

TECHNICAL REPORT
September 1, 1986 through August 31, 1987

Project Title: Desulfurization of Illinois Coals by Thermal, Chemical and Magnetic Methods
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ABSTRACT

The overall goal of this research is to develop an economical process to desulfurize high sulfur Illinois coals by combining thermal, chemical and physical methods. Thermal treatment has been utilized to produce coal chars with less sulfur than the parent coal, and chemical methods have been used to remove additional sulfur by oxidatively converting inorganic sulfur to magnetic monoclinic pyrrhotite and then removing it magnetically, or by hydrodesulfurization of the char at elevated temperatures.

Several magnetic separations on chars produced under slightly oxidizing conditions have shown that significant amounts of inorganic sulfur can be removed. Under the best conditions tested, chars of 2.0 percent sulfur were obtained from a coal initially containing 6.2 percent sulfur, a 1.1% sulfur char was obtained from a 3.23% sulfur coal and 0.88% sulfur chars were obtained from a 2.35% sulfur coal. Extremely low sulfur chars were obtained by hydrodesulfurization. Chars of 0.38 (0.60 lbs SO₂/MMBTU) percent sulfur were obtained from a high sulfur run-of-mine coal having a sulfur content equivalent to 9.8 lbs SO₂/MMBTU. This low sulfur char was obtained by first physically cleaning the coal to remove pyrite, pre-oxidizing the coal prior to pyrolysis and then carrying out the hydrodesulfurization in the presence of an iron oxide acceptor. This char could be combusted in any boiler without flue gas desulfurization and still meet the stringent NSPS of 90 percent sulfur reduction based on run-of-mine coal. Kinetic data indicate that hydrodesulfurization proceeds in two stages where a high rate occurs initially followed by a relatively slow rate of desulfurization at longer residence times.

EXECUTIVE SUMMARY

The overall goal of this project has been to develop a process to desulfurize high sulfur Illinois coals by a combined physical, thermal and chemical approach. It is believed that most inorganic sulfur is best removed by physical means. Organic sulfur, however, is removable only by chemical or thermal methods. In the work described here, thermal processing, or pyrolysis, has been used to convert 30-40 percent of the coal to liquid or gaseous hydrocarbons and produce a char with less sulfur than the parent coal. The remaining sulfur was removed in some coals by converting the iron sulfide in the char to a magnetic form, monoclinic pyrrhotite, by a mild oxidation and then removing the sulfide magnetically. Another approach has been to hydrodesulfurize the char, preferably in the presence of an inorganic hydrogen sulfide scavenger, and then physically remove the scavenger. Iron oxide scavengers have been utilized, and in these cases, the partially sulfided product was removed magnetically.

Data has been collected using a variety of equipment. A quartz pyrolysis system was constructed to produce enough char for X-ray diffraction, magnetic susceptibility, magnetic separation tests and microscopic examinations of the sulfides. The magnetic susceptibility tests were run at the University of Illinois and the X-ray diffraction at the Illinois State Geological Survey. Two fluidized bed reactors were used for pyrolysis and hydrodesulfurization tests and a Perkin-Elmer gas chromatograph equipped with a sulfur-specific flame photometric detector was used to aid in material balance and kinetic data collection.

Several magnetic separation tests on chars produced under slightly oxidizing conditions has demonstrated that significant reductions of inorganic sulfur are possible. Following magnetic separation, chars as low as 2.04 percent were obtained from a coal having 6.17 percent sulfur. Following magnetic separation, chars of 1.1 to 1.9% sulfur were obtained from a coal containing 3.23% sulfur and chars of 0.88-1.15% sulfur were obtained from another coal having a total sulfur content of 2.35%. Thus, high levels of desulfurization are possible by pyrolysis, a mild oxidative treatment and magnetic separation. However, the extent of desulfurization was highly dependent on the nature of the sulfur in the char. High organic sulfur chars would generally not respond well by this method and would need to be hydrodesulfurized to achieve significant sulfur reductions.

A large number of hydrodesulfurization experiments were conducted using Illinois Basin Coal Sample Program (IBCSP) #4 coal. In the first set of experiments, a half-factorial experimental design was employed to determine the effect of hematite as an acceptor on the extent of hydrodesulfurization. The overall effect of the presence of hematite was to lower the specific sulfur content (lbs SO₂/MMBtu) by 0.82, a significant reduction. This enhanced desulfurization was also accompanied by an average 9.25 percent decrease in char yield. In the second series of experiments, hematite or magnetite were employed as acceptors. In general, no statistical difference was observed as each material worked equally well in aiding desulfurization. In a third series of experiments, very high levels of desulfurization (greater than 90 percent) were attained by first physically

cleaning the coal, pre-oxidizing it prior to pyrolysis, and carrying out the desulfurization in the presence of an iron oxide acceptor. Under the best conditions, a char of 0.38 percent sulfur, equivalent to 0.60 lbs SO₂/MMBTU, was obtained. This char was sufficiently desulfurized to meet the stringent NSPS of 90 percent reduction (based on run-of-mine coal), meaning it could be combusted in any boiler without the need for flue gas desulfurization.

Low sulfur chars were obtained more easily with physically cleaned coal. The extent of sulfur removal was further increased by pre-oxidation of the coal prior to pyrolysis and by employing higher temperatures and longer treatment times. Utilizing this material, a compliance char (1.2 lbs SO₂/MMBTU) was obtained without adding an acceptor. Further experimentation led to the optimum process conditions of 866-880°C and chars of 0.5% sulfur were obtained. This is greater than 90% sulfur reduction, based on the run-of-mine coal. The degree of physical cleaning does not necessarily need to be great. In fact, crushing the coal to ultrafine sizes as occurs with any deep cleaning process appears to make the resultant char extremely difficult to handle. Experiments with one Aggregate Flotation coal were not encouraging as desulfurization was inferior compared to physically cleaned char which had not been appreciably size-reduced.

Kinetic data for hydrodesulfurization were obtained in the temperature range of 700-866°C and at atmospheric pressure. Two stages of desulfurization were evident with a markedly higher rate occurring at first followed by a relatively slow rate of desulfurization at longer residence times. This is probably attributable to an equilibrium controlled reaction at first followed by a Knudsen diffusion controlled reaction.

OBJECTIVES

The overall objective of the project has been to develop a process or processes to desulfurize high sulfur Illinois coals by thermal, chemical and magnetic methods. Specific objectives have included the following:

1. Optimize the conditions for the conversion of pyrite to magnetic pyrrhotite.
2. Determine the parameters necessary to achieve the magnetic conversion in a fluidized bed reactor.
3. Test the technical feasibility of using iron-bearing acceptors during char hydrodesulfurization.
4. Demonstrate the feasibility of magnetically separating monoclinic pyrrhotite from char.
5. Investigate the thermodynamics for converting hexagonal pyrrhotite to monoclinic pyrrhotite.
6. Examine the thermodynamics for char hydrodesulfurization with iron oxide acceptors.
7. Obtain a material balance across the hydrodesulfurization reactor.
8. Determine the type of pyrolysis treatment (no treatment, pre-oxidation or post-oxidation) which produces the most suitable char for hydrodesulfurization.
9. Determine combustion and gasification reactivity of selected char samples.

INTRODUCTION AND BACKGROUND

The high sulfur content typical of Illinois coals precludes their use for direct combustion in stationary power plants unless the sulfur is removed after combustion as in flue gas desulfurization, during combustion as in fluidized bed combustion, or before combustion by physical and/or chemical cleaning. Physical cleaning techniques are effective in removing only inorganic sulfur. However, organically bound sulfur can only be removed by chemical or thermal methods. In this project, Illinois coals are being desulfurized by an approach which utilizes both physical and chemical techniques (including thermal processing). Thermal treatment can be used to remove some organic and pyritic sulfur and to produce liquid and gaseous fuels. Additional sulfur can be removed by converting hexagonal pyrrhotite to magnetic monoclinic pyrrhotite and magnetically separating the sulfide or by treating the char with hydrogen, preferably in the presence of an acceptor. A sulfided iron-based acceptor is readily removed by magnetic methods.

EXPERIMENTAL PROCEDURES

Two major efforts have been underway. The magnetic conversion effort has been oriented toward maximizing sulfur removal by converting the pyrite to magnetic monoclinic pyrrhotite and removing the sulfur by magnetic means. The second effort, char hydrodesulfurization, has focused on the removal of organic and inorganic sulfur by treatment with hydrogen.

Magnetic conversion

Initially, pyrolysis experiments to form magnetic (monoclinic) pyrrhotite were carried out using a small bench scale pyrolysis system. This system consisted of a single quartz tube, a split tube furnace, and a programmable temperature controller. The quartz tube was mounted on a trolley which permitted quick extraction of the tube from the furnace and rapid cool down of the charred sample. The quartz tube was purged with pure nitrogen or nitrogen containing a trace amount of oxygen. Gas flow rates were controlled by a set of flow meters and valves. The volatiles were swept out of the quartz reactors and burned off with a bunsen burner inside a laboratory hood. The small pyrolysis system was replaced with a larger bench scale system capable of handling at least 10 times more coal sample.

The new system, designated here as the rotary pyrolysis system and shown in Figure 1, consists of a larger quartz reaction tube (50 mm O.D. x 250 mm), a three zone split tube furnace, a variable speed rotary motor, three programmable temperature controllers, and a temperature recorder. The quartz reaction tube was indented along the length of the tube in order to enhance tumbling of coal particles when the tube was rotated. The three outside thermocouples were calibrated initially against a thermocouple placed inside the tube while the tube was stationary. Temperatures at three zones were controlled by the programmable controllers and recorded by a multichannel temperature recorder. The variable speed rotary motor had an operating speed ranging from 15 to 90 rpm. The system was designed to handle 10 to 15 grams of coal for each pyrolysis run.

Sample preparation

A number of different coal samples were used this year requiring special procedures to ensure uniformity. All coals employed in Part B were obtained from the IBCSP. All coal samples were first size reduced to -28 mesh using a staged crushing and screening procedure in order to minimize the production of fines. A series of riffing operations were performed to produce representative samples for individual coal pyrolysis experiments.

Most of the experiments were performed with IBCSP #4 coal which is a run-of-mine, high sulfur coal from the Illinois (Herrin) No. 6 seam. Two types of physically cleaned coal were prepared from the run-of-mine coal which had 34% ash.

In order to reduce the mineral matter content of the sample to an acceptable level, a desliming step was employed. This step entailed slurring and agitating the sample and then sieving it over a 235 mesh screen. The

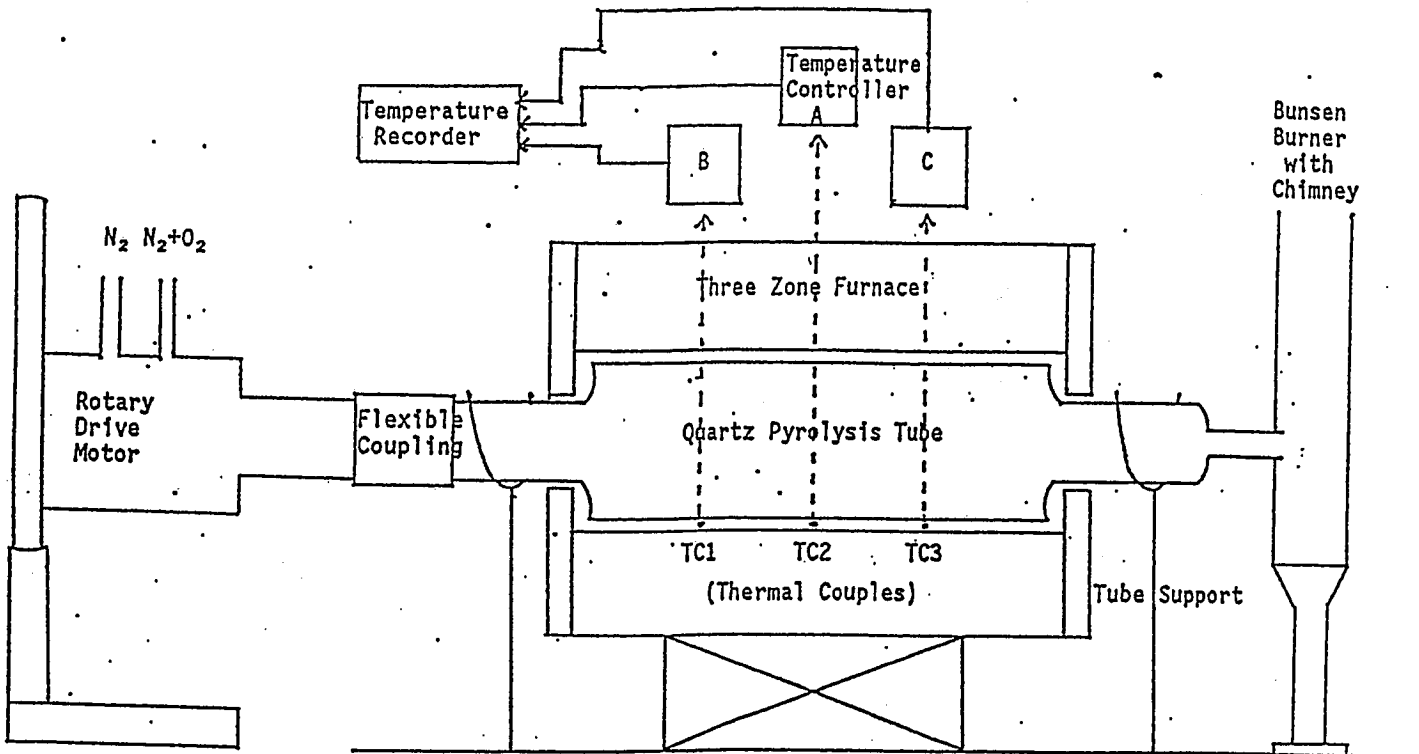


Figure 1. Schematic diagram of rotary pyrolysis system.

step effectively reduced the clay content of the sample, but retained much of the coarser pyrite and other mineral matter. The sample after treatment had 14.8% ash, 2.64% pyrite and 5.13% total sulfur. A 28x200 fraction was prepared from the deslimed coal utilizing a staged crushing and screening technique to ensure that the size fraction was representative of the starting material. This sample is designated here as deslimed.

