2$  and  $\text{H}_2\text{S}$  partial pressures. The atomic percent iron decreased as the  $\text{H}_2\text{S}$  partial pressure increased. A relatively good correlation between the total sulfur content of Illinois no. 6, Kentucky no. 9/14 and West Virginia coals and the pyrrhotite stoichiometry in the liquefaction residues was found (figure 13). As the total sulfur content of the coal increased the atomic percent iron decreased.

In another study, Montano et al. (1981a) showed that the decomposition of coal and mineral pyrite in a hydrogen atmosphere is dependent on particle size. Smaller particle sizes increased the transformation of pyrite to pyrrhotite. This was an expected result as smaller particle sizes result in greater external surface areas and shorter diffusional paths.

Moroni and Fischer (1980) summarized the results of research into the catalytic effects of pyrite as follows:

- 1) pyrites and pyrrhotites are active and effective catalysts for the hydroliquefaction of coal
- 2) pyrite or pyrrhotite addition improves coal conversion as well as product selectivity (i.e. a 5 wt % pyrite addition increases

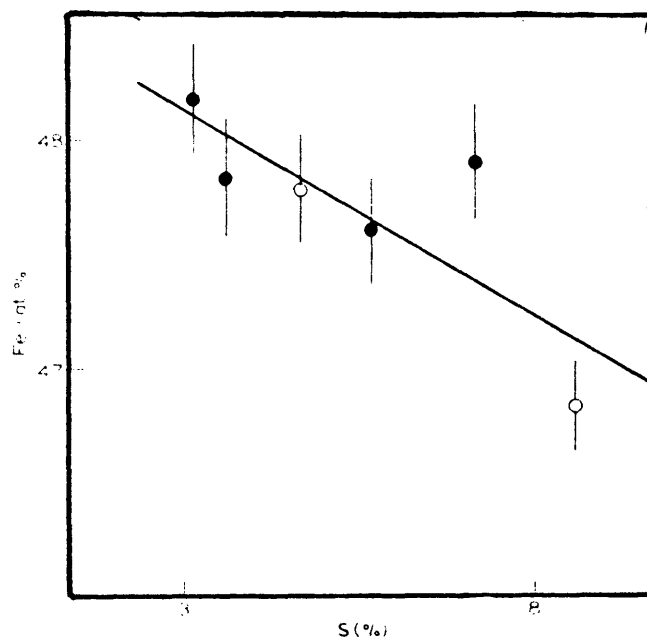


Figure 13. Atomic %Fe in  $\text{Fe}_{1-x}\text{S}$  versus total amount of sulfur. The line is the best fit to the data with  $r=0.8$  (Montano et al., 1981).

coal conversion to benzene solubles equivalent to a 25°C operating temperature increase)

- 3) pyrites from various coals may provide different levels of catalytic activity based on morphological differences of the pyrites and/or related to differences in the inherent surface areas of the pyrites
- 4) pyrites from mineral deposits show in general lower catalytic activity than coal-extracted pyrites

## EXPERIMENTAL

The objective of this study was to determine the effect of pyrite as a coal hydrogenation catalyst both in the presence and absence of added hydrogen sulfide. This section describes the experimental design and operating conditions used to accomplish this objective.

### Experimental Design

In order to determine the catalytic effects of pyrite and hydrogen sulfide, all confounding factors had to be minimized. Operating conditions were thus fixed so as to enable ready evaluation of any catalytic effect.

Initially, base runs (i.e. absence of added pyrite and/or hydrogen sulfide) were made at each of the residence times studied until the non-catalytic results were reproduced. Base runs were also performed after runs using pyrite. These latter runs gave an indication of any memory effect due to the presence of pyrite in a previous run.

In order to more accurately define the residence time and to eliminate any confounding effects due to heat up, coal slurried with solvent was injected into a preheated reactor with high pressure hydrogen. Pyrite, when present, was injected in the same manner.

Guin et al. (1976) have shown that minimal coal

dissolution occurs below 350°C and that thermal destruction of solvent molecules occurs above 425°C. A temperature of 380°C was chosen for this study as a compromise temperature where the rate of reaction was sufficiently high so as to permit substantial thermal coal conversion, but not so high as to mask catalytic effects due to added H<sub>2</sub>S and/or pyrite.

The hydrogen transfer vehicle used in this study was tetralin (1,2,3,4-tetrahydronaphthalene). Tetralin in excess of that required for the complete conversion of coal was used. This eliminated any donor solvent starvation which might have occurred which in turn effects the rate of hydrogenation. To start a run, tetralin in the reactor was preheated to 410°C. Upon coal slurry injection, the desired reaction temperature of 380°C was realized immediately. To accomplish the above criteria, 180 grams of tetralin was used per 20 grams of coal, with 140 grams of tetralin preheated in the reactor and the remaining 20 g coal/40 g tetralin slurry injected into the preheated tetralin.

A coal/pyrite ratio of 10:1 (weight ratio) was employed. This ratio insured that there would be adequate amounts of pyrite while eliminating any diluent effects due to mass transfer limitations.

Reaction pressure was set at 2000 psig in order to minimize coke and gas production. Injection of coal slurry with 1700-1900 psig of hydrogen assured an initial reaction pressure of approximately 2000 psig. Hydrogen sulfide initial partial pressure was based on ideal gas law calculations (see appendix for calculations).  $H_2S$  initial partial pressures of 2, 5, and 10% were used, based on an initial starting pressure of 400 psig before heat up (total "cold" pressure). Hydrogen sulfide was supplied from a gas mixture of 10%  $H_2S$ /90%  $H_2$ , as certified by the gas supplier (Matheson).

Residence times of 10 and 60 minutes were examined. Residence times less than 10 minutes were not considered due to problems in obtaining reproducible results. Shalabi (1977) has shown that overall conversion is not significantly changed after 60 minutes.

A summary of the operating conditions is given in table 5 .

Table 5

## FIXED OPERATING CONDITIONS

Fixed Operating Variables	Explanation
Temperature = 380°C	<ol style="list-style-type: none"> <li>1. Minimal coal dissolution below 350°C.</li> <li>2. Solvent thermal destruction above 425°C.</li> <li>3. Allows minimal but necessary thermal effects on the rate of hydrogenation.</li> </ol>
Pressure = 2000 psig	Minimize coke formation and gas production.
Solvent (Tetralin) = 180 grams	<ol style="list-style-type: none"> <li>1. In excess of theoretical amount required for complete conversion of coal.</li> <li>2. Insures adequate mixing.</li> <li>3. Insures minimal temperature drop after slurry injection.</li> </ol>
Coal = 20 grams	Allows multiple analyses on one product sample.
Slurry = 2:1 solvent to coal ratio	Allows slurry to be easily injected.
10:1 coal to additive ratio	Insures adequate amounts of additive without causing mass transfer limitations.

## EXPERIMENTAL APPARATUS

The batch autoclave system used in this study is shown in figure 14. The system has the following special features:

- 1) allows rapid heat up of solvent
- 2) ability to inject coal and coal/additive slurry
- 3) rapid quenching of reaction mixture
- 4) isothermal operation
- 5) high pressure operation

The reactor was a 300 cc magnedrive batch autoclave reactor supplied by Autoclave Engineers. A variable speed stirrer operated at 1500 rpm extended into the 316 stainless steel reactor. The stirring assembly consisted of a 1- $\frac{1}{4}$ " diameter impeller and baffle. The reactor also contained a thermowell and cooling coils.

The heat source was a jacket-type heater supplied by Autoclave Engineers. The heater was placed on a lab jack and could be raised and lowered from the reactor using a hand crank. A type J (iron constantan) thermocouple was used to monitor the reactor temperature. A Leeds and Northrup Electromax III temperature controller maintained isothermal operation. The temperature profile was recorded on a Honeywell Electronik III chart recorder.

The gas delivery system was designed so that the

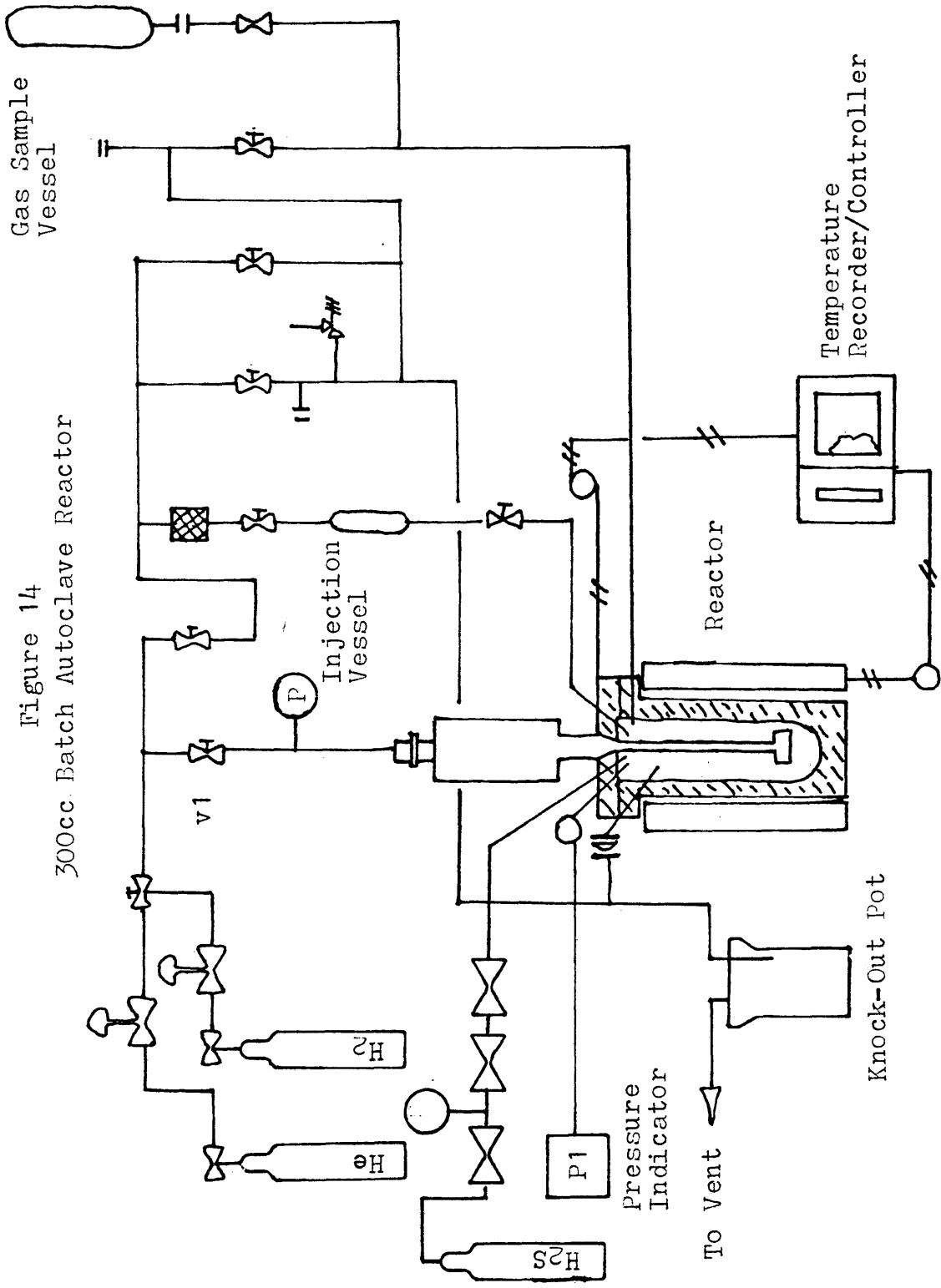


Figure 14  
3000cc Batch Autoclave Reactor

Temperature  
Recorder/Controller

Reactor

Knock-Out Pot

P1  
Pressure  
Indicator

To Vent

P  
Injection  
Vessel

V1

Gas Sample  
Vessel

H<sub>2</sub>

He

H<sub>2</sub>S

reactor could be pressure tested with helium. It was also designed to allow the injection of a coal slurry into the reactor with high pressure hydrogen and thus pressurize the reactor. The injection vessel could be evacuated prior to injection with hydrogen or purged with helium. A gas sample could be taken upon completion of reaction and the remaining gas vented to the atmosphere after passing through a knock-out pot. Hydrogen sulfide (in hydrogen) could be admitted directly into the reactor by a separate gas feed system.

The gas delivery system consisted of a helium cylinder, a hydrogen cylinder and a 10% H<sub>2</sub>S in hydrogen cylinder with associated pressure regulators, pressure gauges, a rupture disk, and valves. The helium and hydrogen pressure regulators were connected directly to the cylinders and were rated at 5000 psig. The pressure regulator system for the H<sub>2</sub>S cylinder was a metering valve used in conjunction with a pressure gauge. The reactor pressure was monitored externally with a Viatran, model 122E, transducer and a Viatran, model 1109, digital pressure gauge. An Ashcroft Maxisafe pressure gauge was positioned between the reactor and valve 1 to aid the operator in the determination of the time at which injection occurred. The rupture disk was designed to fail at 5400 psig at 650<sup>o</sup>F. All valves and

tubing were 316 stainless steel.

Rapid heating of the coal slurry was accomplished by injecting the slurry into the reactor containing preheated solvent. The reaction was quenched rapidly by lowering the heater from the reactor and cooling with a high speed forced convection fan. A typical time/temperature profile is shown in figure 15.

### Materials

This section describes the physical properties and feedstock preparation of the coal, pyrite, and tetralin used in this study. Special properties of the feedstock material which made their choice as a feedstock desirable are also discussed.

### Coal

Coal used for this study was originally obtained from the Energy Mine near Yampa, Colorado. The coal is a high volatile C bituminous coal from the Wadge seam. The proximate, ultimate, ash and sulfur analysis of this coal are given in table 6 and were performed by the Colorado School of Mines Research Institute (CSMRI).

The low ash content of the Energy Mine coal as well as its low sulfur and pyritic sulfur contents made this coal particularly desirable for this study. The low ash

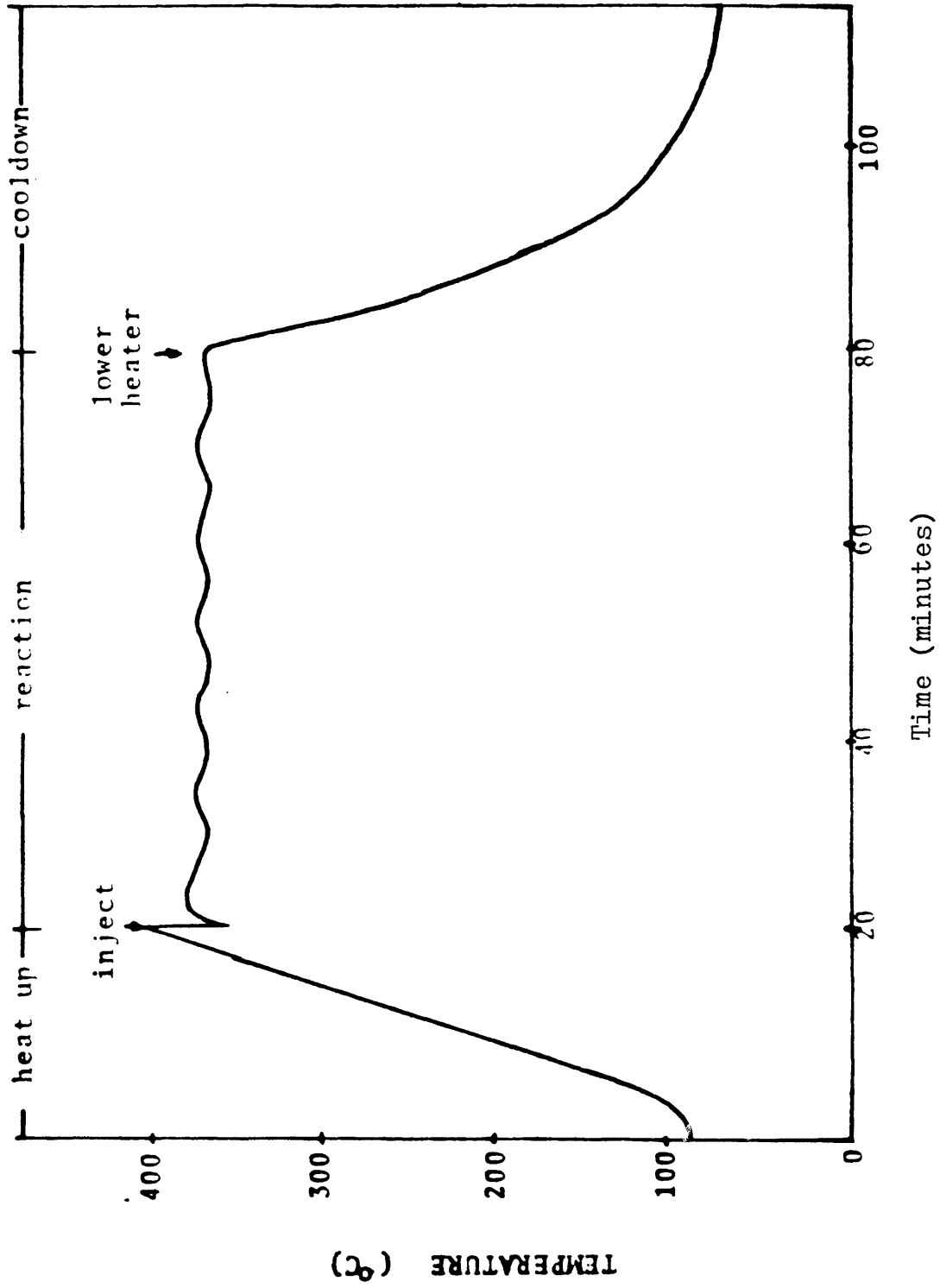


Figure 15. Time/Temperature Profile

Table 6  
Proximate, Ultimate, and Ash Analysis

	<u>As Received (%)</u>	<u>Dry Basis (%)</u>
<u>Proximate Analysis</u>		
Moisture	5.82	---
Ash	5.64	5.99
Volatile	36.9	39.2
Fixed Carbon	51.6	54.8
	<u>99.96</u>	<u>99.99</u>
<u>Ultimate Analysis</u>		
Carbon	69.0	73.3
Hydrogen	5.34	4.98
Nitrogen	1.66	1.76
Sulfur	0.53	0.56
Oxygen	17.83	13.41
Ash	5.64	5.99
	<u>100.00</u>	<u>100.00</u>
<u>Ash Analysis</u>		
SiO <sub>2</sub>	47.1	
Al <sub>2</sub> O <sub>3</sub>	32.6	
Fe <sub>2</sub> O <sub>3</sub>	3.30	
TiO <sub>2</sub>	1.05	
P <sub>2</sub> O <sub>5</sub>	1.74	
CaO	6.48	
MgO	1.48	
Na <sub>2</sub> O	0.14	
K <sub>2</sub> O	0.47	
SO <sub>3</sub>	4.64	
	<u>99.00</u>	

value (especially iron pyrite) effectively eliminated any catalytic effect inherent in the mineral matter of the coal. In addition, this study involved the addition of sulfur in the form of gas phase hydrogen sulfide. The inherently low sulfur content of this coal effectively eliminated any effects due to the presence of sulfur that was not added as pyrite or  $H_2S$ .

