Geol Survey

# Carbon Monoxide-Ethanol Desulfurization of Illinois High Sulfur Coal Demonstration

Final Project Report

for the period

September 1, 1987 through November 30, 1990

submitted to the

ILLINOIS DEPARTMENT OF
ENERGY AND NATURAL RESOURCES

by the

Illinois State Geological Survey

# FINAL PROJECT REPORT
## September 1, 1987 through November 30, 1990

**Project Title:**

Carbon Monoxide-Ethanol Desulfurization of Illinois High Sulfur Coal Demonstration

**Principal Investigators:**

Henry. P. Ehrlinger III and Richard H. Shiley, ISGS, 87-88
Richard H. Shiley and Lawrence Wu, ISGS, 88-89
Lawrence Wu, ISGS, 89-90

**Co-Investigators:**

Donald R. Dickerson, Kristi K. Brewer, Daniel J. Adomaitis, Gwen L. Donnals, Subhash B. Bhagwat and Ronald J. Schaschwary, ISGS

Conrad C. Hinckley, Southern Illinois University, Carbondale

David Buchanan, Eastern Illinois University, Charleston

Curtis L. Knudson, Robert O. Ness, Jr., Ted Aulich, and Laura Sharp, University of North Dakota Energy & Environmental Research Center

**Total Funding:** $1,000,000

**ENR Contract Project Manager:** Michael Purnell

**ENR Project Consultant:** Daniel D. Banerjee

**Report Prepared Under the Supervision of:** Dennis D. Coleman, ISGS

**Report Compiled by:** Lawrence Wu

# INTRODUCTION TO THE REPORT

The Carbon Monoxide-Ethanol (CO/Ethanol) Process of coal desulfurization has been under development since 1982 by a research team principally from the Illinois State Geological Survey (ISGS) and Southern Illinois University at Carbondale (SIU-C). It is a chemical process, tested at the laboratory batch scale on nine Illinois coals, that removes both inorganic and organic sulfur leaving a cleaner solid product. Batch results indicated that the process has the potential to meet the 90 percent sulfur reduction requirement of the Federal Clean Air Act.

The goal of the "Carbon Monoxide-Ethanol Desulfurization of Illinois High Sulfur Coal Demonstration," (Illinois Department of Energy and Natural Resources Contract SSW-2) was the demonstration of a precombustion, coal-cleaning process in which chemical treatments are combined to remove both inorganic and organic sulfur forms from high-sulfur coals producing a low-sulfur, coal-like product in a 1- to 10-kg/hour, continuous-feed, gas-flow reactor (CFU).

This report, in spite of its length, represents only a summary of work, and should not be considered to contain all of the work up to the completion of the SSW-2 contract. This report was intended to serve the purpose of reporting our SSW-2 activities, and also to provide a guide to those interested in continuing this work.

As numerous authors contributed to this report, what may appear to be inconsistencies in data are more likely due to the selective presentation of data to illustrate a specific issue, rather than an error in reporting data. Three different laboratories were utilized for sulfur analyses during the course of the research. Intercomparisons of the different laboratory analyses is not appropriate.

# TABLE OF CONTENTS

# EXECUTIVE SUMMARY

Coal, important for domestic electrical generation, is an abundant fossil fuel in this country. In spite of its significant energy potential, the impact of coal combustion by-products (e.g. sulfur dioxide, $SO_2$) restricts utilization. The Carbon Monoxide-Ethanol Process was directed towards reducing the level of sulfur in coal prior to its combustion. A cleaner burning fuel produced from coal would allow a greater use of this vast domestic energy resource.

The Clean Air Act does not mandate the use of any particular technology as legislators did not wish to hinder development of new competitive technology. If flue-gas scrubbers were considered as the only desirable technology there would be no need for any research programs except those intended to improve scrubbers. Apart from this basic free-market, pro-development consideration, there are good reasons to look forward to markets past the year 2000. The main reason for such a long-term approach is that the Clean Air Act caps total U.S. air pollution (for $SO_2$, 10 million tons/year) by the year 2000. After the year 2000, coal-burning facilities built to meet increased demand cannot exceed the established emission caps. New low emission technologies along with retirement of, or improvements to, existing plants will be necessary.

Many coal users and producers would benefit greatly from a coal cleaning process that could remove enough sulfur prior to combustion to allow utilities to meet federal regulations. The largest obstacle to effective pre-combustion cleaning is the removal of the organic sulfur from the coal. As organic sulfur cannot be separated physically from the coal, some type of chemical, thermal, or biological treatment is necessary. A compliance product that meets the current Federal Clean Air limits cannot be produced from most Illinois coals without significant organic sulfur removal. Very efficient organic sulfur removal has been attained with this process in bench-scale batch reactors. "Coal-like" products containing 0.05 to 0.2 percent organic sulfur have been produced. The process has an additional advantage over other chemical/thermal processes in that it operates at lower temperatures and does not use chemicals that will adversely affect coal quality if not removed.

The Carbon Monoxide-Ethanol (CO/Ethanol) Process of coal desulfurization has been under development since 1982 by a research team principally from the Illinois State Geological Survey and Southern Illinois University at Carbondale. It is a chemical process, demonstrated at the laboratory batch scale on nine Illinois coals, that removes both inorganic and organic sulfur leaving a cleaner solid product. Batch results indicated that the process had the potential to meet the 90 percent sulfur reduction requirement of the Federal Clean Air Act.

The laboratory batch procedure involves three discrete steps carried out at moderate temperatures (300°-550°C/572°-1022°F) and pressures (up to 310 kPa/300 psig), hence its more informal name, "3-Step Process." In Step 1 of the process, carbon monoxide (CO) converts pyrite and marcasite ($FeS_2$) to troilite (FeS) removing up to 50 percent of the inorganic sulfur as carbonyl sulfide (OCS). Additionally, some organic sulfur is removed by pyrolysis as hydrogen sulfide ($H_2S$). In Step 2, the troilite acting as a catalyst, converts ethanol to atomic hydrogen and acetaldehyde. The atomic hydrogen removes organic sulfur (up to 95 percent has been removed in the laboratory) as $H_2S$. If a high degree of sulfur reduction is desired Step 3 can remove much of the troilite, the major form of remnant sulfur after Step 2, by converting it to magnetic monoclinic pyrrhotite ($Fe_7S_8$) and removing it using magnetic separation technology. A prior contract modelled the magnetic separation step in the laboratory with a hydrochloric acid/methylene chloride extraction procedure.

The goal of the "Carbon Monoxide-Ethanol Desulfurization of Illinois High Sulfur Coal Demonstration," was the testing of a precombustion, coal-cleaning process in which chemical treatments are combined to remove both inorganic and organic sulfur forms from high-sulfur coals producing a low-sulfur, coal-like product in a 1- to 10-kg/hour, continuous-feed, gas-flow reactor unit (CFU).

It is widely accepted that many time consuming steps are needed to bring any chemical process to commercialization. In general it is necessary to demonstrate continued success at established goals, or milestones. For this project, the goals can be stated as: 1) basic research, 2) laboratory batch tests, 3) laboratory continuous-feed unit (CFU) tests, 4) process development unit (PDU) tests, 5) pilot-plant tests, and 6) full-scale commercial demonstration. Relying primarily on support from within Illinois, this project was directed towards the demonstration of a CFU reactor. This third stage of the six stages of development was accomplished only by attracting a wide range of private, state, and Federal funds. Even so, work has spanned nearly 15 years and cost over $2.4 million.

The CFU represented a very important milestone for the project as continuous-feed operation is usually considered necessary for viable commercialization. Additionally, the economic and engineering evaluations generated would be the first based on continuous-feed mode data and would eventually provide a more commercially realistic evaluation of economic and engineering viability of the CO/Ethanol process.

A 1- to 10-kg/hour CFU was designed in association with the consulting engineering firm C.W.Nofsinger, Co. in Kansas City, Missouri. Initial design concepts lay in the direction of a conventional fluidized-bed reactor. Due to an incomplete understanding of material mass-balances and the desire to retain maximum flexibility in the design, this configuration was rejected. It was recognized, however, that if commercial development were achieved, a fluidized-bed reactor design would probably be closer to the optimal configuration.

An alternative to the fluidized-bed reactor was a stirred-tank configuration in which mechanical action is used instead of gas flow to maintain bed fluidization. In this particular design, a hollow stirring device was considered for better introduction of the reacting gases. This design was also rejected to avoid difficulties with coal agglomeration and particle comminution.

The initial strategy was, therefore, to move forward with two designs. The first was a modification of a rotary kiln drier design; the second, a modification of a multiple hearth drier design. It was felt that these designs offered a maximum of flexibility with regard to reaction conditions while still allowing for the successful production of a cleaned coal-like product.

The major design considerations for the CFU were: coal agglomeration, material balances, and process conditions (especially material handling). The problem of coal agglomeration can be controlled by pre-oxidation of the coal. Experiments had been performed to study the effect of pre-oxidation on the ability of the process to desulfurize coal. The results indicated that an "optimum" level of pre-oxidation could be found which would inhibit agglomeration while not significantly affecting desulfurization.

The process conditions of the desulfurization reaction were the most serious design considerations. The maximum laboratory defined conditions of 550°C (1022°F) and 2170 kPa (300 psig, for maximum sulfur removal) were deemed too severe for most practical CFU designs. Data from research at SIU-C and Argonne National Laboratory suggested the possibility to reduce the pressure of the reactions significantly. Nonetheless, it was decided to design the CFU to achieve 500°C (932°F) and 3550 kPa (500 psig) in order to produce a reactor that would not only fulfill the criteria of the contract but also serve as a valuable research reactor for the future.

Discussions broached the concerns of the possible weight of the CFU. A preliminary Process Flow Diagram (PFD) was produced. A rough weight estimate for the single modified rotary-kiln would be in the 900-1000 kg range. The handling and safety concerns in a limited laboratory setting could not be ignored because adequate space was not readily available, other options were investigated.

The major concern with this plan was the need of the 3-Step process to work under CFBR conditions. Meetings between the research group, representatives from C.W.Nofsinger Co., and consultant, Dr. Lyle Albright (professor of chemical engineering, Purdue University) led to the conclusion that CFBR operation should be possible.

After it was decided not to perform the demonstration in Illinois (see Appendix C), an existing continuous, fluidized-bed reactor (CFBR) at the Energy & Environmental Research Center, University of North Dakota, Grand Forks (UNDEERC) was contracted for use.

In 1989, a partnership was established with UNDEERC to perform the CFBR tests of the CO/Ethanol process at the 0.5- and 2-kg/hour scales. This collaboration using an existing CFBR permitting the reallocation of project funds from equipment to additional experimentation.

A preliminary contract was signed to perform a feasibility study (Series I). It was shown from Series I that the UNDEERC's CFBR could achieve and maintain the temperature, pressure, gas handling and flow, and coal throughput, deemed necessary for successful operation. Subsequent contracts (Series II and III) were initiated to perform the tests necessary to identify the operating parameters for 3-Step coal desulfurization operation at the CFBR scale.

UNDEERC provided experienced, on-site chemical, chemical engineering, analytical and other service personnel to facilitate the work. Throughout the contract period all work has been closely coordinated through the ISGS. In addition, dollar-for-dollar cost-share funds were made available by UNDEERC through their cooperative agreement with USDOE. (This provision ultimately provided a further $205,000 to support the project.)

During the course of the project it was agreed with the Illinois Department of Energy and Natural Resources (ENR) that the development of the magnetic separation step would be "non-critical path" to the main objectives of demonstrating the CO and ethanol steps. As it will be shown, the demands of the work to accomplish the operation of the first two process steps did not allow for advancement of the magnetic separation step.

Preliminary work was performed to demonstrate the basic operability of the CO/Ethanol desulfurization process in a continuous fluidized-bed reactor (CFBR). The 0.5-kg/hour reactor was a 3.8cm I.D., 316 stainless steel pipe 130cm long. The reactor was operated in a fast fluid-bed mode in which a constant-depth coal bed was maintained. Through devolatilization and particle attrition due to vigorous mixing, the particles become entrained in the gas stream. All products exited at the top of the reactor and the coal-like product was separated by a cyclone. The condensables were separated by indirect glycol cooled condensers. The gas was then metered and sampled. The coal-like product could also be removed through a side-bed drain leg. Fluidization velocities were adjusted so that the majority of the feed coal was removed from the side leg. The remaining coal-like product was removed from the overhead cyclone as fines. Operation with the side-leg was expected to give a more uniform residence time.

Fluidizing conditions (gas and/or liquid flow rates) were established for two feed particle sizes with CO and ethanol. A number of different operating conditions were selected to assess unit operability over the entire range of process variables expected in a more comprehensive program. It was desired to determine whether 1/4"x10-mesh or minus 60-mesh coal should be used in order to minimize the amount of fluidizing gas required. Operating temperatures and residence times (proportional to the inverse of solid-feed rates) were also varied. A number of tests were performed with CO and ethanol with raw coal and two tests were performed with ethanol and coal-like product that had been previously processed with CO. In the initial tests, a total of 20 conditions were used and preliminary data were obtained at various conditions.

After the CFBR had been operating at stable conditions for 1-2.5 hours solid product samples were collected during a known time (≡ material balance period). When the side-leg was present, two samples of solids were collected; one immediately after the cyclone (≡ top coal product) and one from the solid pot at the bottom of the side-leg (≡ bottom coal product). Pre-run coal product (material collected before a material balance period) and blowdown (material blown out of the reactor with bursts of nitrogen following completion of a test) samples were collected but were not usually analyzed.

One concern was the possible occurrence of either agglomeration or size reduction of particles during processing. Sieve data for several runs indicated that the products processed without the use of a side-leg had similar particle size distributions. When operating with 1/4"x10-mesh coal and the side-leg, about 11 wt percent of fine particulates in the feed reported to the cyclone, while with minus 60-mesh coal, 17 wt percent of the total coal product collected was from the cyclone.

Feed coal product samples were analyzed at two external testing laboratories. Analyses were duplicated when it was observed that a larger range of numbers was obtained then expected versus the operating conditions. These data, as did the coal data, indicated a difficulty in obtaining representative samples for analysis.

The necessarily high gas-flow rates decreased the accuracy of determining the amount of OCS, hydrogen sulfide, and other gases produced from the coal, as their concentrations were diluted. The components in the feed gases ($N_2$ and/or CO) and small amounts of $H_2$ and OCS were observed regularly in the product gases. Hydrogen sulfide was not observed, but this may have been due to its low concentration or losses due to adsorption prior to analysis; hydrogen sulfide may have adsorbed on the walls of gas bags and metals in the processing unit.

Analysis of the condensates was outside of the scope of this study. Water, coal tars, and fine coal that got past the cyclone collected in the condensers. When ethanol was used in the process it was also collect in the condensers. For detailed mass balancing the amount of each component present in the condensate would need to be determined. However, the added cost and effort could only be expended on a limited number of tests. Since these preliminary runs were scoping tests, the condensates were not analyzed.

Coal, gas, and ethanol (when desired) were fed to the reactor using calibrated feeding systems. The coal products and condenser material were collected for a known period of time and weighed. Product gas was metered for a known period of time and analyzed. Initial mass-balance recovery values ranged from 85 to 105 percent with one value at 73 percent. The ratio of condenser material to product coal was between 0.040 and 0.051 in five tests and about 0.085 in two tests. The higher amount of condensate material in latter tests may have been due to additional blow-over of coal fines. Collection times were adjusted to yield a 100 percent recovery. The data were then adjusted to a feed of 0.5-kg of coal to provide an easy comparison of the data.

Ash and water recovery values were calculated to check the fit of the mass balanced input-output data. Ash recoveries ranged, as expected, from 82 to 95 percent. The water recoveries were high, if only water was recovered from the condensers. However, if it was assumed that only the amount of water fed into the reaction with the ethanol[1] was recovered in the condensers and that the remaining yield was coal liquids, then coal liquid yields could be estimated. Using this method, liquid yields of 3.0 to 4.7 grams (about 0.8 weight percent of the coal fed) were calculated. Sulfur recoveries were 80 to 97 percent for six of the tests and 70 percent in the test where no CO was present. It was likely that unobserved hydrogen sulfide and sulfur in the condenser material would account for the lower sulfur recoveries. Pyrite recovery data indicated that the pyrite was significantly changed with processing conditions.

In general, during the preliminary runs, the total sulfur was reduced 18-30 percent (from 4.5 wt percent of the feed coal to 3.3-3.9 wt percent of the coal

---

[1] The feed ethanol contained 95% ethanol and 5% water. Additionally, some water would be generated as the coal was heated.

product) during processing. This first initial decrease in total sulfur appeared to be a loss of mainly organic sulfur since the organic sulfur dropped from 1.5 wt percent in the coal to about 0.8 wt percent in the coal products where the highest amount of pyrite was observed. From the data collected, it was unclear as to the destination of the mobilized sulfur. It was not observed as $H_2S$ in the product gas although some was expected. Condensates were not analyzed so it was not known if sulfur was present. OCS was observed in tests where carbon monoxide was present in the feed gas but not enough to balance the sulfur. Essentially all the pyrite was converted to a sulfur form other than pyrite that remained in the coal-like products.

The change in pyrite content with processing conditions was observed in the coal product samples and acid-washed coal samples giving the trend credibility. The total sulfur content stayed relatively constant while the pyrite content significantly decreased with:

1. increasing the CO in the feed gas from 0 to 100 percent at 350°C (662°F),
2. increasing the reaction temperature from 350° to 375°C (662-707°F, 25 percent CO), and
3. doubling the residence time at 350°C (662°F) (25 percent CO).

The effect of residence time and operation with the side-leg resulted in the lowest total sulfur and pyrite values for the bottom coal product. With the side-leg present 15-19 percent of the total coal product enriched in sulfur and pyrite went overhead to the second coal product pot which indicated a beneficial fractionation had occurred.

When ethanol was processed with coal products, the total sulfur content was not influenced. Forms of sulfur are not obtained for the coal-like products produced at these latter conditions.

Modifications to the 0.5-kg/hr reactor were then performed to increase the total through-put capacity to 2-kg/hr. The primary change was to replace the 3.8cm diameter reactor with a 7.5cm diameter reactor.

A test was performed in the CFBR under CO to determine the effect of temperature on sulfur removal. Coal was fed into the reactor at a rate of about 0.5-kg/hr. The initial reactor temperature was 420°C (788°F), the fluidization gas used was a mixture of 35 percent CO/65 percent $N_2$, and the reactor temperature was increased at a rate of 15°C/hr (59°F/hr). Coal product fines were collected from the cyclone and product coals were removed from the coal product collection pot at hourly intervals.

One of the objectives of the test was to determine the temperature at which the coal would agglomerate. Based on experience in the CFBR with other bituminous coals, it was expected that agglomeration would occur in the temperature range of 400-430°C (752-806°F). However, agglomeration did not occur until the reactor temperature reached approximately 540°C (1004°F). The nonagglomeration tendency of the coal may have been a result of its oxidation state; its abnormally high ash content (20.75 percent) showed that the coal may have been partially oxidized.

Since the Illinois Herrin (No.6) coal used in this test behaved unexpectedly, another test was performed using another lot of Illinois No.6. Under similar reaction conditions, this coal agglomerated at about 425°C (797°F).

To study the effects of ethanol on coal product desulfurization, an "ethanol temperature ramping test" was performed, in which coal product produced in the CFBR under an atmosphere of approximately 25 percent carbon monoxide/75 percent nitrogen at 410°C (770°F), was reinjected into the CFBR under an atmosphere of approximately 8 percent ethanol/92 percent nitrogen. The coal product used for this study was produced during an earlier CO run. Initial temperature in the CFBR was 410°C (770°F), temperature was then increased at a rate of 15°C/hour (59°F/hr). The reaction temperature was held constant for 2 hours at 460° and then at 510°C (950°F). When the reactor plugged at about 525°C (977°F), the test was terminated.

