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THE RELATIONSHIP BETWEEN THE PROPERTIES OF IRON SULFIDES AND THEIR CATALYTIC ACTIVITY

by

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ABSTRACT

Iron sulfides, such as pyrite, are known catalysts in coal liquefaction and produce significant increases in both conversion and distillate (850 F^-) yield. The main objective of this work is to increase the catalytic activity of iron sulfides by systematically changing the following properties: composition, source, particle size, surface area, morphology and defect level. Several iron sulfides have been synthesized including pyrite (FeS_2) with 46.6 wt % Fe, pyrrhotite ($Fe_{1-x}S$) with ∿60 wt % Fe and mackinawite (Fe_9S_8) with 66.2 wt % Fe. The source variations have included commercial material and minerals. The pyrite particle sizes ranged from -350 to -5μm, the pyrite surface areas varied from 2 to >10 m^2/g, the mackinawite surface areas ranged from 40 to 80 m^2/g, and pyrite morphologies included massive material and a concentrate of framboids from Iowa coal. Mössbauer studies of the pyrrhotites in coal liquefaction residues have shown that there is a direct correlation between conversion and the number of vacancies in the pyrrhotite. Pyrites with enhanced defect levels were prepared by explosively shock loading Robena pyrite at 15 GPa. All these materials have been tested in either tubing reactor or autoclave runs with West Virginia Blacksville #2 coal and SRC-II heavy distillate (550°F^+). The runs were

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carried out at 425°C, 500 psi H_2 (cold charge) for 30 minutes with a 7.5 wt % catalyst loading. All these materials have shown catalytic effects as compared to uncatalyzed thermal runs.

Introduction

The main objective of DOE's disposable catalyst program in direct coal liquefaction is to find a catalyst which will reduce process costs by decreasing hydrogen consumption and/or increasing the liquid product yield. This catalyst should be cheap and readily available. It has been shown that the mineral matter present in coal is catalytic (Granoff et al., 1978) and that the pyrite in coal is the most catalytic component of the mineral matter (Tarrer et al., 1977; Granoff and Baca, 1979). The addition of pyrite to the charge in a coal liquefaction run causes an increase in benzene and THF conversions, an increase in oil yield, a decrease in preasphaltene yield and an increase in the H/C ratio of the products (Granoff and Baca, 1979). The catalytic effect of pyrite on hydrogen consumption has also been shown by comparing the data from an uncatalyzed liquefaction run with Illinois #6 coal at 425°C with the data from a similar run at 405°C with 5 wt % pyrite. The conversions to benzene solubles and the distillate yields from these two runs were very similar. However, the hydrocarbon gas formation was significantly lower for the catalyzed run at 405°C than for the uncatalyzed run at 425°C (1.8% vs 4.5% on a DAF coal basis) (Granoff, 1979). Pyrite is a good coal liquefaction catalyst, although its effects are not as large as those obtained by some other catalysts such as American Cyanamid's Co/Mo on alumina (HDS 1442A). The purpose of this research was to increase the catalytic activity of pyrite and other iron sulfides by changing their physical properties. The factors which have been tested include concentration, source, particle size, surface area, composition, and defect concentration.

Testing Procedures

All of the tests, which were used to determine catalytic activity, were carried out in either 28 cc tubing reactors or a one liter batch autoclave. The tubing reactors were equipped with an internal thermocouple and pressure transducer to monitor temperature and pressure during a run. These reactors were heated in a Tecann fluidized sand bath and shaken with a wrist-action shaker at 320 strokes/min with a 2 in. stroke displacement. The heat up and quench times for the tubing reactor runs were both two minutes. All the times reported in this work refer to the time at reaction temperature. The following conditions were used in all the tubing reactor runs:

Temperature = 425°C
Pressure = 500 psi H_2 cold charge
(about 750 psi at temperature)
Residence time = 30 minutes
Solvent:Coal = 4:1
Total charge = 8.5 g

The coal used in these runs was West Virginia Blacksville #2 and the solvent was SRC-II heavy distillate which was obtained from the Pittsburgh and Midway solvent refined coal pilot plant at Fort Lewis, Washington. This solvent consisted of 86.6 wt % distillate (850°F$^-$) and contained about 6 wt % asphaltenes. Ultimate and sulfur forms analyses of the coal are given in Table 1.