Fluorescent x-ray spectrography was performed on this coal by Fluo-X-Spec Analytical Laboratory. This analysis was intended to give an approximate concentration of elements with atomic number 22 and higher. The technique employed gives results that are qualitative/semi-quantitative, and are shown for this coal in table 7. These values should be considered to be very rough estimates. The technique does give a good indication of those elements present in the coal.

Coors Spectro-Chemical Laboratory determined the surface area of the coal. It was found to be  $10.9 \text{ m}^2/\text{g}$  by the BET gas adsorption method.

A sample of the Energy Mine coal was low temperature ashed (LTA) by Martin Marieta. The LTA sample was subjected to x-ray diffraction analysis by CSMRI in order to identify the minerals present. The LTA analysis is presented in Appendix E. Kaolinite and quartz were identified. The remainder of the material was amorphous

Table 7

## X-ray fluorescence data

SAMPLE: Coal

Copper	0.007	Iron	1.1	Lanthanum	
Silver		Cobalt		Cerium	
Gold		Nickel		Praseodymium	
Zinc	0.015	Cesium		Neodymium	
Cadmium		Rubidium		Samarium	
Mercury		Barium	0.014	Europium	
Gallium		Strontium	0.022	Gadolinium	
Indium		Titanium	0.097	Terbium	
Thallium		Zirconium		Dysprosium	
Germanium		Hafnium		Holmium	
Tin		Thorium		Erbium	
Lead	0.006	Vanadium		Thulium	
Arsenic	0.002	Columbium		Ytterbium	
Antimony		Tantalum		Lutetium	
Bismuth		Chromium		Yttrium	0.002
Selenium		Molybdenum			
Tellurium		Tungsten			
Bromine		Uranium			
Iodine		Manganese	0.006		

The values above are estimated elemental concentrations in:

\_\_\_\_\_ % per cent      \_\_\_\_\_ parts per million      \_\_\_\_\_ grams per liter

No check was made for elements with atomic numbers less than 22.

and of unknown composition. Further properties of a coal typical to this location (Energy Mine near Yampa, Colorado), as tabulated by Penn State, are shown in Appendix B.

The coal was originally wet ground, filtered with a Buchner funnel, and air dried. It was then screened to -200 mesh on a Sweeco screen. The coal was passed through a riffler to ensure a uniform mixture. The coal was stored under vacuum in a desiccator prior to use.

### Pyrite

A high pyrite coal supplied by the Pittsburgh and Midway Coal Mining Co. was obtained from the Colonial Mine near Madisonville, Kentucky. The coal was ground and pyrite was separated from the coal on a shaker table. Pyrite was ultimately ground to -200 mesh. The pyrite was analyzed for purity using x-ray diffraction and Mossbauer spectroscopy (see Appendix C). These results indicate that between 1 and 20% of the coal derived pyrite may be marcarsite. The Coors Spectro-Chemical Laboratory determined the surface area of the pyrite to be  $1.9 \text{ m}^2/\text{g}$  by the BET gas adsorption method.

### Tetralin

Tetralin was obtained from Union Carbide Corporation. Purity was approximately 98%.

## ANALYTICAL PROCEDURES

This section describes the liquid product and gas analysis that were performed. Results from the liquid product analysis were used directly in the calculation of product yields. The gas analysis aided the interpretation of possible reaction mechanisms.

### Gas Analysis

Product gas samples were analyzed using a model 111H Carle Refinery Gas Analyzer in conjunction with a model 3390A Hewlett-packard integrator. Calibration of the gas chromatograph involved determination of average response factors for pure components relative to methane and an average retention time for each component. Table 8 summarizes the gases investigated and the calibration results.

The gas chromatograph system is shown in figure 16. To analyze a gas sample, a sample cylinder containing the gas to be analyzed was attached to the evacuated gas chromatograph system. The gas sample was admitted to the chromatograph through a metering valve until a pressure of 40 inches of mercury was reached. The start buttons on the chromatograph and preprogrammed integrator were pushed simultaneously. When the gas chromatograph cycle was complete, the integrator produced a printout of the

Table 8

## Gas Chromatograph Calibration Results

<u>Gas</u>	<u>Average Retention Time</u>	<u>Average Relative Response Factor</u>
Hydrogen	87.67	9.0241
Butane	1.03	0.5669
Butene	1.07	0.6047
Iso-Propane	0.48	0.4507
Hydrogen Sulfide	2.19	0.8085
Propane	0.54	0.5160
Carbon Dioxide	1.02	0.7931
Ethene	1.05	0.7203
Ethane	1.08	0.6764
Methane	4.03	1.0000
Carbon Monoxide	2.03	0.8807

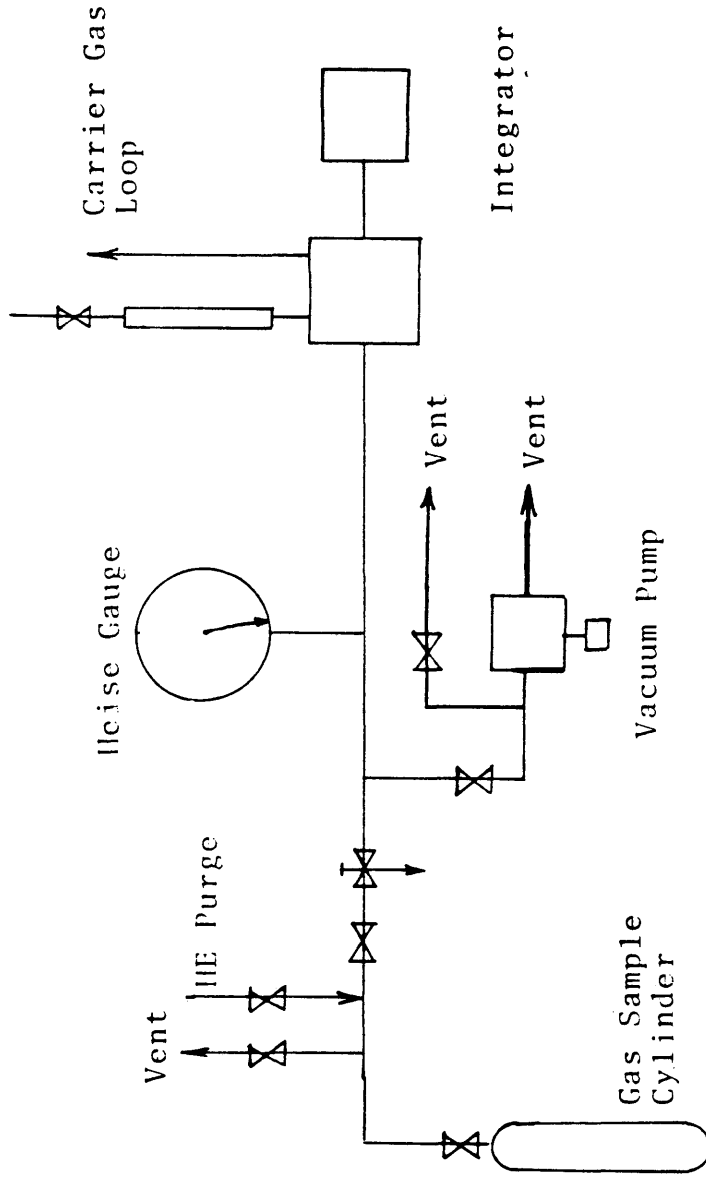
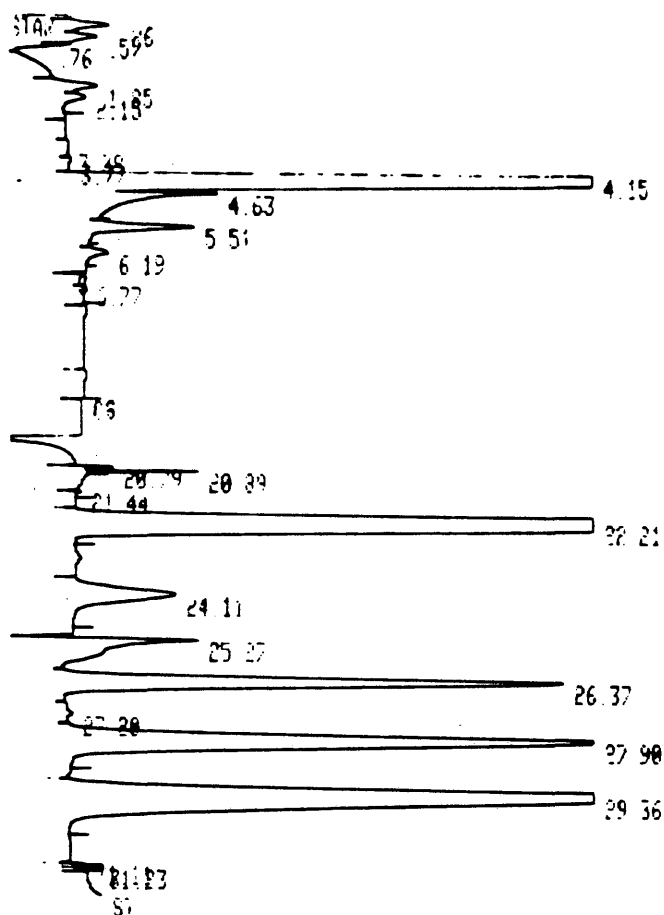


Figure 16. Gas Chromatograph System



RUN # 3 JAN/15/81 16:01:13  
 ID 36--1-15-81

NORM

RT	AREA	TYPE	CAL#	AMOUNT
4.15	1.7052E+07	SHB	1R	96.405
5.51	113060	TPP	2R	0.040
6.19	25003	TPS	3R	0.009
22.21	4952400	BB	7R	1.540
24.11	271330	BB	9R	0.065
27.98	1406600	VB	10R	0.739
29.36	2300400	BB	11R	1.203

TOTAL AREA= 2.6129E+07  
 MUL FACTOR= 1.0000E+00

Figure 17. Gas chromatograph integrator printout.

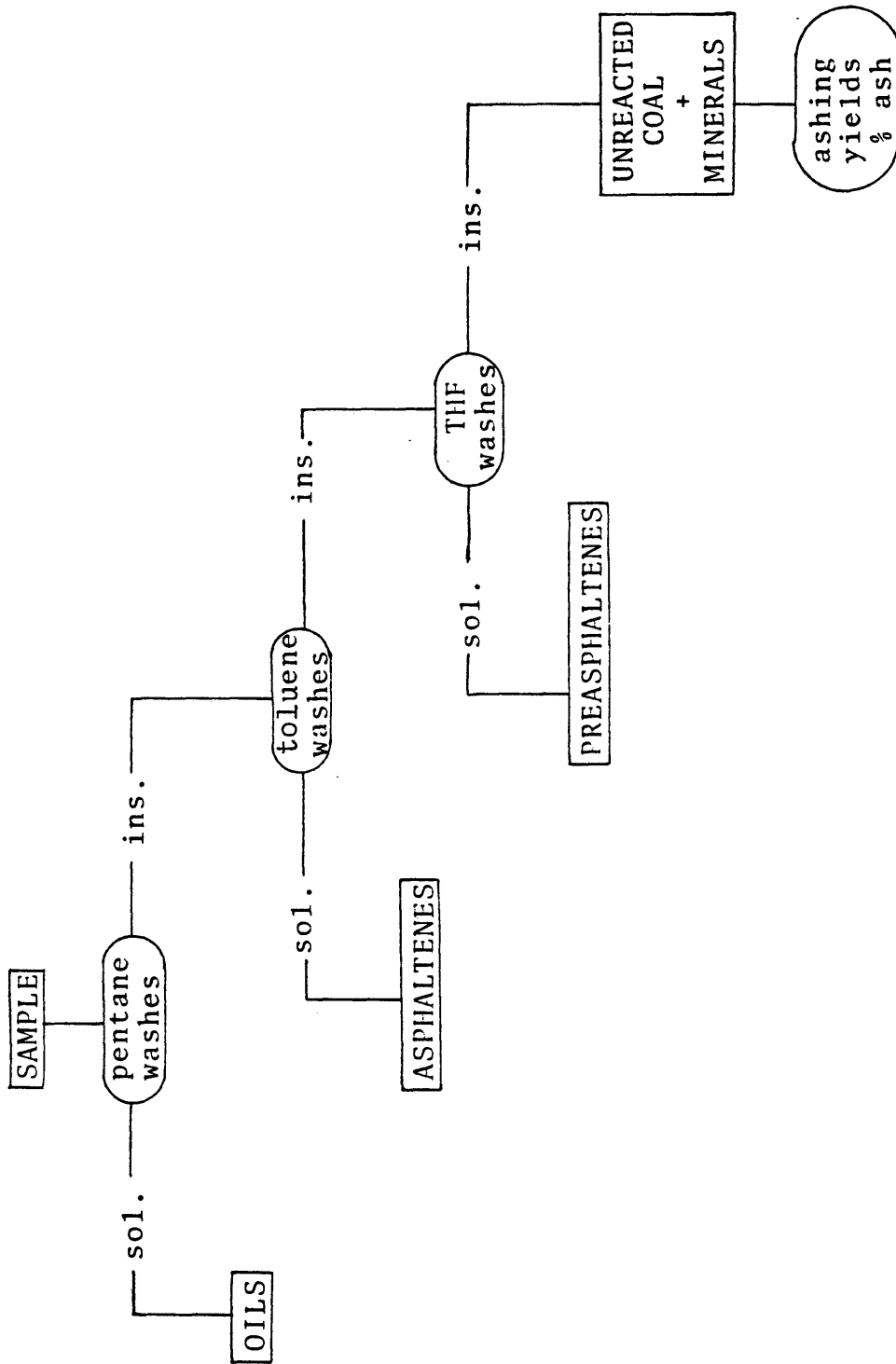
calculated peak areas and gas compositions. A sample printout is presented in figure 17.

### Liquid Analysis

one hundred percent of the liquid products were analyzed using a selective solvent fractionation (SSF) scheme to determine the amounts of oil, asphaltene, preasphaltene, and the overall conversion. The SSF analysis separates the products according to their solubility characteristics through successive extractions with three different solvents: pentane, toluene, and tetrahydrofuran (THF). An outline of the SSF scheme is presented in figure 18.

Liquid product from the reactor was placed in a Waring blender. The liquid product was then blended and pipeted into eight centrifuge tubes such that eight equal and representative liquid product samples were obtained. The weight of each of the eight samples was determined and 150 milliliters (ml.) of pentane were added to each sample. The samples were then sonicated for 5 minutes and centrifuged for 10 minutes to extract the pentane soluble oils. The liquid was decanted and the process repeated twice more with 100 ml. of pentane. After completion of the pentane washes the samples were dried at room temperature and weighed.

Figure 18. Selective solvent fractionation analysis.



After the pentane washes, the samples were washed with toluene to extract the toluene soluble asphaltenes. The samples were first washed with 200 ml. of toluene, sonicated, and then centrifuged as for pentane. The process was repeated three more times with 150 ml. toluene. The toluene insolubles were then dried in an oven set at 100°C and the samples then weighed.

The toluene washes were followed by a set of tetrahydrofuran (THF) washes to extract the THF soluble preasphaltenes. The samples were washed three times with 150 ml. THF, sonicated, and centrifuged. The samples were dried at 100°C and then weighed.

Seven of the eight THF-insolubles were ashed in a muffle furnace at 750°C for a minimum of two hours. The eighth sample was retained for possible future analysis relating to elemental analysis, sulfur determination, and Mossbauer analysis.

A RotoVap was used to strip the solvents from the pentane, toluene, and THF soluble fractions. After removal of the pentane from the pentane solubles, the remaining liquid oils were collected into a sample vial and saved.

The toluene solubles were stripped of all but a small amount of toluene. This liquid was then poured into a set of four centrifuge tubes which were then filled with pentane.

The centrifuge tubes were centrifuged for 5 minutes and the liquid decanted. The solid obtained which contained the asphaltenes was allowed to air dry. The asphaltenes were then collected into a sample vial and stored.

The THF solubles were handled in a similar manner to the toluene solubles. The THF solubles were defined to be preasphaltenes.

## DATA ANALYSIS

The development of the methods used to calculate product yields are discussed in this section. Mass and ash balance calculation methods are also presented. A statistical analysis was not performed as this is an exploratory study geared towards identifying general trends.

### Mass and Ash Balances

In this study a 100% product work-up was done. It was necessary to account for all material entering and leaving the system to ensure representative samples. Figure 19 is a representation of the streams accounted for in the mass and ash balances.