The greatest sulfur content reductions under ethanol occurred at reaction temperatures of 460° and 475°C (860° and 887°F); samples obtained at these temperatures had total sulfur contents of 2.87 and 2.83 weight percent, respectively, compared to the feed coal product sulfur content of 3.14. As reaction temperature increased, pyritic sulfur content decreased (except for an increase at 510°C (950°F)), while organic sulfur content initially decreased, and then increased at higher temperatures.

Several tests were performed under a fluidization gas of 100 percent CO, using -325-mesh coal. Reaction pressure was 450 kPa (50 psig), and reaction temperatures were 300°, 325°, 350°, and 375°C (572°, 617°, 662°, and 707°F). The results showed trends of decreasing total, pyritic, and sulfatic sulfur content and increasing organic sulfur content with increasing temperature. Also observed was a significant increase in the OCS content of the product gas stream and a small decrease in the volatile matter content of the product coal, respectively, with increasing temperature. It was desired to perform tests at higher temperatures, but reactor plugging due to the small particle-size feed coal necessitated shutting down the reactor after the 375°C (707°F) test.

Tests were also performed using a static bed of coal in a Vycor tube in order to define: a) the temperature-time relationships of the reactions; b) the effect of slow heat-up; c) back reactions; and d) the effect of gas-flow rates. In all the tests OCS was first observed at 120° to 160°C (248°-320°F, at 0.1 mol percent concentration), while $H_2S$ was first observed in the product gas at around 200° to 220°C (92°-428°F). Molar concentrations of over 5 percent $H_2S$ (at 400°C/752°F) and over 3 percent OCS (at 200°C/392°F) were observed in the product gas, indicating that high concentrations could exist in the presence of coal. When temperature was held isothermal with CO gas flowing at 215°, 240°, 265°, 300°, and 360°C (410°, 464°, 509°, 572°,and 680°F), the amount of OCS and $H_2S$ observed in the product gas started decreasing within 5 minutes. When the temperature was again increased, the amount of OCS and $H_2S$ observed in the product gas recovered (after an incubation period) to the values observed in other runs where temperature was steadily ramped. The total amount of sulfur removed from the coal was dependent mainly on the final reaction temperature, and to a lesser extent on residence time (up to about 1 hour) at that temperature. Decreasing the heat-up time to reach 360°C (680°F, from 400 minutes to 150 minutes) resulted in slightly lower sulfur removals. Total sulfur content of the product increased ~5 percent, while organic sulfur content increased by 10-20 percent.

The coal devolatilization tests, Vycor tube tests, and CFU tests added information concerning the temperature and residence time requirements of the three-step CO/Ethanol Process to desulfurize bituminous coal. Coal devolatilization was rapid during the initial 10 to 20 minutes after the coal reached reaction temperature. Even after this time the coal steadily losses volatile matter over a period of hours. This volatile matter issuing out of the coal would interfere with the penetration of reactant gaseous molecules such as CO and ethanol.

The Vycor tube test data indicated that the initial reactions that result in desulfurization are primarily temperature dependent (the higher the temperature the more inorganic sulfur removed). The back reactions of $H_2S$ and OCS did not seem important in these slow heat-up tests in that high concentrations (5 mol percent of $H_2S$) could exist in the off gas. However, in tests where absolute ethanol was present, no sustained production of OCS or $H_2S$ gases was observed, nor was any significant reduction in organic sulfur content of the product. The Vycor tube tests were made at a pressure of one atmosphere.

The project demonstrated CFU operation publicly at UNDEERC on 27 September 1990. Operation was at 2-kg/hour. Operation had been sustained for continuous periods as long as 48 hours.

Ultimately, the CFU tests yielded mixed results. Coal was successfully fed to and products were recovered from 0.5- and 2.0-kg/hr continuous fluidized bed reactor systems. A modification (the addition of a side leg) enabled operation at 450 kPa (50 psig) with less fluidizing gases. Initial tests indicated varying degrees of pyrite conversion depending on operating parameters. However, there tended to be an increased conversion of pyritic sulfur to organic (or elemental) sulfur with operating temperature, which resulted in only nominal total sulfur reductions. In selected tests, 30 to 40 percent of the total sulfur was removed during processing. Operation with ethanol present did not result in much additional reduction in sulfur content (total or organic).

Either the reactive troilite catalyst was not successfully made from pyrite, or the low pressure did not allow the ethanol to adequately penetrate the coal due to coal devolatilization, or the reactant mix was not correct, or some other factor inhibited the removal of organic sulfur. About 50 percent of the pyritic sulfur and 20 percent of the organic sulfur was commonly removed in the various batch tests.

Based on the available data, it does not appear that a single fluidized-bed reaction system can effectively prevent back reactions due to the rapid heat-up inherent in such a system. A multiple-staged fluid bed system may be more effective. However, further continuous-mode tests of the 3-step process are not recommended until the coal can be shown to be reactive in smaller scale equipment.

A preliminary economic study was conducted in order to determine market conditions and predict future market conditions for the current co-products of the

CO/Ethanol Desulfurization process. This study included an extensive literature review covering a wide range of books, journals and government reports as well as discussions with members of industry. The results of the study can be summarized as follows:

- Acetaldehyde, the dehydrogenation product of ethanol, may be a marketable co-product if it can be priced low enough to compete with methanol carbonylation for the production of acetic acid (demand for which was growing steadily in 1989).

  Recent environmental interest in the development of a more benign road deicer has led to the development of Calcium Magnesium Acetate (CMA). Acetaldehyde can be used to produce acetic acid which is a CMA feedstock. Prospects for the use of acetaldehyde in the production of an environmentally and economically viable alternative to road salt appear to be rising. Additional investigations will be warranted as more advanced economic evaluations are developed.

- Hydrogen sulfide and carbonyl sulfide are not marketable co-products and should be converted to elemental sulfur.

  The vast majority of hydrogen sulfide, produced as either a co-product from an industrial process or from "sour" natural gas, is converted to elemental sulfur by the Claus process. By 1981, over 200 plants using the Claus process were built in the United States, Japan and 24 other countries. A typical Claus plant will recover 95 to 97 percent of the sulfur feed. Because this is not sufficient to meet current emission standards, the Claus tail gas must also be treated.

  From economic considerations, both hydrogen sulfide and carbonyl sulfide reaction co-products should be converted to elemental sulfur. Hydrogen sulfide is toxic and corrosive, which would lead to serious problems with handling and storage. When industry is faced with the production of hydrogen sulfide as a co-product, it is normally converted to elemental sulfur by the Claus process. There also does not appear to be any market for large scale consumption of carbonyl sulfide. Elemental sulfur is the preferred form of sulfur. It is easily handled and stored and readily converted to sulfuric acid.

- At this time it is premature to try to estimate the market value of the co-product oil. More information about the oil must be known, specifically boiling point range, hydrogen content, and heteroatom content (particularly nitrogen and oxygen).

  There has been much research done on the production of "syncrudes" or synthetic crude oil derived from coal. These oils are similar to petroleum but may require different processing steps before they can be used as fuels. Coal derived oils typically contain high heteroatom contents, particularly nitrogen and oxygen, and also have lower hydrogen contents than petroleum. The oil may also contain a larger portion of distillates in the high boiling point range, which makes it more difficult, and therefore more expensive, to refine.

The Ethanol Coal Desulfurization project continued, beyond this contract, to pursue two separate methods to produce a cleaner coal product (see FUTURE WORK, p. 133). The first method, the 3-Step process, has been described herein at length. In the second method, known as the "1-Step process", ground coal is heated and treated with ethanol in the presence of a "reaction accelerator" in a single process step. This latter technology has been patented with ownership assigned to the Illinois State Geological Survey and the Board of Trustees, Southern Illinois University.

This current project was scheduled to complete demonstration at the PDU reactor level (15- to 50-kg/hr) by August 1991. The work was supported by the Illinois Department of Commerce and Community Affairs, Illinois Corn Marketing Board, Ohio Corn Growers Association, and USDOE through UNDEERC.

The results to date with the 3-Step process will be balanced against the batch and CFU work on the 1-Step process currently being conducted with Ohio University. Preliminary batch results have achieved a 96 percent total sulfur removal at 420°C (788°F) with, perhaps more importantly, 78 percent total sulfur reduction achieved at only 200°C (392°F). Work was underway to transfer the 1-Step technology to UNDEERC.

# INTRODUCTION

The nation's coal resources totals over 250 billion tons of recoverable reserves. These reserves are fairly evenly distributed between low-, medium-, and high-sulfur levels (Table 1). Immediate needs for clean coal can be supplied by large low sulfur coal reserves primarily in Wyoming and Montana. Illinois possesses more than 13 percent of the nation's total recoverable coal reserves. Utilization of most Illinois coals has, however, been greatly inhibited because of their high-sulfur content (3 to 5 percent on average; far above the 0.7 to 0.8 percent limit set by the 1.2 pound $SO_2$/million Btu Federal restriction). An environmentally cleaner coal that meets Federal Clean Air limits cannot be obtained from most Illinois coals without greatly reducing the sulfur content. The largest obstacle to the effective use of this plentiful reserve is the need to remove organic sulfur. The removal of this sulfur before combustion was the primary focus of the Ethanol Coal Desulfurization project. In the laboratory this method has been shown to have the potential for producing products with over a 90 percent sulfur reduction (Webster, et al, 1986 [1] and Warren, et al, 1987 [2]).

**Table 1.** Estimates of 1987 Recoverable Reserves by Coal Type and Region (Million Short Tons).

| | Sulfur Content (pounds/million Btu) | | | |
|---|---|---|---|---|
| Region | Low Sulfur (≤0.60) | Medium Sulfur (0.61-1.67) | High Sulfur (≥1.68) | Total |
| Appalachia | 12,076.5 | 20,968.9 | 22,162.2 | 55,207.6 |
| Interior | 613.4 | 13,325.4 | 55,230.2 | 69,169.0 |
| West | 79,136.1 | 56,407.3 | 7,939.0 | 143,482.4 |
| U.S.Total | 91,826.0 | 90,701.6 | 85,331.4 | 267,859.0 |
| Illinois | 0.0 | 4,353.3 | 31,036.2 | 35,389.5 |

Source: from Table A3, DOE/EIA-0529, 1989.

The Office of Strategic Planning for the Illinois Department of Energy and Natural Resources has reported (Bishop and Baker, 1987 [3]), based on HR 4567 presented during the 99th Congress, that a revised Clean Air Act could have a severe and long-term economic impact on coal users and producers in the state. The impact of the reduced use of Illinois high-sulfur coal, attributable to fuel switching, could decrease coal production by 38 million tons/year (more than a 60 percent decrease from 1988 production), cause the loss of 22,000 jobs (including 6,500 miners), and the compliance cost to utilities alone in the state was estimated to be $395-745 million/annually by the year 2000. The recent amendment to the Clean Air Act (signed by President Bush, 15 November 1990) would further exacerbate these dire estimates.

In 1988, less than 27 percent of Illinois' production was used within the state (Table 2) (USDOE/EIA-0191(88), 1988 [4]). With such large coal resources, it is noteworthy that Illinois coal producers were only able to capture slightly more than half of the market needs of Illinois coal users. Capacity and production are not the problem; these figures are a direct result of the high sulfur content of most Illinois coals and the impact of progressively more stringent restrictions on sulfur dioxide emissions from coal burning. Illinois coal users are increasingly turning to lower sulfur coals produced outside Illinois or by fuel switching (converting coal-fired boilers to use oil or gas).

Table 2. Estimates of 1988 Illinois Coal Production and Usage (Thousand Short Tons).

| Illinois Coal Production (state of destination of coal) | | | Illinois Coal Usage (state of coal origin) | | |
|---|---|---|---|---|---|
| State | Amount | Percentage | State | Amount | Percentage |
| Illinois | 14,351.0 | 26.7 | Illinois | 14,351.0 | 53.3 |
| Missouri | 12,574.7 | 23.4 | Wyoming | 5,854.0 | 21.7 |
| Indiana | 9,000.7 | 16.7 | Montana | 2,729.2 | 10.1 |
| Georgia | 5,580.4 | 10.4 | Kentucky | 2,417.6 | 9.0 |
| Florida | 4,354.9 | 8.1 | Indiana | 1,210.7 | 4.5 |
| Wisconsin | 2,213.6 | 4.1 | West Va. | 357.9 | 1.3 |
| Iowa | 2,034.1 | 3.8 | TOTAL | 26,920.4 | |
| Kansas | 1,211.7 | 2.3 | | | |
| Tennessee | 1,185.5 | 2.2 | | | |
| Mississippi | 840.5 | 1.6 | | | |
| Alabama | 211.6 | 0.4 | | | |
| Minnesota | 122.6 | 0.2 | | | |
| Michigan | 48.0 | 0.1 | | | |
| Kentucky | 19.3 | 0.0 | | | |
| TOTAL | 53,748.6 | | | | |

Note: Data are for steam-electric plants with a generator nameplate capacity of 50 megawatts or larger.
Source: Energy Information Administration, DOE/EIA-0191(88).

Many coal users and producers would benefit greatly from a process that could remove enough sulfur prior to combustion to allow utilities to meet Federal regulations. The largest obstacle to effective pre-combustion cleaning is the removal of the organic sulfur from the coal. As organic sulfur cannot be separated physically from the coal, some type of chemical, thermal, or biological treatment is necessary. A compliance product that meets the current Federal Clean Air limits cannot be produced from most Illinois coals without significant organic sulfur removal. Very efficient organic sulfur removal has been attained with this process in bench-scale batch reactors. "Coal-like" products containing 0.05 to 0.2 percent organic sulfur have been produced, well in excess of a 90 percent reduction. The process has an additional advantage over other chemical/thermal processes in that it operates at lower temperatures and does not use chemicals that will adversely affect coal quality if not removed.

Potentially, thousands of Illinois jobs in the coal and coal-allied industries could be saved, millions of dollars in lost income would be retained, and significant additional benefit to the state would be derived if the impact of the Clean Air Act on Illinois coal production could be reduced by wide-spread use of a process which could utilize high-sulfur coal. This process, in addition, makes use of corn-derived ethanol which could further enhance the state's agricultural economy if the method proves commercial.

## Project Background

Illinois, Indiana, and Kentucky share a vast underground reserve of coal known as the Illinois Coal Basin (Figure 1). The Energy Information Agency estimates the Basin contains 50.8 billion tons of proven recoverable reserves (DOE/EIA-0118(88), [5]). This holding represents nearly 20 percent of the nation's total proven coal resources.

With projections of an expanded role of coal in domestic electricity production, utilization of Illinois Basin coals may become increasingly necessary. Use of most Illinois Basin coals has, however, been greatly inhibited in recent years because of their high sulfur content. These coals typically contain 3 to 5 percent sulfur. It is this sulfur, during coal combustion, that is oxidized to form sulfur dioxide ($SO_2$). Sulfur dioxide emitted into the atmosphere is suspected of being one of the major components of acid rain. Because of this, since 1971 the Federal government has imposed regulations which limit the amount of sulfur dioxide that can be released by coal-burning utility power plants.

For a typical Illinois Basin coal, the current Federal restriction of 1.2 pounds of sulfur dioxide emitted per million Btu coal combusted translates to a sulfur equivalent level of 0.7 to 0.8 percent. As Illinois Basin coals typically contain several times this amount, significant sulfur reduction is necessary in many cases. Future regulations will mandate a 90 percent sulfur reduction which would translate into a sulfur equivalent level of 0.3 to 0.5 percent. Current physical coal cleaning technology can achieve the 1.2 pounds/MM Btu standard with some Illinois Basin coals but cannot meet the 90 percent reduction level.

Competition with low-sulfur coal producing regions will have an increasing large impact on the marketability of high-sulfur coals such as those found in the Illinois Basin. An industry comparison of historic and forecast coal demand (Table 3) states that although coal demand is expected to increase through 1995, the contribution from high sulfur producers is expected to decrease (McMahan and Knutson, 1989 [6]). Future utilization of these high-sulfur coals may depend on the continued advancement of desulfurization technology.

**Table 3. Impact of Sulfur on Regional Coal Demand.**
(U.S. Utility Coal Demand / millions of tons)

| | Historic............. | | | | Forecast......... | | |
|---|---|---|---|---|---|---|---|
| Supply Region | 1985 | 1986 | 1987 | 1988 | 1989 | 1990 | 1995 |
| Illinois Basin | 121 | 122 | 122 | 122 | 119 | 114 | 105 |
| Central Appalachia | 132 | 132 | 140 | 146 | 149 | 157 | 192 |
| Powder River Basin | 154 | 147 | 161 | 180 | 181 | 184 | 206 |

Source: McMahan and Knutson, 1989 [6].

Sulfur in Illinois Basin coals occurs primarily as the iron sulfide minerals pyrite and marcasite ($FeS_2$) and organic sulfur bearing compounds dispersed throughout the organic matrix of the coal. On average, the inorganic sulfur and organic sulfur constituents occur in roughly equal proportions. The methods currently being used to remove sulfur from coal generally involve a physical separation to remove some of the pyrite, followed by some type of post-combustion cleaning in a flue-gas scrubber to remove the $SO_2$ released by the remnant inorganic and organic sulfur.

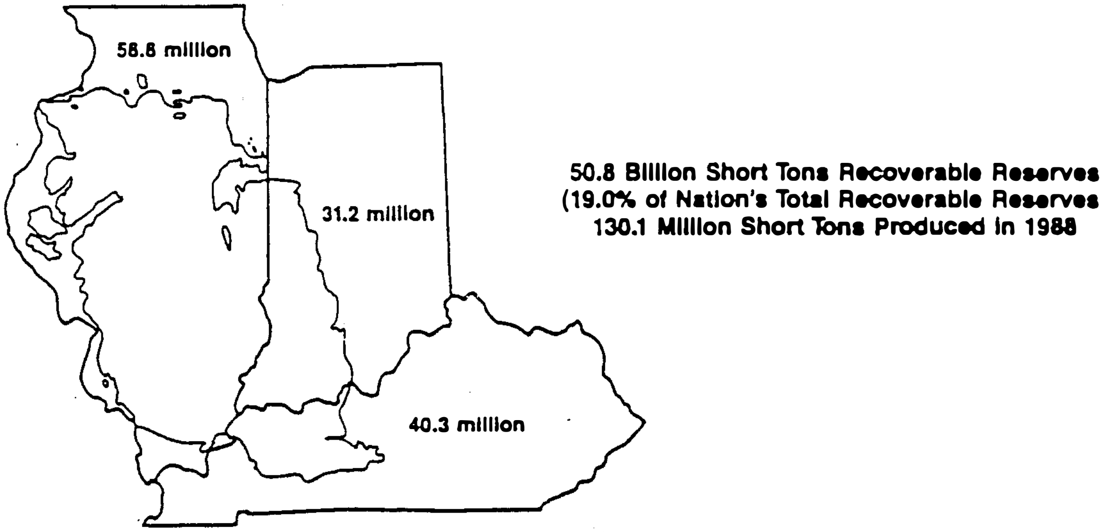


Figure 1. **1988 Coal Production from the Illinois Coal Basin.**
Source: Energy Information Agency, DOE/EIA-0118(88).

## Project Goals and Objectives

The contractual goal of this project was the demonstration of a precombustion, coal-cleaning process in which chemical treatments are combined to remove both inorganic and organic sulfur forms from high-sulfur coals in a continuous-feed, gas-flow reactor. It was planned to develop a small 1- to 10-kg/hour reactor to produce a coal-like product containing total-sulfur concentrations in compliance with Federal emission regulations.