A second sample of IBCSP #4 was prepared by physical cleaning using a gravity concentrating table. Tabling is an effective method for rejecting liberated coarse pyrite and mineral matter. The sample was also deslimed using the above procedure to reject any clays that reported to the coal fraction. This sample is referred to here as tabled. Analyses of these two samples and the parent run-of-mine coal appear in Table 1.

Table 1. Analyses of run-of-mine, deslimed and tabled feed coals.

| Analysis | Run-of-mine | Deslimed | Tabled |
|---|-------------|----------|--------|
| Proximate, wt % as received | | | |
| Moisture | 10.2 | 3.5 | 1.5 |
| Volatile matter | 27.4 | 36.6 | 38.3 |
| Fixed carbon | 28.2 | 45.1 | 50.4 |
| Ash | 34.2 | 14.8 | 9.8 |
| Ultimate, wt % daf | | | |
| Hydrogen | 5.59 | 5.26 | 4.64 |
| Carbon | 74.26 | 77.91 | 81.66 |
| Nitrogen | 1.29 | 1.57 | 1.90 |
| Oxygen | 12.00 | 8.97 | 7.61 |
| Sulfur | 6.77 | 6.28 | 4.18 |
| Pyrite | 3.76 | 3.05 | 1.22 |
| Organic | 2.84 | 3.23 | 2.86 |
| Sulfate | 0.16 | tr | 0.10 |
| Calorific value, Btu/lb | 7,625 | 11,554 | 12,556 |
| Specific sulfur content lbs SO ₂ /MMBtu | 9.84 | 8.88 | 5.91 |

Char hydrodesulfurization

Char production - The fluidized bed reactor system is shown schematically in Figure 2. The reactor was constructed from a 21.5-inch length of 2.25-inch O.D. type 304 stainless steel. The reactor has a 2.01-inch inside diameter and a 0.120 inch wall thickness. A porous metal distributor plate constructed from Hastelloy-X stainless steel was welded to a flanged sleeve which was easily removable from the reactor for periodic cleaning. When assembled, the distributor plate was located 6 inches from the bottom of the reactor leaving 15.5 inches for the bed with freeboard. An additional seven inches of freeboard was added by welding a section of 4-inch diameter type 304 stainless steel to the top of the 2-inch section. The expanded diameter zone was designed to minimize the elutriation of fines. A cyclone separator was added external to the reactor to separate most of the fines which managed to escape.

The top flange of the reactor was fitted with a sample injection chamber and two type K thermocouples. The sample injector was also constructed of type 304 stainless steel and was designed to hold 200 gm of material. The chamber could be pressurized with nitrogen prior to injection. The sample injection took place by opening a ball valve. This feature allowed the system to be heated up prior to introducing the coal charge. One of the two type K thermocouples was mounted dead center in the reactor; this was

used for system temperature control. The other thermocouple, mounted at a distance of 1/2 inch from the wall, was used strictly for monitoring.

The system was heated by a 3-inch, 2260 W, model 3210 Applied Test Systems split tube furnace. The system could be cooled by compressed air emanating from jets in a cooling ring surrounding the reactor. The compressed air was directed into the annular space between the reactor and furnace. This feature permitted rapid cooling following an experimental run. An LFE model 2011 temperature controller was used for system temperature control. This instrument controlled an Asco solenoid valve for cooling and a Payne power controller for heating using the tube furnace. An additional part of the system was a Barber Coleman model 121L limit controller for protecting the furnace from accidental overheating. This device monitored a thermocouple mounted in the furnace. If the furnace temperature exceeded the designated high process set point, power to the furnace was cut off. The LFE temperature controller was quite versatile and allowed for programmable operation including a ramp and soak mode which was especially useful. The reactor system was interfaced with an IBM PC-XT personal computer using a Keithley DAS data acquisition system. The system is used for monitoring and data collection and analysis.

Three different types of chars were prepared and are designated here as pre-oxidized, non-oxidized, and post-oxidized. Several runs were performed to produce several kilograms of char for hydrodesulfurization tests. For each of the three chars, the product chars from the individual runs were combined and riffled into 25-gm portions, and stored under inert conditions in sample bottles which were sealed with paraffin.

The pre-oxidized char was prepared by heating a 200-gm charge of coal to 250°C in the 2-inch FBR using nitrogen as a fluidizing gas. Once at 250°C, the fluidizing gas was switched to five percent oxygen in nitrogen. The coal was fluidized under these conditions for 30 minutes at which time the fluidizing gas was continued. The char was heated to a final temperature of 850°C and held there for 15 minutes. The reactor was cooled to ambient conditions under a slight purge of nitrogen.

Non-oxidized chars were prepared by following a modified FMC COED heating schedule. Multistaged heating permits these caking coals to be pyrolyzed without agglomeration. For IBCSP #4 coal, it was found necessary to employ four soak temperatures, namely 350, 375, 400, and 425°C. Once the temperature reached 850°C, the char was held for 15 minutes before cooling to ambient conditions. Again, a slight purge of nitrogen was used during the cool down period. No effort was made to optimize this heating schedule. Instead, runs were performed until suitable conditions (no agglomeration) were found. All subsequent tests were run under these conditions. Thus, it is entirely possible that one or more soak periods could have been eliminated by further testing and optimization.

The post-oxidized sample was prepared exactly as the non-oxidized sample with one exception. During the cool down period, the bed temperature was allowed to cool to 250°C at which point five percent oxygen was used as a fluidizing gas. This treatment was continued for 30 minutes after which

the gas was switched to a slight purge of nitrogen. The reactor was then cooled to ambient conditions.

Hydrodesulfurization - A 1-inch batch fluidized bed hydrodesulfurizer (HDS) was used for char hydrodesulfurization tests and is shown schematically in Figure 3. The reactor was constructed from a 24-inch length of type 446 stainless steel, schedule 40 pipe. A distributor plate constructed from porous Hastelloy-X stainless steel having an average pore size of 10 microns was located 9 inches from the bottom of the pipe. The space below the plate was filled with 1/4-inch ceramic Raschig rings which served as a gas preheater. Type 446 stainless steel caps were used to seal both ends of the reactor and to allow the reacting gas to enter and exit through 1/4-inch tubing.

For each hydrodesulfurization experiment, an amount of char, usually about 10 grams, was accurately weighed and charged to the reactor. Acceptor, if used, was also accurately weighed before charging to the system. Teflon tape and a silver goop compound were applied to the threads at the end of the reactor pipe to provide a tight seal with the caps and to prevent seizing.

The sample was heated rapidly to the reaction temperature under a nitrogen flow which generally took about 45 minutes. Once the system reached the designated reaction temperature ($\pm 1^\circ\text{C}$), nitrogen was shut off and hydrogen was introduced to the reactor. When the desired treatment time had elapsed, hydrogen was turned off and nitrogen was once again introduced to the reactor. The reactor system was allowed to cool to near room temperature and the desulfurized char was removed, weighed and analyzed. Gas samples were taken at the reactor outlet and analyzed using a Perkin-Elmer model 8500 gas chromatograph equipped with a flame photometric detector specific for sulfur compounds. Generally, gas samples were obtained by syringing from 10-200 microliters from the outlet tube of the hydrodesulfurization reactor. Two columns were used; column one was a 1.5-ft x 0.125-in TFE column packed with 60x80 mesh deactigel and column two was 6-ft x 0.125-in stainless steel column packed with 80x100 mesh chromosorb 102.

Magnetic separations were performed on some reacted char samples using a hand magnet. This procedure was effective in separating magnetic particles from a relatively small sample size. Samples which were originally spiked with iron oxide acceptors were easily handled using this technique and char samples hydrodesulfurized without acceptor had some magnetic particles which were relatively easy to remove.

Experimental design and data analysis - All of the hydrodesulfurization experiments, were statistically designed to maximize the amount of information obtained from a fixed number of experiments. The experimental plans included Plackett-Burman, Box-Wilson, and full and half-factorial designs (1,2,3). The data were analyzed on an IBM-XT computer using a statistical software package (4).

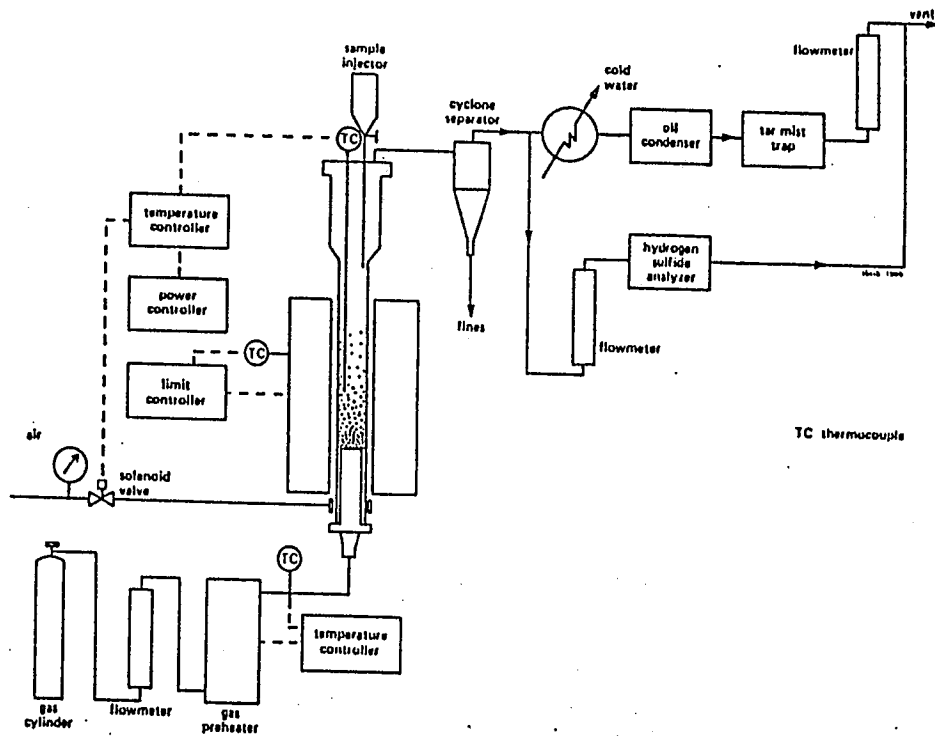


Figure 2. Schematic diagram of 2-inch fluidized bed reactor system.

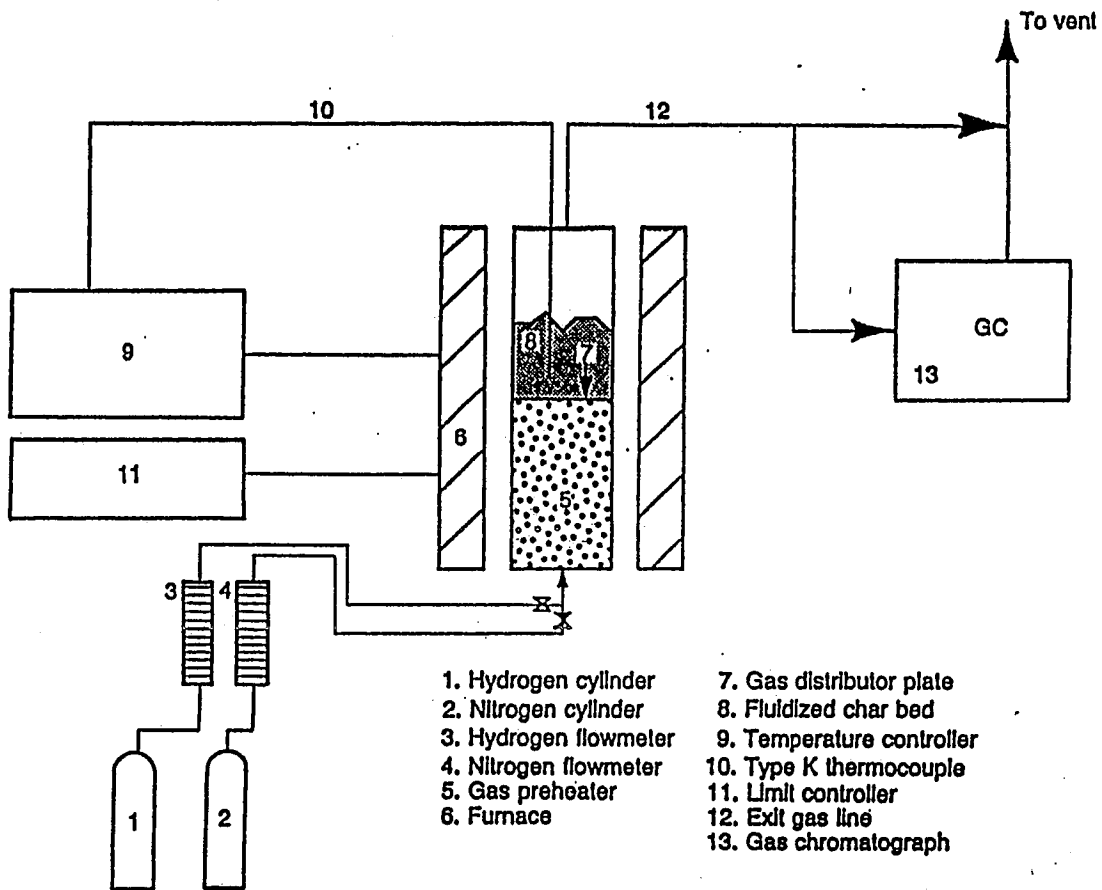


Figure 3. Schematic diagram of 1-inch fluidized bed hydrodesulfurizer.