The amount of material charged to the beaker in figure was known. After the slurry was charged to the injection vessel, the weight of the material remaining in the beaker was determined. This material was then washed with acetone and dried at 100°C. This procedure removed any tetralin from the uncharged slurry. In this manner the quantity of coal and tetralin charged to the injection vessel could be determined. The same procedure was applied to the injection vessel to determine the amounts of coal and tetralin injected into the reactor. When pyrite was present it was necessary to determine the ash content of the

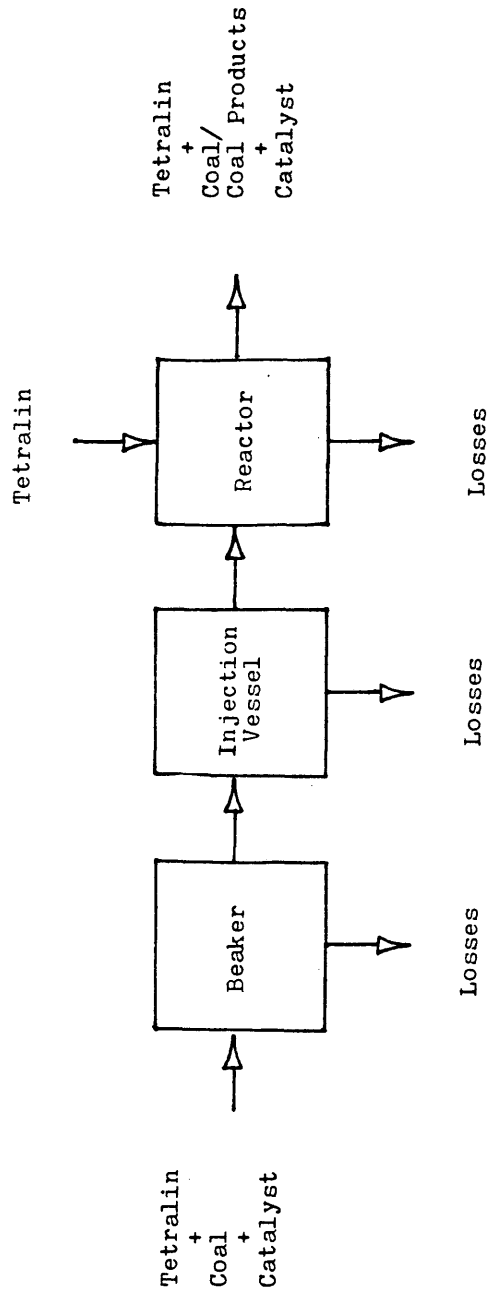


Figure 19. Overall Material Balances.

uncharged slurry in addition to the above procedure. Since the ash content of the coal and pyrite were known, a system of two equations and two unknowns were arrived at which could be solved for the amounts of coal and pyrite which were charged to both the injection vessel and the reactor (see Appendix D for calculation procedure).

After the reaction was completed, the reactor contents were placed in a blender. The purpose of the blender was to adequately mix the products before taking samples. The material remaining in the reactor was washed with acetone to determine the amount of solids present. The weight of the reactor wash sample was used in the determination of the ash balance and the calculation of an ash segregation correction factor which is discussed later.

The results of the ash and mass balances are shown in table 9 . The mass balances ranged from a low of 92% to a high of 97%. The ash balances ranged from a low of 85% to a high of 100%. This range of values and the reason they are less than 100% is primarily due to the inability to recover all of the solids from the reactor.

#### Calculation of Product Yields

Two methods of calculation were used. One of these methods (ATE) used coal-derived ash as a non-reactive tie element to calculate the amounts of unreacted coal,

Table 9

## Mass and Ash Balances

<u>Run #</u>	<u>Residence Time</u>	<u>Additive</u>	<u>Mass Balance(%)</u>	<u>Ash Balance(%)</u>
R2	10	none	94.80	92.69
R7	10	none	96.61	96.83
R8	10	none	96.86	92.97
R10	10	none	96.17	99.63
R19	10	none	95.71	95.45
R4	60	none	96.43	89.46
R6	60	none	96.69	89.81
R9	60	none	95.60	87.42
R15	60	none	95.05	95.57
R26	60	none	96.37	101.28
R28	60	none	96.51	99.11
R16	10	pyrite	92.23	91.91
R42	10	pyrite	96.09	89.63
R43	10	pyrite	94.39	91.59
R40	10	2% H <sub>2</sub> S	96.65	95.40
R30	10	5% H <sub>2</sub> S	96.61	91.30
R29	10	10% H <sub>2</sub> S	95.70	97.05
R36	10	pyrite/2% H <sub>2</sub> S	96.40	91.51
R32	10	pyrite/5% H <sub>2</sub> S	96.48	92.89
R27	10	pyrite/10% H <sub>2</sub> S	95.89	85.13
R14	60	pyrite	93.41	87.99
R11	60	2% H <sub>2</sub> S	92.65	94.55
R31	60	5% H <sub>2</sub> S	95.26	89.49
R41	60	10% H <sub>2</sub> S	94.69	88.12
R38	60	pyrite/2% H <sub>2</sub> S	91.58	87.16
R34	60	pyrite/5% H <sub>2</sub> S	92.90	90.93
R25	60	pyrite/10% H <sub>2</sub> S	93.49	91.87

preasphaltenes, asphaltenes, and oil in the products. This method was very sensitive to variations in the ash content of the product samples or even small variations in the ash value of the parent coal. For these reasons and because of the difficulty in obtaining representative samples, an alternate method, the constant weight ratio (CWR) method, was considered to give more reliable results. Only results from the CWR calculations are presented in the main body of this thesis while the ATE results have been included in the Appendix. This section describes both calculation methods.

For each run eight equal representative product samples were generated. The sample weights and the weights of the pentane insolubles (PI), toluene insolubles (TI), and tetrahydrofuran insolubles (THFI) were determined for each individual sample. The weights for each of these fractions were summed over all samples to give grand totals in each category. In the following discussion, PI, TI, and THFI will refer to the weights represented by the grand totals.

#### Ash Tie Element Method (ATE)

The following assumptions were made in calculations using the ATE method:

- 1) uniform and representative samples
- 2) coal-derived ash remained unchanged
- 3) ash was not carried over with SSF solubles

The calculation of base runs involved the following definitions:

$$\text{ASH} = (\% \text{ ash in THFI})/100$$

$$\text{PASH} = (\% \text{ parent coal ash})/100$$

Using the above definitions it is possible to develop the following equations:

$$\text{WT. ASH} = \text{ASH} * \text{THFI}$$

$$\frac{\text{WT. ASH}}{\text{WT. MAF COAL}} = \frac{\text{PASH}}{1 - \text{PASH}}$$

$$\% \text{ UNREACTED COAL (\%UC)} = \frac{(1-\text{ASH}) * \text{THFI}}{\text{WT. ASH}} * \left( \frac{\text{WT. ASH}}{\text{WT. MAF COAL}} \right) * 100$$

$$\% \text{ PREASPHALTENES (\% PASP)} = \frac{(\text{TI} - \text{THFI})}{\text{WT. ASH}} * \left( \frac{\text{WT. ASH}}{\text{WT. MAF COAL}} \right) * 100$$

$$\% \text{ ASPHALTENES (\% ASP)} = \frac{(\text{PI} - \text{TI})}{\text{WT. ASH}} * \left( \frac{\text{WT. ASH}}{\text{WT. MAF COAL}} \right) * 100$$

$$\% \text{ OIL and GAS (\% OAG)} = 100 - \% \text{ UC} - \% \text{ PASP} - \% \text{ ASP}$$

$$\% \text{ CONVERSION} = 100 - \% \text{ UC}$$

In the above expressions MAF coal refers to moisture and ash-free coal.

In the presence of hydrogen sulfide the above calculations were not effected. If pyrite was present

though, modifications were necessary. The weight of ash (WT. ASH) in the above expressions was generated from unreacted coal in the THF-insolubles. When pyrite was present the total amount of ash ( $ASH_T$ ) included not only coal-derived ash ( $ASH_C$ ) but also ash generated from the added pyrite. It was thus necessary to determine the amount of coal-derived ash. The following expressions enabled this quantity to be calculated:

$$\frac{WT. \text{ ADD ASH}}{WT. \text{ COAL ASH}} = \frac{WT. \text{ CAT}}{WT. \text{ COAL}} * \frac{HOFC}{PASH}$$

IN REACTOR

$$WT. \text{ ASH}_C = (WT. \text{ ASH}_T) * \left( \frac{1}{1 + \frac{WT. \text{ ADD ASH}}{WT. \text{ COAL ASH}}} \right)$$

The term WT. CAT represented the weight of catalyst in the reactor at completion of the run. Pyrite in the course of the run reacted according to the reaction:



The initial weight of pyrite charged to the reactor was thus different from the weight of catalyst at completion of the run due to chemical reaction of pyrite. The composition of the catalyst upon completion of the run was determined by Mossbauer Spectroscopy (see figure 20). The weight of catalyst was able to be calculated from the iron/sulfur



Fe<sub>0.89</sub>S: 69%

FeS<sub>2</sub> : 31%

Figure 20. Mossbauer analysis of run 14.

compositional information determined by the Mossbauer analysis.

HOFC is the highest oxide correction factor. The catalyst represented by WT. CAT was assumed to form its highest oxide,  $\text{Fe}_2\text{O}_3$ , upon ashing. HOFC was the value which took into account the weight change exhibited by the catalyst in forming the highest oxide (i.e. the theoretical percent ash of the catalyst).

The amount of organic material in the THF-insolubles was calculated by subtracting the total weight of ash from the total weight of THF-insolubles. This number was then corrected for the weight change exhibited by the catalyst upon ashing. The resulting relation was:

$$\text{THFI ORGANICS (THFIO)} = \text{THFI (1-ASH)} - (\text{WT. CAT}) * (1-\text{HOFC})$$

The following revised expressions were used in the calculation of runs in which pyrite was added:

$$\% \text{ UC} = \frac{\text{THFIO}}{\text{ASH}_C} * \left( \frac{\text{WT. ASH}}{\text{WT. MAF COAL}} \right) * 100$$

$$\% \text{ PASP} = \frac{(\text{TI} - \text{THFI})}{\text{ASH}_C} * \left( \frac{\text{WT. ASH}}{\text{WT. MAF COAL}} \right) * 100$$

$$\% \text{ ASP} = \frac{(\text{PI} - \text{TI})}{\text{ASH}_C} * \left( \frac{\text{WT. ASH}}{\text{WT. MAF COAL}} \right) * 100$$

$$\% \text{ OAG} = 100 - \% \text{ UC} - \% \text{ PASH} - \% \text{ ASP}$$

$$\% \text{ CONVERSION} = 100 - \% \text{ UC}$$

Constant Weight Ratio Method (CWR)

The following assumptions were made when using the CWR calculation procedure:

- 1) uniform and representative samples
- 2) constant percent of coal + coal products in the reactor

The CWR method was based on the ratio of the weight of coal fed to the reactor to the weight of total material (coal + pyrite + tetralin) fed to the reactor. This ratio was assumed to be constant throughout the experimental run and in the product samples. The following expressions were used to calculate the various product yields for a system in which pyrite was present:

$$\text{CS} = \left( \frac{\text{gm coal injected into reactor}}{\text{gm (coal + pyrite + tetralin in reactor)}} \right) * \text{gm product sample}$$

$$\text{CATS} = \left( \frac{\text{gm pyrite injected into reactor}}{\text{gm (coal + pyrite + tetralin in reactor)}} \right) * \text{gm product sample}$$

$$\% \text{ OIL} = \frac{(\text{CS} + \text{CATS} - \text{PI})}{\text{CS} * (1 - \text{PASH})} * 100$$

$$\% \text{ ASP} = \frac{(\text{PI} - \text{TI})}{\text{CS} * (1 - \text{PASH})} * 100$$

$$\% \text{ PASP} = \frac{(\text{TI} - \text{THFI})}{\text{CS} * (1 - \text{PASH})} * 100$$

$$\% \text{ UC} = 100 - \% \text{ ASP} - \% \text{ PASP}$$

$$\% \text{ CONVERSION} = 100 - \% \text{ UC}$$

The term CS represented the grams of coal present in the product samples while the term CATS represented the grams of pyrite present in the product samples. The reaction of pyrite and the accompanying weight change were not considered here. Little error is introduced though as the weight change was not significant.

Modification of the above equations for the calculation of base runs and H<sub>2</sub>S additive runs is accomplished by eliminating the CATS term.

#### Ash Segregation Correction Factor

Additional modifications to both calculation methods were necessary to account for solids separation in the runs with added pyrite. Solids settled out and adhered to the reactor walls. The reactor wash samples thus had a disproportionately high percentage of ash compared to the product samples. A correction factor was used to account for the ash segregation between the reactor wash sample and the product samples.

The ash segregation correction factor for the ATE

method was calculated as follows:

$$O = \frac{\% \text{ of total THFI}}{\text{organics in product samples}} = \frac{\text{THFI} * (1 - \text{ASH})}{(\text{THFI} * (1 - \text{ASH}) + \text{RW} * (1 - \text{RW ASH}))}$$

$$A = \frac{\% \text{ of total ash}}{\text{in product samples}} = \frac{\text{THFI} * \text{ASH}}{\text{THFI} * \text{ASH} + \text{RW} * (\text{RW ASH})}$$

$f' = O/A =$  ash segregation correction factor for ATE method

RW represented the weight of the reactor wash sample and RW ASH is the % ash of RW divided by 100.

The "f'" correction factor was incorporated into the ATE calculations by multiplying it by the  $\text{ASH}_C$  term. In this way the ash generated from the unreacted coal in the THF-insolubles could be corrected for ash segregation which occurred upon transferring the product samples from the reactor.

The correction factor for the CWR method was arrived at as follows:

$$M = \frac{\% \text{ of total mass}}{\text{in product samples}} = \frac{\text{gm product sample}}{\text{total mass charged to reactor}}$$

$$A = \frac{\% \text{ of total ash}}{\text{in product samples}} = \frac{\text{THFI} * \text{ASH}}{\text{THFI} * \text{ASH} + \text{RW} * (\text{RW ASH})}$$

$f' \text{ mass} = A/M =$  ash segregation correction factor for CWR method

The "f" mass" correction factor was incorporated into the CWR calculations by multiplying it by the CATS term. This allowed the assumed amount of pyrite in the pentane insolubles to be corrected for the occurrence of ash segregation.

## DISCUSSION OF RESULTS

A discussion of the results obtained in this study is presented in this section. Experimental data that have been excluded are also discussed followed by a discussion of the source of errors. Yields of products are presented and general trends are identified. Reaction mechanisms that may account for the observed results are proposed.

### Excluded Data

Data from certain experimental runs were excluded for various reasons as shown in table 10.

### Processing Errors

Fluctuations in reaction temperature were the greatest source of error. Shalabi (1977) has documented the strong effects of temperature on coal conversion. Upon slurry injection, the reaction temperature was approximately 25°C lower than the desired reaction temperature. Recovery to within 5°C of the desired reaction temperature was almost immediate. The temperature oscillated about the set point with an amplitude of  $\pm 5^\circ\text{C}$  and a period of 6½ minutes. The oscillation was due to the lag in the control system with respect to the surface temperature of the heater and the temperature sensed by the thermocouple in the thermowell of the reactor.

Table 10

## Excluded Experimental Runs

<u>Run No.</u>	<u>Residence Time</u>	<u>Additive</u>	<u>Reason for Excluding Data</u>
R1	10	none	Product slurry contaminated with acetone.
R3	60	none	Overall conversion was 20% below comparable runs.
R5	10	none	Pentane washes were not performed.
R12	10	2% H <sub>2</sub> S	Mass recovery was less than 85%.
R21	60	10% H <sub>2</sub> S	
R13	60	pyrite	THF was used in place of toluene
R18	60	none	Material could not be injected due to a plug in a line.
R24	60	10% H <sub>2</sub> S/pyrite	
R39	10	none	
R20	10	pyrite	Temperature controller not properly calibrated resulting in a temperature 25°C low
R33	10	none	Evidence of a memory effect
R35	10	none	
R37	10	none	

Pressure variations were another source of error. The desired reaction pressure was 2000 psig. Due to the variations in the amount of slurry injected and the temperature oscillations, pressure deviations were as great as ten percent. The effect of these pressure variations on coal conversion was assumed to be minimal since the base runs (no additive) experienced similar pressure variations and gave reproducible results.

Tarrer et al. (1976) discovered that catalyst from previous runs effected the conversion of coal in subsequent runs. To avoid this memory effect, base runs were made after runs using pyrite as a catalyst.

#### Effect of Residence Time

An increase in residence time from 10 to 60 minutes increased the conversion from 31.64% to 64.81% for the base runs (no additives). Conversion also increased with increasing residence time for the additive runs. An increase in conversion with time of 19.36% occurred with 2% H<sub>2</sub>S, 26.21% with 5% H<sub>2</sub>S, 29.63% with 10% H<sub>2</sub>S, 16.71% with pyrite, 30.96% with the pyrite/2% H<sub>2</sub>S mixture, 27.53% with the pyrite/5% H<sub>2</sub>S mixture, and 27.03% with the pyrite/10% H<sub>2</sub>S mixture. Table 11 lists the total conversions (to THF-solubles) and the results are shown graphically in figure 21.

Oil, asphaltene, and preasphaltene yields also increased as the residence time was increased as shown in tables 12, 13, and 14. Figures 22, 23, and 24 represent the product yields graphically.

The above results are consistent with the results obtained by Eaton (1981), Shalabi (1977), and Hegarty (1978).

#### Effect of Additives

Hydrogen sulfide, in the absence of any added pyrite, increased the overall conversion at both 10 and 60 minute residence times. The magnitude of the increase was about the same at both residence times for all hydrogen sulfide concentrations except for the 60 minute residence time involving 2% H<sub>2</sub>S addition, where a much smaller increase was observed (see figure 21).

Oil yields were not greatly effected by the presence of H<sub>2</sub>S. A slight increase in oil yields was observed at a residence time of 60 minutes and H<sub>2</sub>S concentration of 5 and 10 percent (see figure 22).

Asphaltene yields increased by a constant amount for the range of H<sub>2</sub>S concentrations employed at a residence time of 10 minutes. A smaller increase was noted for the 60 minute residence time except for the 2% H<sub>2</sub>S concentration, where no increase was observed (see figure 23).