This research addressed a main priority of the Illinois Coal Development Board: production of a high-volatile, coal-like product from coal which can be tested in small-scale equipment and might be used in existing coal-burning plants. This research also involved the study of the multiphase products: oil, gas, carbonyl sulfide (OCS), hydrogen sulfide ($H_2S$), elemental sulfur, and perhaps most importantly - acetaldehyde ($CH_3CHO$), the result of ethanol ($CH_3CH_2OH$) dehydrogenation.

## Specific Goals and Objectives

1. To develop a continuous-feed, gas-flow reactor capable of producing 1- to 10-kg of coal per hour using the carbon monoxide and ethanol steps of the carbon monoxide-ethanol process.

2. To demonstrate the equipment on a continuous basis for a period of approximately 10 to 12 hours.

3. To develop the third step of catalyst removal by the use of magnetic separation and/or oxidation using commercially available equipment.

4. To test representative coals from the Illinois Herrin (No. 6), Springfield (No. 5), and Colchester (No. 2) coals. If adequate amounts exist, one or more coals will be chosen from the Illinois Coal Bank. At least one coal will be run as a public demonstration of 12 hours in length by the end of the contract period.

During the course of the project it was agreed with Mike Purnell, Contract Project Manager, Energy and Natural Resources (ENR) that the development of the magnetic separation step would be a "non-critical path" to the main objectives of goals 1 and 2. As it will be shown, the demands of the work to accomplish the operation of the carbon monoxide and ethanol steps did not allow for significant advancement of the magnetic separation step.

## Project Description

The desulfurization process arising from this research involves three steps (Figure 2). In the first step, carbon monoxide is reacted with the whole coal at moderate temperatures and pressures. Pyrite in the coal is reduced to form catalytically active troilite with the concomitant production of carbonyl sulfide. In the second step, the troilite is used to catalyze ethanol reactions leading to the removal of organic sulfur from coal (Smith, et al, 1982 [7]). The third step of the process effects the removal of the iron sulfide catalyst remaining in the desulfurized coal-like product after ethanol treatment.

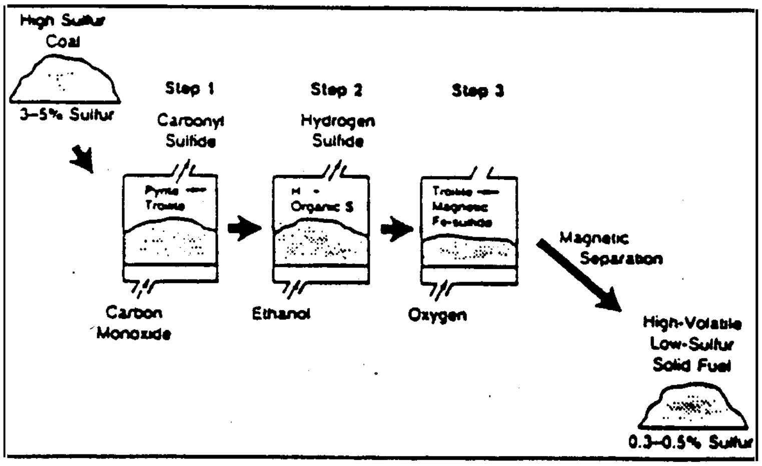


Figure 2. Carbon Monoxide-Ethanol Coal Desulfurization Process.

Although this desulfurization process is considered a departure from past work, it does make use of the results of other desulfurization studies that used reactive gases to treat coal at elevated temperatures. Using hydrogen at 1000°C (1832°F), Snow (1932 [8]) was able to remove 97 percent of the sulfur in coal;

with carbon monoxide, he removed about 50 percent of the sulfur. The first step of this process is a modification of Snow's carbon monoxide treatment. A compendium of methods to desulfurize coal prior to combustion cited 65 patents dealing with sulfur removal from coal and coke (Eliot, 1988 [9]). While some of these methods use electrokinetics, or magnetic separation (Yan, 1987 [10]) most are chemical processes that use various additives and usually require heat and pressure. Some reactants used are gases such as steam (Schroder, 1975 [11]), hydrogen (Sinke, 1978 [12]), oxygen (Longanbach, 1977 [13]), nitrogen dioxide (Diaz and Guth, 1975 [14]), and methane (Whitten, et al, 1973 [15]). In addition to gases, reactants have included metal compounds such as alkali carbonates (Stambaugh and Sachsel, 1977 [16]), iron oxide (Sanders, 1977 [17]), ferric chloride (Meyers, 1973 [18]), phosphines (Ruchfuss, 1984 [19]), and various solvents, including ethanol (Keller, 1977 [20]) have also been used.

There are several processes which have been reported. These include chlorinolysis (Kalvinskas, et al, 1982 [21]), an elaboration of a nitric oxide treatment (DOE/PC/3014T (1980) [22]), microbial techniques (Dugan and Apel, 1984 [23]), the application of microwave technology (Zavitsanos, et al, 1982 [24]), an investigation of the use of aqueous disulfides (Mesher and Peterson, 1979 [25]), chemistry of fused caustic desulfurization of coal (Friedman and Utz, 1985 [26]), coal desulfurization and conversion with formates (Wu and Winschel, 1985 [27]), and chemical desulfurization with Caro's acid (Lin, et al, 1985 [28]). Probably the most prominent recent development involves the use of molten alkali salts (Meyers, et al, 1985 [29]). This last method was being studied by the USDOE and others.

The catalytic role of iron sulfides in liquefaction has been recognized for several years (Guy and Given, 1982 [30]) and (Stohl and Granoff, 1981 [31]). Iron sulfides derived from pyrite and marcasite have also been cited as possible aids in the desulfurization of coal (Eliot, 1978 [9]). The carbon monoxide-ethanol desulfurization process uses the iron sulfide, troilite, as an <u>in situ</u> catalyst for the desulfurization of the organically bound sulfur in coal (Webster, et al, 1985 [32] and Shiley, et al, 1985 [33]).

Two references are of particular interest. In one, an assessment of coal desulfurization prospects, "thiophenic sulfur" (organic sulfur) was identified as one of the central problems in desulfurization (Wrathall, et al, 1979 [34]). Thiophenic sulfur is very difficult to remove, and achieving compliance level coals depends upon removal of this sulfur component. The products obtained by the ISGS/SIU-C process indicate that removal of thiophenic sulfur has occurred (Smith, et al, 1982 [7] and Smith, et al, 1984 [35]). The second article examined the use of iron sulfides as an <u>in situ</u> catalyst for coal processing (NTIS# PB83-15911, 1983 [36]). While acknowledging that iron sulfide catalysis had been observed, and in cases appeared to be important, the author concluded that too little was know for such methods to be reliably applied. The situation which led to this conclusion has changed due to the basic research into iron sulfide chemistry carried out by the project team. From earlier research (Smith, et al, 1982 [7] and Smith, et al, 1984 [35]), a mechanism for the removal of thiophenic sulfur from coal has been identified. In laboratory experiments, thiophene was desulfurized by the catalytic dehydrogenation of ethanol over troilite. Unlike other processes, troilite was formed in the treated coal and was the agent responsible for the removal of thiophenic sulfur.

The unique aspect of the process was the application of the chemical and mineralogical properties of iron sulfides to catalyze sulfur removal. At elevated temperatures, inorganic sulfur, organic sulfur, carbonyl sulfide, and hydrogen sulfide form a complex equilibria. This equilibria was exploited by the process to remove half of the pyritic sulfur from coal in "step 1" and most of the organic sulfur in "step 2." When flowing-gas conditions are employed, the chemical equilibria forces the composition of the iron sulfide from about $Fe_{11}S_{12}$ towards FeS. With the use of pure iron sulfide systems, it has been shown that FeS catalyzes the desulfurization of thiols, and that troilite is the only sulfide that will catalyze the desulfurization of thiophene (Smith, et al, 1982 [7] and Smith, et al, 1984 [35]), the most refractory organic sulfur component in coal.

The success of the process was built around flowing-gas conditions which were found to be one of the most important design aspects. The process was devised to remove sulfur containing gases formed during each reaction. If these gases are not removed, hydrogen sulfide and carbonyl sulfide react rapidly with the coal to form refractory organic sulfur compounds. It has been shown that carbonyl sulfide and hydrogen sulfide react with pure carbon to produce residues containing 3 percent and 8 percent sulfur respectively. Similar findings have been obtained for coal and coal tars. These results are attributed to sulfide back reactions (Kor, et al, 1977 [37]; Boorman, et al, 1977 [38]; and Attar, 1978 [39]).

## SUMMARY OF EARLIER WORK

The overall goal of this research was to develop a desulfurization process for Illinois high sulfur coal. A precombustion coal cleaning process was selected in which chemical treatments were combined in a 3 Step desulfurization process to remove both inorganic and organic sulfur. This research, therefore, addressed two of the main priorities of the Illinois Coal Development Board: Removal of organic sulfur from the coal matrix and the production of high volatile coal-like product. It also involved the production of multiphase products: oil, gas, carbonyl sulfide, elemental sulfur, and acetaldehyde. The objectives of this research were directed toward the development of methods and reagents for chemical coal cleaning, emphasizing substantial removal of organic sulfur. Coal-like products containing organic sulfur in the 0.05 to 0.2 percent range have been produced. The project has demonstrated the following:

1. Carbon monoxide has been shown to reduce pyrite and marcasite to pyrrhotite and a catalytic troilite/troilite "B" mixture ($FeS/Fe_{16}S_{17}$).
2. Catalytic hydrogenation and removal of organic sulfur with ethanol occurs over a catalytic troilite/troilite "B" mixture.
3. Removal of the spent troilite (FeS) catalyst can be achieved with a mild oxidation of the troilite to magnetic monoclinic pyrrhotite ($Fe_7S_8$). The project has not demonstrated this.

The coal desulfurization process takes advantage of the existing mineral matter in coal. The steps in the process manipulate iron sulfide equilibria, catalysis of iron sulfides, and reactor conditions to remove organic sulfur from the coal. The main objectives of the founding study were twofold: first to discover how to prevent the various gaseous sulfur back reactions with the coal matrix; and second, to find a catalyst capable of hydrogenating organic sulfur compounds.

Experiments were conducted that determined reaction rates for atomic hydrogen sources such as 2-propanol, ethanol, methanol, and molecular hydrogen over various synthetically prepared iron sulfides. Through the use of XRD and Mössbauer spectroscopy it was possible to determine the mineralogical changes taking place during the desulfurization.

Since this desulfurization project was initiated in 1982, effort has been applied to the attainment of the goals previously outlined. Listed below are a few of the major accomplishments and conclusions which are considered milestones in the work.

These milestones were instrumental in the design and success of this desulfurization process because they affected the removal of organically bound sulfur from coal.

1. It has been determined that reaction of the coal with oxygen for prolonged periods and high temperatures limits the effectiveness of this process.

2. About 50 percent of the sulfur present as pyrite must be removed as carbonyl sulfide by reaction with CO at temperatures below those at which pyrite thermally decomposes to avoid the formation of elemental sulfur that accompanies thermal decomposition of pyrite to pyrrhotite.

3. Successfully reacting pyrite in coal with carbon monoxide at 250°C (482°F) produces troilite "B" ($Fe_{16}S_{17}$). This is below the critical decomposition temperature (350°C/662°F) which produces elemental sulfur for reaction with the coal matrix.

4. Carbon monoxide converts pyrite and marcasite in coal to a catalytic mixture of troilite and troilite "B" at a much faster rate than does hydrogen.

5. Troilite is a more effective catalyst than pyrite, marcasite, or other members of the pyrrhotite group for the hydrogenation and removal of stable sulfur forms, such as those found in chemical analogues of thiophene. Thus, the proportion of troilite relative to other members of the pyrrhotite group is a significant factor in the effectiveness of this process.

6. Flowing-gas conditions may provide the means necessary to avoid recombination of sulfur products with coal.

7. Over pyrite at low temperatures (below the thermal decomposition point), dehydration of ethanol predominates over dehydrogenation, but, over troilite, dehydrogenation was the predominant reaction.

8. Reaction back pressures of 1480 to 2170 kPa (200-300 psig) have been used to provide a high degree of intimate contact between reactant gases and coal.

9. Reductions in sample size provide a means to decrease agglomeration, increase gas/coal ratio, and increase the contact between the reactant and the coal. For similar conditions the smaller samples undergo a higher degree of desulfurization.

10. X-ray diffraction (XRD) and Mössbauer spectroscopic determinations of changes in iron sulfide stoichiometry and structure have been vital to the study of these catalytic reactions.

    a. Synthesized sulfur minerals found in coal and coal-like product, have been identified and characterized with Mössbauer spectroscopy and XRD.

    b. Study of the thermal decomposition of Colorado pyrite at different temperatures have produced a series of pyrrhotites for use as XRD standards.

11. The ethanol reaction is essential to complete the desulfurization process.

12. It was found difficult to impossible to produce a highly magnetic monoclinic pyrrhotite in coal-like product without an oxidation step.

13. Steam and steam-carbon dioxide methods of sulfide removal were found to be unsuitable for sulfide removal from the product.

14. Illinois high-sulfur coal can be converted to a relatively hard "green" coke at low temperatures in the presence of carbon monoxide.

15. The following catalytic reactions were investigated over iron sulfides:

    a. ethanol dehydration and dehydrogenation

    b. 2-propanol dehydration and dehydrogenation

    c. acetone hydrogenation

    d. 1,3-butadiene hydrogenation

    e. 1-butene hydrogenation

    f. 1-butanethiol desulfurization

    g. thiophene desulfurization

16. The activation energies have been determined for the following reaction:

    a. formation of $H_2S$ from $H_2$ over various iron sulfides

    b. formation of $H_2S$ from ethanol over various iron sulfides

    c. formation of OCS from CO by reaction with iron sulfides

    d. dehydrogenation of ethanol

    e. dehydrogenation of 2-propanol

17. Highly dispersed synthetic iron sulfides on alumina silica, have been prepared, analyzed by Mössbauer spectroscopy, and their catalytic

activities determined. Unexpectedly, their catalytic properties appear different from iron sulfides in coal.

18. Hydrogen molecules were shown to dissociate on iron sulfide surfaces.

19. Iron sulfide surfaces were found to reconstruct in ways which lead to different catalytic activities. That is, iron sulfides with the same composition can have different catalytic properties.

20. Transient structure sensitivity has been discovered in iron sulfides. Specifically, certain iron sulfides can be treated in a way that produce high catalytic activity over a brief period of time and a specific temperature range.

21. A chemical explanation has been proposed for how iron sulfides catalyze the removal of organic sulfur from coal during coal conversion processes.

22. Mass-balance studies and HCl experiments on pyrrhotite dissolution have shown that pyrite and marcasite are converted to pyrrhotite in all neutral or reducing pyrolysis methods, and during pyrolysis with small amounts of oxygen. Samples thought to contain greigite or a related $Fe_2S_3$ mineral contain only pyrrhotite as an identifiable phase, and the quantity of pyrrhotite matches well with the initial pyrite/marcasite content.

In addition to process requirements, the mineralogical results also indicate:

1) that the reactions of pyrite, marcasite, pyrrhotite, and/or troilite in coal with carbon monoxide, ethanol, and $O_2$ are essentially the same as those observed for pure sulfides;

2) the pyrrhotite-group minerals formed in this process are nonequilibrium, metastable phases, and/or lower-temperature equivalents of the phases given in published phase diagrams; and

3) iron sulfides formed during the hydrogenation of pyrite to troilite have the same FeS stoichiometry as those formed by resulfurization with organics such as butanethiol, but, as indicated by their different catalytic properties (butane to butene ratios), they have different surface characteristics.

Taking advantage of these factors has produced coal-like products with high volatile matter retention and very low sulfur contents. Table 4 gives results for the desulfurization of nine Illinois Basin coal samples. Organic sulfur has been reduced, to less than or equal to 0.20 percent for all nine coals. Under an earlier CRSC contractual agreement the magnetic separation step, while demonstrated, has been modelled in the laboratory with a hydrochloric acid/methylene chloride extraction. Nonetheless, on average, only 53 percent of the remnant iron sulfide catalyst must be removed from the product to meet the federal emission requirement of 1.2 pounds $SO_2$/million Btu and 84 percent must be removed to meet the 90 percent reduction of sulfur based upon run-of-mine coal.

**Table 4.** **Desulfurization of Illinois Basin coals.**

| Locale | Seam No.[a] | Coal Wt % Tot. S | Product Wt % Tot. S Before Cat. Removal (Step 3) | | Product Wt % Org S | % Org Sulfur Reduction | % Sulfur Reduction After Cat. Removal |
|---|---|---|---|---|---|---|---|
| | | | Actual | Calc'd. | | | |
| WC[b] | 6 | 4.21 | 1.70 | 1.45 | 0.20 | 93 | 95 |
| WC | 6 | 4.37 | 1.69 | 1.35 | 0.15 | 95 | 97 |
| SW | 6 | 3.56 | 1.75 | 1.29 | 0.20 | 90 | 94 |
| SW | 6 | 2.50 | 1.03 | 0.74 | 0.20 | 89 | 92 |
| SW | 5 | 3.47 | 1.25 | 1.18 | 0.14 | 93 | 96 |
| SC | 6 | 0.89 | 0.12 | 0.45 | 0.05 | 90 | 94 |
| SC | 6 | 3.91 | 1.98 | 2.15 | 0.11 | 91 | 97 |
| SE[b] | 5 | 3.15 | 1.16 | 1.15 | 0.14 | 92 | 96 |
| SE | 5 | 5.36 | 2.10 | 3.11 | 0.16 | 87 | 97 |

a - No. 5 is the Springfield (No. 5) Coal Member, and No. 6 is the Herrin (No. 6) Coal Member. The samples were collected as fresh material at the mine and stored under an argon atmosphere.
b - Preparation plant samples.

An additional attractive feature of the CO/Ethanol process is that the co-products are commercially useful. Not only does this mean there may be a lessened waste material disposal problem, but it may help make the process more cost effective. Carbonyl sulfide can be used to produce thiocarbamates, used in the manufacture of herbicides, as well as chemicals and pharmaceuticals. Hydrogen sulfide can be combined with $SO_2$ to produce elemental sulfur. Acetaldehyde, the dehydrogenation product of ethanol consumed in the process, may be the most promising co-product of this process. Recent environmental interest in the development of a more benign road deicer has led to the development of Calcium Magnesium Acetate (CMA). Acetaldehyde can be used to produce acetic acid which is a CMA feedstock. Additional investigations will be warranted as more advanced economic evaluations are developed.

## Sulfide reactions

In the temperature range studied (380°-420°C/716°-788°F) pyrite and their derived pyrrhotites react substantially faster with carbon monoxide than with hydrogen. This conclusion was derived from both plug-flow results and thermogravimetric studies. While thermogravimetric studies have provided greater detail and quantification, they have also confirmed and validated plug-flow results. The reactions of both gases with pyrite and all of the iron sulfide compositions between pyrite and troilite are first order. The stepwise character of the reactions was a new finding for these systems.

The reaction of carbon monoxide with pyrite appears to occur in two steps. In the first step, the product is pyrrhotite having the composition $Fe_{11}S_{12}$; in the second, the product is troilite. Both the rate constant and the activation energy of the second step are larger than those of the first step at each temperature studied. This indicates significant differences in the pre-exponential factors of the two steps. While the increase in the activation energy of the second step tends to reduce the rate constant, a larger preexponential factor results in a faster rate.