Three response variables were calculated for most hydrodesulfurization experiments. The specific sulfur content (Y_1) relates the sulfur content of the product char to its heating value and is calculated as follows:

$$Y_1 = \frac{\text{wt \% sulfur}}{\text{Btu/lb}} \times 20,000 \quad (1)$$

This parameter depends only on the sulfur content of the char product, thus it reflects the effectiveness of all processing steps that remove sulfur. The second response variable is termed the percent initial sulfur remaining in the char (Y_2). This parameter reveals the effectiveness of the hydrodesulfurization only as it depends on the sulfur contents of the feed and hydrodesulfurized chars. It is defined as:

$$Y_2 = \frac{(\text{wt\% S})_{\text{prod}} (\text{mass})_{\text{prod}}}{(\text{wt\% S})_{\text{feed}} (\text{mass})_{\text{feed}}} \times 100 \quad (2)$$

The third variable is char yield (Y_3) and is simply the mass of char product divided by the mass of feed char multiplied by 100.

RESULTS AND DISCUSSION

Magnetic conversion

To determine the optimum conditions for forming magnetic monoclinic pyrrhotite during pyrolysis with a trace of oxygen numerous pyrolysis experiments were initially conducted in a small bench-scale pyrolysis system. The type of sulfides produced during the pyrolyses were monitored by X-ray diffraction (XRD). A coal sample identified as "RK-B-4" was used for preliminary tests because of its high pyrite content facilitates the detection of sulfides by XRD. Many additional pyrolysis experiments were later made in a larger more dynamic rotary pyrolysis system and finally a few experiments were carried out in a fluidized bed reactor. In later experiments, IBCSP #2 and #3 were used as well due to their lower organic sulfur contents. Magnetic separations and total sulfur analyses were made on several of the chars produced from all three feed coals.

Small bench-scale pyrolysis system - A series of 27 experiments were conducted in the small bench-scale pyrolysis system at various temperatures, oxygen concentrations and oxidative treatment times. The experimental conditions, results of the XRD analysis, and magnetic susceptibility data on the char are shown in Table 2. Trace of oxygen was added only during the soak and cooling periods of the pyrolysis. The XRD data indicated that monoclinic pyrrhotite was formed at all three temperatures.

In general, at 500°C, very little pyrrhotite was formed from the initial pyrite in the coal. This is shown in the pyrrhotite/pyrite ratio (PO/PY) column in Table 2. However, a significant amount of magnetite was formed in nearly all the 500°C chars resulting in the relatively high magnetic susceptibility values. The magnetite probably formed as a surface alteration on the pyrite grains in the char.

During the 550°C pyrolysis more monoclinic pyrrhotite appeared to have been formed, however, significant amounts of pyrite still remained in several of the chars. The optimum formation of monoclinic pyrrhotite at this temperature was obtained with 0.5 percent oxygen concentrations. Some magnetite was also formed when 0.5 and 1 percent oxygen concentrations were used. With lower oxygen concentrations (0.1%), less magnetite was formed which is also reflected in the lower magnetic susceptibility values.

The data for the 600°C runs show that the pyrite was converted to pyrrhotite extensively except in one case. Monoclinic pyrrhotite was observed in the 600°C chars which were pyrolyzed under the higher oxygen concentrations and shorter soak times. No monoclinic pyrrhotite was observed when using a 0.1 percent oxygen concentration at 600°C. Pyrolysis conducted at 600°C and 0.1 percent oxygen concentration consistently formed troilite and hexagonal pyrrhotite and showed the lowest magnetic susceptibilities.

The overall relationship between the formation of monoclinic pyrrhotite and the magnetic susceptibility data for all the chars did not show a positive correlation. This can be explained by the presence of the highly magnetic mineral, magnetite, in many of the chars.

Table 2. X-Ray diffraction and magnetic susceptibility data of chars produced under various pyrolysis conditions^a.

| No. | Pyrolysis Parameters | | | XRD Analysis | | | Magnetic Susceptibility of the chars 10 ⁻⁶ CGS units |
|-----|----------------------|----------------|-----------------|--------------|-------|--------|--|
| | Temp °C | Soak Time(min) | %O ₂ | Types of PO | PO/PY | oxides | |
| 290 | 500 | 2 | 1.0 | mono/hex | 0.2 | M,H | 306 |
| 289 | 500 | 5 | 1.0 | mono/hex | 1.1 | M | 334 |
| 288 | 500 | 10 | 1.0 | mono/hex | 0.2 | M,H | 364 |
| 293 | 500 | 2 | 0.5 | hex/mono | 0.1 | M,H | 316 |
| 292 | 500 | 5 | 0.5 | mono/hex | 0.2 | M | 380 |
| 291 | 500 | 10 | 0.5 | mono/hex | 0.2 | M,H | 319 |
| 302 | 500 | 2 | 0.1 | hex/mon | 0.2 | M | 231 |
| 301 | 500 | 5 | 0.1 | hex/mon | 0.2 | M | 318 |
| 300 | 500 | 10 | 0.1 | hex/mon | 0.3 | M | 334 |
| 284 | 550 | 2 | 1.0 | mono/hex | 0.2 | M,H | 329 |
| 283 | 550 | 5 | 1.0 | mono/hex | 0.7 | M | 201 |
| 282 | 550 | 10 | 1.0 | mono/hex | 0.8 | M,H | 130 |
| 287 | 550 | 2 | 0.5 | mono | 0.2 | M | 209 |
| 286 | 550 | 5 | 0.5 | mono | 5.3 | | 174 |
| 285 | 550 | 10 | 0.5 | mono/hex | 0.6 | M,H | 282 |
| 299 | 550 | 2 | 0.1 | hex/mon | 1.2 | M | 163 |
| 298 | 550 | 5 | 0.1 | mono/hex | 4.0 | | 149 |
| 297 | 550 | 10 | 0.1 | hex/mon | 6.0 | | 150 |
| 278 | 600 | 2 | 1.0 | mono/hex | ∞ | M | 248 |
| 277 | 600 | 5 | 1.0 | hex/mon | ∞ | M,H | 231 |
| 276 | 600 | 10 | 1.0 | hex/troil | ∞ | M | 98 |
| 281 | 600 | 2 | 0.5 | mono | 2.4 | M | 151 |
| 280 | 600 | 5 | 0.5 | mono/hex | ∞ | M | 162 |
| 279 | 600 | 10 | 0.5 | hex/mon | ∞ | M | 202 |
| 296 | 600 | 2 | 0.1 | hex/troil | ∞ | | 51 |
| 295 | 600 | 5 | 0.1 | hex/troil | ∞ | | 26 |
| 294 | 600 | 10 | 0.1 | hex/troil | ∞ | | 20 |

^aPO=Pyrrhotite, PY=Pyrite, M=Magnetite, H=Hematite, ∞ =infinite large, mono=mono clinic, Hex=Hexagonal, Troil=Troilite.

A second set of pyrolyses were conducted in the small pyrolysis system using parameters which were found favorable for the formation of monoclinic pyrrhotite during the initial set of experiments. However, for this second set of experiments the trace of oxygen was added during the heat-up stage (ramp) as well as the soak and cooling stages of the pyrolyses. To study the sulfide mineralogy in more detail and better compare the minerals formed in the two sets of experiments magnetic separations were made on many of the chars. The magnetic separations were made by placing the sample on weighing paper and drawing the paper over a strong magnet. Table 3 shows the XRD results of nine samples which were treated with a trace of oxygen only during the soak and cooling stages of pyrolysis. Table 4 shows the XRD results of eight samples which were treated with a trace of oxygen during the entire pyrolysis run. The results show that monoclinic pyrrhotite was formed in all the chars. According to the XRD patterns more magnetite was formed at 500°C and 550°C when the trace of oxygen was added to the pyrolysis only during the soak and cooling time. No magnetite was observed in the chars which had the trace of oxygen added to the system during the ramp as well as the soak and cooling stages. This was later found to be true only for the small pyrolysis system.

Table 3. X-ray diffraction data for chars and their magnetic fractions (RK-B-4 Coal feed was <60 mesh).

| Pyrolysis Parameters | | | | XRD Analysis | | |
|----------------------|-----------|-----------------|--------------------|--------------|---------------|-----------|
| No. | Temp (°C) | Soak time (min) | O ₂ (%) | Types of Po | Po/Py (ratio) | Fe-oxides |
| 301 | 500 | 5 | 0.1 | hex/mono | 0.2 | M |
| 301-mag | 500 | 5 | 0.1 | mono | 0.05 | <i>M</i> |
| 288 | 500 | 10 | 1.0 | mono/hex | 0.2 | M,H |
| 288-mag | 500 | 10 | 1.0 | mono | 0.18 | M |
| 289 | 500 | 5 | 1.0 | mono/hex | 0.2 | M,H |
| 289-mag | 500 | 5 | 1.0 | mono | 0.1 | <i>M</i> |
| 290 | 500 | 2 | 1.0 | mono/hex | 0.2 | M,H |
| 290-mag | 500 | 2 | 1.0 | mono | 0.07 | <i>M</i> |
| 285 | 550 | 10 | 0.5 | mono/hex | 0.60 | M,H |
| 285-mag | 550 | 10 | 0.5 | mono | 0.42 | <i>M</i> |
| 286 | 550 | 5 | 0.5 | mono | 5.3 | --- |
| 286-mag | 550 | 5 | 0.5 | mono | 4.18 | --- |
| 287 | 550 | 2 | 0.5 | mono | 0.2 | tr,M |
| 287-mag | 550 | 2 | 0.5 | mono | 0.91 | tr,M |
| 280 | 600 | 5 | 0.5 | hex/mono | no-py | --- |
| 280-mag | 600 | 5 | 0.5 | hex/mono | 9.7 | --- |
| 281 | 600 | 2 | 0.5 | mono | 2.4 | --- |
| 281-mag | 600 | 2 | 0.5 | mono | 2.18 | --- |

mag = magnetic fraction, Po = pyrrhotite, Py = pyrite, mono = monoclinic, hex = hexagonal; M = magnetite, *M* = abundant magnetite, H = hematite

Table 4. Results of magnetic separations on chars produced at 500, 550 and 600°C under 0.1, 0.5 or 1.0% oxygen concentration (RK-B-4 coal: 6.17% total sulfur)

| No | Pyrolysis Conditions | | | | XRD Results | | | Sulfur Analysis | |
|-----------------------------------|----------------------|-----------------|------------------|------------|-------------|----------|------------------------------|-----------------|--|
| | Temp °C | Soak time (min) | O ₂ % | Type of Po | Po/Py ratio | % Sulfur | Dif. between char & non-mag. | | |
| <u>A. Small pyrolysis system</u> | | | | | | | | | |
| 350 char | 500 | 5 | 0.1 | hex | 0.2 | 5.77 | 2.36 | | |
| 350A non mag | 500 | 5 | 0.1 | hex | 0.67 | 3.41 | | | |
| 350A mag | 500 | 5 | 0.1 | mono | 0.08 | | | | |
| 351 char | 550 | 2 | 0.1 | hex/mono | 0.47 | 5.26 | 3.03 | | |
| 351A non mag | 550 | 2 | 0.1 | hex | 3.07 | 2.23 | | | |
| 351A mag | 550 | 2 | 0.1 | mono | 1.44 | | | | |
| 352 char | 550 | 5 | 0.1 | hex/mono | 1.16 | 4.95 | 2.36 | | |
| 352A non mag | 550 | 5 | 0.1 | hex | 1.39 | 2.59 | | | |
| 352A mag | 550 | 5 | 0.1 | mono | 1.67 | | | | |
| 353 char | 600 | 2 | 0.1 | mono/hex | no-pyrite | 4.37 | 2.33 | | |
| 353A non mag | 600 | 2 | 0.1 | hex | no-pyrite | 2.04 | | | |
| 353A mag | 600 | 2 | 0.1 | mono | no-pyrite | | | | |
| 354 char | 500 | 5 | 1.0 | hex/mono | 0.16 | 5.52 | 3.00 | | |
| 354A non mag | 500 | 5 | 1.0 | hex | 1.54 | 2.52 | | | |
| 354A mag | 500 | 5 | 1.0 | mono | 0.13 | | | | |
| 355 char | 550 | 2 | 0.5 | hex/mono | 0.49 | 5.13 | 2.64 | | |
| 355A non mag | 550 | 2 | 0.5 | hex/mono | 1.12 | 2.49 | | | |
| 355A mag | 550 | 2 | 0.5 | mono | 0.64 | | | | |
| 356 char | 550 | 5 | 0.5 | mono/hex | 1.03 | 4.81 | 2.55 | | |
| 356A non mag | 550 | 5 | 0.5 | hex | 1.1 | 2.26 | | | |
| 356A mag | 550 | 5 | 0.5 | mono | 0.79 | | | | |
| 357 char | 600 | 2 | 0.5 | hex/mono | no pyrite | 3.79 | 1.55 | | |
| 357A non mag | 600 | 2 | 0.5 | hex | no pyrite | 2.24 | | | |
| 357A mag | 600 | 2 | 0.5 | mono | no pyrite | | | | |
| <u>B. Rotary Pyrolysis System</u> | | | | | | | | | |
| 443 char | 550 | 5 | 0.5 | --- | --- | 4.7 | 2.89 | | |
| 443 non mag | 550 | 5 | 0.5 | --- | --- | 1.81 | | | |

The monoclinic pyrrhotite and magnetite were concentrated in the magnetic fractions while only hexagonal pyrrhotite and pyrite remained in the non-magnetic fractions. The XRD results showed that much of the pyrite was removed with the magnetic fraction for the 500°C and 550°C chars that still had pyrite present. This implies that monoclinic pyrrhotite and magnetite were probably forming on the surface of many of the pyrite grains. We attempted to use a microscopic identification technique to verify this but found the particle sizes of sulfide grains in the chars were too fine for the technique to work well.

