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TECHNICAL REPORT
March 1 through May 31, 1992

Project Title: **INVESTIGATION OF A TECHNIQUE FOR SULFUR REDUCTION OF MILD GASIFICATION CHAR**

DE-FG22-91PC91334

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**ABSTRACT**

The object of this program is to investigate the desulfurization of mild gasification char using $H_2$:$CH_4$ mixtures at the laboratory scale. Mild gasification is a coal conversion technique which produces solid, liquid, and gaseous co-products at 1100°-1500°F and near-ambient pressure. Char comprises about 60 to 70% of the dry coal yield. Form coke for steelmaking and foundries presents potential high-value markets for chars from eastern bituminous coals. Conventional metallurgical cokes generally contain less than 1 wt% sulfur, and mild gasification char from high-sulfur Illinois coals must be upgraded to meet these criteria. One method to accomplish this is desulfurization with reducing gases derived from the co-product gases. Because form coke has a market value up to $200/ton, it can accommodate desulfurization costs and still be economically attractive.

In the first year of the two-year program, granular char is being treated with $H_2$:$CH_4$ blends at temperatures of 1100°-1600°F and pressures of 50-200 psig. The effects of temperature, pressure, residence time, gas velocity, and gas composition on sulfur removal and carbon gasification are being determined. The batch experiments are being performed in a 2-inch-ID stainless-steel batch fluidized-bed reactor. The test chars were produced from Illinois coals by the IGT 100-lb/h process research unit (PRU) in a DOE/METC-sponsored program and by an isothermal free-fall reactor (IFFR) in a related CRSC-sponsored program. These chars contain 1.16 to 4.58 wt% sulfur.

During the third quarter, 10 tests were performed with four chars. Fluidized-bed tests were conducted at 1400-1600°F, 50-200 psig, and 120-240 min residence time. The bed gas velocity was varied from 0.067 to 0.150 ft/s, and the gases used were either 10% or 25% $CH_4$ in $H_2$. The data from these tests show sulfur conversions ranging from 6.0 to 92.4 wt%, with carbon conversions from zero to 25.6 wt%. The maximum sulfur conversion was 92.4 wt% at 1400°F and 200 psig in 90% $H_2$ for 120 minutes residence time, using IFFR char produced from IBC-106 coal at 1200°F in helium. The sulfur content of the char was reduced from 3.78 to 0.39 wt%.

Future tests will focus on determining the key properties that determine the susceptibility of char to hydrodesulfurization with minimal carbon conversion. In the second year, the study will be extended to include form coke briquettes made from desulfurized mild gasification char. Acid-washing of char will also be studied as a method of increasing the susceptibility to desulfurization. The data obtained from the program will be used to design a desulfurization process to be integrated with the IGT MILDGAS process.

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## EXECUTIVE SUMMARY

The object of this program is to investigate the desulfurization of mild gasification char using hydrogen/methane mixtures in a laboratory-scale experimental study. Mild gasification is a coal conversion technique which produces a slate of solid, liquid, and gaseous co-products at conditions of low severity (1000°-1500°F, <50 psig). A mild gasification process which uses a coaxial fluidized-bed/entrained-bed reactor system has been developed by IGT under U.S. DOE sponsorship (DOE Contract DE-AC21-87MC24266). Char is the major co-product, comprising about 60% to 70% of the yield from dry coal.

One major target use for mild gasification char is metallurgical form coke. Form coke for blast furnaces and foundries has a higher market value at low sulfur content. Conventional cokes generally contain about 1 wt% sulfur. Mild gasification chars from high-sulfur Illinois coals contain up to 3 wt% sulfur and must therefore be upgraded. One method that can accomplish this is desulfurization with reducing gases, which can be derived from the mild gasification co-product gases. The desulfurization can be performed on the char particles exiting the mild gasifier, and also on formed briquettes made by a binderless technique, wherein hot (1100°F) char is blended with additional caking coal to provided an *in-situ* binder.

The sulfur content of char from mild gasification is largely dependent on the sulfur content of the parent coal. In the DOE-sponsored study, the parent coal, a conventionally washed Illinois coal, contained 3 to 5 wt% sulfur. The char sulfur content from a series of temperature-dependency tests ranged from 2.1 wt% to 2.8 wt%, which was 27% to 46% lower than that of the coal. It is estimated that desulfurization of the char by an additional 50% or more would be required to yield an attractive product for form coke production.

Research performed in the 1970's at IGT, U.S. Steel, Garrett Research, and elsewhere has shown that coal chars from various types of gasifiers can be effectively desulfurized by exposure to reducing gases at temperatures from 1100°F to 1500°F. Mixtures of hydrogen and methane are effective for this purpose. Although pure hydrogen is much more effective than pure methane, $H_2/CH_4$ mixtures are also more effective than pure methane, and the presence of methane inhibits carbon hydrogasification, thus allowing desulfurization to proceed with reduced carbon losses, compared to treatment with pure hydrogen. Also, the use of a process-derived gas mixture avoids the separation costs associated with the use of pure $H_2$. The product gas from mild gasification, on an inert-free basis, contains 20 to 28 vol% $CH_4$ and 28 to 50% $H_2$, depending primarily on temperature. Estimates show that the amount of $H_2$ gas produced in mild gasification is two to three times the amount required to stoichiometrically react with all of the sulfur in the char.

The ultimate goal of the project is to develop a method for desulfurization of mild gasification char, using process-derived gases. The objectives of the 24-month program are to conduct laboratory studies that assess the technical viability of the process concept, develop a preliminary process flow scheme, and make recommendations for integration of the desulfurization step into an ongoing mild gasification development program.