The reaction of hydrogen with pyrite was found to be similar to that of carbon monoxide, but more complex. Three inflection points are formed in the plot of log $(w_t-w^*)$ versus time (where $w_t$ is the weight of the sample at time "t" and $w^*$ is the weight of the sample at the end of the treatment step), indicating four steps in the transformation of pyrite to troilite. The pyrrhotite composition at the inflection points are the same for each of the temperatures studied within the limits of experimental error. They are $Fe_7S_8$, $Fe_8S_9$, and $Fe_{11}S_{12}$. These compositions are sequential intermediate products of the reduction which in these experiments ended with troilite. Rate constants and activation energies determined for the four steps increase as the reduction proceeds.

Rate constants were determined using the aforementioned first-order rate plots. They were calculated from the sulfur lost in the steps of the reaction and apply to the overall processes occurring between the inflection points. The fact that the pyrrhotite with composition $Fe_{11}S_{12}$ was found at inflection points for both hydrogen and carbon monoxide reactions may have indicated that this pyrrhotite composition has a unique chemical significance which differentiates it from other nearby compositions. A similar significance can also be attached to the compositions $Fe_7S_8$ and $Fe_8S_9$, which nevertheless, lead to inflection points only in the hydrogen reaction. It was supposed that the pyrrhotite compositions $Fe_7S_8$ and $Fe_8S_9$ are also intermediates in the carbon monoxide reaction, but do not appear since the rate constants for the reactions with carbon monoxide are equal throughout the range of compositions from $FeS_2$ to $Fe_{11}S_{12}$.

Activation energies for the reactions of pyrite with both CO and $H_2$ increase in a stepwise fashion as the reductions proceed. Since the activation energies for the two gases are not greatly different, other possible reasons for the faster reaction of CO have been considered. One reason may lie in the difference in reaction mechanism. Curve analyses indicated that the rate determining process in the reactions of carbon monoxide with iron sulfides was a surface reaction. On the other hand, in the case of hydrogen reactions, similar analyses indicated that both surface reaction and solid diffusion provided significant contributions. The likely contribution of solid diffusion to the rate determining process has been suggested by Attar (1978 [39]), and these experiments support that assessment.

Finally, this study demonstrated that the reductions of pyrite to troilite with carbon monoxide and with hydrogen are punctuated by discrete pyrrhotite compositions. The pyrite reductions are not uniform, but proceed through well defined intermediate compositions.

**Development of a laboratory scale reactor (CFU)**

The overall goal of the CO/Ethanol Desulfurization Process was the development of a pre-combustion process in which chemical treatments are combined with physical methods to remove both inorganic and organic sulfur from coals and coal-like products. The objectives are the improvement of the desulfurization process through further experimentation and optimization, establishment of reaction kinetics, characterization of desulfurized products, economic evaluation studies, and most importantly, investigation of the efficacy of a continuous-feed process.

A 1- to 10-kg/hour, continuous-feed, gas-flow coal reactor (CFU) was designed in association with the consulting engineering firm C.W.Nofsinger, Co. in Kansas City, Missouri. Initial design concepts lay in the direction of a conventional fluidized-bed reactor. Due to an incomplete understanding of material mass-balances and the desire to retain maximum flexibility in the design, this configuration was rejected. It was recognized, however, that if commercial development were achieved, a fluidized-bed reactor design would probably be closer to the optimal configuration.

An alternative to the fluidized-bed reactor was a stirred-tank configuration in which mechanical action would be used instead of gas flow to maintain bed fluidization. In this particular design, a hollow stirring device was considered for better introduction of the reacting gases. This design was also rejected to avoid difficulties with coal agglomeration.

The initial strategy was, therefore, to move forward with two designs. The first was a modification of a rotary kiln drier design; the second, a modification of a multiple hearth drier design. It was felt that these designs offered a maximum of flexibility with regard to reaction conditions while still allowing for the successful production of a cleaned coal-like product.

The major design considerations for the CFU were: coal agglomeration, material balances, and process conditions (especially material handling). The problem of coal agglomeration can be controlled by pre-oxidation of the coal. Experiments have been performed to study the effect of pre-oxidation on the ability of the process to desulfurize coal. The results (Figure 3) indicated that an "optimum" level of pre-oxidation could be found which would inhibit agglomeration while not significantly affecting the desulfurization (Webster, et al, 1986 [40]).

The process conditions of the desulfurization reaction were the most serious design considerations. The maximum laboratory defined conditions of 550°C (1022°F) and 2170 kPa (300 psig, for maximum sulfur removal) were deemed too severe for most practical commercial designs. Data from research at SIU-C and Argonne National Laboratory suggested the possibility to reduce the pressure of the reactions significantly. Nonetheless, it was decided to design the CFU to achieve 500°C (932°F) and 3550 kPa (500 psig) in order to produce a reactor that would not only fulfill the criteria of the contract but also serve as a valuable research reactor for the future.

Discussions broached the concerns of the possible weight of the CFU. A preliminary Process Flow Diagram (PFD) was produced (Figure 4). A rough weight estimate for the single modified rotary-kiln would be in the 900-1000 kg range. The handling and safety concerns in a limited laboratory setting could not be ignored.

At that time, an agreement with a laboratory in North Dakota (UNDEERC) was obtained to test the CO/Ethanol process in a 0.5- and 2-kg/hour continuous fluidized-bed reactor (CFBR).

## UNDEERC CONTINUOUS-FEED UNIT (CFU) DESULFURIZATION STUDIES

In 1989, a partnership was established with the University of North Dakota Energy & Environmental Research Center (UNDEERC) to perform the continuous-feed unit (CFU) tests of the CO/Ethanol process at the 0.5- and 2-kg/hour scales. This collaboration allowed for the use of an existing continuous fluidized-bed reactor (CFBR) at UNDEERC, thereby permitting the reallocation of project funds from equipment to additional experimentation.

The major concern with this plan was the need of the 3-Step process to work under CFBR conditions. Meetings between the research group, representatives from the engineering consulting firm C.W.Nofsinger Co., and consultant, Dr. Lyle Albright (professor of chemical engineering, Purdue University) led to the conclusion that CFBR operation should be possible. An earlier proposed horizontal ribbon-stirred reactor would have allowed for more flexible process operating conditions but seemed impracticable with space restrictions at the ISGS.

UNDEERC provided experienced, on-site chemical, chemical engineering, analytical and other service personnel to facilitate the work. Throughout the contract period all work has been closely coordinated through the ISGS. In addition, dollar-for-dollar cost-share funds were made available by UNDEERC through their cooperative agreement with USDOE. (This provision ultimately provided a further $205,000 to support the project.)

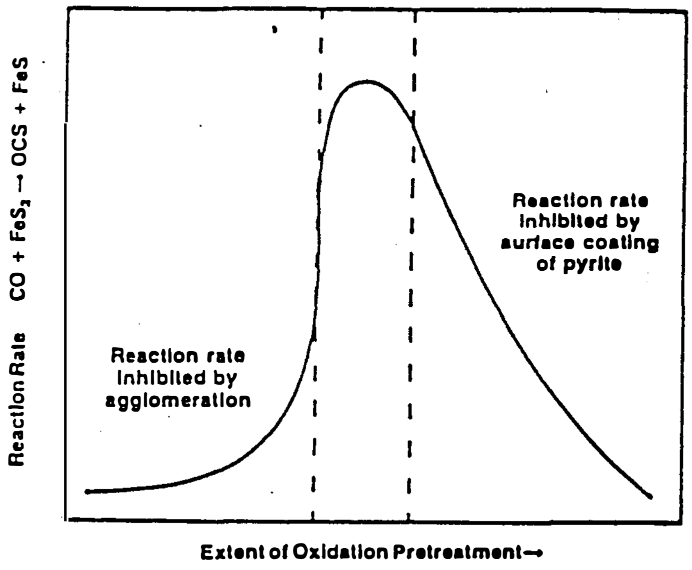
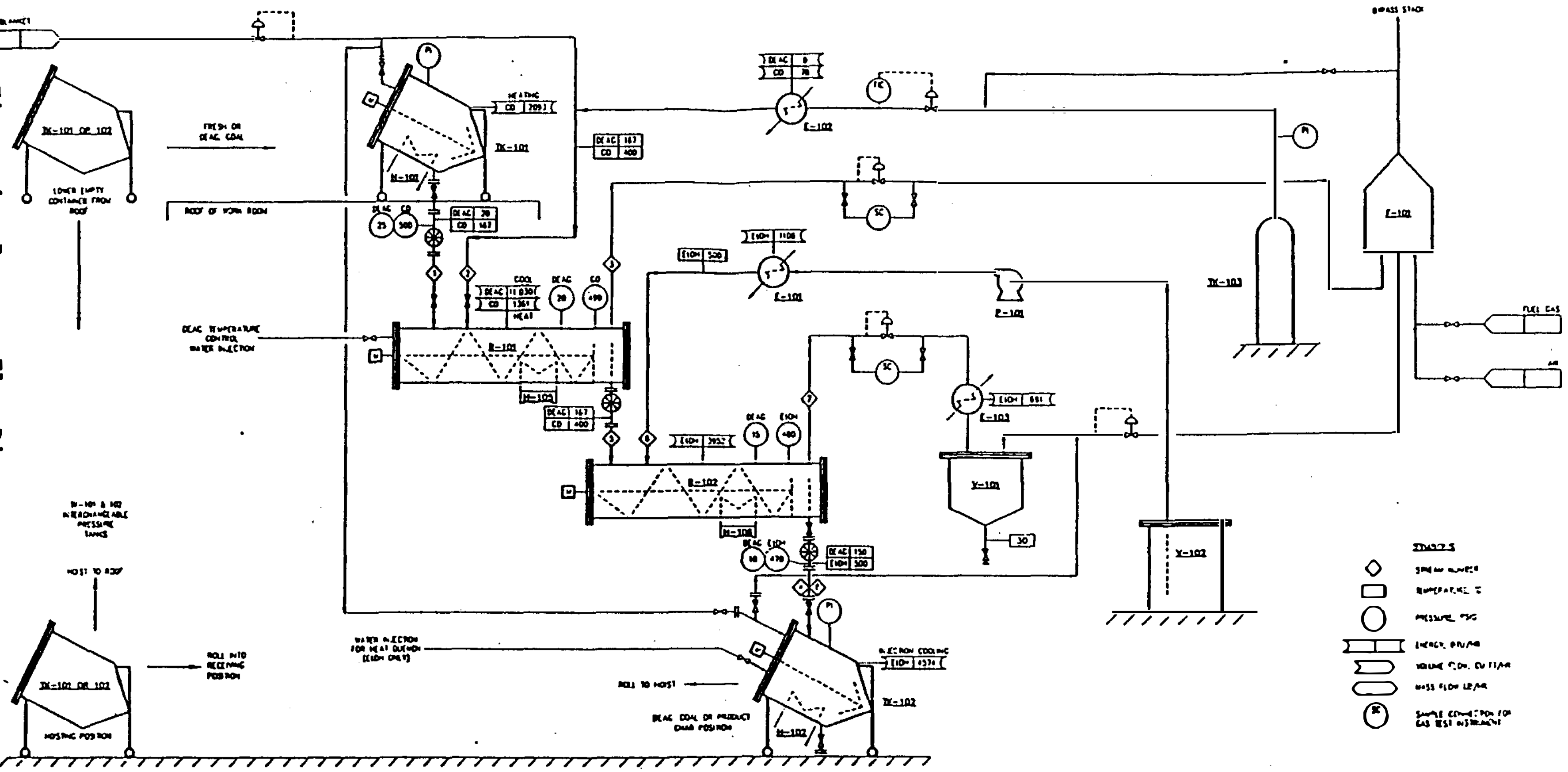


Figure 3. Effect of Pre-oxidation [40].



| 1 | STEP | | NO. 1 DEAGGLOMERATION | | | | NO. 2 CO TREATMENT | | | | NO. 2 ETHANOL TREATMENT | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | COMPONENT | MW | ① LB/HR | ② LB/HR | ③ LB/HR | ④ LB/HR | ① LB/HR | ② LB/HR | ③ LB/HR | ⑤ LB/HR | ⑤ LB/HR | ⑥ LB/HR | ⑦ LB/HR | ⑧ LB/HR |
| 3 | FRESH COAL | | 20,000 | | | | | | | | | | | |
| 4 | DEAG COAL | | | | | 19,000 | 19,000 | | | 19,000 | 19,000 | | | 19,000 |
| 5 | S in OS | 32.07 | 0.500 | | | 0.500 | 0.500 | | | 0.500 | 0.500 | | | |
| 6 | S in FeS₂ OR FeS | 32.07 | 0.500 | | | 0.500 | 0.500 | | | 0.250 | 0.250 | | | 0.250 |
| 7 | OFF GAS & VOLATILES | | | PRESENT | PRESENT | | | | | | | | | |
| 8 | O₂ in FLUE GAS | 32.00 | | 3.072 | | | | | | | | | | |
| 9 | (CO₂) CO | (44.01) 28.01 | | | (3.380) | | | 0.436 | 0.218 | | | | | |
| 10 | COS | 60.08 | | | | | | | 0.440 | | | | | |
| 11 | H₂S | 34.08 | | | | | | | | | | | 0.534 | |
| 12 | ETHANOL | 46.07 | | | | | | | | | | 1.436 | 0.718 | |
| 13 | ACETALDEHYDE | 44.05 | | | | | | | | | | | 0.687 | |
| 14 | FeS₂ | 119.98 | | | | (0.935) | (0.935) | | | | | | | |
| 15 | FeS | 87.92 | | | | | | | | (0.685) | (0.685) | | | (0.685) |
| 16 | COMBUSTION H₂O | 18.02 | | | 0.692 | | | | | | | | | |
| | TOTAL LB/HR | | 20,000 | 3.072 | 4.072 | 20,000 | 20,000 | 0.436 | 0.658 | 19,750 | 19,750 | 1.436 | 1.939 | 19,750 |

NOTES:

1. 100% EXCESSES OF CO AND ETHANOL ARE USED
2. 5% WEIGHT LOSS OF VOLATILES AND SULFUR-FREE COAL CONTENT IS ASSUMED DURING DEAGGLOMERATION WITH FLUE GAS

| | |
|---|---|
| TK-101 & TK-102 | INTERCHANGEABLE COAL FEED & COAL RECEIVING TANKS |
| H-101 & H-102 | COAL HEATERS |
| H-105 & H-106 | REACTOR HEATERS |
| R-101 | PRIMARY REACTOR |
| R-102 | SECONDARY REACTOR |
| E-103 | CONDENSER |
| E-102 | CO/FLUE GAS HEATER |
| E-101 | ETHANOL HEATER |
| V-101 | LIQUID PRODUCT RECEIVER |
| P-101 | ETHANOL FEED PUMP |
| TK-103 | CO STORAGE 1650 PSIG 175 SCF |
| V-102 | ETHANOL STORAGE 55 GALLONS |
| F-101 | FLUE GAS GENERATOR |

| REV | DATE | DESCRIPTION | APPROVED |
|---|---|---|---|
| ISSUE FOR CONSTRUCTION | | DESIGNER APPROVAL | |
| DRAWN ABB | CHECKED | REVIEWED | APPROVED |

TITLE
COAL DESULFURIZATION
DEMONSTRATION UNIT
PROCESS FLOW DIAGRAM

ILLINOIS STATE GEOLOGICAL SURVEY
UNIVERSITY OF ILLINOIS
CHAMPAIGN-URBANA ILLINOIS

THE C.W. NOFSINGER COMPANY
ENGINEERS AND CONTRACTORS
KANSAS CITY, MISSOURI

JOB NO. 80-3??-?
DRAWING NO. 1010-D1

Figure 4. Process Flow Diagram.

### Development of methods for catalyst removal

Magnetic separation techniques were first established with a charcoal/troilite model, then they were used on a Step 2 product of an Illinois No. 5 raw coal. The magnetic strength of the oxidized products were determined using a vibrating sample magnetometer, then separated by use of a hand magnet. Initial work to study the effect of temperature on troilite conversion obtained a maximum magnetic susceptibility near 375°C (707°F) in 2 percent oxygen for 30 minutes.

It has been reported in unpublished works that some of the Step 2 products may contain neoformed pyrrhotite. These pyrrhotites are thought to be formed by sublimation of iron sulfates reacting with hydrogen sulfide or some other sulfide donor. Many of the Step 2 products also contained oldhamite (CaS) which dissolves in HCl during organic sulfur analysis but remains in bottom ash if combusted. Oldhamite therefore represents a non-volatile form of inorganic sulfur and should, therefore, be considered a desulfurization product of chemical cleaning.

An alternative to partial oxidation/magnetic separation was to completely oxidize the iron sulfide catalyst to iron oxides and remove the sulfur as sulfur dioxide ($SO_2$). A few experiments have been carried out to investigate this option. Step 2 products were oxidized in 2 percent $O_2$ flowing at 400 mL/min with a back pressure of 2170 kPa (300 psig) for 1 to 2 hours in a pressure reactor over a temperature range of 300° to 400°C (572°-752°F). The products were analyzed for forms of sulfur to determine the fate of the sulfur. It was found that inorganic sulfur concentrations could be lowered, but that not all of the oxidized inorganic sulfur was actually removed from the final product.

It was agreed that the demonstration of the carbon monoxide and ethanol steps of the 3-Step process was to take precedent over the development of the magnetic separation step. Therefore, this work was deemed "non-critical path." Due to the demands of the scale-up work at UNDEERC no further advancement of this work was possible.

### Series I Results and Discussion

**Fluidization:** The continuous unit was operated in three different ways that greatly affect fluidization: 1) with 1/4"x10-mesh and minus 60-mesh particulate coal, 2) with and without the reactor side-leg, 3) with CO and/or with ethanol.

Gas-flow rates are higher in small scale equipment; small reactors require 1.5 to 2 times more gas to operate at fluidization velocities than do large reactors due to wall effects. Operation at pressure also increases the amount of gas flow required (3.5 times as much at 450 kPa/50 psig as at one atmosphere) to fluidize coal feed particles. Larger particles also require higher gas flows to fluidize and remove them from the reactor. In these tests, 13kg of gas at 450 kPa (50 psig) per 500g of coal (1/4"x10-mesh) was required to provide adequate operation. To process the larger size coal particles it was necessary to use different valves to provide the higher gas flow rates. Half as much gas was required to provide adequate operation with the minus 60 mesh coal. Although coal of both particle sizes was successfully fed to and recovered from the continuous system, the -60 mesh coal required substantially less gas to process.

The addition of the side-leg to the reactor enabled operation at a lower gas flow rate resulting in a more stable residence time for the bulk of the particles.

Some fine coal material (nominally 15 percent) was still recovered from the cyclone. This material would have had a shorter residence time in the reactor and thus was higher in sulfur than the bulk coal product. Pyrite contents were also significantly higher in the top coal product than in the bulk coal product. When operating with ethanol and coal product that had been prereacted with CO, the sulfur contents were similar for both top and bottom coal products. The top coal product was finer than the bottom coal product indicating that sizing occurred during processing.

**Agglomeration and Sieve Analysis:** One potential problem was agglomeration of the coal particles in the reactor. In previous tests, agglomeration was not a problem with an Illinois Herrin coal at temperatures under 425°C (797°F) with 1/4"x10-mesh coal particles. Pretreatment at lower temperatures, preoxidation, and or coal product addition prior to operation at over 425°C (797°F) have been effective in minimizing agglomeration. In these tests, the coal was processed with CO at under 400°C (752°F) no agglomerating problems were encountered. Additional heat was provided to the reactor by external heating's since CO can not be preheated over 300°C (572°F) without adverse carbon deposition reactions occurring.

One series of tests was performed to investigate residence time effects on the CO/coal first stage reaction. Coal segregation during processing makes ash and sulfur values on the products difficult to interpret. Sizing of the coal indicates ash-rich fines are present which are undoubtedly blowing over rapidly during processing.