The autoclave (Granoff et al., 1978) was operated in a constant pressure mode at the reaction temperature. This was accomplished by adding small amounts of hydrogen to the one liter reaction vessel from an auxiliary vessel during the run. The stirrer speed during the run was 1000 rpm. The operating conditions used in these tests were as follows:

Temperature = 425 ± 2°C
Operating pressure = 1800 ± 10 psig
Residence time = 30 ± 0.1 minutes
Coal concentration = 30 wt %
Total charge = 166.5 g

The heat up time for the autoclave is about one hour. The coal used in these tests was Illinois #6 River King and the solvent was the same as used in the tubing reactor runs. The ultimate and sulfur forms analyses of this coal are in Table 1.

Many of the liquefaction runs in this work were compared to uncatalyzed runs and runs with known catalysts including Robena pyrite and a Co/Mo on alumina catalyst. The Robena pyrite is from the beneficiation of coal and was obtained from the Robena Laboratory of the U.S. Steel Corporation. This material contained about 30 wt % impurities consisting of quartz, carbonates, sulfates, clays and about 2 wt % organics (Bickel et al., 1980). A portion of this material was pulverized to -5μm by the Jet Pulverizer Co., Palmyra, N.J. Part of the -5μm Robena pyrite was cleaned by low temperature ashing and acids (HCl and HF) to remove phases other than FeS_2. This is described in Bickel et al. (1980) and was based on a technique reported by Bishop and Ward (1958). A commercial Co/Mo on alumina catalyst (American Cyanamid's HDS 1442A) containing about 9 wt % Mo was also used for comparison. This fresh catalyst was ground to -200 mesh and the ground sample had a surface area of ∿50 m^2/g.

The workups for all liquefaction runs consisted of determining benzene (or toluene) conversions and THF conversions from soxhlet extractions. The conversions were calculated as follows:

$$\text{Conversion} = \frac{\%\ \text{insols in} - \%\ \text{insols out}}{\%\ \text{DAF coal in}}$$

Results and Discussion

Pyrite Concentration

The results from a series of autoclave runs with the -5μm Robena pyrite show the effect of pyrite concentration on liquefaction (Figure 1). The abscissa on the plot in Figure 1 is weight percent pyrite added and does not include the 2.5 wt % pyrite in the Illinois #6 coal. These results show that benzene conversion increases with increasing Robena pyrite concentration.

The curve flattens out at about 8 wt % added Robena pyrite so that higher Robena pyrite concentrations give benzene conversions which are similar to those obtained with an 8 wt % loading.

The cause of the catalytic activity of pyrite is unknown. It may be due to the pyrite itself, the pyrrhotite formed from the pyrite under coal liquefaction conditions, the H_2S gas given off in the pyrite-pyrrhotite transformation, the pyrite-pyrrhotite decomposition reaction, or perhaps free radicals generated in the pyrite-pyrrhotite transformation (Bickel et al., 1980). It is also possible that the iron may be the catalytic species. Some of these possibilities are tested in the following sections where a series of different iron sulfide phases are tested for catalytic activity.

Pyrite Sources

Autoclave runs were also carried out to determine the effects of pyrite sources on catalytic activities. The effects of two pyrites were compared at concentrations of

5 wt % pyrite on a coal basis. The two pyrite samples were the -5μm Robena pyrite and -5μm synthetic pyrite from Cerac/Pure, Inc. The synthetic pyrite gave a benzene conversion of 82% as compared to 86% for the Robena pyrite (Figure 1). The reason for this variation is unknown.