In the first year, granular mild gasification chars are being treated with mixtures of $H_2$ and $CH_4$ at the following ranges of conditions:

- Temperatures of 1100° to 1600°F
- Pressures of 50 to 200 psig
- Residence times of 30 to 240 minutes
- Reducing gas $CH_4$ content of 10 to 25 vol% in $H_2$
- Fluidization gas velocity of 0.067 to 0.150 ft/s

The batch experiments are being performed in a nominal 2-inch-ID stainless-steel, batch fluidized-bed reactor. The chars being desulfurized were produced by the IGT mild gasification process research unit (PRU) in a previous DOE/METC-sponsored technology development program or by an isothermal free-fall reactor (IFFR) in a related CRSC-sponsored program. The parent coal for the PRU chars was Illinois No. 6 coal from Peabody Coal Company's Randolph preparation plant, and the PRU chars were produced at temperatures ranging from 1107° to 1390°F. One IFFR char was produced from a similar Peabody Illinois No. 6 coal at 1392°F under $CO_2$, and the other was produced from IBC-106 Indiana V coal at 1200°F in helium. The chars contain 1.16 - 4.58 wt% sulfur. The effects of char production conditions, temperature, pressure, residence time, gas velocity, and gas composition on sulfur removal and carbon gasification are being determined.

Based on data obtained in the first two quarters, showing large differences in susceptibility to desulfurization between chars prepared under various conditions, efforts are also being directed towards correlating char properties with desulfurization potential.

During the third quarter, we have conducted 10 fluidized-bed tests. Nine tests were conducted on 4 mild gasification chars, and one on coke breeze which had been used as a bed diluent in the mild gasification PRU. The coke breeze test was performed in order to normalize data on PRU chars, which contain varying levels of residual coke breeze. These tests were performed at 1400° to 1600°F, 50 to 200 psig, and with residence times of 30 to 240 minutes.

The analyzed data show dramatic differences in the susceptibility of chars to desulfurization. Sulfur conversion ranged from a low of 6% for one PRU char to a high of 92% for one IFFR char. Sulfur conversion was greater than carbon conversion in all tests. The mean ratio of sulfur conversion to carbon conversion was 3.1 to 1.

The PRU char (Test MG-8) which was tested during the first two quarters continued to be very unreactive, with a maximum sulfur conversion of 17.8% obtained at 1600°F and 100 psig for 240 minutes under 90 vol% $H_2$. This char was produced in a 1320°F PRU test without a bed diluent, and the coal had agglomerated severely, resulting in defluidization. In later tests, coke breeze had been used in the PRU as a 50% bed diluent to simulate char recycle. The MG-8 char was selected for this project because it was uncontaminated with coke breeze and because it had an unusually high sulfur content of 4.58 wt%. However, the conditions of its production may have resulted in anomalous behavior, possibly because of atypical morphology caused by the formation of a monolithic agglomerate in the fluidized bed.

In order to clarify this point, a series of PRU chars produced at temperatures of 1107° to 1390°F, with and without steam in the fluidization gas, were obtained, analyzed, and prepared for testing. The PRU diluent coke breeze was also tested to obtain correction data to be applied to tests with PRU chars, so that the reactivity of the mild gasification char could be determined separate from that of the coke breeze. To date, one of the PRU chars was tested in the desulfurization unit, giving 20.1% sulfur conversion and 4.5% carbon conversion. The coke-free sulfur content was reduced from 3.56 wt% to 3.16 wt% (dry basis).

For comparison, and to gain a perspective on the susceptibility of entrained-bed chars, two chars prepared in the IFFR were also tested. Both chars were desulfurized at 1400°F and 200 psig for 120 minutes in 90% $H_2$/10% $CH_4$. The first char, produced from a Peabody Illinois No. 6 coal at 1392°F in $CO_2$, showed a sulfur reduction from 2.45 wt% to 0.68 wt%, which corresponds to 80% sulfur conversion, while carbon conversion was 26%. The other IFFR char, produced from IBC-106 (Indiana V) coal at 1200°F in helium, was even more susceptible. Sulfur content was reduced from 3.78 wt% to 0.39 wt%, giving a sulfur conversion of 92% and a carbon conversion of only 17%.

Analyses of gas samples showed that $H_2S$ levels in the exit gas dropped rapidly as each test progressed, with 10-minute levels as high as 1610 ppmv dropping as low as 10 ppmv after 240 minutes. Because of the batch nature of the tests, and the varying sulfur contents of the chars, no correlation of $H_2S$ content with extent of desulfurization could be made.

Future tests will complete the evaluation of various MILDGAS PRU chars in the desulfurization reactor. Efforts will be made to determine the key properties that control the susceptibility of chars to hydrodesulfurization with minimal carbon conversion.

In the second year, the correlation of char properties with desulfurization will continue, and acid-washing of chars with HCl will be studied to enhance desulfurization susceptibility. Form coke briquettes will be made from desulfurized mild gasification chars by a binderless technique, wherein hot (1100°F) char is blended with additional parent coal to provided an *in-situ* binder. The briquettes will then be calcined at 1800°F, which is required to cure the binder and develop optimal properties. The study will include calcination under reducing gas atmosphere for further sulfur removal. In addition to the effects of process parameters on sulfur removal and carbon gasification, their effects on the strength, density, tumbler-test stability, and reactivity of the resultant form coke, which are important to their use in blast furnaces, will be investigated.

The data obtained from both years of the program will be used to design a desulfurization process to be integrated with the IGT mild gasification process.

## OBJECTIVES

The ultimate goal of this project is to develop a method for desulfurization of mild gasification char, using process-derived gases. The overall objectives of the 24-month program are to conduct laboratory studies that assess the technical viability of the process concept, develop a preliminary process flow scheme, and make recommendations for integration of the desulfurization step into an ongoing mild gasification development program.

## INTRODUCTION AND BACKGROUND

Mild gasification is an advanced coal carbonization process that emphasizes simple reactor and process design, low-severity processing conditions, and the use of advanced technical knowledge to bring a slate of value-added co-products (char, fuel gas, and oils/tars) to the marketplace in the next five years. The U.S. DOE has been supporting the development of this technology since 1987, and a project team consisting of Peabody Holding Company, Bechtel National, and IGT has completed a literature and market survey and technology development program including the design, construction and operation of a 100-lb/h PRU and the design of a 24-ton/day process development unit (PDU).[1,2,3,4] The mild gasification reactor consists of a coaxial fluidized-bed/entrained-bed vessel which can process all types of coals. IGT has completed 47 mild gasification tests on four coals in the PRU, at temperatures ranging from 1034° to 1390°F.

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[1] Knight, R.A., J. Gissy, M. Onischak, S.P. Babu, J.M. Wootten, and R.G. Duthie, "Development of An Advanced, Continuous Mild Gasification Process for the Production of Co-Products", Task 2 Topical Report to DOE/METC, Contract No. DE-AC21-87MC24266, (July 1990).