A significant increase in the preasphaltene fraction

Table 11

Overall Conversion\*  
(%, maf basis)

	<u>Residence Time (min.)</u>	
	<u>10</u>	<u>60</u>
Base Run	31.64	64.81
2% H <sub>2</sub> S	48.27	67.63
5% H <sub>2</sub> S	52.87	79.08
10% H <sub>2</sub> S	49.64	79.27
FeS <sub>2</sub>	51.21	67.92
FeS <sub>2</sub> /2% H <sub>2</sub> S	52.98	83.94
FeS <sub>2</sub> /5% H <sub>2</sub> S	55.75	83.28
FeS <sub>2</sub> /10% H <sub>2</sub> S	50.05	77.08

\*Measured as THF-solubles

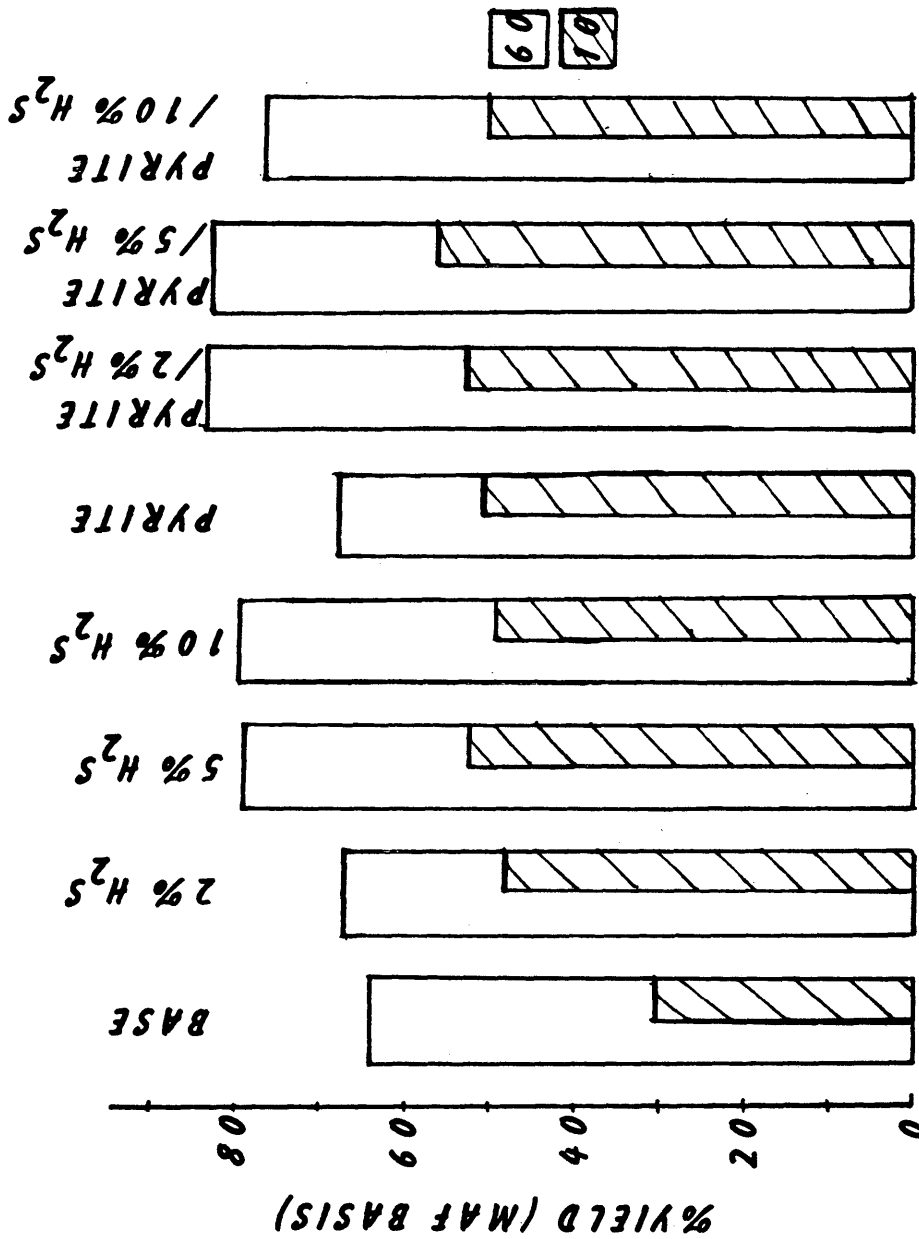


Figure 21. Effect of Time and Additives on Conversion

Table 12

Oil Yields  
(%, maf basis)

	<u>Residence Time (min.)</u>	
	<u>10</u>	<u>60</u>
Base Run	16.50	25.49
2% H <sub>2</sub> S	14.03	25.04
5% H <sub>2</sub> S	17.73	29.95
10% H <sub>2</sub> S	14.37	29.43
FeS <sub>2</sub>	22.01	25.82
FeS <sub>2</sub> /2% H <sub>2</sub> S	18.55	32.36
FeS <sub>2</sub> /5% H <sub>2</sub> S	20.53	32.31
FeS <sub>2</sub> /10% H <sub>2</sub> S	20.56	32.65

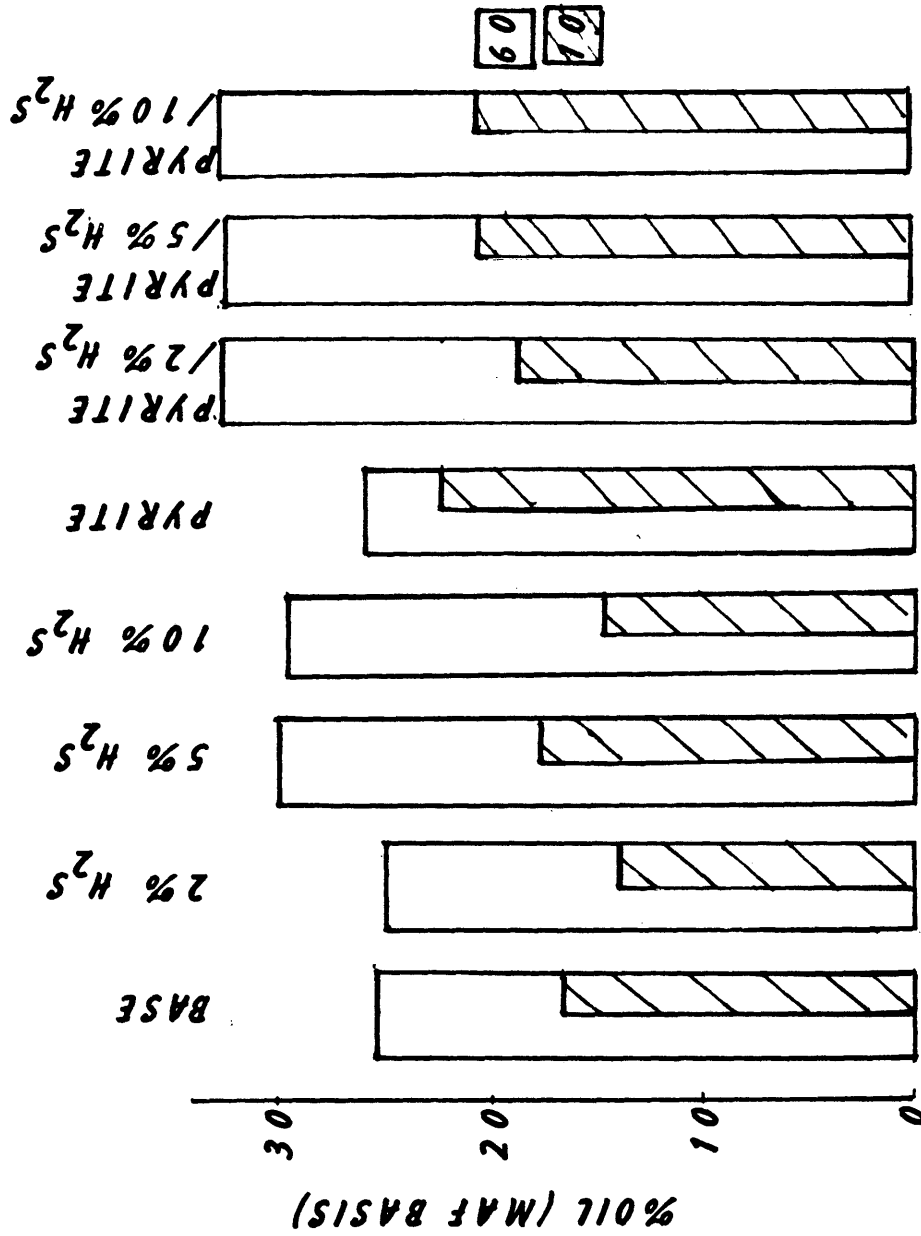


Figure 22. Effect of Time and Additives on Oil Yields

Table 13

Asphaltene Yields  
(%, maf basis)

	<u>Residence Time (min.)</u>	
	<u>10</u>	<u>60</u>
Base Run	8.07	17.22
2% H <sub>2</sub> S	12.94	17.57
5% H <sub>2</sub> S	12.61	20.67
10% H <sub>2</sub> S	13.72	20.82
FeS <sub>2</sub>	11.49	19.15
FeS <sub>2</sub> /2% H <sub>2</sub> S	12.06	19.65
FeS <sub>2</sub> /5% H <sub>2</sub> S	13.22	22.53
FeS <sub>2</sub> /10% H <sub>2</sub> S	12.68	21.24

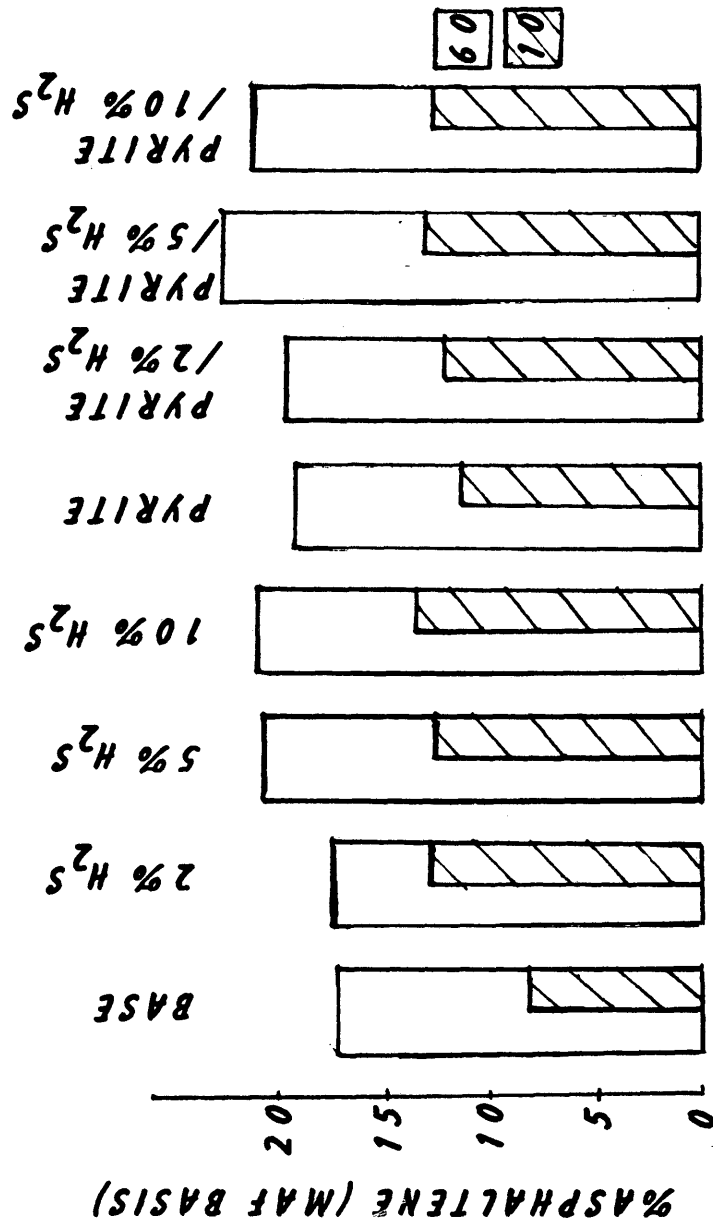


Figure 23. Effect of Time and Additives on Asphaltene Yields

Table 14

PREASPHALTENE YIELDS  
(%, maf basis)

	<u>Residence Time (min.)</u>	
	<u>10</u>	<u>60</u>
Base Run	7.07	22.11
2% H <sub>2</sub> S	21.30	25.02
5% H <sub>2</sub> S	22.53	28.47
10% H <sub>2</sub> S	21.55	29.01
FeS <sub>2</sub>	17.71	22.96
FeS <sub>2</sub> /2% H <sub>2</sub> S	22.36	31.93
FeS <sub>2</sub> /5% H <sub>2</sub> S	22.01	28.44
FeS <sub>2</sub> /10% H <sub>2</sub> S	16.87	23.19

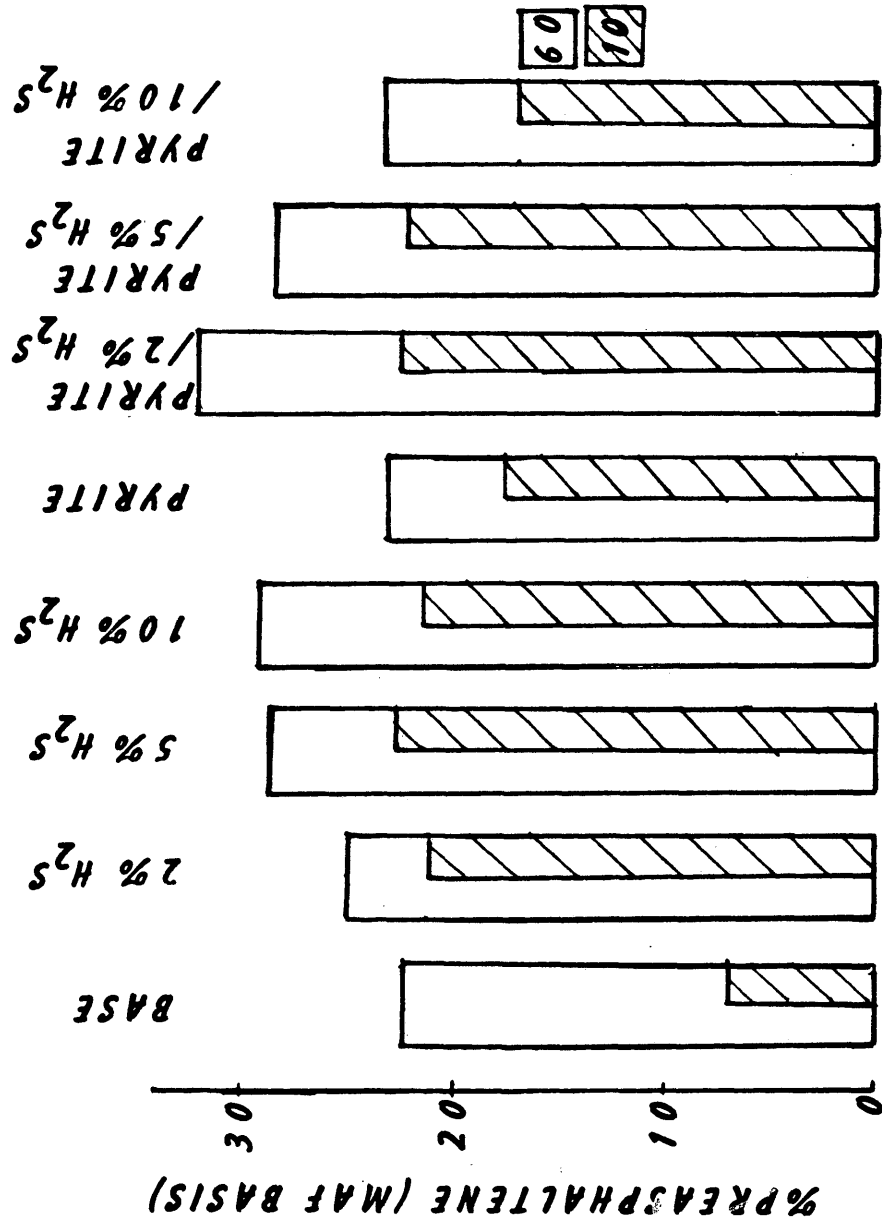


Figure 24. Effect of Time and Additives on Preasphaltene Yields

was seen at the 10 minute residence time. The magnitude of the increase was the same for all  $H_2S$  concentrations. A smaller increase was observed at the 60 minute residence time and appeared to increase as the  $H_2S$  concentration increased (see figure 24). Due to errors in the system, the trend observed with  $H_2S$  concentrations may not be significant.

The addition of pyrite to coal significantly increases the overall conversion at a 10 minute residence time. A smaller increase in conversion is observed at a 60 minute residence time (see figure 21). Oil yields are increased by adding pyrite for a 10 minute residence time, however there was no increase in oil yields indicated at a 60 minute residence time (see figure 22). Slight increases in asphaltene yields were observed at both residence times (see figure 23). There was a significant increase in preasphaltene yields in the presence of pyrite at 10 minutes and little or no effect on the preasphaltene fraction at 60 minutes (see figure 24).

In the presence of  $H_2S$  and pyrite there were no discernable effects different from that of pyrite alone at a 10 minute residence time. Increasing the residence time to 60 minutes significantly increased the oil yields and thus the conversion (see figures 21 and 22). Asphaltene

yields were not greatly effected over that of pyrite alone. A slight increase at  $H_2S$  concentrations of 5 and 10 percent was observed (see figure 23). Preasphaltene yields increased for  $H_2S$  concentrations of 2 and 5 percent. An increase in preasphaltene yields was not observed at a 10%  $H_2S$  concentration. The preasphaltene fraction declined with increasing  $H_2S$  concentration in the presence of pyrite, whereas it appeared to increase in the absence of pyrite (see figure 24).

Mossbauer spectroscopy was used to monitor the conversion of pyrite to pyrrhotite and to establish the stoichiometry of the pyrrhotite that was formed during reaction. The application of  $^{57}Fe$  Mossbauer spectroscopy to determine pyritic and total iron concentrations in coal has been explored by Williamson et al. (1981). Due to the complexity of the Mossbauer spectra that were obtained. The accuracy of the numbers obtained were in question. However, the general trends that were found were accurate.

Pyrrhotite was made from pyrite in run 17. Mossbauer analysis showed the pyrrhotite to be 97%  $Fe_{.90}S$  and 3%  $FeS_2$  (see Appendix C). This pyrrhotite was used to determine a f-value by cooling the sample to liquid nitrogen temperatures and comparing the spectra at room temperature and liquid nitrogen temperature. The f-value for

pyrrhotite was found to be 0.32. A f-value of 0.53 was used for pyrite.