Particle Size Effects

Three Robena pyrite samples, with different particle sizes, have been tested in autoclave runs with 5 wt % pyrite loadings on a coal basis. The compositions for the three samples were the same. Figure 2 shows the benzene conversions from these runs. The benzene conversion for a run without added pyrite is 73%. It is apparent that smaller particle sizes cause increased conversion. The relationship between particle size and conversion is not linear since the change in conversion in going from -149μm to -5μm is 3% whereas the change between -350μm and -149μm is 1%. This particle size effect may be caused by the decomposition of pyrite to pyrrhotite which takes place by diffusion of sulfur through the solid to the surface (Bickel et al., 1980). The larger particle sizes may slow down this reaction and perhaps even give incomplete conversion to pyrrhotite.

Composition and Surface Area Effects

A series of tubing reactor runs was carried out on three groups of synthetic iron sulfides of different compositions and varying surface areas within each compositional group.

The purpose of these tests was to determine the effects of different iron sulfides and varying surface areas on catalytic activity. The three groups studied included synthetic pyrites with 46.6 wt % Fe, pyrrhotites with about 60 wt % Fe and mackinawites (Fe_9S_8) with 66.2 wt % Fe. All of the materials in these three groups were handled under inert atmospheres or vacuum and all liquids used in the preparation or cleaning of these materials were sparged with nitrogen. Several of the syntheses carried out in this work by G. T. Noles of Sandia National Laboratories were based on variations of techniques used by A. Stiller of the West Virginia University. The mackinawite group consisted of two samples which were synthesized at 4°C and room temperature respectively from equivolume aqueous solutions of 2M $FeSO_4 \cdot 7H_2O$(AR) and 2M $Na_2S \cdot 9H_2O$(AR). The resulting black gelatinous precipitates were centrifuged, dried under vacuum and washed with copious quantities of water, methanol and acetone and dried again. The products of these two syntheses were pyrophoric and did not give an X-ray pattern. A small portion of the room temperature material which was heated at 60°C under vacuum gave a weak mackinawite X-ray pattern. Most of the X-ray work was carried out by D. Heinze of Sandia National Laboratories.

The 4°C mackinawite was used as the starting material for several pyrite syntheses. One of these syntheses involved adding a large excess of flowers of sulfur to the uncleaned mackinawite in water and heating this mixture at 85°C for several days under nitrogen. The product was washed with 6M HCl, water, methanol, carbon disulfide, and hexane and then dried. A. Stiller synthesized a large quantity of pyrite using this technique and then divided the material into three portions. One part was untreated whereas the other two were treated in hydrothermal bombs as follows:

Pyrite A: untreated
Pyrite B: annealed at 180°C for 4 days
Pyrite C: annealed at 230°C for 4 days

These three materials were cleaned as indicated above and X-ray patterns of the products only showed pyrite.

The two pyrrhotite samples were residues from tubing reactor liquefaction runs at 425°C for 30 minutes with the 4°C mackinawite and SRC-II heavy distillate and with acid cleaned Robena pyrite and SRC-II heavy distillate.

The results of tubing reactor runs made with these materials have been compared to an uncatalyzed run and runs with known catalysts. The catalyst loadings in all of these runs were 7.5 wt % on a coal basis. All runs were made in duplicate and the average results of the duplicate runs as well as the surface areas for all these materials are given in Table 2. The values for one standard deviation of the toluene conversion and THF conversions for the uncatalyzed run are given in Table 2 and were based on four repeat runs.

The results obtained from these runs show that the additions of pyrite, pyrrhotite or mackinawite give increased conversions as compared to an uncatalyzed run. The increases, however, are not as large as those obtained by the Co/Mo catalyst. It should be noted that the metals loading with the Co/Mo catalyst (9 wt % Mo) is much lower than the metals loading with the iron sulfides (47 to 66 wt % Fe). These runs show that varying the iron concentration between 47 and 66 wt % does not cause significant differences among conversions. The surface areas of the members of the pyrite group show a five-fold variation (2.1 to > 10 m^2/g). The surface areas of the pyrrhotites show about a two-fold variation (5.7 and 10.4 m^2/g). The mackinawites have very high surface areas of 75-80 m^2/g for the 4°C material and 40 m^2/g for the room temperature material. The results of the tubing reactor runs on these materials show that these surface area variations do not cause any significant differences in conversions.