The coal feed was fractionated using sieves and each fraction was analyzed for moisture, ash, and sulfur content using two methods to determine the ash and sulfur content variability. One method (ASTM D-3172-73) uses gram sized samples while the other (a thermogravimetric analysis method, discussed in the Analytical Procedures Section of this report, page 31), uses 40 mg samples.

It must be noted that these were preliminary tests designed primarily to determine the feasibility of running this process with a fluidized bed, and to determine any problems which would need to be addressed if a more comprehensive development program were to be undertaken. The limited amount of process data obtained in these preliminary tests were promising, showing significant sulfur reduction at low process severity.

**Material Balances:** Coal, gas, and ethanol (when desired) were fed to the reactor using calibrated feeding systems. The coal product(s) and condenser material were collected for a known period of time and weighed. Product gas was metered for a known period of time and analyzed. Recovery values for the raw data ranged from 85 to 105 percent with one value at 73 percent. The ratio of condenser material to product coal was between 0.040 and 0.051 in five tests and about 0.085 in two tests. The higher amount of condensate material in latter tests may be due to extra coal fines. The collection time of the CFBR test was adjusted to give a 100 percent recovery (e.g., a feed rate of 0.5-kg/hr would not necessarily accurately deliver that rate. The collecting time would be rather be set by the time necessary to accumulate a given amount of product.). All the data were then adjusted to a feed of 0.5-kg of coal to provide an easy comparison of the data.

Ash and water recovery values were calculated to check the fit of the mass balanced input-output data. Ash recoveries ranged, as expected, from 82 to 95 percent. The water recoveries were high, when assuming that only water was recovered from the condensers. However, if it was assumed that only the amount of water fed into the reaction was recovered in the condensers, coal liquid yields could be estimated. Using this rationale, liquid yields of 3.0 to 4.7 grams (about 0.8 weight percent of the coal fed) were calculated. Sulfur recoveries were 80 to 97 percent for six of the tests and 70 percent in the test where no CO was present. It was likely that unobserved hydrogen sulfide and sulfur in the condenser material would account for the lower sulfur recoveries. Pyrite recovery data indicated that the pyrite was significantly changed with processing conditions.

**Processing Condition Effects on Sulfur Content:** In general, the total sulfur of the products was reduced to 3.3-4.0 wt percent during processing. This initial decrease in total sulfur appeared to be a loss of mainly organic sulfur since the organic sulfur dropped from 1.5 wt percent in the coal to about 0.8 wt percent in the coal products where the highest amount of pyrite was observed. From the data collected it was unclear as to where this sulfur went. It was not observed as $H_2S$ in the product gas although some was expected. Condensates were not analyzed so it was not known if sulfur was present. OCS was observed in tests where carbon monoxide was present in the feed gas but not enough to balance the sulfur. Pyritic sulfur in the coal was 2.86 wt percent while in coal products it ranged from 2.65 wt percent to as low as 0.99 wt percent depending on operating conditions. Due to the characteristic of the fluidized-bed reactor used, it is possible that fractionation of the feed occurred. Essentially, in the coal-like products, all the pyrite was converted to a sulfur form other than pyrite.

The change in pyrite content with processing conditions was observed in the coal product samples and acid-washed coal samples giving the trend credibility (Table 5). The total sulfur content stayed relatively constant while the pyrite content significantly decreased with:

1. increasing CO in the feed gas from 0 to 100 percent at 350°C (662°F),
2. increasing the reaction temperature from 350° to 375°C (662°-7017°F, 25 percent CO), and
3. doubling the residence time at 350°C (662°F) with 25 percent CO.

The effect of residence time and operation with the side-leg resulted in the lowest total sulfur and pyrite values for the bottom coal product. With the side-leg present 15-19 percent of the total coal product enriched in sulfur and pyrite went overhead to the second coal product pot which indicated a beneficial fractionation had occurred.

When ethanol was processed with coal products, the total sulfur content was not influenced. Forms of sulfur are not available for the coal-like products produced at these latter conditions. Budgetary considerations favored additional total sulfur analyses of samples versus a limited number of forms of sulfur analyses.

TABLE 5. Sulfur content at various operating conditions[a].

| Test Number | Temp, °C[b] | Gas, %CO | Rate kg/h | Raw Coal Product Samples<br>Total wt% S | <br>Pyr. wt% S | <br>Sulf. wt% S | Acid Washed Samples<br>Total wt% S | <br>Pyr. wt% S | <br>Sulf. wt% S |
|---|---|---|---|---|---|---|---|---|---|
| Feed Coal, mf[c] | | | | 4.55 | 2.86 | 0.21 | | | |
| -60 mesh Coal | | | | | | | | | |
| 75.40 | 350 | 0 | 0.5 | 3.33 | 2.64 | 0.12 | 3.58 | 2.37 | 0.02 |
| 75.43 | 350 | 25 | 0.5 | 3.83 | 2.65 | 0.10 | 3.65 | 2.35 | 0.07 |
| 75.41 | 350 | 50 | 0.5 | 3.66 | 2.42 | 0.10 | 3.31 | 1.87 | 0.07 |
| 75.42 | 350 | 100 | 0.5 | 3.98 | 1.48 | 0.10 | 3.74 | 1.29 | 0.02 |
| 75.43 | 350 | 25 | 0.5 | 3.83 | 2.65 | 0.10 | 3.65 | 2.35 | 0.07 |
| 75.44 | 375 | 25 | 0.5 | 3.70 | 1.58 | 0.10 | 3.28 | 1.11 | 0.07 |
| 76.45-Top | 350 | 25 | 0.25 | 3.67 | 2.43 | 0.21 | 3.45 | 1.27 | 0.03 |
| -Btm | | | | 3.33 | 0.99 | 0.05 | 2.69 | 1.36 | 0.01 |
| 76.46-Top | 350 | 50 | 0.25 | 3.91 | 2.43 | 0.23 | 3.49 | 2.14 | 0.03 |
| -Btm | | | | 3.42 | 1.13 | 0.01 | 3.14 | 0.90 | 0.02 |

a - All tests were made at 450 kPa (50 psig). The side-leg was present when top and bottom coal product samples are present. No tests included ethanol as a feed.
b - All tests were made at 662° and 707°F
c - Average as received moisture was 4.6 wt percent.

**Processing Condition Effects on Ash Content:** CFBR long residence time tests of 0.5, 1.0, 2.0, and 4.0 hours in pseudo-batch operation (Table 6) to bridge laboratory batch data were complicated by segregation of the coal fed into the reactor during processing. Analyses of the coal feeds show that numerous analyses resulted in low values for ash or sulfur, presumably due to a difficulty in obtaining representative samples. Segregation has not been a problem in the bulk storage container since samples obtained at different times gave similar results. However, the ash contents of the products from the long residence time tests were considerably lower than the ash content of the feed coal. This type of fluid-bed operation will accentuate observation of the effects of high ash material prematurely leaving the reactor. For tests where the coal was in the reactor over 0.5 hours, the ash content of the reactor material was around 15 wt percent, which was lower than the 18 wt percent ash value for the feed coal. Sieving the coal and analyzing the fractions for moisture, ash, and sulfur indicates that there was a high ash fine material present that could preferentially blow-over, resulting in a low ash material remaining in the reactor. Since the purpose of the first stage CO reaction was to convert pyrites into an active form, the analyses of the CO reaction samples for sulfur and iron forms provides useful information.

**Ethanol:** Operation with ethanol present caused some problems. There was a tendency to coke near the inlet of the reactor. Light products, presumably produced from ethanol were found in the gas bag indicating that the condenser was not removing all the condensates. It also appeared that more tars were being produced when ethanol was present.

**TABLE 6.** Pseudo-batch tests.

| Residence Time (hr) | Total Coal Feed (g) | Reactor Product (g) | Moisture AR (wt%) | Moisture Free Ash | Moisture Free Sulfur |
|---|---|---|---|---|---|
| 0.5 | 266 | 60 | 0.12 | 18.68 | 3.72 |
| 1.0 | 213 | 175 | 0.07 | 15.00 | 2.79 |
| 2.0 | 212 | 201 | 0.23 | 15.83 | 3.80 |
| 4.0 | 152 | 105 | 0.04 | 14.39 | 4.40 |

## Series I CFU Conclusions

**CFBR Operation:** CFBR unit operation was successful in that coal was fed and recovered as coal product over a wide range of operating conditions. Agglomeration of the coal particles or excessive fines production in the reactor was not a major problem at any of the conditions studied. Consideration must still be given to the injection of ethanol and the analysis of the liquid and gaseous products.

Tests were performed with 1/4 x 10-mesh and minus 60-mesh coal particles with two reactor configurations, which indicated that operation with the smaller sized particles with a side-leg on the reactor resulted in minimizing the required amount of fluidizing gases. Operation with the side-leg resulted in some fines being carried over to the cyclones which due to the shorter residence time have reacted less. This may necessitate screening the feed coal in order to feed a narrower particle size distribution to minimize carryover to the cyclone. This would also provide a better control when studying a process in a small reaction system. It may also reduce the variability of sampling and decrease the range of analytical values.

**Sulfur Reduction:** The pyrite content of the coal-like product varied with operating conditions. Mössbauer analyses (Table 7) performed at 108°K and 4.2°K indicated the conversion of pyrite to pyrrhotites was occurring as predicted. Forms of sulfur analyses show that the percentage of organic sulfur increases significantly in the final product from the original feed material. It was, therefore, likely that back reactions of the sulfur bearing gases was occurring with the coal. The dimensions of the reactor (3.8cm in diameter by 60cm in reactor length) along with chosen processing conditions could have been increasing the extent of sulfur back reactions.

**TABLE 7. Mössbauer data.**

| Sample | Temp (°C/°F) | %CO | Feed Rate (kg/hr) | % Pyrite | Mössbauer Percentages Pyrite | Pyrrhotite | $FeSO_4$ |
|---|---|---|---|---|---|---|---|
| 75.42 | 350/662 | 100 | 0.5 | 1.48 | 57 | 38 | 5 |
| 75.43 | 350/662 | 25 | 0.5 | 2.65 | 77 | 14 | 9 |
| 75.44 | 375/707 | 25 | 0.5 | 1.58 | 67 | 23 | 10 |
| 76.45-bottom | 350/662 | 25 | 0.25 | 0.99 | 62 | 27 | 11 |

## CFU Development - Series II and III

Modifications to the 0.5-kg/hr were performed to increase the total through-put capacity to 2-kg/hr. The primary change was to replace the 3.8cm diameter reactor with a 7.5cm diameter reactor. This reactor (Figure 5) operated as a fluidized bed.

Equipment needed for the 2-kg/hr unit included: pipe, flanges, and weld reducers for constructing the reactors, valves and mass flow meters capable of handling the increased gas flows necessary for a 2-kg/hr unit, additional modules for the process control system, an ethanol pump, and ceramic fiber heaters for supplying process heat.

**Series II and III analytical procedures:** All coal products produced during desulfurization tests were analyzed for total sulfur content at UNDEERC using a Leco sulfur analyzer; for total sulfur and sulfur forms content at Minnesota Valley Testing Laboratories (MVTL); and for moisture, volatiles, fixed carbon, and ash content (proximate analysis) at UNDEERC. In some cases, particle size distribution analysis was performed on coal products samples using a dry sieve technique and Tyler mesh sizes.

Mössbauer spectroscopy was also used in this work to quantitatively determine forms of iron in coal product samples. The analysis quantified the iron forms of pyrite ($FeS_2$, pyrrhotite ($Fe_{1-x}S$), and iron sulfate ($FeSO_4$) as weight percentages of the total iron in a coal product, which was also quantified as a percentage of the total coal product weight. Another method for obtaining similar data was X-ray diffraction (XRD). XRD was used in the analysis of several coal products to yield a ratio of pyrite concentration to pyrrhotite concentration. However, the technique was not performed rigorously enough to yield absolute concentration data; that is, pyrite and pyrrhotite were not quantified as percentages of the total coal product weight.

In several cases, liquids generated during testing were analyzed using gas chromatography/Fourier Transform infrared spectrometry/mass spectrometry (GC/FT-IR/MS) which enables quantitating ethanol and other species, including potential ethanol degradation products such as acetates and acetals. The following are brief descriptions of the analytical techniques and instrumentation used for this work:

1) Proximate analysis (at UNDEERC) to determine moisture, volatile matter, fixed carbon, and ash contents -- performed using a Fisher 490 coal analyzer according to ASTM D-3172-73, in which fixed carbon content was calculated by difference; and using a thermogravimetric analysis (TGA) technique, which worked as follows: Approximately 40 - 50 mg of sample was heated under argon at a rate of 20°C (68°F) per minute to 100°C (212°F), and held at that temperature for 5 minutes. Weight loss occurring up to this point was designated as moisture content. The sample was then heated at a rate of 100°C (212°F) per minute to 900°C (1652°F) and held at that temperature for about 35 minutes; weight loss occurring during this step was designated as volatile content. After the sample has been totally devolatilized (usually at about the 32-minute mark of the 900°C (1652°F) exposure period), air was introduced into the system to enable combustion of the "fixed carbon." After combustion was completed, the weight of the remaining material was designated as ash content.

2) Ultimate analysis (at UNDEERC) to determine carbon, hydrogen, nitrogen, and sulfur (C, H, N, and S) contents -- performed using a Perkin-Elmer Model

240 elemental analyzer to determine CHN contents and a Leco sulfur analyzer for sulfur content; oxygen content was calculated by difference as the remaining constituent.

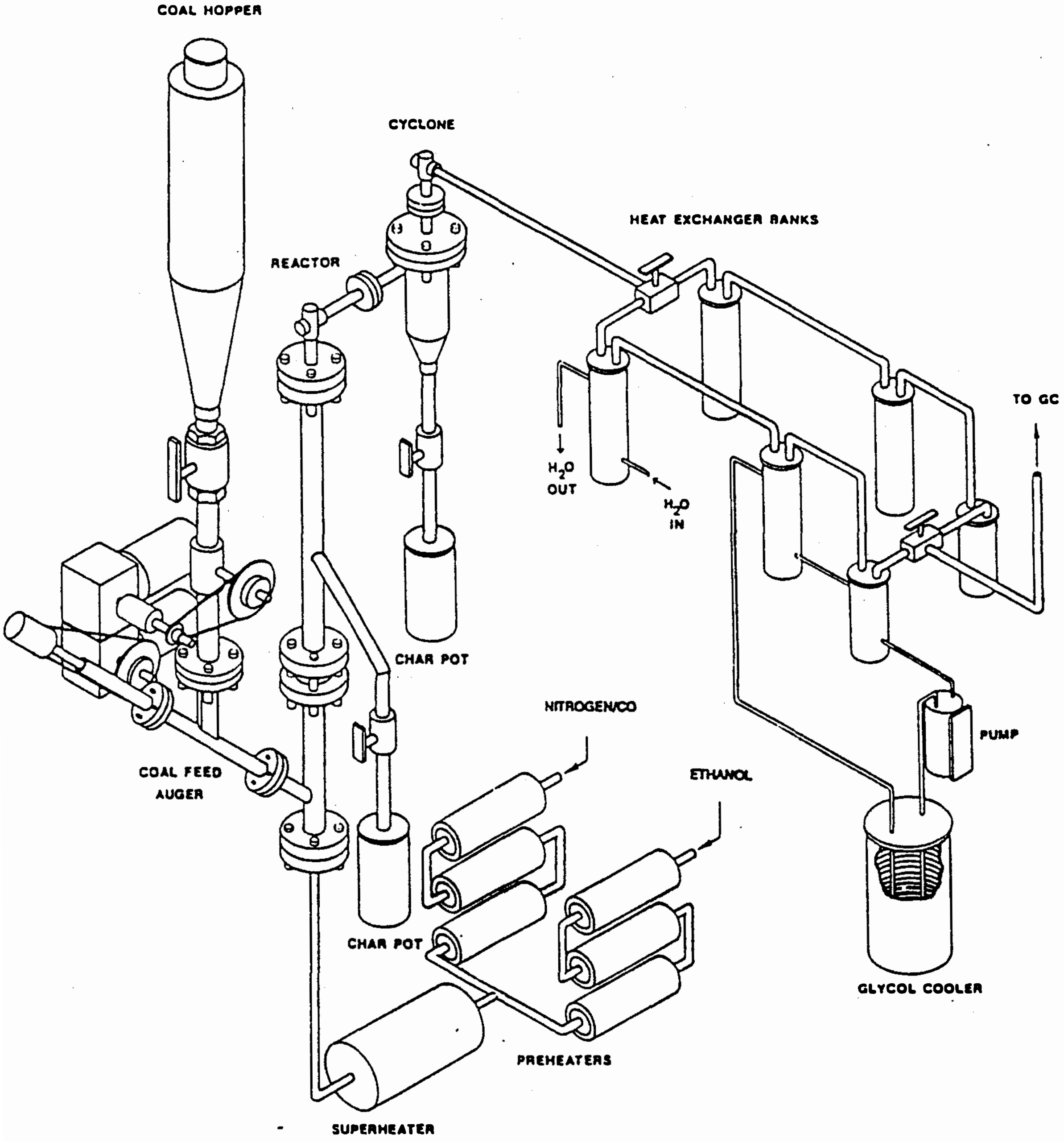


Figure 5. 0.5-kg/Hour CFBR Schematic.

3) Sulfur forms analysis to determine moisture-free weight percentages in coal/coal product of pyritic, sulfatic and organic sulfur -- performed by

Minnesota Valley Testing Laboratories (MVTL) in Bismarck, North Dakota, according to ASTM D-2492-84.

4) Mössbauer spectroscopy analysis to determine weight percentages of the total iron content of a coal/coal product associated as pyrite ($FeS_2$), pyrrhotite ($Fe_{1-x}S$),and iron sulfate ($FeSO_4$). The technique also enables determining the total iron content (in weight percent) a coal/coal product. Series of these analyses were performed by 1) the Dr. Peter DeBrunner, Department of Physics, University of Illinois, Urbana-Champaign; and 2) Dr. William M. Reiff of Mössbauer Spectroscopy Consultants, Burlington, Massachusetts.

   Mössbauer spectroscopy measures the recoilless emission and resonant reabsorption of gamma rays from excited nuclear states of a metal (in our case, iron) atom. This effect can be measured with extreme precision; thus very small differences in the energy of the absorption due to minute changes in the chemical environment of the nucleus can be detected. The energy of the nuclear transition (the chemical shift) varies with the "s" electron density at the nucleus, which in turn depends on the oxidation state and bonding (to surrounding atoms) of the crystal or molecule. Splitting of the absorption line into two or more lines results from interactions of the excited state nonspherical spinning nucleus with an electric field gradient produced by the surrounding atoms. From the energy of the absorption lines and the amount and type of splitting, various iron species in a complex coal or coal product sample can be identified. Pyrite and marcasite give a doublet at 0.314 and 0.277 mm/s, respectively, with splittings of 0.614 and 0.506 mm/s, respectively, at ambient temperature. Stoichiometric FeS (troilite) exhibits a sextuplet Mössbauer spectrum due to magnetic ordering, and nonstoichiometric FeS (pyrrhotite) has a very complex spectrum of overlying sextuplets, owing to three distinct iron environments in the crystal, each in a different magnetic field. Iron (II) salts such as $FeSO_4$ show a doublet with a high chemical shift value (3.104 mm/s) with a very large splitting (1.390 mm/s) at 80°K.

5) X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses (by UNDEERC) to determine the mineralogy and bulk composition, respectively, of coal/coal product samples. In XRD analysis, the sample was ground, spread out, and exposed to a monochromatic X-ray beam, which scans the sample over a range of angles. Each crystalline phase in the sample produces a series of diffraction patterns at particular angles of X-ray beam incidence (Bragg angles). A crystalline phase can be identified by its characteristic "powder diffraction file," in the same way a person can be identified by his or her fingerprints. In XRF analysis, X-rays travelling through a sample are absorbed by atoms in the sample, which causes the atoms to be in an "excited state." The atoms go back to their "ground state" by emitting energy in the form of X-rays. Atoms of each element present in the sample will emit X-rays of specific energy, described by the energy difference between the atom's excited and ground states. A sample element was quantitated by measuring the intensity of its uniquely characteristic X-rays.