The following trends were observed with Mossbauer spectroscopy as shown in table 15.

- 1) The pyrrhotite fraction decreased with increasing  $H_2S$  content.
- 2) The pyrrhotite fraction was always larger for 60 minute versus 10 minute residence time.
- 3) Stoichiometry of the pyrrhotite ( $Fe_xS$ ) varied with  $H_2S$  content. As the  $H_2S$  content increased, x decreased.

It was also apparent from observing the Mossbauer spectra that the non-magnetic phase was not pure pyrite as has been assumed in the calculations. The purity is uncertain. The non-magnetic phase may be amorphous  $Fe_2S_3$ .

Hydrogen sulfide was shown to effect coal conversion as was pyrite. Pyrite in the presence of  $H_2S$  was an effective catalyst at a residence time of 60 minutes but  $H_2S$  had no contributory effect at a 10 minute residence time in this system.

As shown by Mossbauer spectroscopy the stoichiometry of the pyrrhotite is a function of the  $H_2S$  content. It may be that pyrite is able to be maintained in its active

Table 15

## Quantitative Mossbauer Results

Run No.	Residence Time	H <sub>2</sub> S Content (%)	Non-Magnetic Phase 6Fe Fraction	Magnetic Phase (2Fe Fraction)	X-value (Fe <sub>x</sub> S)
R42	10	0	19	81	.900
R16	10	0	29	71	.892
R36	10	2	26	74	.894
R32	10	5	30	70	.891
R27	10	10	41	59	.885
R14	60	0	25	75	.891
R38	60	2	16	84	.899
R34	60	5	24	76	.891
R25	60	10	27	73	.886

sulfide catalytic form at a residence time of 10 minutes and therefore, addition of  $H_2S$  is unnecessary. Increasing the residence time to 60 minutes, as shown by Mossbauer analysis, increased the pyrrhotite fraction. The pyrrhotite fraction decreased with increasing  $H_2S$  content. Therefore, the presence of  $H_2S$  was instrumental in maintaining an active sulfide form. A minimum amount of  $H_2S$  was necessary to maintain the catalyst in its most active form. In the case of the pyrite runs with  $H_2S$  addition at a 10 minute residence time, this minimum amount was met and exceeded for the entire range of  $H_2S$  concentrations tested.

There are several possible mechanisms by which  $H_2S$  may catalyze hydrogen transfer reactions. The first of these is by maintenance of an active sulfide catalyst and has been discussed in relation to pyrite which is a known hydrogenation catalyst for coal liquefaction. Hydrogen sulfide may also react with non-pyritic iron to form an active sulfide catalyst. The Energy Mine coal used in this study had an approximate total iron content of 0.13%. Approximately two-thirds of the total iron was non-pyritic iron and one-third pyrite iron. See Appendix D for the calculation of these values which are based on the ash analysis and sulfur analysis.

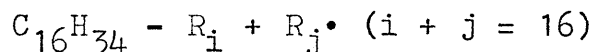
Rebick (1981) studied the homogeneous catalytic participation by  $H_2S$  in a quartz flow reactor at  $500^\circ C$ . Pyrolysis of n-hexadecane was conducted in the presence of 0-0.6 atm.  $H_2S$ . Hydrogen sulfide had three main effects on the pyrolysis as compared with a nitrogen atmosphere:

- 1) Selectivity to methane, ethane, and ethylene was decreased.
- 2) Butane and higher paraffins appeared in the reaction products.
- 3)  $H_2S$  increased the overall rate of hexadecane disappearance.

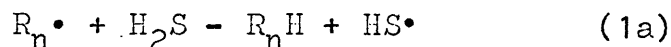
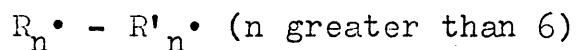
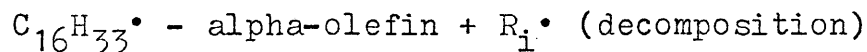
Sulfur compounds were not able to be detected in the liquid products suggesting that noncatalytic participation of  $H_2S$  was unlikely.

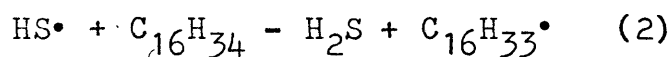
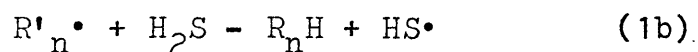
The effect of  $H_2S$  on the pyrolysis of n-hexadecane was explained by the following mechanism:

initiation

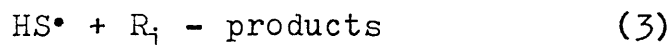


propagation





termination



where  $R_n \cdot$  is a primary radical and  $R'_n \cdot$  is a secondary radical. Reactions 1 and 2, in effect, catalyze the hydrogen transfer reaction. According to the proposed mechanism, if the hydrogen transfer step is rate limiting, the introduction of  $H_2S$  should increase the cracking rate. This was the case as shown in figure 25. There was a half-order dependence on  $H_2S$  concentration and a first order dependence on n-hexadecane. The non-linearity of the relation in figure 25 was consistent with the view that uncatalyzed and catalyzed mechanisms are not additive but the latter replaces the former as the  $H_2S$  concentration increases.

Drawing a parallel between n-hexadecane pyrolysis and coal pyrolysis indicates that homogeneous catalysis by hydrogen sulfide is indeed possible and can produce significant changes in product selectivity and rate of reaction. Free radicals formed by pyrolysis of coal could interact with  $H_2S$  in the following manner:

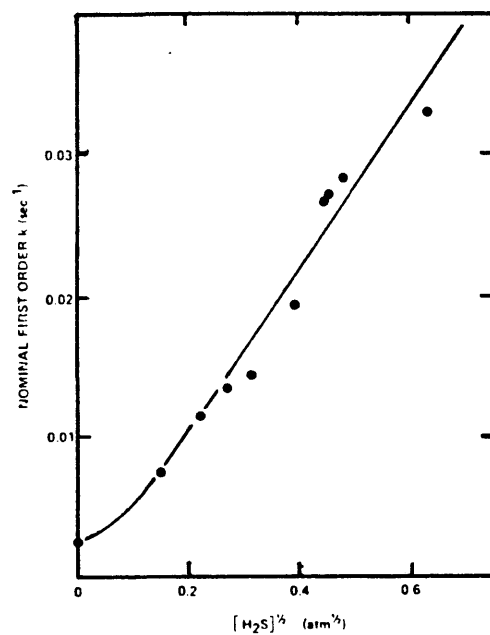
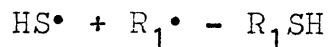
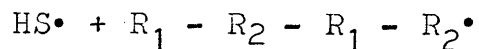
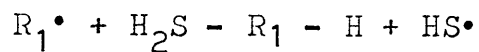
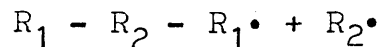


Figure 25. Half-order dependence of  $H_2S$  on the rate of decomposition of n-hexadecane



where  $R_1 - R_2$  is a coal macromolecule. A similar reactor sequence could be written for free radical  $R_2^\bullet$ . This mechanism predicts that the sulfur content of coal liquefaction products could increase. A small, perhaps insignificant, increase in the sulfur content of the oil, asphaltene, and preasphaltene fractions was observed. A factor of two or three increase in sulfur content was observed in the THF-insoluble (insoluble organic matter plus mineral matter) fraction.

## CONCLUSIONS

The conclusion of this study are as follows:

- 1) Pyrite was an effective coal hydrogenation catalyst.
- 2) Hydrogen sulfide enhanced the overall conversion in the presence of pyrite at a 60 minute residence time but not for 10 minutes.
- 3) Hydrogen sulfide catalyzes coal conversion.
- 4) Hydrogen sulfide may catalyze hydrogen transfer reactions by homogeneous and/or heterogeneous mechanisms.

## RECOMMENDATIONS

- 1) Continue the disposable additive screening study with the procedure developed by Eaton (1981). Possible additives to be studied are pyrite with tin added and pyrrhotites.
- 2) Study the effect of impregnating pyrite instead of mechanically mixing pyrite with the coal. Possible methods of impregnation are ball milling of a coal/pyrite mixture, solvent deposition, perhaps with water or another solvent, and vapor-phase deposition of pyrite. The idea behind impregnating with pyrite is to increase the surface area of the pyrite.
- 3) Test promising additives using a continuous flow reactor.
- 4) Investigate the kinetics of marcarsite versus pyrite catalysis as the pyrite used in this study may have as much as 20% marcarsite.
- 5) Follow up on the possibility of using  $H_2S$  as a homogeneous catalyst.

## LITERATURE CITED

- Berkowitz, N., 1979, An Introduction to Coal Technology, Academic Press, New York, New York.
- Bicket, T.C., Stohl, F.V., and Thomas, M.G., 1980, Coal Liquefaction Process Research, Sandia National Laboratories Energy Report Sand-80-2793.
- Donath, E.E. and Hoering, M., 1977, Early Coal Hydrogenation Catalysis, Fuel Processing Technology, 1, 3-20.
- Eaton, W.J., 1981, Disposable Additive Screening Study in Coal Liquefaction, Unpublished Thesis, Colorado School of Mines.
- Garg, D. and Givens, E.N., 1982, Pyrite Catalysis in Coal Liquefaction, Ind. Eng. Chem. Process Des. Dev., 21 (1), 113-117.
- Gates, B.C., 1979, Liquefied Coal Hydrogenation, Chemtech, 97-102.
- Granoff, B. and Thomas, M.G., 1977, Mineral Matter Effects in Coal Liquefaction, 1. Autoclave Screening Study, American Chemical Society Division of Fuel Chemistry Preprints, 22 (6), 183-193.
- Granoff, B. and Traeger, R.K., 1978, Mineral Matter Effects in Coal Liquefaction, Paper Presented at the 85th National Meeting of AIChE, Philadelphia, Pa.
- Guin, J.A., Tarrer, A.R., Prather, J.W., Johnson, D.R., and Lee, J.M., 1978, Effects of Coal Minerals on the Hydrogenation, Desulfurization, and Solvent Extraction of Coal, Ind. Eng. Chem. Process Des. and Dev., 17 (2), 118-126.
- Guin, J.A., Tarrer, A.R., Lee, J.M., Lo, L., Curtis, C.W., Further Studies of the Catalytic Activity of Coal Minerals in Coal Liquefaction. 1. Verification of Catalytic Activity of Mineral Matter by Model Compound Studies, Ind. Eng. Chem. Process Des. Dev., 18 (3), 371-376.

## LITERATURE CITED

- Guin, J.A., Lee, J.M., Fan, C.W., Curtis, C.W., Lloyd, J.L., and Tarrer, A.R., 1980, Pyrite-Catalyzed Hydrogenolysis of Benzothiophene at Coal Liquefaction Conditions, *Ind. Eng. Chem. Process Des. Dev.*, 19 (3), 440-446.
- Hegarty, M., 1978, The Effects of Mineral Matter in Donor Solvent Coal Conversion, Unpublished Thesis, Colorado School of Mines.
- Kawa, W., Hiteshue, R.W., Anderson, R.B., and Greenfield, H., 1960, Reactions of Iron and Iron Compounds with Hydrogen and Hydrogen Sulphides, Bureau of Mines Report of Investigations 5690.
- Kawa, W., and Hiteshue, R.W., 1963, Iron-Catalyzed Hydrogenation of Phenyl Ether, Benzyl Ether, and Phenyl Sulfide, Bureau of Mines Report of Investigations 6179.
- Lee, J.M., Tarrer, A.R., Guin, J.A., and Prather, J.W., 1977, The Selectivity of Coal Minerals as Catalysts in Coal Liquefaction and Hydrodesulfurization, American Chemical Society Division of Fuel Chemistry Preprint, 22 (6), 120-130.
- Lowry, H.H., 1945, *Chemistry of Coal Utilization*, Vol. II: New York, Wiley, 1751.
- Montano, P.A. and Granoff, B., 1980, Stoichiometry of Iron Sulphides in Liquefaction Residues and Correlation with Conversion, *Fuel*, 59 (3), 214-216.
- Montano, P.A., Bommannavar, A.S., and Shah, V., 1981, Mossbauer Study of Transformations of Pyrite Under Conditions of Coal Liquefaction, *Fuel*, 60 (8), 703-711.
- Montano, P.A., Vaishnava, P.P., King, J.A., and Eisentrout, E.N., 1981a, Mossbauer Study of Decomposition of Pyrite in Hydrogen, *Fuel*, 60 (8), 712-716.
- Moroni, E.C. and Fischer, R.H., 1980, Disposable Catalysts for Coal Liquefaction, American Chemical Society Division of Fuel Chemistry Preprints, 25 (1), 16.

## LITERATURE CITED

- Mukherjee, D.K. and Chowdhury, P.B., 1976, Catalytic Effect of Mineral Matter Constituents in a North Assam Coal on Hydrogenation, *Fuel*, 55 (1), 4-8.
- Neavel, R.C., 1976, Liquefaction of Coal in Hydrogen-Donor and Non-Donor Vehicles, *Fuel*, 55 (7), 237-242.
- Rapoport, I.B., 1955, Chemistry and Technology of Synthetic Liquid Fuels, Second Ed. Moskow. Translation Published for the National Science Foundation, 1962, Washington, D.C. by the Israel Program for Scientific Translations, Jerusalem, 96-97.
- Rebick, C., 1981, H<sub>2</sub>S Catalysis of n-hexadecane Pyrolysis, *Ind. Eng. Chem. Fundam.*, 20 (1), 54-59.
- Richardson, J.T., Thermo-Magnetic Studies of Iron Compounds in Coal Char, 1972, *Fuel*, 51, 150.
- Ruether, J.A., Kinetics of Heterogenously Catalyzed Coal Hydroliquefaction, 1977, *Ind. Eng. Chem. Process Des. Dev.*, 16 (2), 249-253.
- Shalabi, M.A., 1977, Kinetics of Coal Liquefaction to Preasphaltenes, Asphaltene, and Oils, Unpublished Ph.D. Thesis, Colorado School of Mines.
- Tarrer, A.R., Guin, J.A., Pitts, W.S., Henley, J.P., Prather, J.W., and Styles, G.A., 1976, Effects of Coal Minerals on Reaction Rates During Coal Liquefaction, *American Chemical Society Division of Fuel Chemistry Preprints*, 21 (5), 59-77.
- Weller, S.W., 1956, Catalysis in the Liquid-Phase Hydrogenation of Coal and Tar, Ch. 7 in *Catalysis*, Vol. 4, P.H. Emmett (Ed.), Reinhold, New York, New York.
- Williamson, D.L., Guettinger, T.W., and Dickerhoof, D.W., 1981, Quantitative Investigations of Pyrite and Coal, *Advances in Chemistry Series*, No. 194, Mossbauer Spectroscopy and its Chemical Applications.
- Wright, C.H. and Severson, D.E., 1972, Experimental Evidence for Catalytic Activity in Coal Minerals, *American Chemical Society Division of Fuel Chemistry Preprints*, 16 (2), 68-88.

APPENDIX A

RAW DATA

RUN NUMBER: R2

CONDITIONS:

Residence Time : 10 min. Additive: none  
 Coal Injected : 19.38 gm  
 Injection Pressure: 1650 psig  
 Maximum Pressure : 2015 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 183.67  
 Total Weight of Pentane Insolubles (gm): 15.16  
 Total Weight of Toluene Insolubles (gm): 13.99  
 Total Weight of THF Insolubles (gm) : 13.15  
 Average % ASH in THF Insolubles : 6.73  
 % ASH in Parent Coal : 5.41

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	7.08		15.89
% Asphaltene	7.64		6.96
% Preasphaltene	5.42		4.93
% Conversion	20.14		27.79

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	98.806
CO <sub>2</sub>	.680
CH <sub>4</sub>	.145
CO	.347

RUN NUMBER: R4

CONDITIONS:

Residence Time : 60 min.                    Additive: none  
 Coal Injected : 19.22 gm  
 Injection Pressure: 1850 psig  
 Maximum Pressure : 1950 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 185.24  
 Total Weight of Pentane Insolubles (gm): 13.62  
 Total Weight of Toluene Insolubles (gm): 10.89  
 Total Weight of THF Insolubles (gm) : 7.17  
 Average % ASH in THF Insolubles : 12.46  
 % ASH in Parent Coal : 5.38

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	18.95		26.82
% Asphaltene	17.39		15.81
% Preasphaltene	23.69		21.54
% Conversion	60.03		64.17

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	97.783
CO <sub>2</sub>	.923
CH <sub>4</sub>	.599
CO	.616

RUN NUMBER: R6

CONDITIONS:

Residence Time : 60 min.            Additive: none  
 Coal Injected : 18.86 gm  
 Injection Pressure: 1640 psig  
 Maximum Pressure : 2094 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 183.89  
 Total Weight of Pentane Insolubles (gm): 13.70  
 Total Weight of Toluene Insolubles (gm): 10.81  
 Total Weight of THF Insolubles (gm) : 7.18  
 Average % ASH in THF Insolubles : 12.13  
 % ASH in Parent Coal : 5.40

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	15.92		24.28
% Asphaltene	18.94		17.18
% Preasphaltene	23.79		21.57
% Conversion	58.65		63.03

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	97.602
CO <sub>2</sub>	1.002
CH <sub>4</sub>	.675
CO	.646

RUN NUMBER: R7CONDITIONS:

Residence Time : 10 min. Additive: none  
 Coal Injected : 17.07 gm  
 Injection Pressure: 1575 psig  
 Maximum Pressure : 1868 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 181.50  
 Total Weight of Pentane Insolubles (gm): 13.36  
 Total Weight of Toluene Insolubles (gm): 12.07  
 Total Weight of THF Insolubles (gm) : 10.75  
 Average % ASH in THF Insolubles : 7.40  
 % ASH in Parent Coal : 5.45

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	10.37		17.62
% Asphaltene	9.20		8.50
% Preasphaltene	9.42		8.70
% Conversion	28.99		34.81

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	98.729
CO <sub>2</sub>	.659
CH <sub>4</sub>	.163
CO	.406