The surface areas in Table 2 show several interesting things. First, the pyrrhotite derived from acid cleaned Robena pyrite has a surface area of 5.7 m^2/g whereas the acid cleaned Robena only has a surface area of 2.2 m^2/g. In addition, the pyrrhotite from the 4°C mackinawite has a surface area of only 10.4 m^2/g as compared to a surface area of about 80 m^2/g for the mackinawite. Therefore, two additional tubing reactor runs were made to determine how the surface area changes during liquefaction. The runs were made with 4°C mackinawite and SRC-II heavy distillate at 250°C and 350°C for 30 minutes with a 500 psi H_2 cold charge pressure. The surface areas which were determined on the residues of these runs were 52 and 12 m^2/g, respectively. An X-ray pattern of these residues showed very weak, broad lines which were attributed to pyrrhotite. The pattern for the 250°C residue was weaker than the 350°C pattern. The mackinawites do not give a pattern.

The surface area changes of the pyrite and the mackinawite may be related to the conversion of the initial iron sulfides to pyrrhotite. Work that has been done on the kinetics of the pyrite-pyrrhotite transformation (Bickel et al., 1980) indicates that this reaction is very rapid at 350°C. It is therefore possible that the pyrites (and perhaps the mackinawites) may be almost completely converted to pyrrhotite during the two minute heat up of the tubing reactors and that the surface areas of the catalysts may have changed considerably before liquefaction temperatures are reached. It is also possible that there is a build-up of organic material on the surfaces of the iron sulfides which results in lower surface areas. This is currently being tested.

One additional point that should be noted from the data in Table 2 is that the acid cleaned Robena pyrite has a reduced surface area as compared to the whole Robena pyrite with the 30 wt % impurities. These two materials, however, still show the same conversions.

Defects in Pyrite

Montano and Granoff (1980) have recently observed an inverse linear relationship between the iron content of pyrrhotites in liquefaction residues and the yield of benzene soluble liquid products. The iron content of pyrrhotites is inversely related to the vacancy concentrations in the pyrrhotites so that higher vacancy concentrations in the pyrrhotites from liquefaction residues are directly related to higher benzene conversions. It is not known if the increased number of vacancies is a cause of increased conversion or an effect.

A recent study of the Soviet effort (Adadurov et al., 1973) in shock-induced solid state chemistry has revealed a major effort in activation of catalysts with shock loading. The Soviets have demonstrated substantial improvements in catalytic activity due to shock-induced introduction of massive numbers of point defects. Therefore, we have carried out a study on the effects of increased vacancy concentrations in pyrite on liquefaction.

A shock-loading test was carried out by R. Graham of Sandia National Laboratories on cleaned Robena pyrite. This material was packed to a density of 2.5 g/cc in a copper capsule and was explosively loaded to a pressure of about 15 GPa in the copper. The sample recovery after shocking was 96%. An X-ray powder pattern (taken by B. Morosin of Sandia National Laboratories) of the product from this run showed the presence of pyrite and small amounts of marcasite (present in the starting material) and smythite (Fe_9S_{11}) which was formed during the shock-loading. The high 2θ pyrite lines were broadened relative to the unshocked material thereby indicating an increase in defect concentration. The marcasite and smythite patterns were very weak so that the relative defect levels in these phases could not be determined.

The product obtained in this shock-loading test was tested in tubing reactor runs for catalytic activity. The run was made in duplicate and the average results are shown in Table 2. The shock-loading has resulted in a decrease in surface area from 2.2 m^2/g to 1.6 m^2/g. The conversions show that there is no significant difference between the runs with unshocked cleaned Robena and the runs with the shocked material. It is not known, however, if the enhanced defect level in pyrite yields an enhanced defect level in the resulting pyrrhotite. Therefore, we may not be testing the same effect observed by Montano and Granoff (1980).