6) GC/FT-IR/MS analysis (by UNDEERC) to determine the species present in the condensate recovered from the reactions. The technique was useful in monitoring for ethanol decomposition. The serially interfaced GC/FT-IR/MS system consists of a Hewlett Packard 5890 GC, which separates the volatile components of a sample and then routs them to the light pipe of a Nicolet 20SXB FT-IR; the effluent from the light pipe was then routed to a

Finnigan 800ITD ion trap detector. The data system enables real time GC analysis.

**Series II and III Test Descriptions:** Initial tests were performed in a 0.5-kg/hr continuous fluid bed reactor (CFBR) (see the Series I test results). Following completion of several series of tests, this reactor was modified to handle a coal/coal product feed rate of up to 2-kg/hr. To achieve the 2-kg/hr capacity, the original one-section reactor was replaced with a larger, two-section reactor with an expanded freeboard. The bottom section of the 2-kg/hr unit was a 7.5cm Schedule 80 stainless steel pipe, and the freeboard section was a 9.0cm Schedule 80 stainless steel pipe. Because of the greater thickness of its walls, the 2-kg/hr unit was rated for operation at a maximum temperature and pressure of 825°C (1517°F) and 1480 kPa (200 psig), respectively.

## Engineering Development

The objective of this preliminary work was to demonstrate the CO/Ethanol desulfurization process in a 0.5-kg/hour continuous fluidized-bed reactor (CFBR). The equipment was being utilized for Mild Gasification research funded by the U.S. Department of Energy (USDOE).

The 0.5-kg/hour CFBR is shown in Figure 5. The reactor was a 3.8cm I.D., 316 stainless steel pipe 130cm long. The reactor was operated in a fast fluid bed mode in which a constant-depth coal bed was maintained. Through devolatilization and particle attrition due to vigorous mixing, the particles become entrained in the gas stream. All products exited at the top of the reactor and the coal-like product was separated in a cyclone. The condensables were separated by one of the two sets of three indirect glycol cooled condensers. The gas was then metered and sampled. The coal-like product could also be removed through a side bed drain leg that is shown in Figure 5. In this mode of operation, the coal-like product was removed just above the middle flange at approximately 60 cm above the distribution plate. Fluidization velocities were adjusted so that the majority of the feed coal was removed from the side leg. The remaining coal-like product was removed from the overhead cyclone as fines. Operation with the side-leg was expected to give a more uniform residence time.

As part of this work, the unit was fitted with a back pressure regulator to perform tests at pressures of 450 kPa (50 psig). Safety equipment was installed to enable operating with carbon monoxide and a liquid injection system was installed to enable the injection of ethanol. In selected tests, the side-leg was added to the reactor so that the bulk of the product was not blown over to the cyclone but removed from the top of the fluidized bed.

## Operating Conditions

Fluidizing conditions (gas and/or liquid flow rates) were established for the two feed particle sizes with CO and ethanol. A number of different operating conditions were selected to assess unit operability over the entire range of process variables expected in a more comprehensive program (see Table 8). It was desired to determine whether 1/4" or minus 60-mesh coal should be used in order to minimize the amount of fluidizing gas required. Operating temperatures and residence times (proportional to the inverse of solid-feed rates) were also varied. A number of tests were performed with CO and ethanol with raw coal while two tests were performed with ethanol and coal-like product that had been previously processed with CO. In the initial tests, a total of 20 conditions were used and preliminary data were obtained at various conditions.

**TABLE 8. Operating conditions investigated[a].**

| Run Number | Temperature °C[b] | Feed Gas % CO | Ethanol % | Feed Rate kg/h | Side-leg |
|---|---|---|---|---|---|
| 1/4" Coal | | | | | |
| 78.49 | 350 | 0 | 0 | 0.25 | yes |
| 77.47 | 350 | 25 | 0 | 0.25 | yes |
| 77.48 | 350 | 50 | 0 | 0.25 | yes |
| 78.50 | 350 | 100 | 0 | 0.25 | yes |
| -60 mesh Coal | | | | | |
| 75.40 | 350 | 0 | 0 | 0.5 | no |
| 75.43 | 350 | 25 | 0 | 0.5 | no |
| 75.41 | 350 | 50 | 0 | 0.5 | no |
| 75.42 | 350 | 100 | 0 | 0.5 | no |
| 75.44 | 375 | 25 | 0 | 0.5 | no |
| 76.45 | 350 | 25 | 0 | 0.25 | yes |
| 76.46 | 350 | 50 | 0 | 0.25 | yes |
| 85.64 | 350 | 25 | 0 | 0.375 | yes |
| 82.57 | 350 | 25 | 11 | 0.375 | yes |
| 83.61 | 400 | 25 | 11 | 0.375 | yes |
| 82.59 | 300 | 25 | 14 | 0.375 | yes |
| 82.58 | 350 | 25 | 14 | 0.375 | yes |
| 83.60 | 400 | 25 | 14 | 0.375 | yes |
| Coal product Preparation | | | | | |
| 80.51-54 | 350 | 25 | 0 | 0.375 | yes |
| Operation with Coal Product | | | | | |
| 84.62 | 350 | 0 | 14 | 0.375 | yes |
| 84.63 | 400 | 0 | 14 | 0.375 | yes |

---

a - All tests were made at 450 kPa (50 psig).
b - All tests were made at 572°, 662°, and 752°F

## Samples Obtained and Analyses

**Feed materials:** Feed gases (nitrogen and carbon monoxide) were obtained from DOW Welding Supply Company. Two 55 gallon drums of Illinois Herrin coal were procured directly from the mine and stored under nitrogen. This coal was pulverized and sized into 1/4" x 10-mesh and minus 60-mesh lots (Table 9 lists but a few of the analyses). The indications from the coal data obtained was that representative samples were difficult to obtain.

**Product Solids:** Solid product samples were collected from the CFBR, after it had been operating at stable conditions for 1-2.5 hours, during a known time (material balance period). When the side-leg was present, two samples of solids were collected; one immediately after the cyclone (top coal product) and one from the solid pot at the bottom of the side-leg (bottom coal product). Pre-run coal product (material collected before a material balance period) and blowdown (material blown out of the reactor with bursts of nitrogen following completion of a test) samples were collected but were normally not analyzed.

**TABLE 9. Variability of Selected Feed Coal Analyses.**[2]

| **Lab** | **Mesh** | **Moisture wt% AR** | **Ash wt% mf** | **Sulfur wt% mf** |
|---|---|---|---|---|
| UNDEERC | 1/4" | 8.00 | 22.22 | 4.42 |
| UNDEERC | -60 mesh | 4.69 | 17.52 | 3.58 |
| CTL[1] | -60 mesh | 3.48 | 25.68 | 5.73 |
| CTL | -60 mesh | 2.37 | 26.59 | 4.46 |
| Average |  | 4.63 | 23.00 | 4.55 |

1 - Cepheus Testing Laboratories, Marion, Illinois

One concern was the possible occurrence of agglomeration or size reduction of particles during processing. Sieve data for runs 75.40 to 75.44 indicates that the products processed without the use of a side-leg have similar particle size distributions. When operating with 1/4" x 10-mesh coal and a side-leg, about 11 wt percent of fine particulates in the feed went to the cyclone, while with minus 60-mesh coal, 17 wt percent of the total coal product collected was from the cyclone.

---

[2] Table 29 illustrates the difficulty encountered in obtaining a consistent coal sample. At one point, three separate coal testing laboratories were used for total sulfur analyses: Cepheus Testing Laboratory, Marion, Illinois (CTL); the coal laboratory at the Energy & Environmental Research Center, University of North Dakota, Grand Forks (EERC); and the Minnesota Valley Testing Laboratory, Bismarck, North Dakota (MVTL).

After encountering large variations with "identical" samples, two decisions were made: a single testing laboratory would be used. MVTL was selected to provide the sole basis from which conclusions would be drawn. Throughout this report, values from CTL and EERC are reported. These values have been included to allow the reader to observe the variability of the sulfur data. As both inorganic and organic sulfur should be effected by the CO and ethanol steps, it was felt that total sulfur analyses would provide sufficient information concerning the success of each test. Therefore, as a cost saving factor, forms of sulfur analyses were only performed on selected samples. Because of the problems in collecting representative samples, the later experiments included contemporaneous analyses of the feed coal and their products.

Feed coal product samples were analyzed at two testing laboratories. Analyses were duplicated when it was noticed that a larger range of numbers was obtained then expected versus the operating conditions. These data, as did the coal data, indicated a difficulty in obtaining representative samples for analysis.

**Gas:** The high gas flow rates decreased the accuracy of determining the amount of OCS, hydrogen sulfide, and other gases produced from the coal, since their concentrations were small. Hydrogen sulfide had a tendency to adsorb on the walls of gas bags and metals in the processing unit, resulting in a loss prior to analysis. The components in the feed gases ($N_2$ and/or CO) and small amounts of $H_2$ and OCS were observed regularly in the product gases. Hydrogen sulfide was not observed, but this may have been due to its low concentration or losses due to adsorption prior to analysis.

**Condenser material:** Analysis of the condensates was outside of the scope of this study. Water, coal tars, and fine coal that got past the cyclone collected in the condenser. When ethanol was used in the process it would also collect in the condenser. For detailed mass balancing the amount of each component present in the condensate would need to be determined. However, the added cost and effort could only be expended on a limited number of tests. Since these were scoping tests, the condensates were not analyzed.

**TABLE 10. Some Gas Species Collected during Processing with Ethanol.**

| Empirical Formula | Component |
|---|---|
| $CO_2$ | Carbon Dioxide |
| $C_2H_4O$ | Acetaldehyde |
| $C_7H_{16}$ | 2,3-Dimethylpentane |
| $C_6H_{14}$ | 3-Methylpentane |
| $C_6H_{14}$ | Hexane |
| $C_4H_8O_2$ | Acetic acid, ethyl ester |
| $C_6H_{12}$ | Cyclohexane |
| $C_6H_{12}O$ | 2-Hexanone |

A complex GC trace was obtained for gas bags that had been collected when ethanol was used in the process. One sample of this gas was analyzed by GC/MS in order to obtain preliminary information. The carbon and hydrogen content of some peaks and some tentative identifications found in the gas are presented in Table 10. The data indicates that a wide range of light material passed through the condenser when ethanol was used in the processing. Special trapping will be required to collect and quantify this material.

## CFU PROJECT DATA AND DISCUSSION

### Microwave studies

The investigations of microwave-assist catalysis have been carried out at Argonne National Laboratory. Conversion of pyrite/marcasite to pyrrhotite can be accomplished at temperatures lower than those required by thermal heating alone.

The conversion also occurs at atmospheric pressure versus 2170 kPa (300 psig) backpressure in the thermal process. Acetaldehyde and hydrogen, the expected products from ethanol dehydrogenation, have been produced over the iron sulfide catalyst by the required reaction pathway in preference to water and ethylene produced by dehydration of ethanol. Additional efforts into this research area were discontinued but it was hoped to eventually reinvestigate this very promising technology as it applies to the CO/Ethanol desulfurization process.

### Carbon Monoxide Residence Time Study

Four tests were performed with carbon monoxide (CO) gas to study the effect of residence time on desulfurization. The tests were performed in the 0.5-kg/hr continuous fluid bed reactor (CFBR). The CFBR was normally operated in a continuous mode; however, for these tests the system was operated as a batch reactor.

Coal was fed into the CFBR at a rate of approximately 0.8-kg/hour for 17 minutes, to charge about 0.25-kg of coal in the reactor, which was the weight of a coal bed that would exist during continuous operation. After 17 minutes, coal feeding was stopped, and the coal charged was allowed to remain in the reactor for the desired residence time (0.5, 1, 2, or 4 hours). The reactor temperature was held at 375°C (707°F) during both the coal feeding and the residence time sequence of each test. A fluidization gas mixture of approximately 68 percent nitrogen/32 percent carbon monoxide was fed to the reactor at a flow rate of about 0.5 feet per second (ft/s). Throughout this work, fluidization gas flow rates are reported as ft/s instead of metric units to enable easy comparison of fluidization velocities in different-size reactors.

Table 11. CO Residence time study (1-4-90).

| Run # | Ill #6 | Leftover | M111 | M095 | M113 | M112 |
|---|---|---|---|---|---|---|
| Sample | Feedcoal | Feedcoal | 83 | | | |
| Residence Time, min | | | 0.5 hr | 1 hr | 2 hr | 4 hr |
| MVTL Prox. | | | | | | |
| % Moist | 4.36 | 4.75 | 1.03 | 0.19 | 0.36 | 0.00 |
| % Vol Mat | 31.14 | | | | | |
| % Fixed C | 47.44 | | | | | |
| % Ash | 17.06 | 15.95 | 18.66 | 14.99 | 15.79 | 14.38 |
| BTU/lb | 10941 | | | | | |
| S, wt%, dry (EERC) | 3.43 | 3.49 | 3.72 | 2.97 | 3.80 | 4.40 |
| Ash S, wt% (EERC) | 2.31 | 2.02 | 2.51 | 1.67 | 2.45 | 1.76 |
| S, wt%, dry (MVTL) | | | | | | |
| Total | 3.67 | 3.81 | 3.14 | 3.68 | 3.91 | 4.26 |
| Pyritic | 1.66 | 1.78 | 1.77 | 1.46 | 1.67 | 1.48 |
| Sulfatic | 0.40 | 0.39 | 0.24 | 0.17 | 0.25 | 0.17 |
| Organic | 1.61 | 1.63 | 1.13 | 2.05 | 2.00 | 2.61 |
| Coal product wt, g | | | 266 | 213 | 212 | 152 |
| Condensate wt, g | | | 14 | 10 | 13 | 9 |
| Total, g | | | 280 | 223 | 225 | 161 |

EERC - Analyzed at the Energy and Environmental Research Center
MVTL - Analyzed at Minnesota Valley Testing Laboratories, Bismarck, ND

Operating conditions described in "Description of CO Residence Time Tests." Reaction Temp -- 375 C
Feed Gas -- Approximately 32 percent CO/68 percent N2
Ash S -- Sulfur content of the ash made from the coal or coal product

A small amount of fine material became entrained in the fluidization gas stream and was deposited in the cyclone and the coal product collection pots during the tests. At the completion of each test, the reacted coal product was removed, or "blown out" from the reactor with high-pressure bursts of nitrogen. This coal product "blow over" was analyzed for ash, moisture, and sulfur content. Also, ash samples prepared from the feed coal and each of the coal products were analyzed for sulfur. The test results, shown in Table 11, indicate that (under the described conditions) a residence time of <1 hour provides the best sulfur removal. It appears that sulfur content decreases significantly during initial heat exposure, then increases, due to loss of organic matter through devolatilization. Table 11 also shows that while pyritic and sulfatic sulfur contents decrease with residence time, organic sulfur content increases.

Table 12. CO temperature ramp study.

| | M116<br>Ill #6<br>-60<br>Feed coal | 420°C[a] | 435°C | 450°C | 465°C | 480°C | 495°C | 510°C | 530°C |
|---|---|---|---|---|---|---|---|---|---|
| TGA Prox | | | | | | | | | |
| % Moist | 5.41 | 0.61 | 0.56 | 0.54 | 0.59 | 0.55 | 0.61 | 0.68 | 0.87 |
| % Vol Mat | 30.29 | 29.26 | 27.30 | 24.74 | 21.18 | 20.25 | 18.96 | 25.99 | 25.72 |
| % Fixed C | 43.56 | 47.73 | 47.20 | 50.88 | 52.68 | 52.54 | 51.48 | 52.61 | 52.00 |
| % Ash | 20.75 | 22.41 | 24.96 | 24.04 | 25.55 | 26.67 | 28.95 | 20.72 | 21.41 |
| % Ash (ASTM) | 20.83 | 20.94 | 23.70 | 22.40 | 25.11 | 26.07 | 26.41 | 19.05 | 22.56 |
| Particle Size | | | | | | | | | |
| +60 | 0.32 | 0.33 | 0.42 | 0.41 | 0.88 | 3.30 | 24.96 | 1.20 | 2.13 |
| -60+80 | 12.23 | 5.57 | 7.58 | 6.25 | 9.40 | 16.73 | 23.53 | 4.87 | 8.99 |
| -80+100 | 25.40 | 14.04 | 17.43 | 15.29 | 19.38 | 21.84 | 17.47 | 11.49 | 19.65 |
| -100+140 | 23.00 | 32.74 | 38.07 | 40.32 | 38.61 | 31.92 | 19.03 | 32.92 | 36.30 |
| -140+200 | 15.04 | 23.78 | 19.64 | 21.81 | 16.54 | 13.50 | 7.38 | 24.15 | 16.66 |
| -200+325 | 12.36 | 17.64 | 12.70 | 12.23 | 11.09 | 9.19 | 5.18 | 16.75 | 11.95 |
| -325 | 11.64 | 6.35 | 4.29 | 3.83 | 4.26 | 3.51 | 2.43 | 8.63 | 4.16 |
| S, wt%, dry | | | | | | | | | |
| Total | 5.01 | 3.65 | 3.84 | 3.78 | 3.89 | 4.35 | 3.66 | 3.30 | 3.67 |
| Pyritic | 2.70 | 1.38 | 1.76 | 1.38 | 1.02 | 1.10 | 1.01 | 1.02 | 1.35 |
| Sulfatic | 0.60 | 0.45 | 0.46 | 0.47 | 0.43 | 0.44 | 0.45 | 0.44 | 0.51 |
| Organic | 1.71 | 1.82 | 1.62 | 1.93 | 2.44 | 2.81 | 2.20 | 1.84 | 1.81 |
| Coal product wt, g | | | | | | | | | |
| Top | | 4 | 2 | 5 | 4 | 13 | 3 | 8 | 1 |
| Bottom | | 77 | 150 | 144 | 209 | 325 | 376 | 92 | 306 |
| Total | | 81 | 152 | 149 | 213 | 338 | 379 | 100 | 307 |

---

a - Conversion of temperatures are as follows: 420°C=788°F, 435°C=815°F, 450°C=842°F, 465°C=869°F, 480°C=896°F, 495°C=923°F, 510°C=950°F, 530°C=986°F.

## CO Temperature Ramp Study

A test was performed in the CFBR under CO to determine the effect of temperature on sulfur removal. Coal was fed into the reactor at a rate of about 0.5-kg/hr. The initial reactor temperature was 420°C (788°F), the fluidization gas used was a mixture of 35 percent CO/65 percent $N_2$, and the reactor temperature was increased at a rate of 15°C/hr (59°F/hr). Coal product fines (referred to as "top" in Table 12) were collected from the cyclone and product coals (referred to as "bottom" in Table 12) were removed from the coal product collection pot at hourly intervals.

One of the objectives of the test was to determine the temperature at which the coal would agglomerate. Based on experience in the CFBR with other bituminous coals, it was expected that agglomeration would occur in the temperature range of 400° to 430°C (752°-806°F). However, agglomeration did not occur until the reactor temperature reached approximately 540°C (1004°F). The nonagglomeration tendency of the coal may have been a result of its oxidation state; its abnormally high ash content (20.75 percent) showed that the coal may have been partially oxidized.

Table 12 shows that the lowest total, pyritic, and sulfatic sulfur contents, and the highest organic sulfur contents were achieved at temperatures of 465° to 495°C (869°-923°F). Since the Illinois #6 coal used in this test behaved unexpectedly, another test was performed using another lot of Illinois #6. Under similar reaction conditions, this coal agglomerated at about 425°C (797°F).