RUN NUMBER: R8

CONDITIONS:

Residence Time : 10 min. Additive: none  
 Coal Injected : 18.94 gm  
 Injection Pressure: 1629 psig  
 Maximum Pressure : 2000 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 187.63  
 Total Weight of Pentane Insolubles (gm): 15.23  
 Total Weight of Toluene Insolubles (gm): 13.67  
 Total Weight of THF Insolubles (gm) : 12.28  
 Average % ASH in THF Insolubles : 7.31  
 % ASH in Parent Coal : 5.48

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	7.53		16.98
% Asphaltene	10.07		9.10
% Preasphaltene	8.97		8.11
% Conversion	26.56		34.19

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	98.562
CO <sub>2</sub>	.779
CH <sub>4</sub>	.182
CO	.455

RUN NUMBER: R9

CONDITIONS:

Residence Time : 60 min. Additive: none  
 Coal Injected : 20.14 gm  
 Injection Pressure: 1645 psig  
 Maximum Pressure : 2189 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 188.07  
 Total Weight of Pentane Insolubles (gm): 14.08  
 Total Weight of Toluene Insolubles (gm): 11.16  
 Total Weight of THF Insolubles (gm) : 7.22  
 Average % ASH in THF Insolubles : 12.52  
 % ASH in Parent Coal : 5.39

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	17.11		27.24
% Asphaltene	18.44		16.33
% Preasphaltene	24.70		21.88
% Conversion	60.25		65.44

GAS ANALYSIS: Not Available

RUN NUMBER: R10

CONDITIONS:

Residence Time : 10 min. Additive: none  
 Coal Injected : 18.67 gm  
 Injection Pressure: 1910 psig  
 Maximum Pressure : 2100 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 188.56  
 Total Weight of Pentane Insolubles (gm): 14.96  
 Total Weight of Toluene Insolubles (gm): 13.45  
 Total Weight of THF Insolubles (gm) : 12.17  
 Average % ASH in THF Insolubles : 7.55  
 % ASH in Parent Coal : 5.50

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	11.16		16.42
% Asphaltene	9.55		9.02
% Preasphaltene	8.10		7.65
% Conversion	28.82		33.09

GAS ANALYSIS: Not Available

RUN NUMBER: R11

CONDITIONS:

Residence Time : 60 min. Additive: 2% H<sub>2</sub>S  
 Coal Injected : 18.87 gm  
 Injection Pressure: 1653 psig  
 Maximum Pressure : 1840 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 177.04  
 Total Weight of Pentane Insolubles (gm): 13.10  
 Total Weight of Toluene Insolubles (gm): 10.25  
 Total Weight of THF Insolubles (gm) : 6.21  
 Average % ASH in THF Insolubles : 14.72  
 % ASH in Parent Coal : 5.53

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	22.35		25.04
% Asphaltene	18.16		17.57
% Preasphaltene	25.86		25.02
% Conversion	66.37		67.63

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	
H <sub>2</sub> S	
CO <sub>2</sub>	
C <sub>2</sub> H <sub>6</sub>	
CH <sub>4</sub>	
CO	

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	96.503
C <sub>3</sub> H <sub>8</sub>	.161
H <sub>2</sub> S	.281
CO <sub>2</sub>	1.497
C <sub>2</sub> H <sub>6</sub>	.105
CH <sub>4</sub>	.839
CO	.674

RUN NUMBER: R14

CONDITIONS:

Residence Time	: 60 min.	Additive:	pyrite
Coal Injected	: 19.33 gm	Pyrite Injected:	1.66 gm
Injection Pressure:	1700 psig		
Maximum Pressure	: 1940 psig		

PRODUCT ANALYSIS

Total Weight of Samples (gm)	:	189.17
Total Weight of Pentane Insolubles (gm):		15.01
Total Weight of Toluene Insolubles (gm):		11.79
Total Weight of THF Insolubles (gm)	:	7.93
Average % ASH in THF Insolubles	:	21.03
% ASH in Parent Coal	:	5.53

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	7.56		25.61
% Asphaltene	22.73		19.20
% Preasphaltene	27.24		23.02
% Conversion	57.54		67.82

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	98.517
H <sub>2</sub> S	.046
CO <sub>2</sub>	.678
CH <sub>4</sub>	.374
CO	.328

RUN NUMBER: R15

CONDITIONS:

Residence Time : 60 min. Additive: none  
 Coal Injected : 19.97 gm  
 Injection Pressure: 1650 psig  
 Maximum Pressure : 1850 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 188.22  
 Total Weight of Pentane Insolubles (gm): 14.30  
 Total Weight of Toluene Insolubles (gm): 11.28  
 Total Weight of THF Insolubles (gm) : 7.79  
 Average % ASH in THF Insolubles : 12.65  
 % ASH in Parent Coal : 5.41

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	22.93		25.23
% Asphaltene	17.48		17.00
% Preasphaltene	20.20		19.64
% Conversion	60.61		61.86

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	98.856
CO <sub>2</sub>	.571
CH <sub>4</sub>	.279
CO	.250

RUN NUMBER: R16CONDITIONS:

Residence Time : 10 min. Additive: pyrite  
 Coal Injected : 17.96 gm Pyrite Injected: 1.51 gm  
 Injection Pressure: 1700 psig  
 Maximum Pressure : 1850 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 181.74  
 Total Weight of Pentane Insolubles (gm): 13.70  
 Total Weight of Toluene Insolubles (gm): 12.21  
 Total Weight of THF Insolubles (gm) : 10.35  
 Average % ASH in THF Insolubles : 12.00  
 % ASH in Parent Coal : 5.53

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	-4.67		25.84
% Asphaltene	12.83		9.64
% Preasphaltene	16.02		12.03
% Conversion	24.18		47.51

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	99.434
H <sub>2</sub> S	.032
CO <sub>2</sub>	.336
CH <sub>4</sub>	.066
CO	.121

RUN NUMBER: R19

CONDITIONS:

Residence Time : 10 min.            Additive: none  
 Coal Injected : 18.72 gm  
 Injection Pressure: 1700 psig  
 Maximum Pressure : 1875 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 188.05  
 Total Weight of Pentane Insolubles (gm): 15.06  
 Total Weight of Toluene Insolubles (gm): 10.50  
 Total Weight of THF Insolubles (gm) : 9.75  
 Average % ASH in THF Insolubles : 6.98  
 % ASH in Parent Coal : 5.52

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	8.31		15.61
% Asphaltene	7.30		6.76
% Preasphaltene	6.44		5.96
% Conversion	22.06		28.33

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	99.50
CO <sub>2</sub>	.329
CH <sub>4</sub>	.044
CO	.121

RUN NUMBER: R25CONDITIONS:

Residence Time : 60 min. Additive: pyrite/10% H<sub>2</sub>S  
 Coal Injected : 18.90 gm Pyrite Injected: 1.58 gm  
 Injection Pressure: 1900 psig  
 Maximum Pressure : 2170 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 183.78  
 Total Weight of Pentane Insolubles (gm): 13.40  
 Total Weight of Toluene Insolubles (gm): 9.93  
 Total Weight of THF Insolubles (gm) : 6.14  
 Average % ASH in THF Insolubles : 26.82  
 % ASH in Parent Coal : 5.37

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	17.06		32.40
% Asphaltene	24.49		21.31
% Preasphaltene	26.74		23.27
% Conversion	68.29		76.98

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	95.948
H <sub>2</sub> S	4.044

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	92.118
H <sub>2</sub> S	3.554
CO <sub>2</sub>	2.204
C <sub>2</sub> H <sub>6</sub>	.182
CH <sub>4</sub>	1.342
CO	.546

RUN NUMBER: R26

CONDITIONS:

Residence Time : 60 min. Additive: none  
 Coal Injected : 19.63 gm  
 Injection Pressure: 1900 psig  
 Maximum Pressure : 2250 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 191.06  
 Total Weight of Pentane Insolubles (gm): 13.98  
 Total Weight of Toluene Insolubles (gm): 10.86  
 Total Weight of THF Insolubles (gm) : 6.40  
 Average % ASH in THF Insolubles : 15.00  
 % ASH in Parent Coal : 5.14

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	26.58		26.82
% Asphaltene	17.60		17.55
% Preasphaltene	25.13		25.05
% Conversion	69.31		69.42

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	96.127
CO <sub>2</sub>	1.840
C <sub>2</sub> H <sub>6</sub>	.150
CH <sub>4</sub>	1.022
CO	.737

RUN NUMBER: R27

CONDITIONS:

Residence Time	:	10 min.	Additive:	pyrite/10% H <sub>2</sub> S
Coal Injected	:	18.76 gm	Pyrite Injected:	1.69 gm
Injection Pressure:		1900 psig		
Maximum Pressure	:	2150 psig		

PRODUCT ANALYSIS

Total Weight of Samples (gm)	:	190.78
Total Weight of Pentane Insolubles (gm):		15.86
Total Weight of Toluene Insolubles (gm):		13.74
Total Weight of THF Insolubles (gm)	:	10.92
Average % ASH in THF Insolubles	:	14.69
% ASH in Parent Coal	:	5.80

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	-9.30		20.19
% Asphaltene	16.25		12.73
% Preasphaltene	21.62		16.93
% Conversion	28.58		49.85

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	96.621
H <sub>2</sub> S	3.374

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	95.114
H <sub>2</sub> S	2.895
CO <sub>2</sub>	1.176
CH <sub>4</sub>	.341
CO	.410

RUN NUMBER: R28

CONDITIONS:

Residence Time : 60 min. Additive: none  
 Coal Injected : 19.62 gm  
 Injection Pressure: 1900 psig  
 Maximum Pressure : 2070 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 189.97  
 Total Weight of Pentane Insolubles (gm): 14.73  
 Total Weight of Toluene Insolubles (gm): 11.29  
 Total Weight of THF Insolubles (gm) : 7.23  
 Average % ASH in THF Insolubles : 14.14  
 % ASH in Parent Coal : 5.52

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	21.70		22.57
% Asphaltene	19.65		19.45
% Preasphaltene	23.19		22.95
% Conversion	64.54		64.97

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	96.706
CO <sub>2</sub>	1.576
C <sub>2</sub> H <sub>6</sub>	.107
CH <sub>4</sub>	.839
CO	.692

RUN NUMBER: R29

CONDITIONS:

Residence Time : 10 min. Additive: 10% H<sub>2</sub>S  
 Coal Injected : 19.51 gm  
 Injection Pressure: 1900 psig  
 Maximum Pressure : 2150 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 187.72  
 Total Weight of Pentane Insolubles (gm): 15.90  
 Total Weight of Toluene Insolubles (gm): 13.52  
 Total Weight of THF Insolubles (gm) : 9.78  
 Average % ASH in THF Insolubles : 10.06  
 % ASH in Parent Coal : 5.67

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	8.92		14.37
% Asphaltene	14.53		13.72
% Preasphaltene	22.84		21.55
% Conversion	46.29		49.64

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	96.790
H <sub>2</sub> S	3.204

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	95.068
H <sub>2</sub> S	2.803
CO <sub>2</sub>	1.286
CH <sub>4</sub>	.342
CO	.441

RUN NUMBER: R30

CONDITIONS:

Residence Time : 10 min.                    Additive: 5% H<sub>2</sub>S  
 Coal Injected : 19.33 gm  
 Injection Pressure: 1900 psig  
 Maximum Pressure : 2250 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 189.92  
 Total Weight of Pentane Insolubles (gm): 15.36  
 Total Weight of Toluene Insolubles (gm): 13.16  
 Total Weight of THF Insolubles (gm) : 9.23  
 Average % ASH in THF Insolubles : 9.89  
 % ASH in Parent Coal : 5.47

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	8.48		17.73
% Asphaltene	13.94		12.61
% Preasphaltene	24.89		22.53
% Conversion	47.31		52.87

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	98.324
H <sub>2</sub> S	1.672

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	96.125
H <sub>2</sub> S	1.786
CO <sub>2</sub>	1.291
CH <sub>4</sub>	.333
CO	.400

RUN NUMBER: R31CONDITIONS:

Residence Time : 60 min. Additive: 5% H<sub>2</sub>S  
 Coal Injected : 19.38 gm  
 Injection Pressure: 1900 psig  
 Maximum Pressure : 2260 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 186.25  
 Total Weight of Pentane Insolubles (gm): 13.05  
 Total Weight of Toluene Insolubles (gm): 9.50  
 Total Weight of THF Insolubles (gm) : 4.61  
 Average % ASH in THF Insolubles : 19.22  
 % ASH in Parent Coal : 5.59

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	18.79		29.95
% Asphaltene	23.70		20.67
% Preasphaltene	32.65		28.47
% Conversion	75.14		79.08

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	97.691
H <sub>2</sub> S	2.304

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	94.987
H <sub>2</sub> S	1.108
CO <sub>2</sub>	1.900
C <sub>2</sub> H <sub>6</sub>	.163
CH <sub>4</sub>	1.190
CO	.583

RUN NUMBER: R32

CONDITIONS:

Residence Time : 10 min.                    Additive: pyrite/5% H<sub>2</sub>S  
 Coal Injected : 18.49 gm                    Pyrite Injected: 1.62 gm  
 Injection Pressure: 1900 psig  
 Maximum Pressure : 2240 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 190.16  
 Total Weight of Pentane Insolubles (gm): 15.65  
 Total Weight of Toluene Insolubles (gm): 13.44  
 Total Weight of THF Insolubles (gm) : 9.76  
 Average % ASH in THF Insolubles : 16.27  
 % ASH in Parent Coal : 5.02

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	.38		20.30
% Asphaltene	15.66		13.27
% Preasphaltene	26.07		22.09
% Conversion	42.10		55.66

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	97.597
H <sub>2</sub> S	2.398

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	96.615
H <sub>2</sub> S	.955
CO <sub>2</sub>	1.382
CH <sub>4</sub>	.439
CO	.539

RUN NUMBER: R34

CONDITIONS:

Residence Time : 60 min.                      Additive: pyrite/5% H<sub>2</sub>S  
 Coal Injected : 18.77                              Pyrite Injected: 1.61 gm  
 Injection Pressure: 1900 psig  
 Maximum Pressure : 2345 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 184.24  
 Total Weight of Pentane Insolubles (gm): 13.39  
 Total Weight of Toluene Insolubles (gm): 9.73  
 Total Weight of THF Insolubles (gm) : 5.11  
 Average % ASH in THF Insolubles : 31.55  
 % ASH in Parent Coal : 5.37

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	10.47		32.08
% Asphaltene	27.82		22.60
% Preasphaltene	35.12		28.53
% Conversion	73.41		83.21

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	97.425
H <sub>2</sub> S	2.571

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	94.938
H <sub>2</sub> S	.781
CO <sub>2</sub>	1.909
C <sub>2</sub> H <sub>6</sub>	.178
CH <sub>4</sub>	1.407
CO	.725

RUN NUMBER: R36CONDITIONS:

Residence Time	: 10 min.	Additive:	pyrite/2% H <sub>2</sub> S
Coal Injected	: 18.26 gm	Pyrite Injected:	1.60 gm
Injection Pressure:	1800 psig		
Maximum Pressure	: 2210 psig		

PRODUCT ANALYSIS

Total Weight of Samples (gm)	:	190.90
Total Weight of Pentane Insolubles (gm):		15.77
Total Weight of Toluene Insolubles (gm):		13.79
Total Weight of THF Insolubles (gm)	:	10.12
Average % ASH in THF Insolubles	:	15.83
% ASH in Parent Coal	:	5.40

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	-2.83		18.29
% Asphaltene	14.37		12.10
% Preasphaltene	26.64		22.43
% Conversion	38.18		52.82

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	98.985
H <sub>2</sub> S	1.014

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	96.987
H <sub>2</sub> S	.854
CO <sub>2</sub>	1.293
CH <sub>4</sub>	.352
CO	.498

RUN NUMBER: R38CONDITIONS:

Residence Time : 60 min. Additive: pyrite/2% H<sub>2</sub>S  
 Coal Injected : 18.79 gm Pyrite Injected: 1.60 gm  
 Injection Pressure: 1800 psig  
 Maximum Pressure : 2190 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 181.32  
 Total Weight of Pentane Insolubles (gm): 13.23  
 Total Weight of Toluene Insolubles (gm): 10.08  
 Total Weight of THF Insolubles (gm) : 4.96  
 Average % ASH in THF Insolubles : 31.36  
 % ASH in Parent Coal : 5.40

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	8.01		32.14
% Asphaltene	24.82		19.71
% Preasphaltene	40.34		32.03
% Conversion	73.17		83.87

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	99.219
H <sub>2</sub> S	.780

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	94.454
H <sub>2</sub> S	.490
CO <sub>2</sub>	2.516
C <sub>2</sub> H <sub>6</sub>	.222
CH <sub>4</sub>	1.526
CO	.720

RUN NUMBER: R40

CONDITIONS:

Residence Time : 10 min.            Additive: 2% H<sub>2</sub>S  
 Coal Injected : 19.39 gm  
 Injection Pressure: 1800 psig  
 Maximum Pressure : 2200 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 189.92  
 Total Weight of Pentane Insolubles (gm): 16.01  
 Total Weight of Toluene Insolubles (gm): 13.75  
 Total Weight of THF Insolubles (gm) : 10.03  
 Average % ASH in THF Insolubles : 9.97  
 % ASH in Parent Coal : 5.40

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	14.27		14.03
% Asphaltene	12.91		12.94
% Preasphaltene	21.25		21.30
% Conversion	48.43		48.27

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	98.933
H <sub>2</sub> S	1.065

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	97.075
H <sub>2</sub> S	.519
CO <sub>2</sub>	1.385
CH <sub>4</sub>	.386
CO	.575

RUN NUMBER: R41CONDITIONS:

Residence Time : 60 min. Additive: 10% H<sub>2</sub>S  
 Coal Injected : 19.41 gm  
 Injection Pressure: 1800 psig  
 Maximum Pressure : 2250 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 185.17  
 Total Weight of Pentane Insolubles (gm): 13.04  
 Total Weight of Toluene Insolubles (gm): 9.48  
 Total Weight of THF Insolubles (gm) : 4.52  
 Average % ASH in THF Insolubles : 20.43  
 % ASH in Parent Coal : 5.44