[2] Knight, R.A., J. Gissy, M. Onischak, R.H. Carty, S.P. Babu, J.M. Wootten, and R.G. Duthie, "Development of An Advanced, Continuous Mild Gasification Process for the Production of Co-Products", Task 4 Topical Report to DOE/METC, Contract No. DE-AC21-87MC24266, (December 1990).

[3] Wootten, J.M., M. Nawaz, R.G. Duthie, R.A. Knight, M. Onischak, S.P. Babu, and W.G. Bair, "Development of An Advanced, Continuous Mild Gasification Process for the Production of Co-Products", Task 1 Topical Report to DOE/METC, Contract No. DE-AC21-87MC24266, (August 1988).

[4] Carty, R.H., M. Onischak, S.P. Babu, R.A. Knight, J.M. Wootten, and R.G. Duthie, "Development of An Advanced, Continuous Mild Gasification Process for the Production of Co-Products", Task 3 Topical Report to DOE/METC, Contract No. DE-AC21-87MC24266, (December 1990).

Figure 1 shows the variation of char sulfur content with mild gasification temperature from a series of PRU tests using Illinois No. 6 coal from Peabody's Randolph preparation plant. The parent coal, containing 3 to 5 wt% sulfur, is typical of a conventionally washed Illinois coal. As shown, the char sulfur content, ranging from 2.1 wt% to 2.8 wt%, is 27% to 46% lower than that of the coal. Expressed on a Btu basis, this represents a sulfur reduction of 20% to 38%.

For form coke made from mild gasification char, the guidelines on sulfur content are not strictly defined. In the blast furnace, coke acts as both a fuel and as a reductant for iron ore. Limestone is added to the furnace charge to bind the sulfur, and the amount of limestone added directly affects the economics of the process by limiting the steel output, consuming sensible heat, and adding material cost for the limestone. For these reasons, in this project, the target sulfur limit of 1.0 wt% for the form coke has been selected.

In the 1970's, research on coal and char desulfurization increased along with synfuels research in general. U.S. Steel Corporation, with ERDA support, developed the Clean Coke process, in which desulfurization of the char with recycled product gas played an important role.[5] The recycle gas used for fluidization in the PDU was 71% $CH_4$, 13% $C_2H_6$, 10% CO, 2% $H_2$, and 4% higher hydrocarbons. At 1400°F, char was reduced in sulfur content from 1.7 wt% to 0.3 wt% in 180 min residence time, which is an 82% reduction. The $H_2S$ concentration in the recycle gas was identified as a critical factor in achieving effective desulfurization, as shown by the finding that increasing the volumetric $H_2S$ concentration in the recycle gas from 50 ppm to 500 ppm increased the char sulfur content from 0.21 wt% to 0.71 wt%. An associated study of char-sulfur chemistry[6] found that, with an Illinois No. 6 hydro-gasification char, desulfurization with reducing gases occurred in two steps: an initial rapid-rate step associated with reduction of $FeS_2$ to FeS, and a slower secondary step where FeS is reduced to elemental iron. The study determined that, while $H_2$ is more effective than $CH_4$ for char desulfurization, mixtures of $CH_4$ and $H_2$ were also effective and, furthermore, the presence of methane inhibited carbon gasification at longer residence times while allowing desulfurization to continue.

The same study also found that, for a given char, the relationship between sulfur removal and carbon loss through gasification in the first 15-30 minutes follows a monotonic curve, regardless of the temperature, pressure, or gas atmosphere used. Figure 2 shows this relationship for an Illinois No. 6 char prepared at 1112°F. Based on this relationship, a 50% to 65% sulfur reduction, such as may be required for mild gasification char to meet the selected form coke requirement of 1 wt% sulfur, could be achieved with an

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[5] Boodman, N.S., T. F. Johnson, and K.C. Krupinski, "Fluid-Bed Carbonization/Desulfurization of Illinois Coal by the Clean Coke Process: PDU Studies", ACS Div. of Fuel Chem. Prepr. 22:2, 28-44 (1977).

[6] Kor, G.J.W., "Desulfurization and Sulfidation of Coal and Char", ACS Div. of Fuel Chem. Prepr. 22:2, 1-27 (1977)

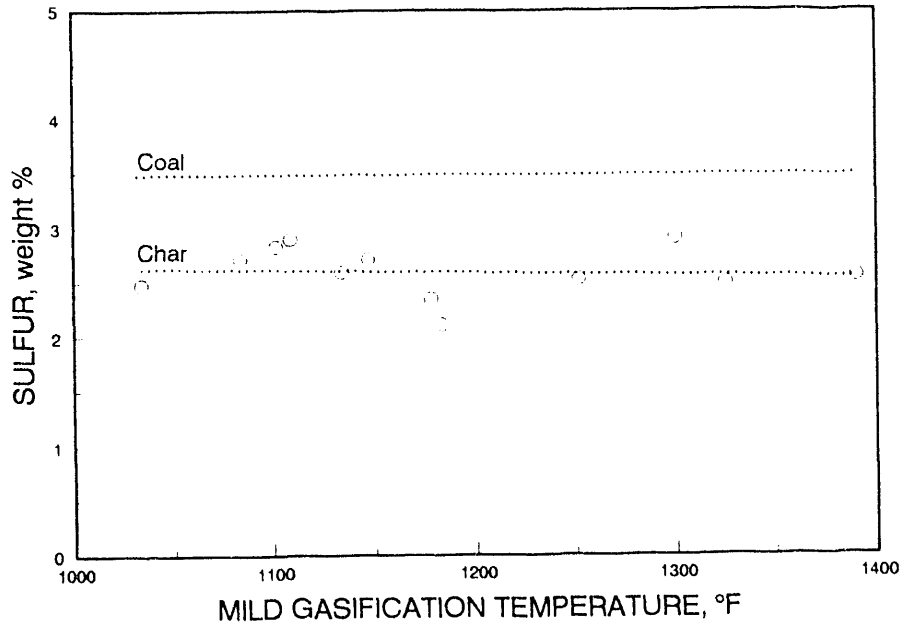


Figure 1. SULFUR CONTENT OF MILD GASIFICATION CHAR AS A FUNCTION OF TEMPERATURE

accompanying 10% to 13% carbon conversion.