## Low CO Concentration Study

To investigate how low concentrations of CO affect desulfurization, a series of tests was performed in which CO concentration in the fluidization gas was increased from 0 to 25 percent. In all tests, the reaction temperature was maintained at 410°C (770°F), the coal feed rate at 0.5-kg/hr, and the fluidization gas flow rate at 0.35 ft/s. Each CO concentration test was performed for 6 hours, and coal product samples were collected at 2-hour intervals. Coal product fines (top) were collected from the cyclone, and product coals (bottom) were removed from the coal product collection pot. The results of the tests (Tables 13-17) show that as CO concentration in the feed gas is increased, pyrite conversion increases, total sulfur content decreases, and organic sulfur content increases; and fixed carbon and ash contents increase as a function of decreasing volatile material.

## Sequential Solvent Extraction

For coal products from UNDEERC the "tops" contained less non-polar extractable material than either the "bottoms" or "run" products. Since polar extracts are usually the largest contributors to the total extract yields, the "tops" produced the lowest extract yields.

Size Exclusion Chromatography (SEC) of the extracts revealed changes in molecular size distributions of the solvent extracts due to heating with CO. Compared with extracts from the feed coals, all product extracts showed the loss of high molecular weight, polar material - probably phenolics. Molecular weight distributions of non-polar extracts became broader.

Table 13. Concentration study (10 percent).

| Run # | M118 | M117 | M117 | M117 | M117 | M117 | M117 | | |
|---|---|---|---|---|---|---|---|---|---|
| Period | Feed | 101 | 101 | 102 | 102 | 103 | 103 | Average | Average |
| Sample | Coal | bottom | top | bottom | top | bottom | top | bottom | top |
| TGA Prox | | | | | | | | | |
| % Moist | 2.41 | 0.37 | 0.66 | 0.43 | 0.65 | 0.42 | 0.64 | 0.41 | 0.65 |
| %Vol Mat | 34.57 | 29.17 | 31.62 | 26.96 | 31.22 | 27.62 | 32.29 | 27.92 | 31.71 |
| % Fixed C | 50.48 | 58.02 | 54.76 | 58.68 | 54.84 | 57.32 | 53.90 | 58.01 | 54.50 |
| % Ash | 12.54 | 12.43 | 12.97 | 13.93 | 13.29 | 14.63 | 13.18 | 13.66 | 13.15 |
| % Ash (ASTM) | 12.72 | 12.57 | 13.06 | 14.53 | 13.40 | 14.24 | 13.56 | 13.78 | 13.34 |
| Particle Size | | | | | | | | | |
| +60 | 0.12 | 0.25 | 0.34 | 0.43 | 0.26 | 0.35 | 1.05 | 0.34 | 0.55 |
| -60+80 | 5.10 | 2.28 | 0.61 | 6.10 | 0.40 | 5.64 | 0.85 | 4.67 | 0.62 |
| -80+100 | 16.44 | 9.79 | 1.57 | 33.57 | 1.06 | 22.00 | 1.26 | 21.79 | 1.30 |
| -100+140 | 24.64 | 42.80 | 53.28 | 23.06 | 18.44 | 28.75 | 2.66 | 31.54 | 24.79 |
| -140+200 | 16.42 | 15.32 | 1.44 | 13.37 | 9.69 | 17.16 | 8.36 | 15.28 | 6.50 |
| -200+325 | 19.04 | 20.29 | 8.78 | 16.87 | 32.95 | 18.97 | 52.48 | 18.71 | 31.40 |
| -325 | 17.99 | 9.40 | 33.69 | 6.85 | 37.26 | 7.48 | 33.31 | 7.91 | 34.75 |
| S, wt%, dry | | | | | | | | | |
| Total | 3.38 | 3.18 | 3.17 | 3.16 | 3.11 | 3.16 | 3.24 | 3.17 | 3.17 |
| Pyritic | 1.69 | 1.25 | 1.20 | 1.25 | 1.16 | 1.33 | 1.32 | 1.28 | 1.23 |
| Sulfatic | 0.20 | 0.14 | 0.19 | 0.14 | 0.21 | 0.14 | 0.21 | 0.14 | 0.20 |
| Organic | 1.49 | 1.79 | 1.78 | 1.77 | 1.74 | 1.69 | 1.70 | 1.75 | 1.74 |

| | M117,101 | M117,102 | M117,103 | | |
|---|---|---|---|---|---|
| Coal product | 84 | 117 | 134 | | 112 |
| wt, g | 243 | 415 | 605 | 421 | |
| Top | 327 | 532 | 739 | | |
| Bottom | 31 | 13 | 8 | | |
| SubTotal | 358 | 545 | 747 | | |
| Condensate | | | | | |
| Total | | | | | |

(continued)

(Table 3 continued)

| Run #<br>Period<br>Sample | M118<br>Feed<br>Coal | M117<br>101<br>bottom | M117<br>101<br>top | M117<br>102<br>bottom | M117<br>102<br>top | M117<br>103<br>bottom | M117<br>103<br>top | Average<br>bottom | Average<br>top |
|---|---|---|---|---|---|---|---|---|---|
| Product Gas Composition, Mole % | | | | | | | | | |
| N2 | | 88.42 | | 90.62 | | | | 89.52 | |
| CO | | 11.40 | | 9.11 | | | | 10.26 | |
| CO2 | | 0.07 | | 0.11 | | | | 0.09 | |
| H2 | | 0.05 | | 0.07 | | | | 0.06 | |
| OCS | | 0.04 | | 0.04 | | | | 0.04 | |
| H2S | | | | 0.04 | | | | 0.02 | |
| Propane | | | | | | | | | |
| Total | | 99.98 | | 99.99 | | | | 99.99 | |

For tests described in Tables 11 - 16:
Fluidization Gas Flow Rate - 0.35 ft/s
Coal Feed Rate - 0.5-kg/hr
Temperature - 410°C (770°F)

(Table 3 continued)

**Table 14.** CO concentration study (3%).

| Run # | M118 | M118 | M118 | M118 | | |
|---|---|---|---|---|---|---|
| Period | 98-99 | 98-99 | 100 | 100 | Average | Average |
| Sample | bottom | top | bottom | top | bottom | top |
| TGA Prox | | | | | | |
| % Moist | 0.53 | 0.59 | 0.57 | 0.73 | 0.55 | 0.66 |
| % Vol Mat | 27.47 | 31.71 | 27.94 | 31.68 | 27.71 | 31.70 |
| % Fixed C | 58.52 | 54.72 | 57.33 | 54.86 | 57.93 | 54.79 |
| % Ash | 13.49 | 12.97 | 14.17 | 12.94 | 13.83 | 12.96 |
| % Ash (ASTM) | 14.14 | 13.25 | 14.04 | 13.11 | 14.09 | 13.18 |
| Particle Size | | | | | | |
| +60 | 0.45 | 0.95 | 0.31 | 0.32 | 0.38 | 0.64 |
| -60+80 | 7.42 | 0.97 | 4.02 | 0.40 | 5.72 | 0.69 |
| -80+100 | 22.78 | 1.88 | 17.95 | 0.95 | 20.37 | 1.42 |
| -100+140 | 36.36 | 27.71 | 29.81 | 2.01 | 33.09 | 14.86 |
| -140+200 | 8.84 | 23.35 | 17.39 | 3.39 | 13.12 | 13.37 |
| -200+325 | 17.31 | 21.48 | 20.82 | 23.92 | 19.07 | 22.70 |
| -325 | 7.25 | 23.65 | 9.69 | 68.82 | 8.47 | 46.24 |
| S, wt%, dry | | | | | | |
| Total | 3.30 | 3.17 | 3.11 | 3.11 | 3.21 | 3.14 |
| Pyritic | 1.46 | 1.26 | 1.50 | 1.26 | 1.48 | 1.26 |
| Sulfatic | 0.14 | 0.20 | 0.14 | 0.20 | 0.14 | 0.20 |
| Organic | 1.70 | 1.71 | 1.47 | 1.64 | 1.59 | 1.68 |
| | M118,98 | M118,99 | | M118,100 | | |
| Coal product | | | | | | |
| wt, g | 74 | 116 | | 124 | | 105.00 |
| Top | 220 | 434 | | 501 | 385 | |
| Bottom | 294 | 550 | | 625 | | |
| SubTotal | 27 | 7 | | 38 | | |
| Condensate | 321 | 557 | | 663 | | |
| Total | | | | | | |

(continued)

| Product Gas Composition, Mole % | | |
|---|---|---|
| N2 | 98 | 99.00 |
| CO | 95.09 | 97.41 |
| CO2 | 4.60 | 2.41 |
| H2 | 0.08 | 0.10 |
| OCS | 0.05 | 0.05 |
| H2S | 0.03 | 0.03 |
| Propane | 0.14 | 0.01 |
| Total | | |

Products from Tests 98 and 99 were combined for analysis.

## Table 15. CO concentration study (3.8 percent).

| Run # | M119 | M119 | | Average |
|---|---|---|---|---|
| Period | 95-97 | 95-97 | | |
| Sample | bottom | top | | |
| TGA Prox | | | | |
| % Moist | 0.47 | 0.65 | | |
| % Vol Mat | 27.31 | 32.32 | | |
| % Fixed C | 58.08 | 53.77 | | |
| % Ash | 14.15 | 13.25 | | |
| % Ash (ASTM) | 14.31 | 13.25 | | |
| Particle Size | | | | |
| +60 | 0.47 | 2.26 | | |
| -60+80 | 6.14 | 1.75 | | |
| -80+100 | 34.39 | 2.38 | | |
| -100+140 | 19.34 | 39.86 | | |
| -140+200 | 15.77 | 19.34 | | |
| -200+325 | 18.16 | 23.92 | | |
| -325 | 6.00 | 10.33 | | |
| S, wt%, dry | | | | |
| Total | 3.26 | 3.16 | | |
| Pyritic | 1.44 | 1.32 | | |
| Sulfatic | 0.12 | 0.21 | | |
| Organic | 1.70 | 1.63 | | |
| | M119,95 | M119,96 | M119,97 | |
| Coal product | | | | |
| wt, g | 148 | 89 | 104 | 114.00 |
| Top | 516 | 244 | 326 | 362.00 |
| Bottom | 664 | 333 | 430 | |
| SubTotal | 58 | 24 | 28 | |
| Condensate | 722 | 357 | 458 | |
| Total | | | | |
| Product Gas composition, Mole % | | | | |
| N2 | 95.00 | 96.00 | 97.00 | |
| CO | 95.35 | 96.26 | 96.41 | 96.01 |
| CO2 | 4.49 | 3.54 | 3.33 | 3.79 |
| H2 | 0.06 | 0.06 | 0.08 | 0.07 |
| OCS | 0.02 | 0.01 | 0.01 | 0.01 |
| H2S | 0.03 | | | 0.01 |
| Propane | | | | |
| Total | | | | |

Products from Tests 95-97 were combined for analysis.

Table 16. CO concentration study (0 percent).

| Run #<br>Period<br>Sample | M120<br>93<br>bottom | M120<br>93<br>top | M120<br>92<br>bottom | M120<br>92<br>top | M120<br>94<br>bottom | M120<br>94<br>top | Average<br>bottom | Average<br>top |
|---|---|---|---|---|---|---|---|---|
| TGA Prox | | | | | | | | |
| % Moist | 0.51 | 0.46 | 0.38 | 0.44 | 0.52 | 0.74 | 0.47 | 0.55 |
| % Vol Mat | 28.11 | 29.41 | 29.92 | 30.15 | 30.03 | 32.40 | 29.02 | 30.65 |
| % Fixed C | 57.63 | 56.67 | 56.96 | 55.46 | 56.08 | 53.34 | 56.89 | 55.16 |
| % Ash | 13.76 | 13.46 | 13.73 | 13.95 | 13.37 | 13.53 | 13.62 | 13.65 |
| % Ash (ASTM) | 12.95 | 13.44 | 14.06 | 14.32 | 13.78 | 13.61 | 13.60 | 13.79 |
| Particle Size | | | | | | | | |
| +60 | 0.18 | 0.50 | 0.24 | 0.32 | 0.20 | 0.45 | 0.21 | 0.42 |
| -60+80 | 1.59 | 1.50 | 3.48 | 3.48 | 4.01 | 0.45 | 3.03 | 1.81 |
| -80+100 | 7.80 | 4.55 | 22.46 | 11.58 | 24.08 | 1.22 | 18.11 | 5.78 |
| -100+140 | 26.86 | 11.71 | 36.24 | 21.71 | 45.62 | 1.72 | 36.24 | 11.71 |
| -140+200 | 26.57 | 13.16 | 13.63 | 10.51 | 6.66 | 3.05 | 15.62 | 8.91 |
| -200+325 | 23.14 | 26.40 | 17.24 | 24.66 | 14.06 | 39.86 | 18.15 | 30.31 |
| -325 | 13.86 | 41.81 | 6.63 | 27.57 | 5.29 | 53.36 | 8.59 | 40.91 |
| S, wt%, dry | | | | | | | | |
| Total | 3.23 | 3.22 | 3.43 | 3.36 | 3.29 | 3.22 | 3.32 | 3.27 |
| Pyritic | 1.60 | 1.46 | 1.70 | 1.64 | 1.76 | 1.35 | 1.69 | 1.48 |
| Sulfatic | 0.13 | 0.17 | 0.13 | 0.16 | 0.13 | 0.25 | 0.13 | 0.19 |
| Organic | 1.50 | 1.59 | 1.60 | 1.56 | 1.40 | 1.62 | 1.50 | 1.59 |
| | | M120,93 | | M120,92 | | M120,94 | | |
| Coal product | | | | | | | | |
| wt, g | | 111 | | 254 | | 138 | | 168 |
| Top | | 181 | | 486 | | 626 | 431 | |
| Bottom | | 292 | | 740 | | 764 | | |
| SubTotal | | 28 | | 68 | | 75 | | |
| Condensate | | 320 | | 808 | | 839 | | |
| Total | | | | | | | | |

(Table 6 continued)

Table 17. **Preparation of first stage product for ethanol temperature ramp test.**

| Run # | M114 | M114 | M114 |
|---|---|---|---|
| Period | Feed coal | 105 | 105 |
| Sample | | bottom | top |
| TGA Prox | | | |
| % Moist | 2.69 | 0.47 | 0.99 |
| % Vol Mat | 34.52 | 30.23 | 32.02 |
| % Fixed C | 50.68 | 56.56 | 54.22 |
| % Ash | 12.09 | 12.75 | 12.78 |
| % Ash (ASTM) | 12.16 | 12.79 | 13.47 |
| Particle Size | | | |
| +60 | 0.06 | 0.13 | 0.53 |
| -60+80 | 1.75 | 0.73 | 0.28 |
| -80+100 | 11.44 | 8.18 | 1.28 |
| -100+140 | 34.05 | 37.64 | 4.70 |
| -140+200 | 19.33 | 17.94 | 10.40 |
| -200+325 | 22.21 | 21.55 | 24.69 |
| -325 | 10.90 | 13.73 | 58.52 |
| S, wt%, dry | | | |
| Total | 3.38 | 3.19 | 3.11 |
| Pyritic | 1.44 | 1.34 | 1.22 |
| Sulfatic | 0.24 | 0.15 | 0.25 |
| Organic | 1.70 | 1.70 | 1.64 |

M114,105 was a 24-hour coal product production run.
The above data are from samples obtained at about the midpoint of the run.
Used feed gas of 25 percent CO, 75 percent N2
Reaction Temperature = 410°C (770°F)

Table 18. Temperature ramp test with ethanol.

| Run # | M114 | M114 | M121 | M121 | M121 | M121 | M121 | M121 | M121 | M121 | M121 | M121 | M121 | M121 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Period | Feedcoal | 105 | 109 | 109 | 109 | 109 | 109 | 109 | 109 | 109 | 109 | 109 | 109 | 109 |
| Sample | Ill #6 | CLP | 5:00 | 6:00 | 7:20 | 8:20 | 9:20 | 10:20 | 11:20 | 12:40 | 13:40 | 14:40 | 15:40 | 16:40 |
| Reaction Temp (°C)[a] | | | 425 | 440 | 460 | 460 | 460 | 475 | 490 | 510 | 510 | 510 | 525 | 540 |
| S, wt%, dry (MVTL) | | | | | | | | | | | | | | |
| Total | 3.31 | 3.14 | 3.12 | 2.92 | 2.91 | 3.00 | 2.87 | 2.83 | 3.02 | 2.89 | 3.04 | 3.18 | 3.06 | 3.06 |
| Pyritic | 1.30 | 1.08 | 1.01 | 0.99 | 0.90 | 0.94 | 0.87 | 0.90 | 0.99 | 0.85 | 1.06 | 1.12 | 0.82 | 0.85 |
| Sulfatic | 0.28 | 0.15 | 0.14 | 0.14 | 0.12 | 0.14 | 0.14 | 0.13 | 0.12 | 0.12 | 0.15 | 0.14 | 0.13 | 0.11 |
| Organic | 1.73 | 1.91 | 1.97 | 1.79 | 1.89 | 1.92 | 1.86 | 1.80 | 1.91 | 2.01 | 1.83 | 1.92 | 2.10 | 2.10 |
| S, wt%, dry (EERC) | | | | | | | | | | | | | | |
| Total | 2.76 | 2.45 | 2.54 | 2.54 | 2.33 | 2.48 | 2.39 | 2.48 | 2.59 | 2.57 | 2.45 | 2.57 | 2.64 | 2.59 |
| EERC/MVTL | 0.83 | 0.78 | 0.81 | 0.87 | 0.80 | 0.83 | 0.83 | 0.88 | 0.86 | 0.86 | 0.81 | 0.81 | 0.86 | 0.85 |
| CLP wt, g | | | | | | | | | | | | | | |
| Top | | | 80 | 62 | 65 | 9 | 9 | 15 | 1 | 400 | 32 | 43 | 179 | 7 |
| Bottom | | | 295 | 291 | 384 | 283 | 294 | 101 | 258 | 122 | 33 | 140 | 19 | 56 |
| Subtotal | | | 365 | 353 | 449 | 282 | 303 | 116 | 259 | 522 | 65 | 183 | 198 | 63 |
| Condensate | | | | | 478 | | 302 | | | 540 | | 359 | 237 | |
| Total | | | 365 | 353 | 927 | 292 | 605 | 116 | 259 | 1062 | 65 | 542 | 435 | 63 |

[a] - Conversion of temperatures are as follows: 425 °C=797 °F, 440 °C=824 °F, 460 °C=860 °F, 475 °C=887 °F, 490 °C=914 °F, 510 °C=950 °F, 525 °C=977 °F, and 540 °C=1004 °F.

The above data are from "bottom" samples only. Feed Gas -- 8 percent ethanol/92 percent nitrogen. Coal Feed Rate -- 0.5-kg/hr. Operating conditions described in "Analysis of Ethanol. Ramping Test Feedstocks and Products." Condensate weights are cumulative and include condensate produced during previous sampling periods for which no weights are given. CLP -- coal-like product. MVTL -- Analyzed at Minnesota Valley Testing Labs. EERC -- Analyzed at the Energy and Environmental Research Center. EERC/MVTL -- Ratio of sulfur analyses from the two labs.

SEC curves of pyridine extracts are always the most variable and the UNDEERC samples were no exception. It was deemed significant that the 100 percent CO produced a pyridine extract with a very small detector response for the same concentration of solution. This usually means a low content of heteroatoms - an explanation consistent with the highly reducing reaction conditions.

In general, CO seemed to broaden the molecular size distributions, mainly by increasing the amount of material at lower molecular size. In terms of burning characteristics of the coal products, for most desulfurization reaction conditions examined, the loss in total extractable material may be partly offset by a shift from polar to non-polar material.