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	25.12		29.43
% Asphaltene	22.00		20.82
% Preasphaltene	30.65		29.01
% Conversion	77.77		79.27

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	93.795
H <sub>2</sub> S	6.187

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	93.761
H <sub>2</sub> S	1.879
CO <sub>2</sub>	2.147
C <sub>2</sub> H <sub>6</sub>	.186
CH <sub>4</sub>	1.478
CO	.489

RUN NUMBER: R42

CONDITIONS:

Residence Time : 10 min. Additive: pyrite  
 Coal Injected : 19.19 gm Pyrite Injected: 1.58 gm  
 Injection Pressure: 1800 psig  
 Maximum Pressure : 2270 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 189.50  
 Total Weight of Pentane Insolubles (gm): 16.01  
 Total Weight of Toluene Insolubles (gm): 13.90  
 Total Weight of THF Insolubles (gm) : 9.99  
 Average % ASH in THF Insolubles : 16.11  
 % ASH in Parent Coal : 5.40

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	-.51		20.27
% Asphaltene	14.73		12.38
% Preasphaltene	27.29		22.95
% Conversion	41.51		55.60

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	97.386
H <sub>2</sub> S	.215
CO <sub>2</sub>	1.388
CH <sub>4</sub>	.403
CO	.572

RUN NUMBER: R43

CONDITIONS:

Residence Time : 10 min. Additive: pyrite  
 Coal Injected : 18.68 gm Pyrite Injected: 1.67 gm  
 Injection Pressure: 1800 psig  
 Maximum Pressure : 2185 psig

PRODUCT ANALYSIS

Total Weight of Samples (gm) : 189.31  
 Total Weight of Pentane Insolubles (gm): 15.94  
 Total Weight of Toluene Insolubles (gm): 13.85  
 Total Weight of THF Insolubles (gm) : 10.80  
 Average % ASH in THF Insolubles : 15.27  
 % ASH in Parent Coal : 5.24

CALCULATED YIELDS

<u>Product</u>	<u>ATE</u>	<u>Method</u>	<u>CWR</u>
% Oil	1.98		19.39
% Asphaltene	14.69		12.51
% Preasphaltene	21.43		18.26
% Conversion	38.10		50.16

GAS ANALYSIS

Initial Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	100.0

Product Gas:

<u>Component</u>	<u>Mole %</u>
H <sub>2</sub>	97.548
H <sub>2</sub> S	.259
CO <sub>2</sub>	1.349
CH <sub>4</sub>	.314
CO	.478

APPENDIX B

PENN STATE COAL DATA BANK INFORMATION

\*\* PFNN STATE COAL DATA BASE \*\*

\*\*\*\*\*  
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\*\* PAGE 1 \*\*  
\*\*\*\*\*

\*\*\*\*\*  
\*  
\* SAMPLE HISTORY \*  
\*  
\*\*\*\*\*

PFNN STATE NUMBR PSOC-233  
COLLECTED BY PFNNSYLVANIA STATE UNIVERSITY  
COLLECTION DATE 9/25/71  
COLLECTOR'S NUMBER 233

REPORTED RANK

SAMPLE TYPE CHANNEL WHOLE SEAM  
OTHER SAMPLE INFORMATION BRIGHT COAL  
SAMPLE RESERVE

SFAM NAME WADGE  
ALTERNATE SFAM NAME

TOTAL SFAM THICKNESS 8 FT. 7 IN.  
THICKNESS OF SFAM SAMPLED  
PORTION RECOVERED IN CORE  
DIAMETER OF CORE

\*\*\*\*\*  
\*  
\* SAMPLE LOCATION \*  
\*  
\*\*\*\*\*

COUNTRY U.S.A.  
STATE COLORADO  
COUNTY ROUTT  
TOWNSHIP  
NEAREST TOWN ENERGY  
COAL PROVINCE ROCKY MOUNTAIN  
COAL REGION GREEN RIVER  
COAL FIELD

MAP REFERENCE: LATITUDE 40D 29M 00S  
LONGITUDE 106D 50M 00S  
QUADRANGLE

\*\* PENN STATE COAL DATA BASE \*\*

\*\*\*\*\*  
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\*\* PAGE 2 \*\*  
\*\*\*\*\*

SFAM NAME WADGE  
APPARENT RANK HIGH VOLATILE C BITUMINOUS (HVCB)

COUNTRY U.S.A.  
STATE COLORADO

\*\*\*\*\*  
\* \*  
\* GEOLOGIC INFORMATION \*  
\* \*  
\*\*\*\*\*

SYSTEM (AGE) UPPER CRETACEOUS  
SERIES  
GROUP MESA VERDE  
FORMATION WILLIAMS FORK

OVERBURDEN LITHOLOGY  
FLOOR LITHOLOGY

\*\*\*\*\*  
\* \*  
\* SFAM STRATA INFORMATION \*  
\* \*  
\*\*\*\*\*

THICKNESS      LITHOLOGY

\*\*\*\*\*  
\* \*  
\* MINE INFORMATION \*  
\* \*  
\*\*\*\*\*

MINE NAME  
MINING METHOD  
MINE RESERVES  
MINE PRODUCTION  
MINE LIFE EXPECTANCY  
OVERBURDEN THICKNESS

ENERGY  
STRIP  
  
769 THOUSAND TONS/YEAR

\*\* PENN STATE COAL DATA BASE \*\*

\*\*\*\*\*  
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 \*\*\*\*\*

SFAM NAME WADGE COUNTRY U.S.A.  
 APPARENT RANK HIGH VOLATILE C BITUMINOUS (HVCB) STATE COLORADO

\*\*\*\*\*  
 \* \*  
 \* CHEMICAL DATA 1 \*  
 \* \*  
 \*\*\*\*\*

PROXIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF (PARR)	DMMF (PARR-G)	DMMF (DIR MM)
% MOISTURE	7.54					
% ASH	8.40	9.09				
% VOLATILE MATTER	35.61	38.51	42.36	41.80	41.46	
% FIXED CARBON	48.45	52.40	57.64	58.20	58.54	

CALORIFIC VALUE	DRY	AS REC'D	EQUIL.
(GROSS BTU/LB)		MOIST.	MOIST.

MM-FREE, DIRECT  
 MM-CONTAINING 12372 11439  
 MM-FREE (PARR) 13733 12591  
 MM-FREE (MOD.P) 13790 12617  
 BEST MM FREE 12617  
 NET CV, DMMF BTU/LB 13276  
 ASH-FREE 13609

MOTT-SPOONER DIFFERENCE = 21.

ASSOCIATED ANALYSIS	DRY	MMF
% EQUILIBRIUM MOISTURE		
% TOTAL SULFUR	0.51	

\*\*\*\*\*  
 \* \*  
 \* RANK CALCULATIONS \*  
 \* \*  
 \*\*\*\*\*

APPARENT RANK (AS REC'D MOIST) HIGH VOLATILE C BITUMINOUS (HVCB)  
 ASTM RANK (EQUIL. MOIST.)  
 REFLECTANCE RANK CATEGORY HIGH VOLATILE B BITUMINOUS (HVBV)  
 INTERNATIONAL RANK  
 AS REC'D MOIST.  
 EQUIL. MOIST.  
 REPORTED RANK

\*\* PFNN STATE COAL DATA BASE \*\*

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 \*\* PSOC-233 \*\*  
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 \*\*\*\*\*

SFAM NAME WADGE COUNTRY U.S.A.  
 APPARENT RANK HIGH VOLATILE C BITUMINOUS (HVCB) STATE COLORADO

\*\*\*\*\*  
 \* \*  
 \* CHEMICAL DATA 2 \*  
 \* \*  
 \*\*\*\*\*

ULTIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF (PARR)
				(10.10 %MM)
% ASH	8.40	9.09		
% CARBON	65.03	70.33	77.36	78.23
% HYDROGEN	4.60*	4.98	5.48	5.54
% NITROGEN	1.61	1.74	1.91	1.94
% SULFUR	0.47	0.51	0.56	
% CHLORINE	0.01	0.01	0.02	0.02
% OXYGEN (DIFF)	12.33*	13.34	14.67	14.28

SULFUR FORMS	% PYRITIC	% SULFATIC	% ORGANIC	% TOTAL
DRY	0.08	0.01	0.42	0.51
DAF	0.09	0.01	0.46	0.56

ELEMENTAL ANALYSIS	DRY	DMMF (MOD.P)	DMMF (DIR.)
		(10.32%MM)	( %MM)
% CARBON	70.20	78.28	
% HYDROGEN	4.86	5.42	
% NITROGEN	1.74	1.94	
% ORGANIC SULFUR	0.42	0.47	
% OXYGEN (DIFF)	12.46	13.88	
% CHLORINE	0.01	0.02	
% MINERAL MATTER	10.32		
(INCLUDES 0.15 % FFS2)			

ATOM RATIOS (DMMF)	PARR	MOD. PAR	DIRRECT
ATOMIC H/C	0.850	0.832	
ATOMIC O/C	0.137	0.148	

MISC. CHEMICAL DATA	DRY	OF DMMF COAL	OF DMMF OXYGEN
% O AS COOH			
% O AS OH	4.90	5.46	39.32
% S AS SO4, IN ASH			
% CARBONATE AS CO2			
% CHLORINE	0.03		

INFRA-RED ANALYSIS

(\*)-EXCLUDES MOISTURE

\* PENN STATE COAL DATA BASE \*

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 \*\* PSOC-233 \*\*  
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 \*\*\*\*\*

SEAM NAME WADGF  
 APPARENT RANK HIGH VOLATILE C BITUMINOUS (HVCB)

COUNTRY U.S.A.  
 STATE COLORADO

\*\*\*\*\*  
 \* CHEMICAL DATA 3 \*  
 \* \* \*  
 \*\*\*\*\*

% MOISTURE IN COAL = 9.00 AT 550 DEGREES C  
 % HIGH TEMPERATURE ASH = 9.67

TRACE ELEMENT ANALYSIS	PPM HTA	PPM TOTAL COAL	MAJOR ELEMENT ANALYSIS	OXIDE % OF HTA DRY COAL	ELEMENT % OF TOTAL
AG	< 1	0	SIO2	51.70	2.34
B			AL2O3	24.50	1.25
BA	4400	425	TIO2	0.70	0.04
BF	5	0	FF2O3	2.63	0.18
BJ	< 20	2	MGO	1.20	0.07
CF	< 100	10	CA0	4.55	0.31
CO	< 20	2	NA2O	0.97	0.07
CR	44	4	K2O	0.72	0.06
CU	130	13	P2O5	1.40	0.06
GA	34	3	S03	4.60	0.18
GF	< 25	2			
LA	70	7			
LJ					
MN	77	7			
MO					
NJ	< 25	2			
NB	< 20	2			
PB	80	8			
RB					
SC	12	1			
SN	70	7			
SR	3300	319			
TH					
U					
V	54	5			
Y	36	3			
YB	< 5	0			
ZN	140	14			
ZR	210	20			

VOLATILES                      PPM TOTAL COAL

AS  
 BR  
 CD  
 CL  
 F  
 HG  
 SB  
 SF



\*\* PENN STATE COAL DATA BASE \*\*

\*\*\*\*\*  
 \*\* PSOC-233 \*\*  
 \*\* PAGE 7 \*\*  
 \*\*\*\*\*

SFAM NAME WADGE  
 APPARENT RANK HIGH VOLATILE C BITUMINOUS (HVCB)

COUNTRY U.S.A.  
 STATE COLORADO

\*\*\*\*\*  
 \* \*  
 \* PETROGRAPHIC DATA \*  
 \* \*  
 \*\*\*\*\*

MACERAL COMPOSITION

	DRY VOLUME %	DMMF VOLUME %	DRY WEIGHT %
VITRINITE (CALC.)	84.2	88.8	79.9
INFERTINITE	6.2	6.5	6.4
LIPTINITE	4.5	4.7	3.6
MINERAL MATTER	5.1		10.1

VITRINOIDS			
VITRINITE	72.4	76.3	68.7
PSEUDOVITRINITE	11.9	12.5	11.2
FUSINITE	3.4	3.6	3.6
SEMI-FUSINITE	1.5	1.6	1.5
MACRINITE	0.7	0.7	0.7
MICRINITE	0.6	0.6	0.6
SCLEROTINITE	0.0	0.0	0.0
SPORINITE	2.5	2.6	2.0
CUTINITE	0.0	0.0	0.0
EXINITE (ANAL)			
RFSINITE	2.0	2.1	1.6
EXUDATINITE	0.0	0.0	0.0
FLUORINITE	0.0	0.0	0.0
BITUMINITE	0.0	0.0	0.0
ALGINITE	0.0	0.0	0.0
LIPTODETRINITE	0.0	0.0	0.0
MINERAL MATTER (ANAL)			
INFERTINITE			
LIPTINITE			

REFLECTANCE DATA (% IN OIL)	HIGH	LOW	RANGE	MFAN MAX	STAND. DEV.
VITRINITE	0.76	0.47	0.29	0.61	
PSEUDOVITRINITE	0.72	0.54	0.18	0.63	
VITRINOIDS			0.00		

\*\* PENN STATE COAL DATA BASE \*\*

\*\*\*\*\*  
 \*\* PSOC-233 \*\*  
 \*\* PAGE 8 \*\*  
 \*\*\*\*\*

SEAM NAME WADGE COUNTRY U.S.A.  
 APPARENT RANK HIGH VOLATILE C BITUMINOUS (HVCB) STATE COLORADO

\*\*\*\*\*  
 \* \*  
 \* PETROGRAPHIC DATA \*  
 \* CONTINUED \*  
 \* \*  
 \*\*\*\*\*

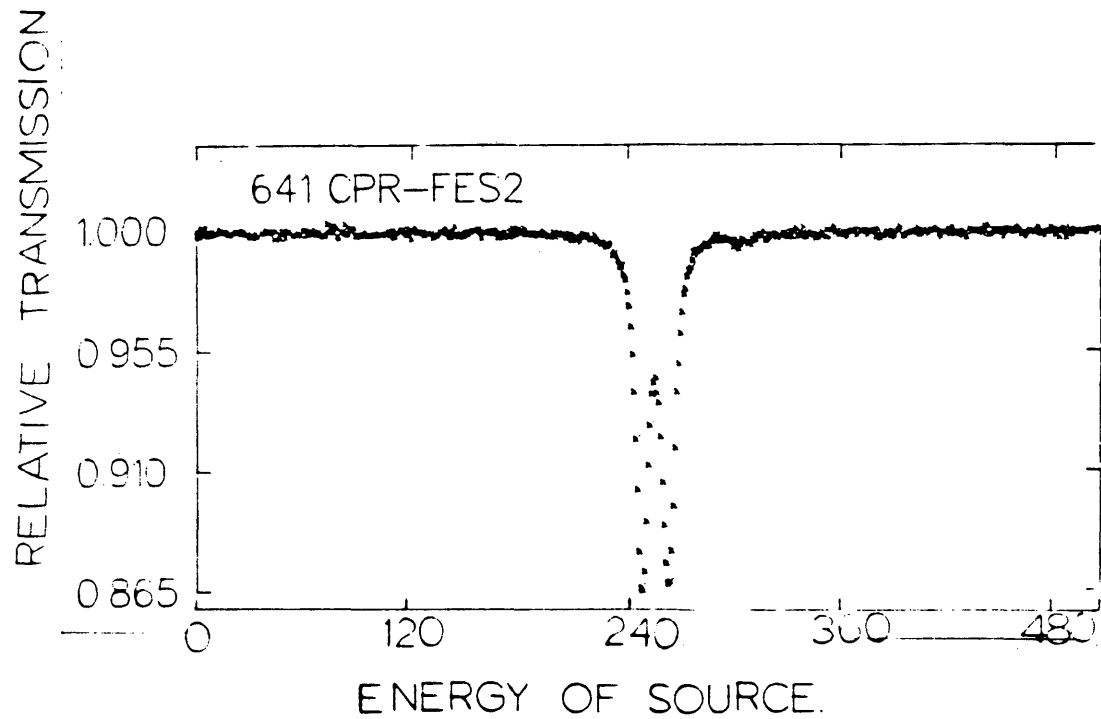
<u>% VITRINOID</u>		<u>VOLUME</u>	<u>% VITRINOID</u>		<u>VOLUME</u>
<u>REFLECTANCE</u>	<u>HALF-TYPE</u>	<u>PERCENT</u>	<u>REFLECTANCE</u>	<u>V-TYPE</u>	<u>PERCENT</u>
0.40-0.44	VHT 0.425	1.29			
0.45-0.49	VHT 0.475	1.29	0.50-0.59	V4	2.58
0.50-0.54	VHT 0.525	14.20			
0.55-0.59	VHT 0.575	14.20	0.50-0.59	V5	28.40
0.60-0.64	VHT 0.625	30.62			
0.65-0.69	VHT 0.675	30.62	0.60-0.69	V6	61.24
0.70-0.74	VHT 0.725	3.88			
0.75-0.79	VHT 0.775	3.88	0.70-0.79	V7	7.76





APPENDIX C

MOSSBAUER ANALYSIS



Fraction of Fe as:

Pyrite ( $\text{FeS}_2$ ): 98%

$\text{Fe}^{2+}$ : 2%

Figure 26. Mossbauer Spectroscopy Analysis of Coal-Derived Pyrite.