One property of pyrite is still being tested to determine its effect on catalytic activity. This is the morphology of the pyrite. Pyrite can occur in coal as a bulk material, such as the Robena pyrite, or as small discrete particles, or as raspberry-shaped clusters of crystals known as framboids. A sample of concentrated framboidal pyrite from an Iowa coal which was sent to us by R. Greer of the Iowa State University is currently being characterized. This material will be tested in tubing reactors and the results compared to those obtained with Robena pyrite.

Summary

The purpose of this study was to increase the catalytic activity of pyrite and other iron sulfides by changing their concentration, source, particle size, surface area, composition and defect concentration. The results of this work were as follows:

1. Autoclave experiments have shown that benzene conversion increases with increasing concentrations of Robena pyrite and levels off at about 8 wt % pyrite on a coal basis.
2. Different sources of pyrite (coal-derived versus synthetic) give different conversions even with the same particle size.

3. Autoclave tests on Robena pyrite of varying particle size have shown that -5μm material gives a significant increase in conversion as compared to -350μm material and -149μm material.
4. Three different iron sulfides (with iron compositions between 47 and 66 wt %) have been tested in tubing reactors. The results show that there are no significant differences in conversion as a result of variations in iron concentration.
5. Synthetic pyrites (with surface areas from 2.1 m^2/g to > 10 m^2/g), synthetic mackinawites (with surface areas of 40 m^2/g and 80 m^2/g) and pyrrhotites (with surface areas of 5.7 and 10.4 m^2/g) have been tested as catalysts in tubing reactor runs. The results show that there is no significant increase in conversion with surface area.
6. The pyrrhotites which are formed from iron sulfides during liquefaction have surface areas which are very different from the starting materials.
7. All iron sulfides studied show significant increases in conversion relative to uncatalyzed runs although none of the increases are as high as those obtained with fresh Co/Mo on alumina catalyst.

8. The introduction of defects into the pyrite structure does not increase catalytic activity.

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	West Virginia	Illinois #6
Carbon	73.64	67.23
Hydrogen	5.03	4.87
Nitrogen	1.41	1.42
Sulfur	2.76	4.03
Oxygen (difference)	5.38	8.82
Ash	11.78	13.63
Sulfur Forms		
Pyritic	1.34	1.35
Sulfate	0.03	0.15
Organic	1.39	2.53

Table 1 Ultimate and sulfur forms analyses of coals used in this study reported as weight percent on a dry basis.

Catalyst	Surface Area (m^2/g)	Toluene Conv. (%)	THF Conv. (%)
Uncatalyzed	-	43 ± 2	65 ± 4
Co/Mo	50	56	77
Robena pyrite	3.5	49	69
Cleaned Robena	2.2	50	71
Pyrite A	>10	49	70
Pyrite B	4.9	50	72
Pyrite C	21	48	74
Pyrrhotite (4°C mack.)	10.4	47	70
Pyrrhotite (Cleaned Robena)	5.7	47	69
Mackinawite (4°C)	75-80	48	73
Mackinawite (Room Temp)	40	47	67
Shocked cleaned Robena	1.6	49	70

Table 2 The conversions for these tubing reactor runs are average results from duplicate runs. All runs were made with West Virginia Blacksville #2 coal and SRC-II heavy distillate.

Figure Captions

Figure 1. Changes in benzene conversion with increasing concentrations of -5μm Robena pyrite.

Figure 2. The change in benzene conversion as a function of the particle size of Robena pyrite.