In similar work, IGT studied the hydrodesulfurization of four bituminous coals at 1300° to 1500°F for 30 min in hydrogen.[7] A reduction of 74% in the lb $SO_2$/MMBtu was achieved with Illinois No. 6 coal. This study emphasized the importance of maintaining a low $H_2S$ concentration in the treatment gas, suggesting the use of a solid sulfur sorbent such as calcium oxide. The investigators also concluded that a mild pre-oxidation of the coal substantially increases subsequent sulfur removal by hydrodesulfurization. However, a more recent CRSC-funded study[8] found that this interaction was dependent on the coal tested and the type of physical cleaning to which the coal had been subjected.

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7 Fleming, D.K., R.D. Smith, and M.R.Y. Aquino, "Hydrodesulfurization of Coals", ACS Div. of Fuel Chem. Prepr. 22:2, 45-49 (1977)

8 Stephenson, M.D., A.D. Williams, M. Rostam-Abadi, and C.W. Kruse, "The Effect of Mild Oxidation on the Thermal Desulfurization and Hydrodesulfurization of two Illinois Bituminous Coals in a Fluidized-Bed Reactor", ACS Div. of Fuel Chem. Prepr. 33:4, 960-967 (1988)

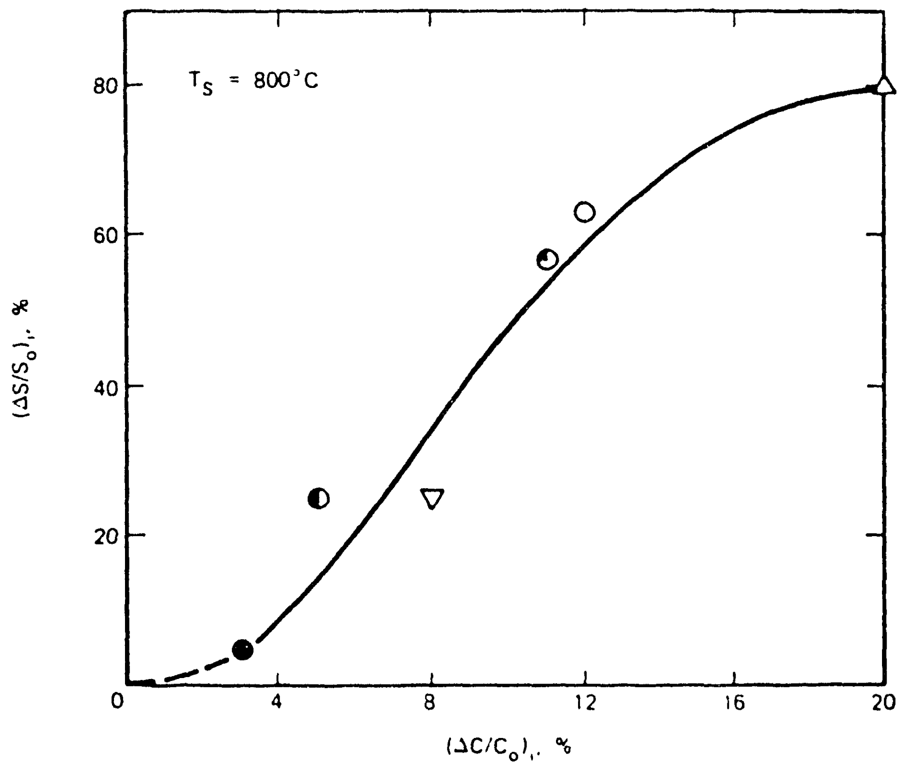


Figure 2. GENERAL RELATIONSHIP BETWEEN INITIAL LOSS OF SULFUR AND CARBON FOR ILLINOIS NO. 6 CHAR PREPARED AT 1112°F

Research on char hydrodesulfurization was also done by Garrett Research and Development (later Occidental Petroleum). A 1976 paper[9] discusses the effectiveness of acid-washing of char to remove Ca and Fe compounds which appear to contribute to the severity of $H_2S$ inhibition. The hydrogen requirement with an acid-washed char was 12% of that required for an untreated char.

This study is evaluating the technical feasibility of desulfurizing mild gasification char and/or form coke briquettes with process-derived reducing gases. The unique aspects of this research are: the application of this technique to mild gasification char and/or briquettes made therefrom, and the integration of the technique with form coking. In the IGT fluidized-bed mild gasification process, bituminous coal is not pre-oxidized to prevent caking as has been done in other processes.[5,7] The intrinsic caking tendency of the coal is instead overcome by a systematic control over the relationship of the incoming coal feed rate to the volumetric char inventory in the fluidized bed.

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9 Robinson, L., "Hydrodesulphurization of Char", *Fuel* **55:3**, 193-201 (1976)

The char thus differs in physical and chemical properties from both coal and from gasification or hydrogasification chars that have previously been studied. In form coke production, the hot (1100°F) char would be contacted with fresh coal which would supply an *in-situ* binder for briquetting. The resulting "green" briquettes would then be calcined in a shaft furnace at about 1800°F. The relative feasibility and impact on overall process efficiency of desulfurization before and after briquetting must be evaluated.

The product gas from mild gasification, on an inert-free basis, contains 20 to 28 vol% $CH_4$ and 28 to 50% $H_2$, where the $H_2$:$CH_4$ mole ratio increases monotonically from about 0.4 at 1100°F to 1.0 at 1300°F.[2] In addition to the presence of methane inhibiting the carbon gasification during desulfurization, the use of a process-derived gas mixture would be more economical than using pure hydrogen. If necessary, the hydrogen content of the desulfurizing gas can be adjusted via the shift reaction or partial steam reforming of the methane and other hydrocarbon gases. The effectiveness of varying mixtures of $H_2$ and $CH_4$ for desulfurization are being determined in the program.

The information thus obtained will be unique in its direct applicability to mild gasification, and thus will be of immediate value to further process development and the expanded utilization of high-sulfur Illinois coals.