Rotary Pyrolysis System - Three different coals were used in the rotary pyrolysis system: RK-B-4, IBCSP #2 and IBCSP #3. The IBCSP #2 and #3 tended to agglomerate easily. Pre-oxidation with 5% oxygen in the nitrogen purging gas was used from room temperature to 250°C to alleviate the agglomeration problem. At 250°C, the oxygen was reduced to the desired trace of oxygen. Initially there were some problems forming monoclinic pyrrhotite in the rotary system. Tables 5, 6 and 7 show the XRD results of the chars formed from RK-B-4, IBCSP #2 and #3 respectively.

As observed in Table 5,6 and 7 the non-magnetic hexagonal pyrrhotite dominated the inorganic sulfides in the initial chars produced in the rotary system. When gas flow rates were increased the formation of monoclinic pyrrhotite improved in most cases. The optimum formation of monoclinic pyrrhotite in the rotary system appears to be at 550°C with 0.25 and 0.5% oxygen and a short soak time (0 to 5 minutes). The longer soak times appear to produce less monoclinic pyrrhotite and more magnetite rather than converting more hexagonal pyrrhotite to monoclinic pyrrhotite.

Table 5. Results of sulfide mineralogy produced in the larger scale rotary pyrolysis system using the RK-B-4 coal sample (<60 mesh).

| Pyrolysis Conditions | | | | | XRD Results | |
|----------------------|-----------|--------------------|-----------------|--------------------|-------------------|-------------|
| No. | Temp (°C) | Flow Rate (cc/min) | Soak Time (min) | O ₂ (%) | Type of Po | Po/Py ratio |
| 389 | 550 | 162 | 5 | 1.0 | hex/mono | 4.5 |
| 390 | 500 | 162 | 5 | 1.0 | hex/troilite | 0.3 |
| 391 | 600 | 162 | 5 | 0.5 | hex | no-py |
| 392 | 600 | 162 | 2 | 0.5 | hex | no-py |
| 393 | 550 | 162 | 10 | 0.25 | hex | no-py |
| 394 | 500 | 162 | 20 | 0.25 | hex/mono,troilite | .9 |
| 395 | 550 | 162 | 20 | 0.1 | hex | no-py |
| 396 | 500 | 162 | 20 | 0.1 | hex/mono | 1.1 |
| 443 | 550 | 1350 | 5 | 0.5 | mono/hex | no-py |

Table 6. Results of sulfide mineralogy produced in the larger scale rotary pyrolysis system using IBCSP #2 coal (<60 mesh).

| Pyrolysis No. | Pyrolysis Conditions | | | | XRD Results | | | |
|---------------|----------------------|-----------|--------------------|-----------------|-----------------------|------------|-------------|----------------|
| | Mat'l Type | Temp (°C) | Flow Rate (cc/min) | Soak Time (min) | O ₂ ** (%) | Type of Po | Iron oxides | Percent sulfur |
| 412 | --- | 550 | 162 | 5 | .5 | hex | --- | --- |
| 413 | --- | 550 | 162 | 20 | .5 | troilite B | --- | --- |
| 414 | --- | 550 | 162 | 5 | 1.0 | troilite B | --- | --- |
| 415 | --- | 550 | 162 | 20 | .25 | hex | --- | --- |
| 416 | --- | 550 | 378 | 20 | 1.0 | hex | tr m | --- |
| 416 | mag | 550 | 378 | 20 | 1.0 | mono | m | --- |
| 417 | --- | 550 | 1350 | 20 | 0.1 | troilite B | --- | --- |
| 417 | mag | 550 | 1350 | 20 | 0.1 | hex/mono | m | --- |
| 418 | --- | 550 | 1350 | 20 | 0.5 | hex | m | --- |
| 418 | non-mag | 550 | 1350 | 20 | 0.5 | hex | --- | 1.31 |
| 418 | mag | 550 | 1350 | 20 | 0.5 | mono/hex | m | --- |
| 418 | non-mag* | 550 | --- | 20 | 0.5 | --- | --- | 1.10 |
| 419 | mag | 550 | 1350 | 20 | 0.25 | mono | m | --- |
| 419 | non-mag | 550 | --- | 20 | 0.25 | --- | --- | 1.46 |
| 420 | mag | 550 | 675 | 20 | 0.25 | hex | m | --- |
| 421 | mag | 550 | 1350 | 20 | 0.25 | hex/mono | m | --- |
| 421 | char | 550 | --- | 20 | 0.25 (S) | --- | --- | 2.03 |
| 421 | non-mag | 550 | --- | 20 | 0.25 (S) | --- | --- | 1.67 |
| 422 | mag | 550 | 1350 | 20 | 0.10 | hex | tri m | --- |
| 422 | char | 550 | --- | 20 | 0.10 (S) | --- | --- | 2.27 |
| 422 | non-mag | 550 | --- | 20 | 0.10 (S) | --- | --- | 1.92 |
| 439 | mag | 600 | 1350 | 5 | 0.50 | hex | m | --- |
| 440 | mag | 550 | 1350 | 20 | 0.50 | hex/mono | m | --- |
| 440 | char | 550 | --- | 20 | 0.50 | --- | --- | 2.21 |
| 440 | non-mag | 550 | --- | 20 | 0.50 | --- | --- | 1.37 |
| 447 | mag | 550 | 1350 | 5 | 0.25 | mono/hex | m | --- |
| 447 | non-mag | 550 | --- | 5 | 0.25 | --- | --- | 1.23 |
| 448 | mag | 550 | 1350 | 5 | 0.10 | hex/mono | m | --- |

* This sample was passed through the magnetic separation process 4 times. The others were passed through twice.

** Normally the O₂ was added during both the ramp and soak time, (S) means O₂ was only added during the soak period.

Table 7. Results of sulfide mineralogy obtained using IBCSP #3 coal in rotary system (feed was <60 mesh).

| No. | Pyrolysis Conditions | | | | XRD Results | |
|-----|----------------------|--------------------|----------------|-----------------|-------------------------|------------------------|
| | Temp (°C) | Flow Rate (cc/min) | Percent Oxygen | Soak Time (min) | Pyrrhotite ^a | Magnetite ^b |
| 449 | 680 | 600 | 0.1 | 2 | hex | tr m |
| 450 | 680 | 600 | 0.25 | 2 | hex | tr m |
| 451 | 680 | 550 | 0.25 | 20 | hex/mono? | m |
| 452 | 680 | 600 | 0.5 | 2 | hex | m |
| 453 | 680 | 550 | 0.1 | 60 | hex | m |
| 454 | 1350 | 550 | 0.5 | 3 | mono/hex | m |
| 455 | 1350 | 550 | 0.5 | 2 | mono/hex | m |
| 456 | 1350 | 550 | 0.5 | 0 | mono/hex | m |
| 457 | 1350 | 550 | 0.25 | 0 | mono/hex | m |
| 458 | 1350 | 550 | 0.1 | 0 | hex/mono | m |

^a (HEX), hexagonal pyrrhotite; (MONO), monoclinic pyrrhotite; (MONO?), only a small amount of monoclinic pyrrhotite present.

^b qualitative amounts of magnetite indicated by symbols; m=magnetite, M=abundant magnetite, and tr. m = trace of magnetite

Fluidized bed system - A few pyrolysis experiments were carried out in the fluidized bed system using IBCSP #3 as a feed coal. The parameters of the pyrolyses were to be 550°C with 0.5% oxygen and zero soak time. Unfortunately the controller did not work correctly on one of the experiments and only took the temperature to 526°C. The pyrrhotite formed during the 526°C pyrolysis was primarily hexagonal with a slight amount of monoclinic pyrrhotite present. A significant amount of pyrite was also present as well as some magnetite.

Sulfur removed by magnetic separation - To test the effectiveness of sulfur removal by magnetic separation on chars produced under a trace of oxygen, sulfur determinations were made on many chars and their corresponding non-magnetic fractions. Tables 4, 6 and 8 contain the results of the sulfur analyses.

Table 4 shows the results of sulfur removal by magnetic separation on chars produced from the RK-B-4 coal. The sulfur analyses indicate that a significant amount of sulfur was removed by the magnetic separation of the inorganic sulfides. RK-B-4 is a very high sulfur coal containing 6.17 percent total sulfur (3.77% pyritic sulfur and 2.38% organic sulfur). Magnetic separation of the sulfides by a hand magnet resulted in non-magnetic fractions having sulfur contents of 1.81 to 3.41 percent. Most of the non-magnetic fractions contained from 2.2 to 2.5 percent sulfur. According to most of the XRD patterns there is very little sulfide mineral-

ogy remaining in the non-magnetic fractions of these chars. It is assumed that most of the sulfur remaining in the non-magnetic fractions of these chars is organic sulfur.

Table 6 shows the results of magnetic separations made on chars produced from the IBCSP #2 coal. The magnetic separations resulted in non-magnetic fractions with sulfur contents of 1.1 to 1.9% sulfur from a coal with 3.23% total sulfur. The lowest sulfur contents were obtained with those chars showing good monoclinic pyrrhotite formation. Pyrolyses #422 showed no monoclinic pyrrhotite formation and very little magnetite, consequently the reduction in sulfur content due to magnetic separation was small.

Table 8 shows the results of magnetic separations made on chars produced from the IBCSP #3 coal. The magnetic separations on the chars produced in the rotary pyrolysis system resulted in non-magnetic fractions with sulfur contents of 0.88 to 1.15% sulfur from a coal with 2.35% total sulfur. The magnetic separation on the 526°C char produced in the fluidized bed system resulted in a non-magnetic fraction with 1.29% sulfur. The magnetic separation results on the fluidized bed char could be improved with more optimized pyrolysis conditions.

The magnetic separation results were very encouraging and show that significant amounts of sulfur can be removed by magnetic separation after pyrolysis with a trace of oxygen. However, yields of clean char after magnetic separation were low, and significant amounts of carbon were removed with the magnetic fraction. Total yields after magnetic separations were approximately 40-55% of the original coal. The yield could probably be increased with improved magnetic separation techniques.

Table 8. Results of magnetic separations on chars produced in the rotary pyrolysis system and the fluidized bed system using IBCSP #3 as feed coal. (Total Sulfur 2.35%).

| Pyrolysis No. | Mat'l Type | Temp (°C) | %O ₂ add. | Soak time | % sulfur |
|---------------------------------|------------|-----------|----------------------|-----------|----------|
| A. Rotary System: | | | | | |
| 452 | char | 600 | 0.5 | 2 | 1.47 |
| 452 | non-mag | 600 | 0.5 | 2 | 0.96 |
| 455 | char | 550 | 0.5 | 2 | 1.40 |
| 454 | non-mag | 550 | 0.5 | 3 | 0.88 |
| 456 | char | 550 | 0.5 | 0 | 1.49 |
| 456 | non-mag | 550 | 0.5 | 0 | 1.15 |
| B. Fluidized bed system: | | | | | |
| FBR-119 | char | 526 | 0.5 | 0 | 1.71 |
| FBR-119 | non-mag | 526 | 0.5 | 0 | 1.29 |

Most Illinois Basin coals contain pyrite which is very finely disseminated within the organic matter making physical separation difficult. Finer particle sizes for the feed coals would improve the yield of clean char after magnetic separation. The particle size of the feed coals used in these experiments were -60 mesh for RK-B-4 and IBCSP #2 coals and -60/+100 mesh for IBCSP #3 coal.

Char hydrodesulfurization - Approximately 300 statistically designed char hydrodesulfurization tests were run this contract year. A brief summary of the individual designs appears in Table 9.