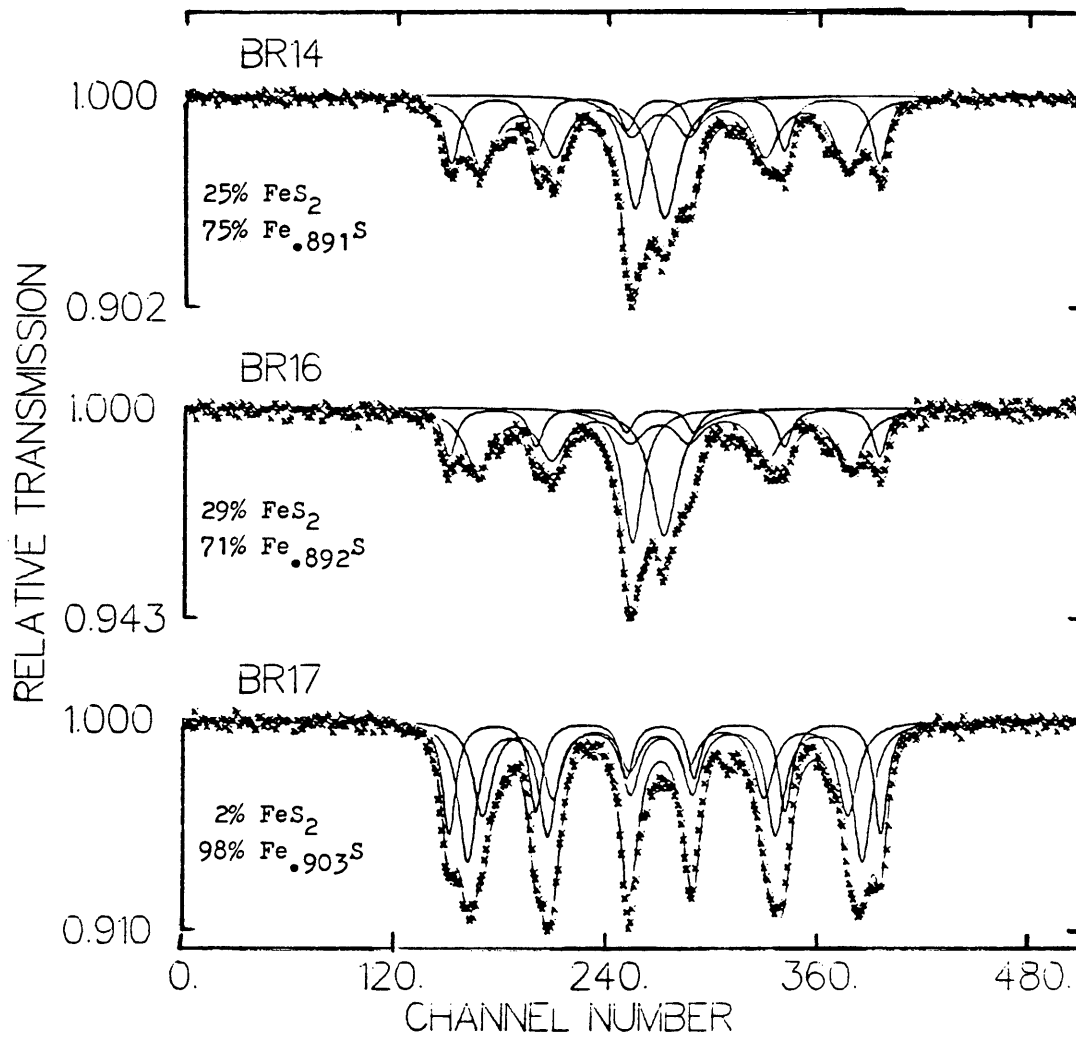


Figure 27. Mossbauer Spectra  
of Runs 14, 16, and 17

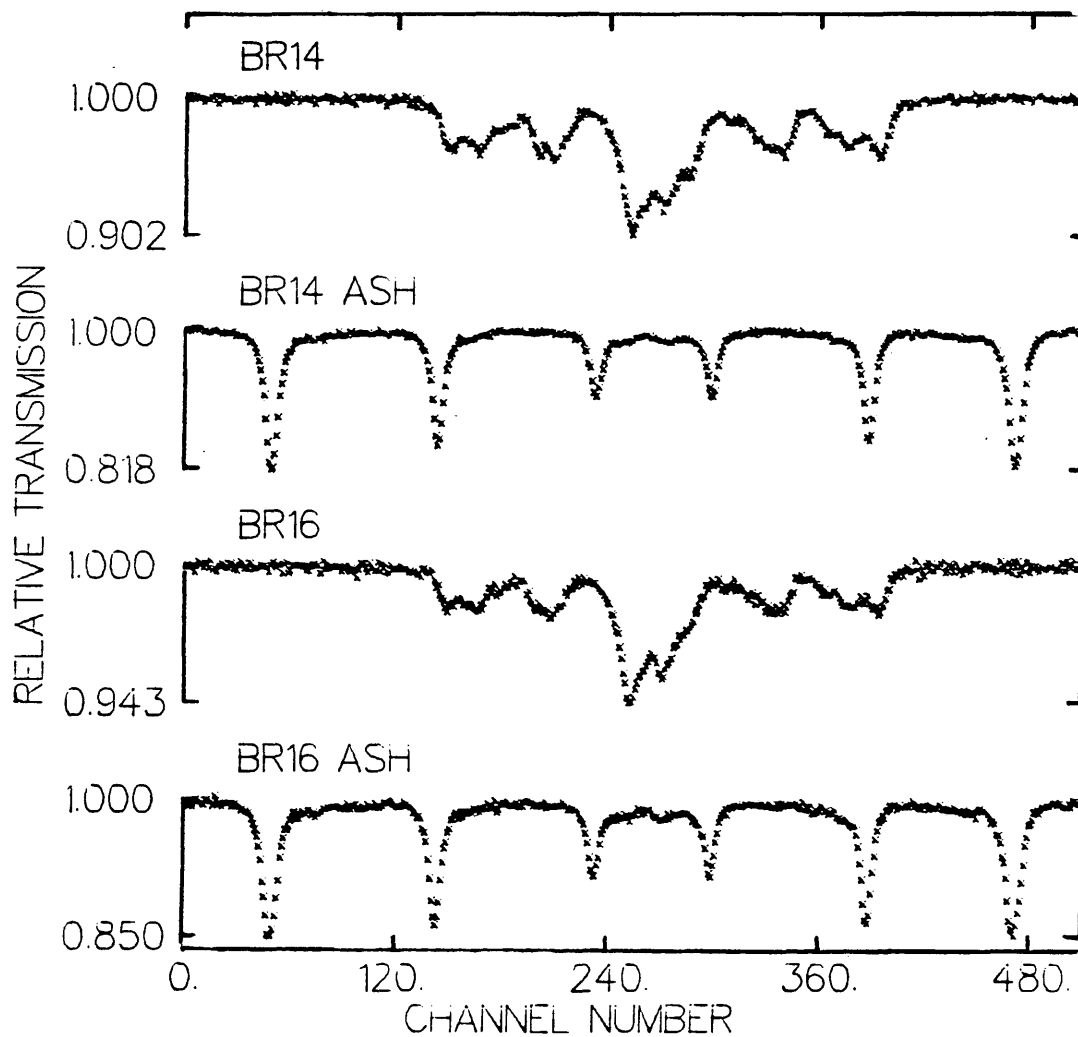


Figure 28. Comparison of THF-Insolubles and Ash.

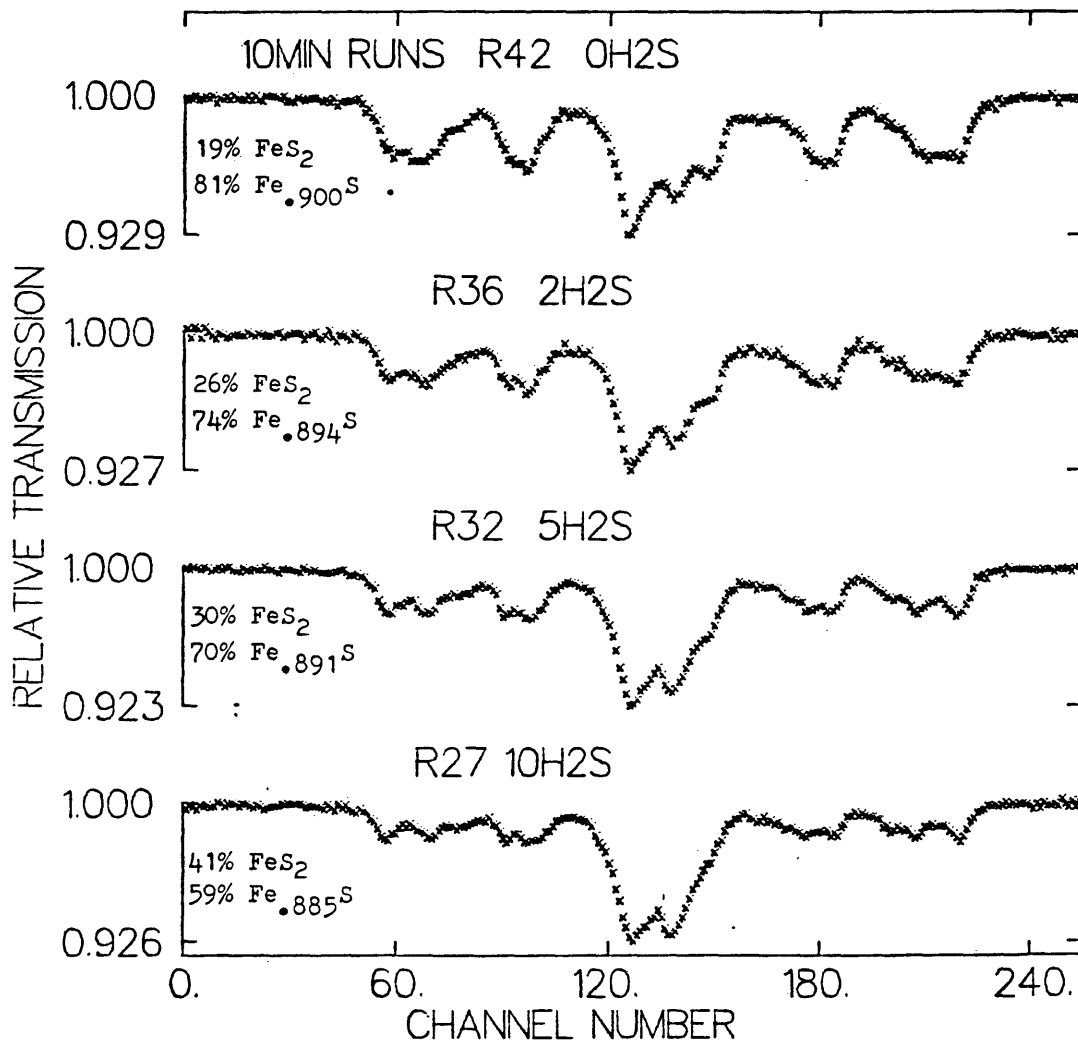


Figure 29. Effect of H<sub>2</sub>S Concentration on Fe<sub>x</sub>S Stoichiometry at a 10 Minute Residence Time

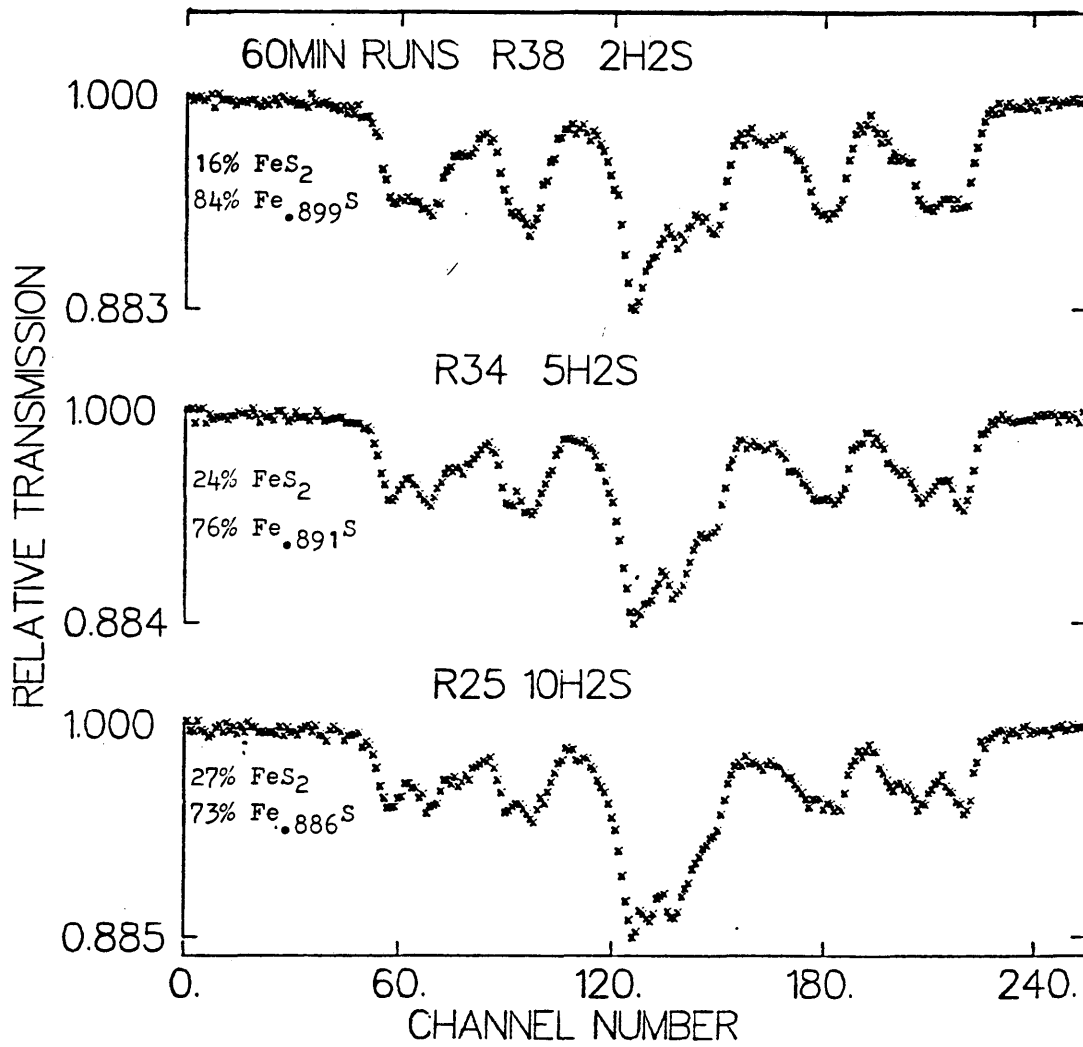


Figure 30. Effect of H<sub>2</sub>S Concentration on Fe<sub>x</sub>S Stoichiometry at a 60 Minute Residence Time

APPENDIX D  
CALCULATIONS

Slurry Calculations  
(in presence of pyrite)

slurry = tetralin + coal + pyrite

known information:

XB = grams uncharged slurry from beaker

AXB = grams coal + pyrite (acetone wash of XB)

AXB ASH = % AXB ASH

XI = grams uncharged slurry from injection vessel

AXI = grams coal + pyrite (acetone wash of XI)

AXI ASH = % AXI ASH

PASH = % parent coal ash

ADD ASH = % pyrite ash

now for beaker:

$$\begin{aligned} \text{total grams ash} &= (\text{AXB ASH}) * \text{AXB} \\ &= (\text{AXB ASH}) * (\text{coal} + \text{pyrite}) \end{aligned}$$

or since the ash is generated from coal and pyrite,

$$\text{total grams ash} = (\text{PASH}) * \text{coal} + (\text{ADD ASH}) * \text{pyrite}$$

This reduces to two equations and two unknowns which can be solved for the amount of coal and pyrite not charged to the injection vessel. Thus,

$$\text{coal lost} = \frac{\text{AXB} * (\text{AXB ASH} - \text{ADD ASH})}{(\text{PASH} - \text{ADD ASH})}$$

$$\text{pyrite lost} = \text{AXB} - \text{coal lost}$$

$$\text{tetralin lost} = \text{XB} - \text{AXB}$$

now for injection vessel:

by a similar development,

$$\text{coal lost} = \frac{\text{AXI} * (\text{AXI ASH} - \text{ADD ASH})}{(\text{PASH} - \text{ADD ASH})}$$

$$\text{pyrite lost} = \text{AXI} - \text{coal lost}$$

$$\text{tetralin lost} = \text{XI} - \text{AXI}$$

CALCULATION OF H<sub>2</sub>S INITIAL PERCENTAGES

H<sub>2</sub>S gas bottle: 10.19% H<sub>2</sub>S in H<sub>2</sub>

total initial pressure = 400 psig

H<sub>2</sub>S initial partial pressures used: 80, 200, 400 psig

Therefore, assuming ideal gasses:

$$\text{@ 400 psig H}_2\text{S} \quad \frac{400}{400} * 10.19 = 10.19\% \text{ H}_2\text{S}$$

$$\text{@ 200 psig H}_2\text{S} \quad \frac{200}{400} * 10.19 = 5.095\% \text{ H}_2\text{S}$$

$$\text{@ 80 psig H}_2\text{S} \quad \frac{80}{400} * 10.19 = 2.038\% \text{ H}_2\text{S}$$

## IRON IN COAL

Coal ash contains 3.30%  $\text{Fe}_2\text{O}_3$

% coal ash = 5.64%

Basis: 1 g coal

thus:

$$(.0330) * (.0564) = .00186 \text{ g Fe}_2\text{O}_3$$

$$(.00186 \text{ g Fe}_2\text{O}_3) * \frac{(55.85 \text{ g Fe})}{(\text{mole Fe})} * \frac{(2 \text{ mole Fe})}{(\text{mole Fe}_2\text{O}_3)} * \frac{(\text{mole Fe}_2\text{O}_3)}{(159.70 \text{ g Fe}_2\text{O}_3)}$$

$$= .00130 \text{ g Fe or } .13\% \text{ Fe}$$

Pyritic Sulfur = .05%

thus,

$$(.0005 \text{ g pyritic sulfur}) * \frac{(\text{mole S})}{(32.06 \text{ g Fe})} * \frac{(\text{mole Fe})}{(2 \text{ mole S})} * \frac{(55.85 \text{ g Fe})}{(\text{mole Fe})}$$

$$= .00044 \text{ g pyrite iron}$$

$$= .00044 / .00130 = 33.5\% \text{ pyrite}$$

result:

total iron .13%

pyritic iron 33.5%

non-pyritic iron 66.5%

APPENDIX E  
LOW TEMPERATURE  
ASH ANALYSIS

## LTA Analysis

<u>Coal Ash</u>		
<u>Mineral (or Material)</u>	<u>Composition</u>	<u>Est. Amount (Wt %)</u>
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	20-30
Quartz	$\text{SiO}_2$	10-15
Unidentified (Crystalline)	?	<u>&lt;5</u>
Amorphous	?	Remainder