## EXPERIMENTAL PROCEDURES

Existing samples of mild gasification char from PRU tests conducted under a DOE/METC contract are being used in addition to chars made from IBCSP coals in previous projects. The coal used in PRU tests was an Illinois No. 6 fines (-1/4-inch) circuit from the Peabody Coal Company's Randolph preparation plant. In order to control agglomeration, dilution of the incoming coal feed with recycled char is an integral part of the MILDGAS design. In most of the PRU tests, this process feature was simulated by blending the feed coal with coke breeze in a 1:1 weight ratio. Chars chosen for testing contain from 0% to 64% residual coke breeze in the sample. Other chars were produced in the IFFR, including one from IBC-106 (Indiana V) coal.

### Task 1. Sample Preparation and Characterization

For the first-year experiments on granular char, samples are being crushed and screened to -80+100 mesh, divided by riffling into representative portions, and characterized in IGT laboratories according to the following protocol:

- proximate and ultimate analyses
- heating value
- pore volume and surface area
- sieve analysis
- forms of sulfur

Task 2. Equipment Preparation and Shakedown

The desulfurization experiments are being conducted in a nominal 2-inch batch reactor, which is being employed in a fluidized-bed mode for granular char experiments. The schematic diagram of the reactor system is shown in Figure 3. Existing furnaces, controls, instruments, and gas supply equipment are being used. A reactor vessel was fabricated from Sch40 316 stainless steel to safely operate up to 1800°F at atmospheric pressure and up to 1400°F at 200 psig. The reactor system has also been modified to allow operation up to 200 psig by the addition of high-pressure mass flow controllers and a high-capacity sintered metal filter to retain fines, replacing the existing low-pressure cyclone.

In the first year, this task covers the reactor fabrication, system cleanup, mechanical and electronic testing of components, and shakedown testing of the system.

Task 3. Desulfurization

This Task is divided into two Subtasks as shown below. In the first year, the experimental work is being performed with granular char.

Subtask 3.1. Parametric Experiments

Char desulfurization experiments are being performed to determine the effects of temperature, pressure, residence time, and gas composition on the char sulfur content. Table 1 shows the specific values of these parameters to be tested. Not all of the combinations in the test matrix will be used. The combinations of parameters will be selected, based on the ongoing data interpretation, to maximize char desulfurization. Approximately 24 experiments are scheduled for each year of the program.

Table 1. EXPERIMENTAL PARAMETERS TO BE TESTED

| | |
|---|---|
| Temperature, °F | 1100, 1300, 1400, 1600 |
| Pressure, psig | 50, 100, 200 |
| Residence time, min | 30, 60, 120, 240 |
| Gas composition, vol% $CH_4$[a] | 10, 25 |
| Superficial gas velocity, ft/s[b] | 0.065 to 0.150 |

[a] Balance $H_2$; $CH_4$ concentrations are based on gas stability with respect to solid carbon deposition

[b] For first-year fluidized-bed experiments only

In a typical experiment, 50 to 100 grams of char are charged to the reactor, which is then sealed. The reactor and associated tubing are leak-tested and purged with inert gas. The reactor is then heated to the desired desulfurization temperature while continuing the flow of inert gas. When the

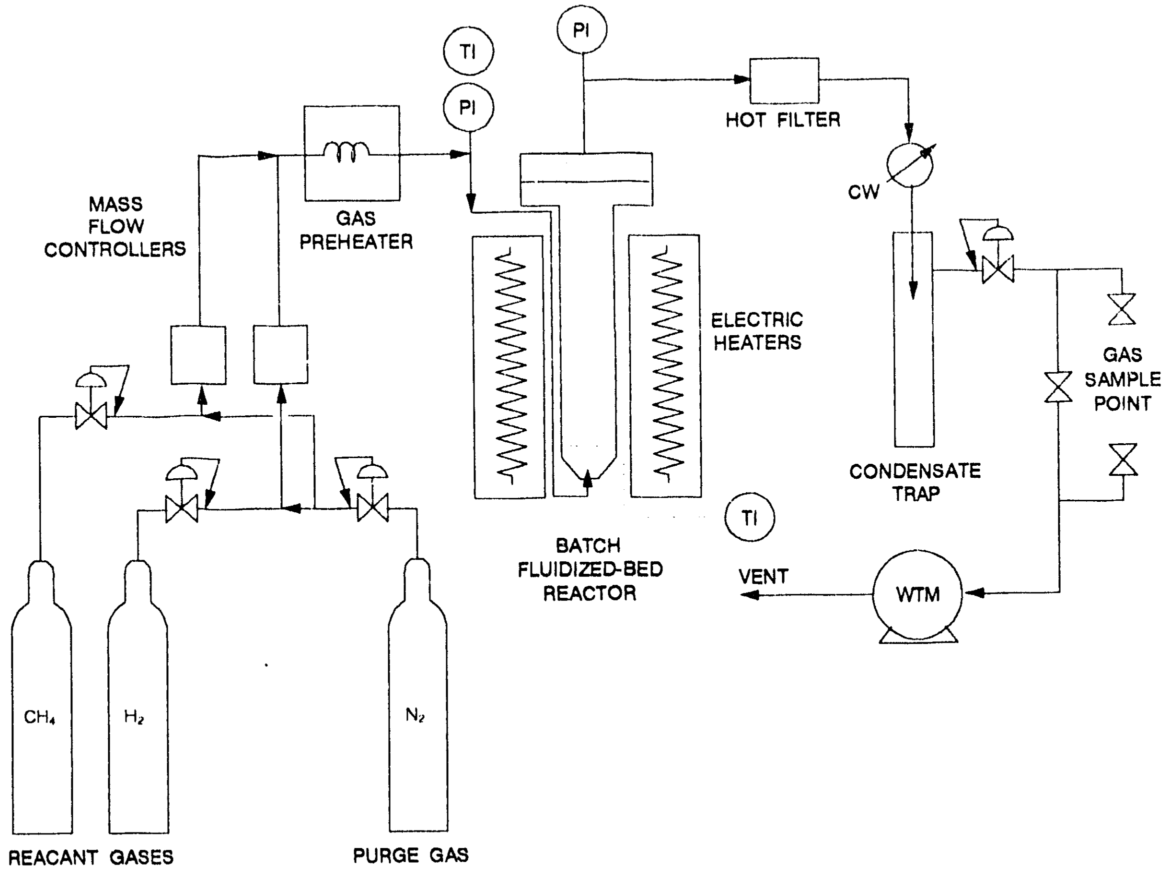


Figure 3. SCHEMATIC OF EXPERIMENTAL DESULFURIZATION REACTOR

desired temperature is attained, the gas flow is switched to the desired premixed gas (10 vol% to 25 vol% $CH_4$ in $H_2$). Gas samples are retrieved at 10- to 30-minute intervals until the end of the desired residence time. Inert gas flow then replaces the reactive gas mixture, and the reactor is rapidly cooled. When cooled to room temperature, the reactor will is opened to retrieve the desulfurized sample (product char) for analysis.