Table 9. Experimental designs for char hydrodesulfurization.

| Series No. | Design type | Factors ^a | Purpose |
|------------|-------------------------------------|----------------------|--|
| I | Factorial | CT, t | Effect of pyrolysis method on hydrodesulfurization |
| II | Plackett-Burman | T,F,t,d,A | Screening experiments for five factors |
| III | Factorial | d | Effect of particle size |
| IV | Half-factorial | T,F,t,A | Effect of hematite acceptor |
| V | Half-factorial | T,F,t,A | Effect of magnetite acceptor |
| VI | Factorial | F,A | Effect of acceptor on physically cleaned coal |
| VII | Half-factorial | CT,ChT,T,F,t | Effect of type of hydrodesulfurization feed |
| VIII | Path of steepest ascent, Box-Wilson | T,t | Optimization study |
| IX | Factorial | T,F,t,A | HDS of IBCSP #6 coal |
| X | Factorial | T,t | Kinetic study |
| XI | --- | --- | Combustion tests |

^a ChT (char type), CT (coal type), T (temperature), F (hydrogen flow rate), t (time), d (particle diameter), A (acceptor)

Series I experiments - A factorial design of three levels of char type (pre-oxidized, non-oxidized, and post-oxidized) and two levels of residence time (15 and 90 min) was chosen to investigate the influence of char type on hydrodesulfurization. Three response variables were examined which have been defined earlier in the experimental procedures section. The specific sulfur content, i.e., the weight (in lbs) of sulfur dioxide liberated per million btus of char burned, is used to normalize the sulfur content data with respect to any changes in calorific value. A second response variable, the percent initial sulfur remaining in the char, reflects the effectiveness of hydrodesulfurization alone. It is simply the amount of sulfur removed during hydrodesulfurization divided by the amount of sulfur present initially in the char. A third response variable, char yield, was chosen to correlate changes in char yield with respect to char type and residence time. The experimental data and the calculated response variables are shown in Table 10.

The statistical analysis is shown in Table 11. Examination of the regression coefficients shows that pre-oxidized chars are easier to desulfurize than non-oxidized chars which are easier to desulfurize than post-oxidized chars. As expected, longer residence times result in lower sulfur chars. The interaction of char type and residence time is negligible, however.

Char yield is most sensitive to residence time with decreasing yield occurring with longer treatment times. This could be due to weight loss from deoxygenation and denitrogenation as well as desulfurization. In addition, some weight loss probably occurs by gasification from hydrogen and perhaps steam as well. The effect of char type on char yield was negligible.

Series II experiments - An initial set of experiments designed to screen a large number of factors has been completed. A Plackett-Burman design (3) was chosen to determine those factors which appear to exert the most influence on the response variable. For these experiments, the response variable, the specific sulfur content (lbs SO₂/MMBtu), was measured as a function of temperature, hydrogen flow rate, particle size, time, presence (or absence) of hematite, and type of char (pre-oxidized or non-oxidized). The data were then analyzed statistically to rank the factors in order of importance.

The raw data for these experiments is shown in Table 12. Note that the design consisted of experiments at two levels for each factor. Temperature was investigated at 750 and 850°C, hydrogen flow rate at 500 and 1000 cc/min, and time at 45 and 90 min. Coded levels (-1, +1) were used for the more qualitative factors. For particle size (DP), +1 indicates char of -28 mesh whereas -1 represents -60 mesh material. Visual inspection of the char revealed that the -28 mesh material was primarily comprised of discrete particles with very few fines whereas the -60 mesh material was essentially all fines with the consistency of a fine powder. In the case

Table 10. Experimental data for hydrodesulfurization series I experiments

| HDS run No. | Char type | Time, min | Sulfur content, wt% Feed | Product | Specific sulfur content lb SO ₂ /MMBtu | Char yield % | Calorific Value BTU/lb | Percent init. Sulfur remaining in char |
|-------------|-----------|-----------|-----------------------------|---------|--|-----------------|---------------------------|---|
| 67 | PRE-OX | 15 | 4.10 | 3.62 | 6.31 | 96.3 | 11524 | 85.1 |
| 70 | PRE-OX | 15 | 4.10 | 2.82 | 4.82 | 96.4 | 11747 | 66.3 |
| 73 | PRE-OX | 15 | 3.80 | 3.44 | 6.16 | 97.4 | 11231 | 88.2 |
| 74 | PRE-OX | 90 | 3.80 | 1.84 | 3.23 | 93.4 | 11410 | 45.2 |
| 77 | PRE-OX | 90 | 4.01 | 1.95 | 3.36 | 93.6 | 11679 | 45.5 |
| 66 | NO-OX | 15 | 4.58 | 4.27 | --- | 97.9 | --- | 91.3 |
| 68 | NO-OX | 15 | 4.58 | 3.27 | 5.83 | 97.3 | 11281 | 69.5 |
| 71 | NO-OX | 15 | 4.58 | 3.47 | 6.17 | 96.3 | 11282 | 73.0 |
| 75 | NO-OX | 90 | 4.58 | 1.95 | 3.44 | 93.9 | 11468 | 40.0 |
| 78 | NO-OX | 90 | 4.09 | 1.67 | 2.80 | 94.0 | 12012 | 38.4 |
| 81 | NO-OX | 90 | 4.09 | 2.04 | 3.50 | 92.6 | 11720 | 46.2 |
| 69 | POST-OX | 15 | 4.06 | 3.41 | 5.95 | 97.5 | 11488 | 81.9 |
| 72 | POST-OX | 15 | 4.06 | 3.57 | 6.25 | 97.0 | 11482 | 85.3 |
| 76 | POST-OX | 90 | 4.06 | 1.90 | 3.34 | 93.4 | 11427 | 43.7 |
| 79 | POST-OX | 90 | 4.06 | 2.27 | 3.97 | 93.1 | 11525 | 52.1 |

Table 11. Regression analysis of effect of char type and time on specific sulfur content, percent, initial sulfur remaining in the char, and char yield^a

| Term | Regression coefficients | | |
|----------------|-------------------------|--|------------|
| | specific sulfur content | Percent initial sulfur remaining in the char | Char yield |
| 1 (constant) | 4.664 | 0.6236 | 95.24 |
| Char type | 0.1762 | 0.01425 | 0.08237 |
| Time | -1.287 | -0.1791 | -1.810 |
| Char type*time | 0.003824 | -0.001497 | -0.2074 |
| coeff of detmn | 0.9182 | 0.8716 | 0.9317 |

^aregression equations use coded variables. Char type: -1 = pre-oxidized, 0 = non-oxidized, 1 = post-oxidized. Time: -1 = 15 minutes, 1 = 90 minutes.

of hematite acceptor, +1 indicates the presence and -1 the absence of hematite. Pre-oxidized char is denoted by +1, non-oxidized char by a -1. A Plackett-Burman design is useful in determining main effects only; generally, it is not possible to calculate interactions between factors. Such a design, therefore, can only be modeled linearly where the response variable (specific sulfur content) is simply a linear combination of all factors. When the data were fitted to a linear model, a regression equation was obtained with a coefficient of determination (r-squared) of 96.01 percent. This is an excellent fit, especially when one considers the number of factors involved.

The regression coefficients for this equation are shown in Table 13. One method for ranking factors is to compare the level of confidence that the coefficient for the factor is non-zero. In other words, the higher the confidence, the more important the factor. Using this criterion, the factors are ranked as follows:

Time > Hematite > Temp > Oxidation > Flow > DP

The signs of the regression coefficient are negative for all factors indicating that the upper level for each factor leads to lower levels of specific sulfur content, i.e., higher desulfurization. Longer treatment times, presence of hematite, higher temperatures, pre-oxidized char (vs. non-oxidized char), higher hydrogen flow rates and larger particle sizes should all lead to increased desulfurization. Note that the confidence for particle size is so low that changes in this variable should not effect the response variable at all.

Table 12. Experimental data for hydrodesulfurization series II experiments

| HDS Run No. | Temp., °C | Flow rate cc/min | Particle size ^a | Time, min | Hematite ^b | Oxidation ^c | Sulfur content, wt% Feed | Product | Calorific Value Btu/lb | Specific S cont lbs SO ₂ /MMBtu |
|-------------|-----------|------------------|----------------------------|-----------|-----------------------|------------------------|--------------------------|---------|------------------------|--|
| 80 | 850 | 1000 | 1 | 45 | 1 | -1 | 4.09 | 2.17 | 11,802 | 3.68 |
| 88 | 850 | 1000 | 1 | 45 | 1 | -1 | 4.09 | 2.02 | 11,679 | 3.45 |
| 81 | 850 | 1000 | -1 | 90 | -1 | -1 | 4.09 | 2.13 | 11,324 | 3.77 |
| 89 | 850 | 1000 | -1 | 90 | -1 | -1 | 4.09 | 2.26 | 11,550 | 3.91 |
| 82 | 850 | 500 | 1 | 45 | -1 | 1 | 4.01 | 2.47 | 11,563 | 4.27 |
| 90 | 850 | 500 | 1 | 45 | -1 | 1 | 4.01 | 2.40 | 11,337 | 4.23 |
| 83 | 750 | 1000 | -1 | 45 | 1 | 1 | 4.01 | 2.37 | 10,998 | 4.32 |
| 91 | 750 | 1000 | -1 | 45 | 1 | 1 | 4.01 | 1.67 | 12,112 | 2.74 |
| 98 | 750 | 1000 | -1 | 45 | 1 | 1 | 4.01 | 2.63 | 11,417 | 4.61 |
| 84 | 850 | 500 | -1 | 90 | 1 | 1 | 4.01 | 1.57 | 11,244 | 2.79 |
| 92 | 850 | 500 | -1 | 90 | 1 | 1 | 4.01 | 1.64 | 11,819 | 2.78 |
| 85 | 750 | 500 | 1 | 90 | 1 | -1 | 4.09 | 2.34 | 10,982 | 4.27 |
| 93 | 750 | 500 | 1 | 90 | 1 | -1 | 4.09 | 2.32 | 11,634 | 3.99 |
| 86 | 750 | 1000 | 1 | 90 | -1 | 1 | 4.01 | 2.14 | 11,458 | 3.74 |
| 94 | 750 | 1000 | 1 | 90 | -1 | 1 | 4.01 | 1.65 | 11,411 | 2.89 |
| 99 | 750 | 1000 | 1 | 90 | -1 | 1 | 4.01 | 2.35 | 11,718 | 4.01 |
| 87 | 750 | 500 | -1 | 45 | -1 | -1 | 4.09 | 2.28 | 9,179 | 4.98 |
| 95 | 750 | 500 | -1 | 45 | -1 | -1 | 4.09 | 3.15 | 11,674 | 5.39 |

^a coded variable 1=28x200 mesh, -1=-60 mesh
^b coded variable 1=hematite present, -1=hematite absent
^c coded variable 1=pre-oxidized char, -1=non-oxidized char

Table 13. Statistical analysis of series II hydrodesulfurization experiments^a

| Coefficient | Term or factor | Standard error | T-Value | Confidence coeff is non-zero, % | Correlation coefficient between factor and response variable | Effect of factor |
|-------------|----------------|----------------|---------|---------------------------------|--|------------------|
| 10.06 | constant | 2.131 | 4.72 | 78.0 | -- | -- |
| -0.0058 | temp | 0.003 | 2.25 | 69.4 | -0.449 | -0.578 |
| -0.0008 | Flow | 0.001 | 1.47 | 60.4 | -0.293 | -0.377 |
| -0.0260 | DP | 0.128 | 0.20 | 21.7 | -0.040 | -0.052 |
| -0.0144 | time | 0.006 | 2.52 | 71.3 | -0.503 | -0.647 |
| -0.3065 | hematite | 0.128 | 2.39 | 70.4 | -0.477 | -0.613 |
| -0.2810 | oxidation | 0.128 | 2.19 | 68.9 | -0.437 | -0.562 |

^aregression equation is $10.059 - 0.00578(\text{temp}) - 0.0007540(\text{flow}) - 0.0260(\text{DP}) - 0.0144(\text{time}) - 0.307(\text{hematite}) - 0.281(\text{Oxidation})$

It is also possible to rank the factors by examining the magnitude of the correlation coefficients between each factor and the specific sulfur content. When this is done, the same ranking of variables is obtained (see Table 13 for these values). Still another approach is to calculate the effects of each factor. The effects are simply the differences in the averages of the response variable at the two levels of the factor in question. These values are displayed in Table 13 and result in the same ranking of factors. The low particle size dependence is not surprising. Char is believed to contain a high percentage of micropores of molecular dimensions. For the case of hydrodesulfurization, the mean free path of hydrogen sulfide is several fold greater than the average micropore diameter. Consequently, Knudsen diffusion of hydrogen sulfide out of the micropores is possibly a rate controlling phenomenon. If this is the case, particle size effects would be non-existent. The lack of a particle size effect is in accord with previous hydrodesulfurization studies (5,6).

The sulfur analysis of the char and reacted magnetite indicated that the amount of sulfur liberated to the off-gas was substantially less with the acceptor present.

Series III experiments - Experiments with char prepared from IBCSP #1 coal have shown high sulfur removals achieving compliance levels in some cases (see Table 14). This high sulfur coal (4.03%) was pre-oxidized at 250°C before pyrolysis.

Table 14. Hydrodesulfurization of char from IBCSP #1 coal^a

| HDS run no. | Particle size | Sulfur content, wt. % | | Specific S content lbs SO ₂ /MMBtu |
|-------------|---------------|-----------------------|---------|--|
| | | Feed | Product | |
| 100 | -150 | 2.90 | 0.806 | 1.28 |
| 101 | - 20 | 2.90 | 0.598 | 0.95 |
| 102 | -150 | 2.90 | 0.915 | 1.46 |
| 103 | - 20 | 2.90 | 0.677 | 1.08 |

^ahydrodesulfurization at 850°C, 1000 cc/min hydrogen, 90 min

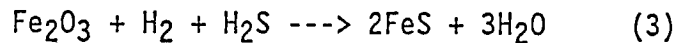
Series IV experiments - A half-factorial design of two levels of acceptor (present and absent), hydrogen flow rate (500 and 1000 cc/min), temperature (750 and 850°C) and time (45 and 90 minutes) was chosen to determine the effect of a hematite acceptor on char desulfurization. In all hydrodesulfurization runs a pre-oxidized char made from IBCSP #4 deslimed coal was used. The factors flow, temperature and time were varied to determine their interactions with the hematite acceptor.