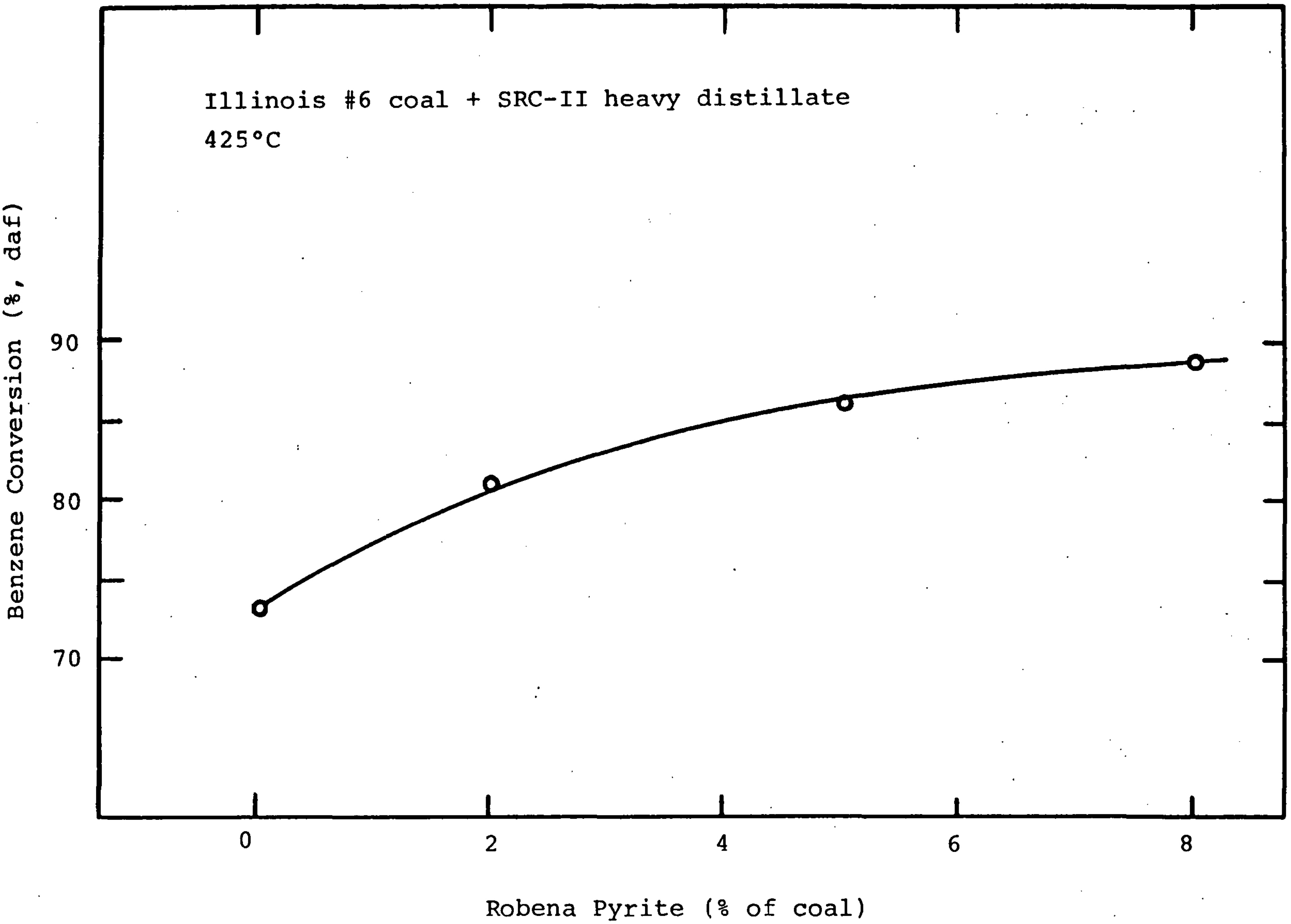
Illinois #6 coal + SRC-II heavy distillate
425°C
Benzene Conversion (%, daf)
90
80
70
0
2
4
6
8
Robena Pyrite (% of coal)