For first-year tests, the gas flow to the fluidized-bed reactor is based on the required minimum fluidization velocity ($u_{mf}$). The parameters selected for gas velocity are slightly below and slightly above three times the $u_{mf}$ for the largest (80-mesh) char particles. The required gas flow to attain the desired gas velocity is calculated for each experiment based on the density and viscosity of the gas mixture used at the conditions of the experiment.

Subtask 3.2. Product Characterization and Evaluation

The desulfurized char or briquettes from each experiment are evaluated by proximate and ultimate analyses. The amount of sulfur removal is calculated based on the weight% of sulfur in the parent sample. The heat content of the product char is calculated according to the following formula from the IGT Databook:[10]

$$Q_v \text{ (Btu/lb, dry basis)} = 146.58C + 568.78H + 29.4S - 6.58A - 51.53(O+N)$$

where C, H, S, A, and (O+N) are the respective weight % of carbon, hydrogen, total sulfur, ash and oxygen + nitrogen by difference.

Selected char samples (approximately one in eight) are also analyzed for sulfur by type and measured calorific value, in order to study effects on the distribution of inorganic or organic sulfur removed. Gas samples from the desulfurization unit are analyzed for $H_2S$ content by the GC/FPD method and for standard light gases by the GC/TCD method.

Task 4. Data Analysis and Interpretation

The experimental data are analyzed and interpreted to determine the effects of the selected parameters (temperature, pressure, residence time, gas velocity, and gas composition) on the following properties of the granular mild gasification char:

- Sulfur content, wt% of dry char

- Percent S conversion, $100\left(1 - \frac{m_p(\%S_p/100)}{m_f(\%S_f/100)}\right)$

  where $m_f$ = feed char mass, $m_p$ = product mass, $\%S_f$ = feed char S content, and $\%S_p$ = product S content.

- Percent C conversion, $100\left(1 - \frac{m_p(\%C_p/100)}{m_f(\%C_f/100)}\right)$

  where $m_f$ = feed char mass, $m_p$ = product mass, $\%C_f$ = feed char C content, and $\%C_p$ = product C content.

- Higher heating value of char, Btu/lb (dry)

For PRU samples which were produced with coke breeze diluent, a normalization of the data to include only coal char is being performed. One test has been conducted with coke breeze to determine conversion of coke, sulfur, and carbon. Based on this test, the product char composition can be corrected to eliminate the contribution of the coke residue, and the desulfurization of the coal char alone can be determined.

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10 *Coal Conversion Systems Technical Data Book*, U.S. DOE Document HCP/T2286-01, Section IA.30.5 (Feb 1978), pp. 1-2

## RESULTS AND DISCUSSION

Task 1. Sample Preparation and Characterization

Five samples have been characterized for testing: two PRU chars, one coke breeze, and two IFFR chars. MG-8 PRU char, which was received in the form of 3"-5" chunks, was crushed and screened to -80+100 mesh. The 40301MG1 IFFR char, which contained a significant amount of fines, was screened to -80+100 mesh. The other two samples, RC040688 IFFR char and IST-9 PRU char, were used as received. The proximate and ultimate analyses of these samples are shown in Table 2 below. Surface area and pore volume analyses are also being conducted on the chars but these data are not yet available.

Table 2. ANALYSES OF MILD GASIFICATION CHARS TESTED IN THIRD QUARTER

| Sample | PRU Test MG-8 | PRU Test IST-9 | PRU coke breeze | IFFR Test RC04688 | IFFR Test 40301MG1 |
|---|---|---|---|---|---|
| Proximate | | | | | |
| Moisture | 1.46 | 0.91 | 0.16 | 2.16 | 2.63 |
| V. M. | 11.64 | 9.36 | 1.14 | 13.33 | 22.17 |
| Ash | 34.81 | 22.63 | 8.79 | 13.08 | 14.47 |
| Fixed Carbon | 52.09 | 67.10 | 89.91 | 71.43 | 60.73 |
| Ultimate | | | | | |
| Ash | 35.33 | 22.84 | 8.80 | 13.37 | 14.86 |
| Carbon | 54.63 | 68.07 | 88.49 | 74.21 | 68.00 |
| Hydrogen | 0.94 | 0.79 | 0.17 | 2.27 | 3.36 |
| Nitrogen | 1.11 | 1.08 | 1.30 | 1.85 | 1.54 |
| Sulfur | 4.58 | 3.14 | 0.72 | 2.45 | 3.78 |
| Oxygen | 3.41 | 4.08 | 0.52 | 5.85 | 8.46 |

Task 2. Equipment Preparation and Shakedown

Preparation and shakedown of the hydrodesulfurization unit was completed in previous quarters. The schematic diagram of the reactor system was shown in Figure 3.

Task 3. Desulfurization

Ten char desulfurization tests were conducted during the quarter. Six tests, (0325 - 0409) were conducted with MG-8 PRU char, one test (0424) with IST-9 PRU char, one test (0505) with RC040688 IFFR char, one test (0515) with 40301MG1 IFFR char, and one test (0518) with PRU coke breeze.

The reaction temperature and residence times were increased over previous tests, which were limited to 1550°F and 60 minutes. Tests 0325 through 0409 were performed for 120 to 240 minutes residence time, and the temperature in three of these tests was increased to 1600°F. After the tests with MG-8 char, concluding with test 0409, it became apparent that this particular char was unreactive to desulfurization even at the increased severity.