The specific sulfur content, defined in experimental procedures section, and the char yield were the response variables examined. Each run was replicated and the average specific sulfur content was used in the statist-

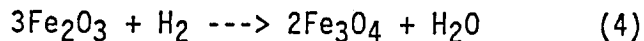
ical analysis. The experimental data and the calculated response variables are shown in Table 15.

The statistical analysis is shown in Table 16. When the data were fitted to a linear model, a regression equation was obtained with a coefficient of determination (r-squared) of 99.04 percent. This is an excellent fit and indicates that interactions between factors are negligible. The effect of each factor is calculated by taking the difference in the averages of the response variable at the two levels of the factor. From Table 16 it can be seen that the average effect of the presence of hematite was to lower the specific sulfur content by 0.82 which is a significant reduction.

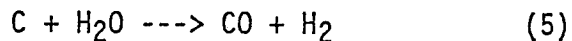
The effect of the presence of hematite on char yield was to lower the yield by 9.25 percent. The lower char yield when the acceptor was present is most likely due to reactions involving the acceptor which produce steam. The reaction of hydrogen sulfide with hematite occurs in a hydrogen environment according to:



Steam also is produced in the reaction of hematite with hydrogen to produce magnetite:



The steam also reacts with the char, gasifying a portion of it:



Series V experiments - Hydrodesulfurization experiments were conducted with magnetite as the acceptor. In these experiments a pre-oxidized char made from IBCSP #4 deslimed coal was used. The results were compared to previous runs which were identical except that hematite was used as the acceptor. The raw data and the calculated specific sulfur content are shown in Table 17. The average specific sulfur content at 1000 cc/min flow rate of hydrogen with hematite acceptor is 2.34 as compared to 2.42 with magnetite acceptor. At 500 cc/min flow rate the average specific sulfur content with hematite is 2.68 and with magnetite it is 2.42. In both cases there is only a slight difference between the level of desulfurization with hematite and magnetite. This indicates that there is very little difference in the effectiveness of hematite and magnetite as sulfur acceptors.

Series VI experiments - In these experiments an IBCSP #4 coal was used which had been tumbled, deslimed and pyrolyzed with a pre-oxidation treatment. All of these experiments were conducted for 90 minutes at 850°C. The raw data, the calculated specific sulfur content and run-of-mine percent sulfur reduction are shown in Table 18. As can be seen from the table very high levels of desulfurization were achieved with this char. Low sulfur levels were achieved in experiments without acceptor and those with acceptor present were well below the compliance level of 1.2 lbs SO₂/MMBTU. Coal-burning utilities built after 1979 have the added restriction on sulfur emissions of greater than 90 percent sulfur reduction from

Table 15. Experimental data for hydrodesulfurization series IV experiments

| HDS Run No. | Temp., °C | Flow rate cc/min | Time min | Hematite ^a | Sulfur content, wt% Feed | Product | Calorific value BTU/lb | Char Yield | Specific S cont lbs SO ₂ /MMBTU |
|-------------|-----------|------------------|----------|-----------------------|--------------------------|---------|------------------------|------------|--|
| 104 | 750 | 500 | 45 | -1 | 4.01 | 3.12 | 11815 | .96 | 5.28 |
| 111 | 750 | 500 | 45 | -1 | 4.01 | 3.68 | 11352 | .97 | 6.48 |
| 105 | 750 | 500 | 90 | 1 | 4.01 | 2.61 | 11913 | .89 | 4.38 |
| 113 | 750 | 500 | 90 | 1 | 4.01 | 2.53 | 12233 | .90 | 4.14 |
| 106 | 750 | 1000 | 90 | -1 | 4.01 | 2.51 | 11781 | .95 | 4.26 |
| 114 | 750 | 1000 | 90 | -1 | 4.01 | 2.76 | 11716 | .95 | 4.71 |
| 107 | 750 | 1000 | 45 | 1 | 4.01 | 2.62 | 11665 | .91 | 4.49 |
| 116 | 750 | 1000 | 45 | 1 | 4.01 | 2.64 | 11949 | .92 | 4.42 |
| 109 | 850 | 500 | 90 | -1 | 4.01 | 2.51 | 11677 | .94 | 4.30 |
| 157 | 850 | 500 | 90 | -1 | 4.01 | 2.04 | 12039 | .92 | 3.41 |
| 108 | 850 | 500 | 45 | 1 | 4.01 | 3.13 | 11636 | .90 | 5.38 |
| 119 | 850 | 500 | 45 | 1 | 4.01 | 1.84 | 12392 | .81 | 2.97 |
| 110 | 850 | 1000 | 45 | -1 | 4.01 | 2.71 | 11717 | .95 | 4.63 |
| 117 | 850 | 1000 | 45 | -1 | 4.01 | 2.30 | 11575 | .92 | 3.97 |
| 112 | 850 | 1000 | 90 | 1 | 4.01 | 1.47 | 12225 | .80 | 2.40 |
| 118 | 850 | 1000 | 90 | 1 | 4.01 | 1.23 | 10858 | .69 | 2.27 |

^a coded variable; 1 = hematite; -1 = hematite absent

Table 16. Statistical analysis of series IV hydrodesulfurization experiments^a

| Coefficient | Term or factor | Standard error | T-value | Confidence Coeff is non-zero, % | Effect of factor on the Specific S content |
|-------------|----------------|----------------|---------|---------------------------------|--|
| 15.45 | constant | 0.8483 | 18.21 | 98.4% | --- |
| -0.4100 | acceptor | 0.0512 | 8.015 | 97.6% | -0.820 |
| -0.0013 | flow | 0.0002 | 6.353 | 97.1% | -0.650 |
| -0.0110 | temperature | 0.0010 | 10.75 | 98.0% | -1.100 |
| -0.0216 | time | 0.0023 | 9.48 | 97.8% | -0.970 |

^a regression equation is 15.45 - 0.4100 (acceptor) - 0.0013 (flow) - 0.0110 (temp) - 0.0216 (time)

Table 17. Experimental data for hydrodesulfurization series V experiments^a

| HDS Run No. | Flow rate cc/min | Flow rate | Acceptors | Sulfur content, wt% Feed | Sulfur content, wt% Product | Calorific Value BTU/lb | Specific S cont lbs SO ₂ /MMBTU |
|-------------|------------------|-----------|-----------|--------------------------|-----------------------------|------------------------|--|
| 140 | 1000 | | magnetite | 4.01 | 1.42 | 12313 | 2.31 |
| 141 | 1000 | | magnetite | 4.01 | 1.52 | 11954 | 2.54 |
| 146 | 500 | | magnetite | 4.01 | 1.46 | 12176 | 2.42 |
| 147 | 500 | | magnetite | 4.01 | 1.46 | 11995 | 2.43 |
| 112 | 1000 | | hematite | 4.01 | 1.47 | 12225 | 2.40 |
| 118 | 1000 | | hematite | 4.01 | 1.23 | 10858 | 2.27 |
| 115 | 500 | | hematite | 4.01 | 1.51 | 12268 | 2.46 |
| 84 | 500 | | hematite | 4.01 | 1.57 | 11244 | 2.79 |
| 90 | 500 | | hematite | 4.01 | 1.64 | 11819 | 2.78 |

^aall experiments run for 90 minutes at 850°CTable 18. Experimental data for hydrodesulfurization series VII experiments^a

| HDS Run No. | Flow rate cc/min | Flow rate | Acceptors | Sulfur content, wt% Feed | Sulfur content, wt% Product | Calorific Value BTU/lb | Specific S cont lbs SO ₂ /MMBTU | ROM of S reduction |
|-------------|------------------|-----------|-----------|--------------------------|-----------------------------|------------------------|--|--------------------|
| 138 | 1000 | | none | 2.77 | 0.72 | 12641 | 1.14 | 88.4 |
| 139 | 1000 | | none | 2.77 | 0.85 | 12485 | 1.36 | 86.2 |
| 158 | 500 | | none | 2.77 | 0.94 | 12365 | 1.70 | 82.8 |
| 159 | 500 | | none | 2.77 | 0.80 | 12484 | 1.28 | 87.0 |
| 160 | 500 | | hematite | 2.77 | 0.60 | 12549 | 0.94 | 90.5 |
| 161 | 500 | | hematite | 2.77 | 0.49 | 12547 | 0.78 | 92.1 |
| 162 | 1000 | | hematite | 2.77 | 0.38 | 12574 | 0.60 | 93.9 |
| 163 | 1000 | | hematite | 2.77 | 0.39 | 12616 | 0.62 | 93.7 |

^aall experiments run for 90 minutes at 850°C

the run-of-mine coal (if the run-of-mine coal has 3 to 6 percent sulfur content). Again, without acceptor present the level of desulfurization is close to the compliance level and with acceptor present compliance levels were attained.

Series VII experiments - Hydrodesulfurization experiments were carried out according to a five factor, half-factorial design at two levels as shown in Table 19 (7). This resulted in experiments being run under 16 different conditions of coal type (deslimed or tabled), char type (untreated or pre-oxidized), temperature (750 or 850°C), hydrogen flow rate (500 or 1000 cc/min) and treatment time (45 or 90 minutes). This half-factorial design enabled all main effects and second-order interactions to be calculated directly. Higher order interactions were assumed to be negligible.

The experimental data are shown in Table 20. Product char sulfur contents varied from 0.77 to 3.40 percent which corresponds to specific sulfur contents of 1.2 to 5.9 lbs SO₂/MMBTU. When these data are expressed as percent initial sulfur remaining in the char, a range of 27.2 to 86.0 percent was obtained. Char yields varied slightly from 93.4 to 96.8 percent.

A summary of the main effects and second-order interactions for the three response variables is shown in Table 21. The magnitude of the effect is a direct indicator of the influence of factor. Thus, the use of a physically cleaned coal, i.e., the upper level of coal type (+1), results in a decrease (-2.33) in Y₁, or a lower sulfur char. Likewise, a pre-oxidized coal, increasing temperatures, hydrogen flow rates and treatment times all lead to a lower value of Y₁. The ranking of the factors lowering Y₁ from most to least important are:

coal type > temperature > time > char type > flow rate

Consequently, it is highly desirable to physically clean the coal to remove as much pyrite as possible.

The same ranking of effects is seen for Y₂, the percent initial sulfur remaining in the char. While a physically cleaned coal leads to a high percentage of sulfur removed during hydrodesulfurization (a lowering of Y₂), increased temperatures and treatment times are nearly as effective.

The effects of pre-oxidizing the coal and increasing the hydrogen flow rates are roughly equivalent, as both decrease the value of Y₂ (increasing the extent of hydrodesulfurization). Temperature and treatment time are the two most important factors influencing char yield. Increasing temperatures and treatment times resulted in lower char yields. The interaction of time and temperature is quite small, indicating these are mostly independent factors. Increasing temperature and treatment times resulted in lower char yields. Part of the weight loss is due to sulfur removal, although nitrogen and oxygen are removed by hydrogen as well. The remaining weight loss is probably due to hydrogasification whereby methane is generated from carbon in the char.

Table 19. Series VIII half-factorial experimental design.

| Coal type ^a | Char type ^b | Temperature, °C | Hydrogen flow rate, cc/min | time, min | Conditions | Run no |
|------------------------|------------------------|-----------------|----------------------------|-----------|------------|---------|
| -1 | -1 | 750 | 500 | 90 | A | 164,176 |
| 1 | -1 | 750 | 500 | 45 | B | 182,184 |
| -1 | 1 | 750 | 500 | 45 | C | 104,111 |
| 1 | 1 | 750 | 500 | 90 | D | 165,172 |
| -1 | -1 | 850 | 500 | 45 | E | 166,173 |
| 1 | -1 | 850 | 500 | 90 | F | 183,185 |
| -1 | 1 | 850 | 500 | 90 | G | 109,157 |
| 1 | 1 | 850 | 500 | 45 | H | 167,175 |
| -1 | -1 | 750 | 1000 | 45 | I | 170,177 |
| 1 | -1 | 750 | 1000 | 90 | J | 186,187 |
| -1 | 1 | 750 | 1000 | 90 | K | 106,114 |
| 1 | 1 | 750 | 1000 | 45 | L | 168,178 |
| -1 | -1 | 850 | 1000 | 90 | M | 171,174 |
| 1 | -1 | 850 | 1000 | 45 | N | 188,189 |
| -1 | 1 | 850 | 1000 | 45 | O | 110,117 |
| 1 | 1 | 850 | 1000 | 90 | P | 169,179 |

^acoded coordinates: -1 denotes deslimed, +1 denotes tabled

^bcoded coordinates: -1 denotes no-oxidation, +1 denotes pre-oxidation

Table 20. Experimental data for series VIII design^a

| Conditions | Sulfur content, wt% | Y ₁ | Y ₂ | Y ₃ |
|------------|---------------------|----------------|----------------|----------------|
| A | 2.77 | 4.88 | 64.55 | 95.5 |
| B | 2.01 | 3.30 | 66.40 | 96.8 |
| C | 3.40 | 5.88 | 86.00 | 96.7 |
| D | 1.14 | 1.82 | 40.95 | 95.3 |
| E | 2.57 | 4.53 | 59.40 | 94.4 |
| F | 1.41 | 2.31 | 45.60 | 94.8 |
| G | 2.28 | 3.86 | 53.05 | 93.4 |
| H | 1.22 | 1.97 | 43.70 | 94.6 |
| I | 2.99 | 5.25 | 70.05 | 96.0 |
| J | 1.76 | 2.85 | 57.25 | 95.7 |
| K | 2.64 | 4.49 | 63.10 | 95.1 |
| L | 1.50 | 2.42 | 54.30 | 95.9 |
| M | 2.24 | 3.99 | 51.20 | 94.4 |
| N | 1.62 | 2.65 | 52.30 | 95.0 |
| O | 2.51 | 4.30 | 58.85 | 94.2 |
| P | 0.77 | 1.24 | 27.15 | 93.7 |

^aeach value is the average of two experiments.