Figure 1

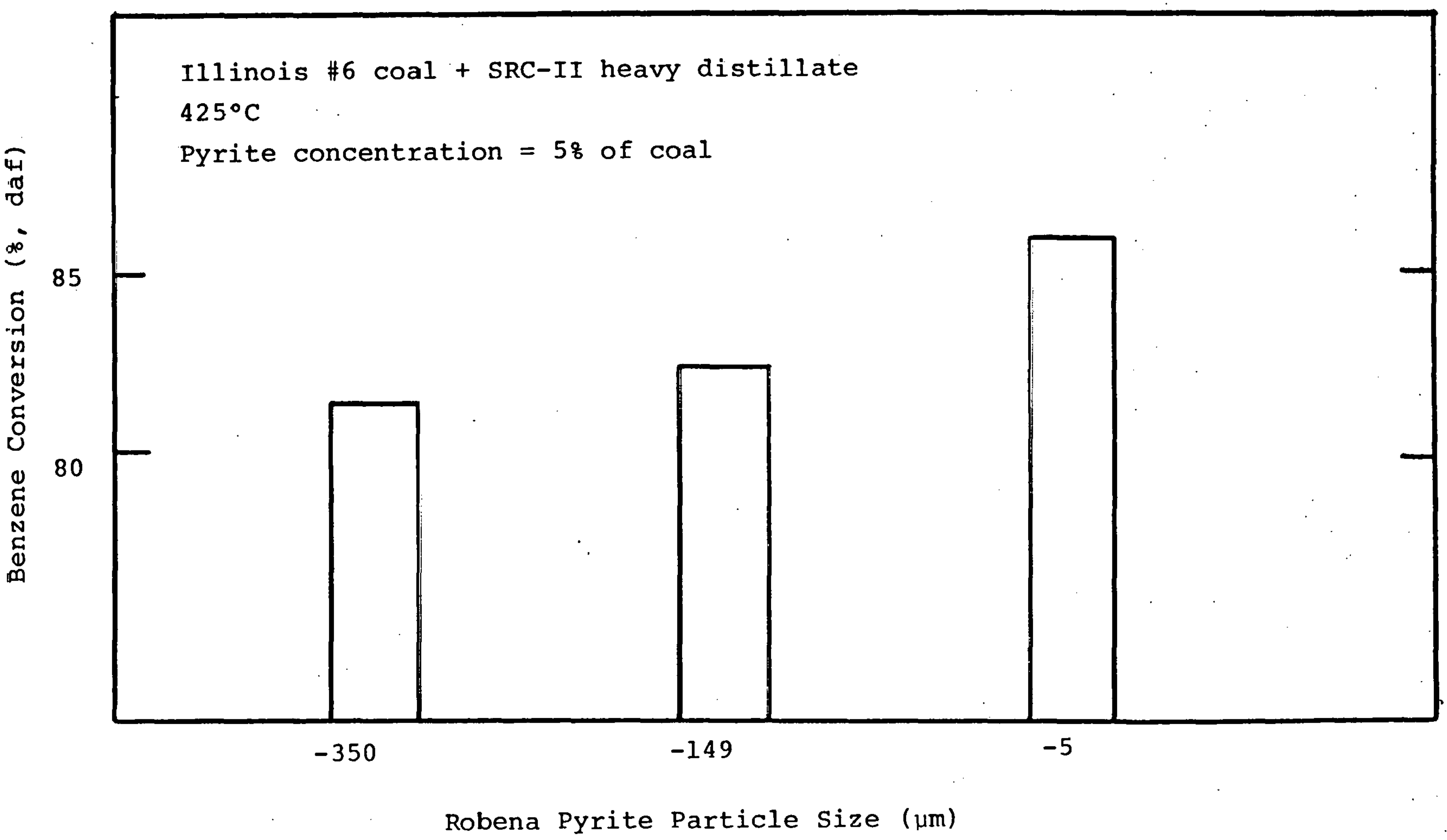
Illinois #6 coal + SRC-II heavy distillate
425°C
Pyrite concentration = 5% of coal
Benzene Conversion (%, daf)
85
80
-350
-149
-5
Robena Pyrite Particle Size (μm)

Figure 2