A single test with IST-9 char showed similar behavior, with only about 11% reduction in sulfur content in a 240-minute test. Consequently, an assortment of mild gasification chars produced in the PRU and IFFR were then obtained for comparison testing at a single set of conditions, to determine the range of reactivities that could be expected.

The two IFFR chars were successfully desulfurized, indicating that these chars are much more reactive than PRU chars. Sulfur conversion was 80% and 92%, while carbon conversion was 26% and 17%. These findings will be discussed in more detail in the next section.

A summary of test conditions and resulting data from tests conducted in the third quarter is shown in Table 3.

Task 4. Data Analysis and Interpretation

The following discussion refers to the analyzed data shown in Table 3. As in previous reports, carbon, sulfur, and HHV conversions were calculated on the basis of a forced ash balance. Table 4 shows the feed and product char proximate and ultimate analyses for the IST-9 PRU char test (0424) and the two IFFR char tests (0505 and 0515).

For the MG-8 char (tests 0325-0409), sulfur conversions ranged from 6.0% to 17.2%. The maximum sulfur conversion was obtained at 1600°F, 100 psig for 240 minutes residence time in 90% $H_2$. Carbon conversion data were less than sulfur conversion in all cases. However, in two tests, the ash-balanced carbon conversions are negative, which probably signifies zero conversion within the random error limits of the standard analytical techniques. In such cases, the S/C conversion ratio, which in two cases results in a negative number, is meaningless. Overall, the reduction in sulfur content of this char was not significant at any conditions. The MG-8 char was originally chosen for testing because it was obtained from a test which did not use a coke breeze diluent, avoiding the complication of having to make corrections for residual coke breeze content in the char. It also contained an unusually high sulfur content of 4.58 wt%. It is speculated that the atypical nature of this char responsible for the low reactivity may have resulted from severe caking in the PRU fluidized bed during mild gasification.

An IGT computer model for coal gasification/combustion was modified to examine the sensitivity of hydrodesulfurization and hydrogasification to temperature and pressure. The model was modified to accommodate a batch fluidized-bed operation. The results of this exercise suggested that desulfurization was more sensitive to hydrogen partial pressure (74 to 588 psia) than to temperature (1000° to 1600°F). On this basis, subsequent test conditions for screening various chars were set at 1400°F and 200 psig with 90 vol% $H_2$. These conditions represent the operational limits of the reactor flanges. The

Table 3. TEST CONDITIONS AND DATA FOR CHAR DESULFURIZATION TESTS 0325 TO 0518

| Test | 0325 | 0330 | 0401 | 0403 | 0407 |
|---|---|---|---|---|---|
| Feed char | MG-8 | MG-8 | MG-8 | MG-8 | MG-8 |
| Temperature, °F | 1600 | 1600 | 1400 | 1400 | 1600 |
| Pressure, psig | 100 | 100 | 50 | 100 | 50 |
| Residence time, min | 240 | 240 | 240 | 120 | 120 |
| Bed velocity, ft/s | 0.10 | 0.10 | 0.15 | 0.10 | 0.15 |
| $CH_4$ conc, vol% | 10 | 25 | 10 | 25 | 25 |
| Total gas flow, scfh | 11.4 | 11.4 | 10.6 | 12.6 | 9.6 |
| Feed char wt% sulfur | 4.58 | 4.58 | 4.58 | 4.58 | 4.58 |
| Product char wt% sulfur | 4.36 | 4.36 | 4.33 | 4.41 | 4.63 |
| Sulfur reduction, % | 4.8 | 4.8 | 5.5 | 3.7 | -1.1 |
| Sulfur conversion, wt% | 17.2 | 9.0 | 15.6 | 13.5 | 6.0 |
| Carbon conversion, wt% | 8.6 | -5.0 | 5.8 | 5.5 | -0.3 |
| HHV conversion, wt% | 8.9 | -3.5 | 5.0 | 4.9 | 0.4 |
| S/C conversion ratio | 2.0 | -1.8 | 2.7 | 2.5 | -20.2 |

| Test | 0409 | 0424 | 0505 | 0515 | 0518 |
|---|---|---|---|---|---|
| Feed char | MG-8 | IST-9 | RC040688 | 40301MG1 | PRU coke |
| Temperature, °F | 1400 | 1400 | 1400 | 1400 | 1400 |
| Pressure, psig | 50 | 200 | 200 | 200 | 200 |
| Residence time, min | 120 | 240 | 240 | 120 | 120 |
| Bed velocity, ft/s | 0.10 | 0.065 | 0.065 | 0.065 | 0.065 |
| $CH_4$ conc, vol% | 10 | 10 | 10 | 10 | 10 |
| Total gas flow, scfh | 7.1 | 15.3 | 15.3 | 15.3 | 15.3 |
| Feed char wt% sulfur | 4.58 | 3.57[a] | 2.45 | 3.78 | 0.72 |
| Product char wt% sulfur | 4.53 | 3.18[a] | 0.68 | 0.39 | 0.66 |
| Sulfur reduction, % | 1.1 | 10.8[a] | 72.2 | 89.7 | 8.3 |
| Sulfur conversion, wt% | 10.7 | 20.1[a] | 80.4 | 92.5 | 9.4 |
| Carbon conversion, wt% | 5.6 | 5.2[a] | 25.6 | 17.2 | 1.7 |
| HHV conversion, wt% | 5.3 | 5.0[a] | 28.7 | 24.8 | 2.0 |
| S/C conversion ratio | 1.9 | 3.9[a] | 3.1 | 5.4 | 5.4 |

[a] Corrected for residual coke in the feed char; values represent mild gasification char only