Table 21. Estimates of effects^a

| | Response variable | | |
|---------------------------|-------------------|----------------|----------------|
| | Y ₁ | Y ₂ | Y ₃ |
| Average | 3.48 | 55.87 | 95.06 |
| Main effects | | | |
| coal type (A) | -2.33 | -14.82 | 0.26 |
| char type (B) | -0.47 | -4.96 | -0.45 |
| temperature (C) | -0.76 | -13.92 | -1.58 |
| flow rate (D) | -0.17 | -3.18 | -0.18 |
| time (E) | -0.61 | -11.02 | -0.71 |
| Second-order interactions | | | |
| AB | -0.44 | -8.91 | -0.24 |
| AC | 0.20 | 1.38 | 0.14 |
| AD | 0.11 | 1.77 | -0.14 |
| AE | 0.08 | -0.42 | -0.001 |
| BC | -0.06 | -1.48 | -0.23 |
| BD | -0.10 | -1.89 | -0.08 |
| BE | -0.18 | -3.63 | -0.26 |
| CD | 0.05 | -0.12 | 0.23 |
| CE | 0.10 | 1.71 | 0.24 |
| DE | 0.09 | 1.82 | 0.16 |

^aassumes interactions above third-order are negligible

A regression model was used to fit each of the three response variables (specific sulfur content, percent initial sulfur remaining in the char, and char yield) as a function of each of the five factors. A linear model was used with added terms for all second-order interactions. The coefficients of the regression equation are equal to exactly one-half the estimates of the effects. Thus, the equations for the specific sulfur content is:

$$Y_1 = 3.48 - 1.16(A) - 0.24(B) - 0.38(C) - 0.086(D) - 0.30(E) - 0.22(AB) + 0.10(AC) + 0.055(AD) + 0.039(AE) - 0.028(BC) - 0.049(BD) - 0.092(BE) + 0.025(CD) + 0.048(CE) + 0.047(DE)$$

Coal type, char type, temperature, hydrogen flow rate and time are represented by A, B, C, D, E, respectively. Equations for Y₂ and Y₃ were obtained similarly. The regression equations fit the data very well and indicated that optimum desulfurization occurred at the upper level of each factor. Thus, the true optimum lies somewhere outside the ranges studied here.

For the most part, the second-order interactions were quite small. However, there is a measurable interaction between coal type and char type on Y_1 and Y_2 . In fact, a marked synergism occurs when a preoxidized char, prepared from a tabled coal, is hydrodesulfurized. This is evident by examining the regression equations for Y_1 and Y_2 . If factors C, D, and E are set equal to plus one (the upper level), then two equations can be written, one for each level of coal type, as a function of char type. For tabled coal ($A=+1$), the equations are:

$$Y_1 = 1.87 - 0.63(B)$$

$$Y_2 = 37.47 - 10.44(B)$$

and for deslimed coal ($A=-1$),

$$Y_1 = 3.80 - 0.19(B)$$

$$Y_2 = 49.56 - 1.53(B)$$

For Y_1 , the slope is over three times greater for the tabled sample and for Y_2 , there is nearly a sevenfold difference. Therefore the regression models indicate that increasing the level of oxidation results in a steeper decline in Y_1 and Y_2 for tabled coal than for deslimed coal.

In addition to studies with IBCSP#4 tabled and deslimed coal, some experiments were conducted with char prepared from an ISGS Aggregate Flotation (AF) cleaned coal (also IBCSP#4). Chemical analyses revealed that the pyritic sulfur content of the AF product was roughly equivalent to that of the tabled and deslimed sample (1.08 vs 1.22% daf). In general, superior results were obtained with the tabled and deslimed product. Under the best conditions tested, an AF char of 3.24 lbs SO_2 /MMBtu whereas with the tabled and deslimed coal, several chars of 1.2 lbs SO_2 /MMBtu or less were produced.

Processing the AF product, due to its ultrafine size, was especially difficult in a fluidized bed reactor. A 50 percent reduction in superficial velocities was necessary simply to keep the material in the reactor. Even so, char losses were inordinately high. Furthermore, no increase in hydrodesulfurization reaction rates occur when using ultrafine particles due to the nature of the rate controlling phenomenon. Assuming that equilibrium controls the rate of desulfurization at short residence times and Knudsen diffusion at longer times, then decreased particle sizes will have absolutely no positive impact on hydrodesulfurization. Under equilibrium control, increasing space velocities increases rates and conversions; however, ultrafine sized particles necessitates the use of low superficial velocities, and thus forces the use of low space velocities. Thus, the use of an ultrafine char can actually decrease reaction rates. Inasmuch as the ultrafine sized material would need to be pyrolyzed first, problems of particle entrainment into the oil product can be envisioned. Consequently, the use of an ultrafine sized coal as a feed to pyrolysis and hydrodesulfurization does not appear to be a sound and viable concept. Thus, further studies with AF coals and chars prepared from AF coals were suspended.

Series VIII experiments - Inasmuch as the lowest sulfur chars for the Series VII experiments occurred at the upper level of each factor, a new set of experiments was designed to optimize the extent of hydrodesulfurization. Pre-oxidized char prepared from the tabled and deslimed coal was used. Basically, the experimental strategy involved expanding the previous design to a full factorial, developing a regression model from this to determine a path to follow in order to bracket where the optimum lies. Once this new region was discovered (using the path-of-steepest ascent approach), a Box-Wilson composite design was used to determine the conditions for optimum conversion (2).

The regression model from the Box-Wilson design indicated the optimum conversion is equivalent to 0.92 lbs SO₂/MMBtu and this optimum can be achieved at 880°C for a residence time of 106 minutes. It is important to note that desulfurization is not especially sensitive to changes in time and temperature in the immediate region and very high sulfur conversions are possible in any part of this region (866°C-885°C). The actual regression equation was found to be:

$$Y_1 = -189.9 + .457*T - 0.104*t + 0.00018*T*t - 0.000276*T^2 - 0.000323*t^2$$

Since the run-of-mine coal contained a sulfur content equivalent to 9.81 lbs SO₂/MMBtu, then hydrodesulfurization under optimum conditions would yield a char which could be combusted under present law in any boiler.

Series IX experiments - The hydrodesulfurization of IBCSP #6 coal was investigated using a four factor, two-level factorial design. The experimental data is shown in Table 22, and the regression analysis appears in Table 23. Increasing times and temperatures lead to lower sulfur chars, although increasing flow rates and the presence of a magnetite acceptor does not appear to have any appreciable benefit. Upon examining the main effects for Y₂, it can be seen that increasing times and temperatures with an acceptor present is somewhat beneficial in increasing the extent of hydrodesulfurization. The data presented here are not intended to suggest that optimum conditions for this particular sample have been attained, although chars of one percent sulfur or less were produced.

Series X experiments - Hydrodesulfurization kinetic data were obtained at 700, 750, 800, 850, and 866°C using char prepared from IBCSP #4 coal. The starting coal was tabled and deslimed and pre-oxidized for the pyrolysis treatment. Sulfur conversion data were obtained at times ranging from 5-120 minutes and are shown in Figure 4 as percent initial sulfur remaining in the char (Y₂). As expected, increasing temperatures resulted in higher levels of desulfurization with optimum sulfur conversion occurring at the highest temperature employed (866°C). At 700°C, the lowest temperature for which kinetic data were obtained, some 60 percent of the char's initial sulfur remained whereas at 866°C, approximately 30 percent remained. Furthermore, the initial rate at 866°C was much faster and the amount of sulfur removed in 10 minutes was roughly equivalent to that removed in two hours at 700°C.

Table 22. Hydrodesulfurization data for IBCSP #6 coal

| HDS No. char | Conditions | | | | | | | | | | Product | | | Sulfur Balance | | |
|-----------------|------------|------|------|------------|---------------|---------|---------|----------------|----------------|----------------|---------|-------|----------|----------------|-----|--|
| | Temp | Time | Flow | Space Vel. | Acceptor Type | Wt% Acc | %S Char | Y ₁ | Y ₂ | Y ₃ | in | char | acceptor | out | gas | |
| 221 | 750 | 45 | 500 | 0.328 | --- | 0.00 | 0.8 | 1.28 | 25.62 | 93.84 | 0.219 | 0.056 | 0.000 | 0.163 | | |
| 222 | 850 | 45 | 500 | 0.307 | --- | 0.00 | 1.17 | 1.90 | 36.83 | 92.23 | 0.234 | 0.086 | 0.000 | 0.148 | | |
| 223 | 750 | 45 | 1000 | 0.675 | --- | 0.00 | 1.32 | 2.15 | 42.45 | 94.22 | 0.213 | 0.090 | 0.000 | 0.123 | | |
| 224 | 850 | 45 | 1000 | 0.615 | --- | 0.00 | 1.12 | 1.82 | 35.06 | 91.73 | 0.234 | 0.082 | 0.000 | 0.152 | | |
| 225 | 750 | 90 | 500 | 0.337 | --- | 0.00 | 1.17 | 1.90 | 36.97 | 92.59 | 0.214 | 0.079 | 0.000 | 0.135 | | |
| 226 | 850 | 90 | 500 | 0.338 | --- | 0.00 | 1.14 | 1.85 | 35.05 | 90.08 | 0.213 | 0.075 | 0.000 | 0.138 | | |
| 227 | 750 | 90 | 1000 | 0.701 | --- | 0.00 | 1.03 | 1.66 | 32.39 | 92.14 | 0.205 | 0.066 | 0.000 | 0.139 | | |
| 228 | 850 | 90 | 1000 | 0.636 | --- | 0.00 | 1.08 | 1.73 | 33.27 | 90.27 | 0.226 | 0.075 | 0.000 | 0.151 | | |
| 229 | 750 | 45 | 500 | 0.329 | Mag. | 28.78 | 1.52 | 2.48 | 44.43 | 85.64 | 0.218 | 0.097 | 0.056 | 0.065 | | |
| 230 | 850 | 45 | 500 | 0.363 | Mag. | 31.02 | 1.15 | 1.87 | 33.91 | 86.39 | 0.198 | 0.067 | 0.033 | 0.098 | | |
| 231 | 750 | 45 | 1000 | 0.669 | Mag. | 29.32 | 1.32 | 2.17 | 40.01 | 88.81 | 0.215 | 0.086 | 0.040 | 0.088 | | |
| 232 | 850 | 45 | 1000 | 0.624 | Mag. | 28.09 | 1.11 | 1.80 | 22.75 | 60.05 | 0.230 | 0.052 | 0.036 | 0.142 | | |
| 233 | 750 | 90 | 500 | 0.319 | Mag. | 28.89 | 1.15 | 1.83 | 30.31 | 77.21 | 0.225 | 0.068 | 0.067 | 0.090 | | |
| 234 | 850 | 90 | 500 | 0.332 | Mag. | 29.42 | 0.81 | 1.29 | 21.44 | 77.54 | 0.217 | 0.046 | 0.034 | 0.137 | | |
| 235 | 750 | 90 | 1000 | 0.636 | Mag. | 28.01 | 1.13 | 1.81 | 32.96 | 85.47 | 0.226 | 0.074 | 0.039 | 0.113 | | |
| 236 | 850 | 90 | 1000 | 0.624 | Mag. | 28.19 | 0.87 | 1.38 | 22.49 | 75.73 | 0.231 | 0.052 | 0.039 | 0.140 | | |

Table 23. Estimates of effects of hydrodesulfurization of IBCSP #6 coal

| | Response variables | | |
|---------------|--------------------|----------------|----------------|
| | Y ₁ | Y ₂ | Y ₃ |
| Average | 1.808 | 32.87 | 85.87 |
| Main effects | | | |
| A (temp) | -0.103 | -2.77 | -2.87 |
| B (flow rate) | -0.008 | -0.20 | -1.07 |
| C (time) | -0.126 | -2.26 | -0.74 |
| D (acceptor) | 0.021 | -1.83 | -6.27 |
| Interactions | | | |
| AB | -0.030 | -1.51 | -2.49 |
| AC | -0.016 | 0.22 | 1.15 |
| AD | -0.141 | -3.12 | -1.81 |
| BC | -0.141 | -3.12 | -1.81 |
| CD | -0.125 | -1.98 | 0.13 |
| ABC | 0.059 | 1.66 | 1.31 |
| ABC | 0.074 | 0.47 | -2.46 |
| ACD | 0.018 | 0.83 | 1.18 |
| BCD | 0.100 | 2.54 | 1.86 |
| ABCD | -0.075 | -1.02 | 1.12 |

The shapes of the kinetic curves suggest that hydrodesulfurization might be controlled by two different phenomenon; one at short residence times and one at long residence times. Reaction rates were relatively fast in the first 20 minutes but were quite slow for the duration of the run. This was evident at all temperatures, but is clearly evident at 866°C where most of desulfurization occurred in the first 20 minutes. FMC data, (5) showed similar trends for hydrodesulfurization of a COED char (derived from an Illinois No. 6 coal). Their data were modeled by assuming an equilibrium controlled reaction at short residence time and a Knudsen diffusion controlled reaction, which is very slow, at longer residence times. Calculations using the kinetic data generated here, showed that in the initial stages of the reaction and at all temperatures tested, the outlet hydrogen sulfide concentrations were in the same range expected for a thermodynamically controlled reaction of hydrogen with ferrous sulfide. Thus, even in small bench-scale equipment, back-reactions occur to such an extent that they determine the rate of reaction. Consequently, an acceptor is an absolute requirement on a commercial scale as it would not be feasible to achieve space velocities which are high enough for sufficiently high conversions.

Series XI experiments - Inasmuch as the envisioned end use of hydrodesulfurized char would be as an industrial or utility boiler fuel, a number of tests were conducted to evaluate combustion characteristics. All chars were pyrolyzed to 850°C regardless of the hydrodesulfurization temperature which ranged from 750-850°C.

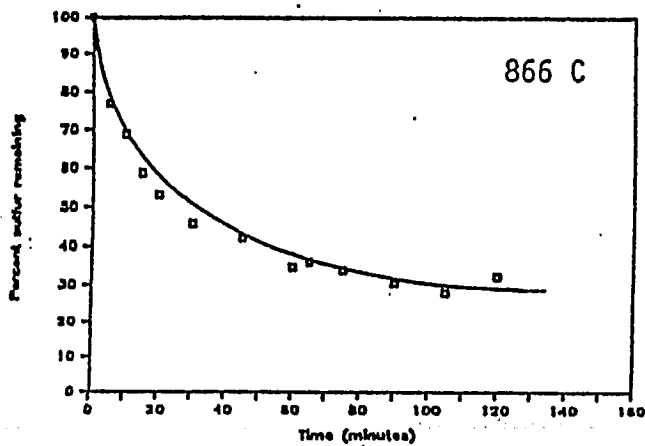
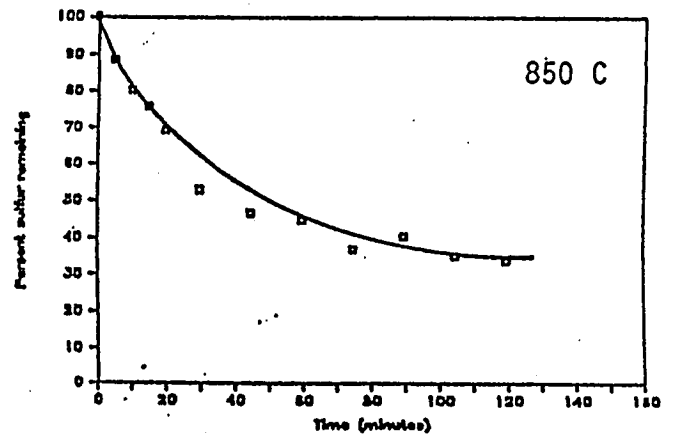
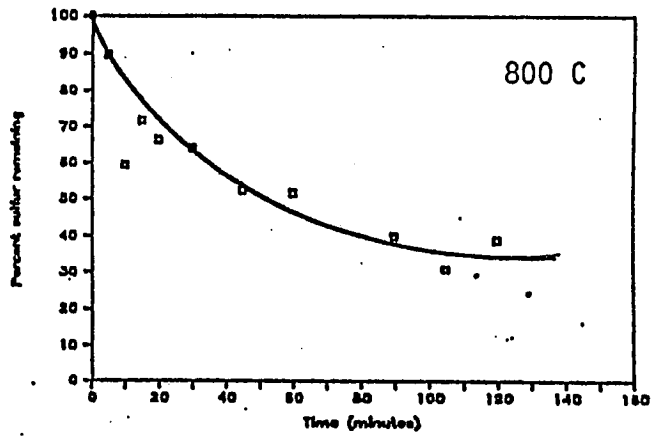
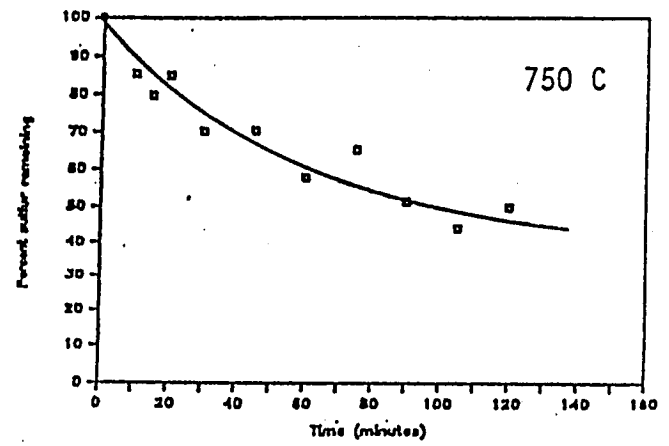
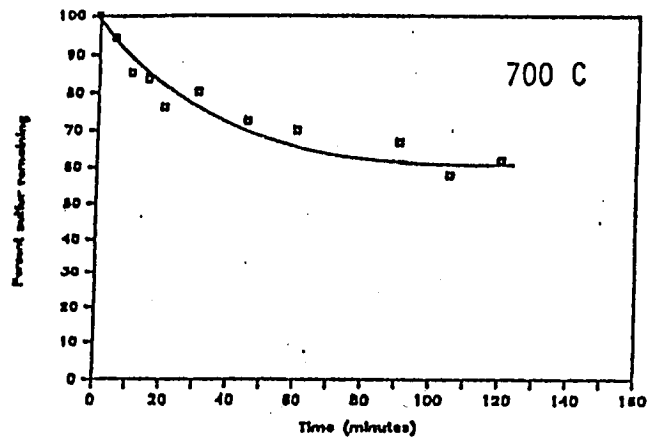


Figure 4. Percent initial sulfur remaining in the char (Y_2) as a function of time at various temperatures.

A burn-off curve of several chars appears in Figure 5. As expected, the untreated coal starts burning at a lower temperature than any of the chars. All of the chars exhibit similar behavior with combustion beginning about 500°C and essentially complete by 600°C. It is noteworthy that the temperature at which complete combustion occurs is roughly equivalent for all of the chars and the raw coal.

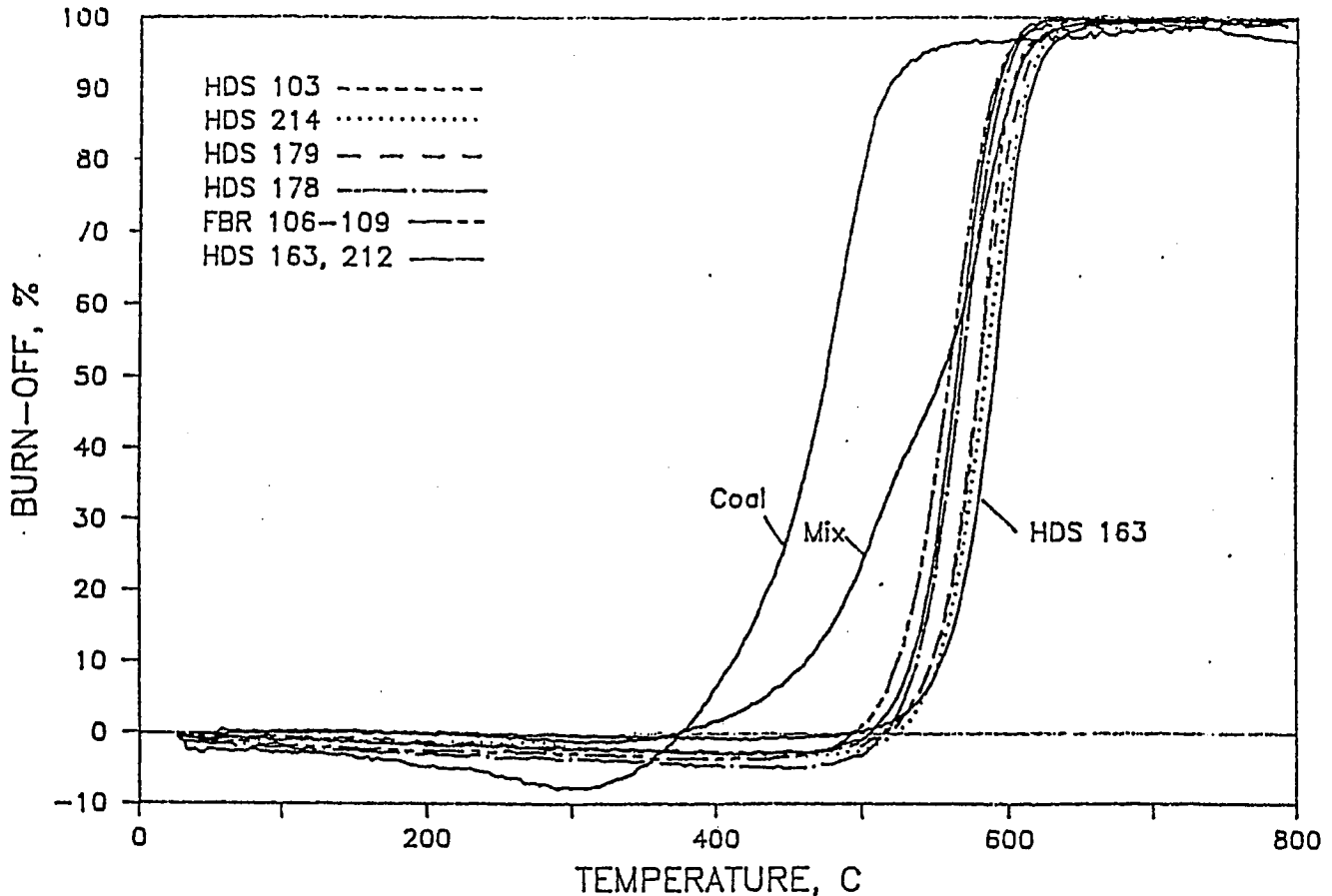


Figure 5. Burn-off curves for various chars and raw coal.

CONCLUSIONS AND RECOMMENDATIONS

The concentration of oxygen, the pyrolysis temperature and the soak time were found to be the primary factors affecting the conversion of pyrite to magnetic pyrrhotite. Several pyrolysis experiments were made at 500, 550 and 600°C with oxygen concentrations ranging from 0.1 to 1.0 percent. While monoclinic pyrrhotite was produced at all three temperatures, the conversion was more complete at 550 and 600°C. Magnetic separation tests

on several of these chars have demonstrated that significant reductions of inorganic sulfur are possible. Chars as low as 1.87%, 1.1% and 0.9% sulfur were obtained from coal originally containing 6.2%, 3.2% and 2.4% sulfur, respectively. The optimum monoclinic pyrrhotite formation and magnetic separation results were obtained at 550 and 600°C with 0.5 and 0.1 percent oxygen. The removal of sulfur by magnetic separation was very encouraging, however, the yield of clean char was low after magnetic separation. Improved magnetic separation techniques could probably increase the yield of clean char. However, the extent of desulfurization is highly dependent on the nature of the sulfur in the char. High organic sulfur chars would not respond well to this method and would need to be hydrodesulfurized to achieve significant sulfur reductions.

A number of conclusions have been drawn from the hydrodesulfurization data.

- Compliance level chars (<1.2 lbs SO₂/MMBtu) were obtained from all three IBCSP coals tested. With IBCSP #4 coal, >90% reduction was attained as well.
- For chars produced from IBCSP #4 coal, the reactivity towards hydrogen depends on the method of char preparation. Pre-oxidized chars are more reactive than non-oxidized chars which are more reactive than post-oxidized chars.
- The yield of char decreases with increasing times and temperatures and decreases in the presence of an acceptor. In the first two cases (time and temperature), hydrogasification could be responsible. In the latter case, it could be due to increased carbon-steam gasification or due to losses during magnetic separation.
- Particle size has absolutely no effect on the rate of hydrodesulfurization. This is consistent with a reaction rate controlled by thermodynamic equilibrium or Knudsen diffusion or both.
- Magnetite and hematite appear to be roughly equivalent as sulfur scavengers. Each acceptor has been found to appreciably reduce the outlet concentration of hydrogen sulfide, to lower the final sulfur content of the char and to effect a generally small but measurable decrease in char yield. The decreased char yield could be due to an increased portion of the char undergoing gasification or it could have resulted from carbon loss to the magnetic fraction during magnetic separation.
- An increased extent of hydrodesulfurization of IBCSP #4 coal can be attained by increasing the treatment times, temperatures and hydrogen flow rates, by using a physically cleaned coal sample as feed, by pre-oxidizing it before pyrolysis and by carrying out the hydrodesulfurization in the presence of an acceptor. Optimization studies indicated optimum conditions of 880°C and 106 minutes would result in a char of 0.91 lbs SO₂/MMBtu in the absence of an acceptor. Specific sulfur contents of 0.6 lbs SO₂/MMBtu were attained when the hydrodesulfurization was carried out with an acceptor present.

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