Table 4. ANALYSES OF FEED AND PRODUCT CHARS FOR TESTS 0325 TO 0518

| Test(s) | ---- 0424[a] ---- | | ---- 0505 ---- | | ---- 0515 ---- | |
|---|---|---|---|---|---|---|
| Sample | Feed | Product | Feed | Product | Feed | Product |
| PROXIMATE, wt% as rec'd | | | | | | |
| Moisture | 0.91 | 0.11 | 2.16 | 0.38 | 2.63 | 0.69 |
| Volatile Matter | 9.36 | 1.78 | 13.33 | 3.54 | 22.17 | 3.86 |
| Ash | 22.63 | 25.05 | 13.08 | 18.85 | 14.47 | 20.17 |
| ULTIMATE, wt% dry | | | | | | |
| Ash | 25.32 | 28.25 | 13.37 | 18.92 | 14.86 | 20.31 |
| Carbon | 64.47 | 68.21 | 74.21 | 78.14 | 68.00 | 76.93 |
| Hydrogen | 0.90 | 0.47 | 2.27 | 1.02 | 3.36 | 1.07 |
| Nitrogen | 1.04 | 0.81 | 1.85 | 0.96 | 1.54 | 1.25 |
| Sulfur | 3.57 | 3.18 | 2.45 | 0.68 | 3.78 | 0.39 |
| Oxygen (by difference) | 4.71 | -0.91 | 5.85 | 0.28 | 8.46 | 0.05 |
| HHV, Btu/lb (calculated) | 9,603 | 10,177 | 11,756 | 11,866 | 11,377 | 11,696 |

[a] Corrected for residual coke in the feed char; values represent mild gasification char only

IST-9 PRU char (test 0424), which contained an estimated 15% residual coke breeze, showed slightly higher sulfur conversion of 20.1% after correcting for residual coke content. With a carbon conversion of 4.5%, the S/C conversion ratio was 4.5:1. However, the sulfur reduction was unacceptably low.

The IFFR chars (tests 0505 and 0515), in contrast, showed very high conversions under conditions identical to those used in test 0424. These tests both yielded chars with sulfur content well under the 1% target set for this study. Both of these chars were produced from undiluted coal in the IFFR, which more closely simulates the entrained section of the MILDGAS process than the fluidized bed. However, it is not yet known how the reactor geometry affects char reactivity towards hydrodesulfurization, or whether other process conditions are involved.

These data are encouraging, indicating that chars produced from Illinois coals under mild gasification conditions can be satisfactorily desulfurized at relatively mild conditions. However, it is important to determine what conditions during mild gasification influence char susceptibility to desulfurization, and how this knowledge can be applied to the process design.

Average exit gas $H_2S$ concentrations were measured at 10, 20, 30, 60, 120, and (in 240-minute tests) at 180 and 240 minutes from the start of the test. These concentrations are shown in Table 5. $H_2S$ levels in the exit gas dropped rapidly as each test progressed, with 10-minute levels as high as 1610 ppmv dropping as low as 10 ppmv after 240 minutes. Because of the batch nature of

Table 5. $H_2S$ CONCENTRATIONS IN TESTS 0325 TO 0518

| Test | 0325 | 0330 | 0401 | 0403 | 0407 |
|---|---|---|---|---|---|
| Feed char | MG-8 | MG-8 | MG-8 | MG-8 | MG-8 |
| Temperature, °F | 1600 | 1600 | 1400 | 1400 | 1600 |
| Pressure, psig | 100 | 100 | 50 | 100 | 50 |
| Residence time, min | 240 | 240 | 240 | 120 | 120 |
| Bed velocity, ft/s | 0.10 | 0.10 | 0.15 | 0.10 | 0.15 |
| $CH_4$ conc, vol% | 10 | 25 | 10 | 25 | 25 |
| $H_2S$ concentration, ppmv | | | | | |
| 10 minutes | 1610 | 1570 | 720 | 700 | 850 |
| 20 " | 790 | 810 | 510 | 530 | 430 |
| 30 " | 160 | 440 | 410 | 400 | 230 |
| 60 " | 150 | 190 | 270 | 300 | 160 |
| 120 " | 130 | 120 | 120 | 150 | 20 |
| 180 " | 110 | 130 | 70 | -- | |
| 240 " | 50 | 70 | 50 | -- | |

| Test | 0409 | 0424 | 0505 | 0515 | 0518 |
|---|---|---|---|---|---|
| Feed char | MG-8 | IST-9 | RC040688 | 40301MG1 | PRU coke |
| Temperature, °F | 1400 | 1400 | 1400 | 1400 | 1400 |
| Pressure, psig | 50 | 200 | 200 | 200 | 200 |
| Residence time, min | 120 | 240 | 240 | 120 | 120 |
| Bed velocity, ft/s | 0.10 | 0.065 | 0.065 | 0.065 | 0.065 |
| $CH_4$ conc, vol% | 10 | 10 | 10 | 10 | 10 |
| $H_2S$ concentration, ppmv | | | | | |
| 10 minutes | 730 | 1050 | 790 | 930 | 550 |
| 20 " | 550 | 480 | 440 | 810 | 450 |
| 30 " | 480 | 335 | 230 | 670 | 360 |
| 60 " | 160 | 150 | 70 | 640 | 220 |
| 120 " | 170 | 50 | 60 | 490 | 270 |
| 180 " | -- | 20 | 40 | -- | -- |
| 240 " | -- | 10 | 20 | -- | -- |

content could with extent of desulfurization could be made. Neither the initial or average $H_2S$ concentrations could satisfactorily be correlated with any other data at this time. It is apparent that the rate of release of $H_2S$ into the gas stream follows complex unsteady-state kinetics, and varies considerably between chars and test conditions.

## CONCLUSIONS AND RECOMMENDATIONS

Mild gasification chars made in the IFFR can be successfully desulfurized by a $H_2$:$CH_4$ mixture at 1400°F and 200 psig. The IFFR simulates conditions of entrained flash pyrolysis. Sulfur conversion, which reached 92% in one case, exceeds carbon conversion by about three to one. For Illinois No. 6 coal, this results in a char with sulfur content well below the target of 1 wt% required for form coke.

Chars produced in the PRU appear to be much less reactive, but their susceptibility to desulfurization may be strongly dependent on the mild gasification conditions. Further tests are being conducted to determine the effects of mild gasification temperature and steam input on desulfurization susceptibility of the char. PRU chars produced at temperatures from 1034°F to 1390°F are being examined.

Future work will focus on determining the relationship between char desulfurization potential and physicochemical properties of the char.



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**PROJECT MANAGEMENT REPORT**
March 1 - May 31, 1992

Project Title: **Investigation of a Technique for Sulfur Reduction of Mild Gasification Char**

Principal Investigator: Richard Knight, Institute of Gas Technology

Project Monitor: Frank Honea, CRSC

**COMMENTS**

No change to the budget or management were implemented this quarter.

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