## Ethanol Temperature Ramp Study

To study the effects of ethanol on coal product desulfurization, an "ethanol temperature ramping test" was performed, in which coal product produced in the continuous fluid bed reactor (CFBR) under an atmosphere of approximately 25 percent carbon monoxide/75 percent nitrogen at 410°C (770°F), was reinjected into the CFBR under an atmosphere of approximately 8 percent ethanol/92 percent nitrogen. The coal product used for this study was produced during Test M114; analytical data for this coal product is shown in Table 17. Initial temperature in the CFBR was 410°C (770°F), and temperature was increased at a rate of 15°C/hour (59°F/hr). Also, the reaction temperature was held constant for 2 hours at 460° and 510°C (860° and 950°F). When the reactor plugged at about 525°C (977°F), the test was terminated.

As shown in Table 18, the greatest sulfur content reductions under ethanol occurred at reaction temperatures of 460° and 475°C (860° and 887°F); samples obtained at these temperatures had total sulfur contents of 2.87 and 2.83 weight percent, respectively, compared to the feed coal product sulfur content of 3.14. As reaction temperature increased, pyritic sulfur content decreased (except for an increase at 510°C/950°F), while organic sulfur content initially decreased, and then increased at higher temperatures.

To investigate how CO and ethanol affected the mineralogy of the original coal, proximate, ultimate, X-ray fluorescence (XRF), and X-ray diffraction (XRD) analyses were performed on the feed coal, the coal product produced under carbon monoxide, and the coal product produced under ethanol. The proximate, ultimate, and XRD analyses were performed on samples of as-received coal and coal product, and the XRF analyses were performed on ash samples made from the coal and coal products. An important consideration when examining the XRF data (shown in Table 19) was that the ASTM ashing procedure used to prepare the ashes involves heating the coal/coal product to 750°C (1382°F) under flowing air. This oxidizes essentially all minerals and vaporizes much of the sulfur, which was why the sulfur contents shown in the XRF analyses are low, and why no information was provided regarding the mineralogical associations of iron and calcium.

The XRD analyses (Figure 6) were performed on the raw coal and coal products, and show the presence of both pyrite and pyrrhotite in the coal products, and only pyrite in the coal. With the use of relative quantitation, pyrrhotite-to-pyrite ratios were calculated to compare the amounts of the two minerals in the coal products. For the coal product made under carbon monoxide, the pyrrhotite-to-pyrite ratio was 0.35; for the coal product made under ethanol (using the carbon monoxide coal product as feed) this ratio was 0.79. These results show that pyrrhotite was formed during coal product production under carbon monoxide, and more was formed during coal product production under ethanol.

Table 19. **XRF Data.**

| | Normalized wt% of ash | | |
|---|---|---|---|
| Oxide | Feed Coal | CO-Treated | CO- and Ethanol-Treated |
| $SiO_2$ | 45.4 | 51.9 | 47.6 |
| $Al_2O_3$ | 20.8 | 21.7 | 21.4 |
| $Fe_2O_3$ | 22.5 | 18.4 | 20.6 |
| $TiO_2$ | 1.1 | 0.8 | 1.1 |
| CaO | 2.9 | 1.9 | 2.5 |
| MgO | 1.5 | 1.3 | 1.4 |
| $K_2O$ | 3.4 | 1.7 | 3.3 |
| $SO_3$ | 2.4 | 2.3 | 2.1 |

## Ethanol Concentration Variation

Another study was performed in which coal product made under a mixture of 25 percent CO/75 percent nitrogen at 360°C (680°F) was reacted under two different ethanol/nitrogen mixtures (10 percent ethanol/90 percent nitrogen and 25 percent ethanol/75 percent nitrogen). Also, reaction pressure was increased during both stages of the testing, from 450 to 790 kPa (50-100 psig). During the CO stage, coal was fed at a rate of 2-kg/hr to give a residence time of 30 minutes, and during the ethanol stage, coal product was fed at a rate of 0.5-kg/hr to give a residence time of 4 hours. In addition to these two-stage tests, a separate single-stage test was performed in which coal was reacted under a mixture of 7 percent ethanol/25 percent CO/68 percent nitrogen. The reaction temperature was 410°C (770°F) and the coal feed rate was 0.5-kg/hr to give a residence time of 4 hours.

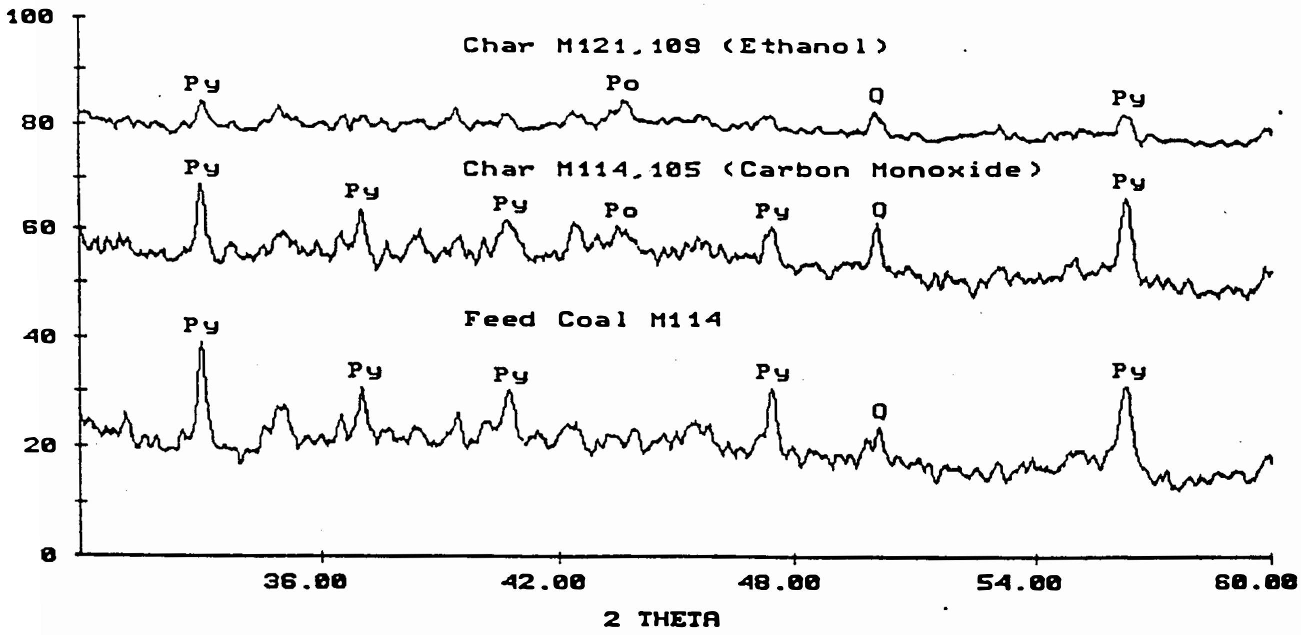


Figure 6. XRD of samples M114, M114,105 (CO), and M121,109 (EtOH)

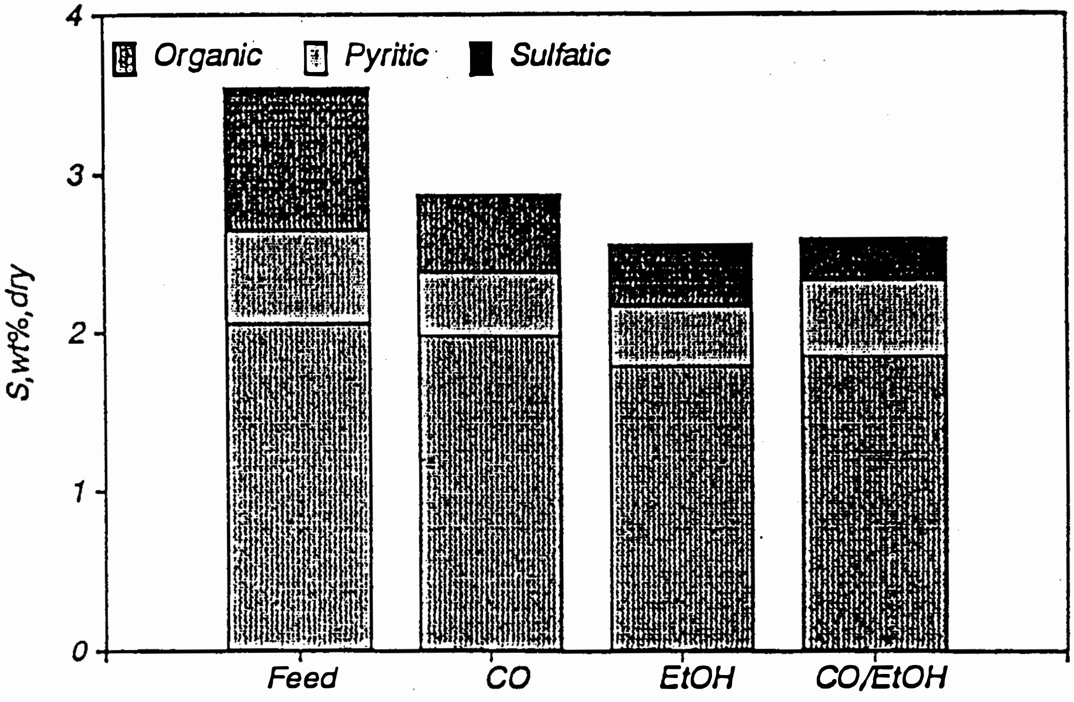


Figure 7. One/two stage comparison, 410°C (770°F).

Table 20. Ethanol concentration variations -- preliminary study.

| | Ill #6 Feed coal 20x60-mesh | M134,181 CO/EtOH | M131,180 CO | M132,180 CO Sample 1 | M132,180 CO Sample 2 | M135,182 CLP Feed EtOH 5:30 | M135,182 CLP Feed EtOH 6:30 | M135,183 CLP Feed EtOH Pre-run |
|---|---|---|---|---|---|---|---|---|
| mf S, EERC | 2.95 | 2.61 | 2.37 | 2.64 | 2.63 | 2.43 | 2.42 | 2.33 |
| mf S, MVTL | 3.55 | 2.60 | 2.62 | 2.87 | 3.02 | 2.64 | 2.56 | 2.53 |
| Organic | 2.06 | 1.85 | 1.82 | 1.98 | 1.98 | 1.91 | 1.79 | 1.89 |
| Pyritic | 0.59 | 0.48 | 0.38 | 0.40 | 0.49 | 0.35 | 0.38 | 0.32 |
| Sulfatic | 0.90 | 0.27 | 0.42 | 0.49 | 0.55 | 0.38 | 0.39 | 0.31 |
| Moisture | 4.74 | 0.57 | 0.33 | 0.42 | 0.43 | 0.52 | 0.54 | 0.71 |
| Volatiles | 33.03 | 35.23 | 32.37 | 32.83 | 32.90 | 33.15 | 32.97 | 33.71 |
| Fixed C | 49.16 | 54.37 | 54.46 | 53.28 | 51.42 | 55.01 | 54.64 | 54.26 |
| Ash | 13.07 | 9.83 | 12.86 | 13.46 | 15.25 | 11.33 | 11.86 | 11.33 |

M134,181 -- 7 percent EtOH/25 percent CO/68 percent nitrogen, 0.5 ft/s fluidization velocity, 790 kPa/100 psig, 410 °C/770 °F, 0.5-kg/hr coal feed rate for residence time of 4 hours

M131+132,180 -- 25 percent CO/75 percent nitrogen, 0.5 ft/s fluidization velocity, 790 kPa/100 psig, 360 °C/680 °F, 2-kg/hr coal feed rate for residence time of 30 minutes

M135,182 -- 10 percent EtOH/90 percent nitrogen, 0.5 ft/s fluidization velocity, 790 kPa/100 psig, 410 °C/770 °F, 0.5-kg/hr coal-like product (M131,180) feed rate for a residence time of 4 hours

M135,183 -- 25 percent EtOH/75 percent nitrogen, 0.5 ft/s fluidization velocity, 790 kPa/100 psig, 410 °C/770 °F, 0.5-kg/hr coal-like product (M131,180) feed rate for a residence time of 4 hours

The test results (Table 20) show that similar sulfur content reductions were achievable under all of the conditions tested. No trend of decreasing sulfur content with increasing ethanol concentration was evident. Figure 7 compares results from the single-stage process with those from the two-stage process, and shows that while both processes yield products with similar total and organic sulfur contents, fairly significant differences are evident in pyritic and sulfatic sulfur contents. A noteworthy data point in Table 20 is the sulfatic sulfur content of the feed coal, which, at 0.90 weight percent, is high. In previous tests, sulfatic sulfur content in the feed coal (with the exception of the coal used in Test M116, which may have been partially oxidized) ranged from 0.14 to 0.40 weight percent, and averaged about 0.25 weight percent.

**Table 21.** **Ethanol concentration variations -- second study.**

| | Ill #6<br>Feed Coal<br>6-14-90<br>-20-mesh | M146,194<br>EtOH + CO<br>6-20-90 | M141,191<br>CO<br>6-14-90 | M144,192<br>EtOH<br>6-15-90<br>Sample 1 | M144,192<br>EtOH<br>6-15-90<br>Sample 2 |
|---|---|---|---|---|---|
| mf S, EERC | 3.10 | 2.41 | 2.60 | 2.86 | 2.86 |
| mf S, MVTL | 3.13 | | 2.75 | 3.14 | 2.87 |
| Organic | 1.97 | | 1.93 | 2.22 | 1.89 |
| Pyritic | 0.61 | | 0.41 | 0.49 | 0.50 |
| Sulfatic | 0.55 | | 0.41 | 0.43 | 0.48 |
| Moisture | 4.17 | 0.33 | 0.19 | 0.25 | 0.46 |
| Volatiles | 34.33 | 27.57 | 32.50 | 31.25 | 31.62 |
| Fixed C | 49.57 | 59.29 | 55.91 | 55.42 | 56.43 |
| Ash | 11.74 | 12.85 | 11.21 | 12.84 | 11.51 |
| Mesh size | | | | | |
| +20 | 0.08 | | | | |
| -20+40 | 37.64 | | | | |
| -40+60 | 28.15 | | | | |
| -60+100 | 14.88 | | | | |
| -100+230 | 12.58 | | | | |
| -230+325 | 2.32 | | | | |
| -325 | 4.26 | | | | |

1. Undried feed coal was sealed in 5-gallon pails with dry ice prior to reaction
2. M146,194 -- 15 percent EtOH/50 percent CO/35 percent nitrogen, 0.65 ft/s fluidization velocity, 420°C/788°F, 450 kPa/50 psig, 2-kg/hr coal feed for residence time of 30 minutes, 1.8-kg/hr coal product collection rate
3. M141,191 -- 50 percent CO/50 percent nitrogen, 0.5 ft/s fluidization velocity, 360°C/680°F, 450 kPa/50 psig, 2-kg/hr coal feed for residence time of 30 minutes, 2-kg/hr coal product collection rate
4. M144,192 -- 15 percent EtOH/85 percent nitrogen, 0.5 ft/s fluidization velocity, 420°C/788°F, 450 kPa/50 psig, 2-kg/hr coal product (M141,191) feed for residence time of 30 minutes, 2.4-kg/hr coal product collection rate

Another series of tests was performed to investigate the effect of ethanol concentration and compare a single-stage reaction with a two-stage process. The fluidization gas used to prepare the first-stage coal product was a mixture of 50 percent CO/50 percent nitrogen, the reaction temperature was 360°, and the reaction pressure was 450 kPa (50 psig). The second-stage fluidization gas was a mixture of 15 percent ethanol/85 percent nitrogen, and the reaction temperature and pressure were 420°C (788°F) and 450 kPa (50 psig), respectively. The single-stage process was performed using a fluidization gas of 15 percent ethanol/50 percent CO/35 percent nitrogen, and a reaction temperature and pressure of 420°C (788°F) and 450 kPa (50 psig), respectively. All tests used a coal/coal product feed rate of 2-kg/hr to give a residence time of 30 minutes. The test results (Table 21) show that the lowest sulfur content coal product may have been the one produced with the simultaneous CO/Ethanol treatment. Unfortunately, no sulfur forms data are available for this coal product and so this conclusion is based only on 1 total sulfur analysis.

**Table 22.** **Test with low sulfur coal.**

| | New Ill #6 Feed Coal -20 mesh | *CO* M153 | *Ethanol* M155 |
|---|---|---|---|
| Moisture | 9.02 | | |
| Volatiles | | | |
| Fixed C | | | |
| Ash | | | |
| S, wt%, dry EERC | 0.96 | 0.75 | 0.84 |
| MVTL | 1.11 | 0.97 | 1.04 |
| Pyritic | 0.36 | 0.20 | 0.27 |
| Sulfatic | 0.04 | 0.01 | 0.01 |
| Organic | 0.71 | 0.76 | 0.76 |

M153 product was used as feed coal product for M155

M153 -- 360 C reaction temp, 450 kPa/50 psig pressure, 25 percent CO/75 percent N2 fluidization gas, 1-kg/hr coal feed rate, 0.40 ft/s fluidization velocity

M155 -- 400°C/752°F reaction temp, 450 kPa/50 psig pressure, 15 percent ethanol/85 percent N2 fluidization gas, 1-kg/hr coal product feed, 0.40 ft/s fluidization velocity

## Low Sulfur Coal Test

A test series was performed using a low sulfur coal (1.11 weight percent, moisture-free basis, as determined at UNDEERC) obtained from the Illinois State Geological Survey Coal Bank. The coal was known as IBC-109. The results of the two-stage test -- the first stage done under 25 percent CO/75 percent nitrogen, and the second under 15 percent ethanol/85 percent nitrogen -- are shown in Table 22. No significant change in the sulfur content is observed.

## Temperature Effects Under 100 percent CO

Several tests were performed under a fluidization gas of 100 percent CO, using -325-mesh coal. Reaction pressure was 450 kPa (50 psig), and reaction temperatures were 300°, 325°, 350°, and 375°C (572°, 617°, 662°, and 707°F). The results (Table 23 and Figure 8) showed trends of decreasing total, pyritic, and sulfatic sulfur content and possibly increasing organic sulfur content with increasing temperature. Also, Figures 9 and 10 showed a significant increase in the OCS content of the product gas stream and a small decrease in the volatile matter content of the product coal, respectively, with increasing temperature. It was desired to perform tests at higher temperatures, but reactor plugging due to the small particle-size feed coal necessitated shutting down the reactor after the 375°C (707°F) test.

Table 23. Temperature effects, 100 percent CO.

| | Ill #6 Feed Coal -325 mesh | M161 | M162 | M163 | M164 |
|---|---|---|---|---|---|
| Moisture | 3.53 | 0.86 | 0.88 | 1.00 | 1.03 |
| Volatiles | 34.42 | 35.71 | 34.70 | 33.16 | 28.27 |
| Fixed C | 49.71 | 50.98 | 52.34 | 53.30 | 56.55 |
| Ash | 12.33 | 12.94 | 12.07 | 12.54 | 14.06 |
| S, wt%, dry | | | | | |
| EERC | 2.80 | 2.95 | 2.64 | 2.62 | 2.49 |
| MVTL | 3.29 | 2.99 | 2.84 | 2.66 | 2.50 |
| Pyritic | 1.12 | 1.06 | 0.85 | 0.56 | 0.37 |
| Sulfatic | 0.39 | 0.29 | 0.25 | 0.24 | 0.23 |
| Organic | 1.77 | 1.64 | 1.74 | 1.86 | 1.90 |
| Prod. Gas | | | | | |
| H2 | | 0.06 | 0.06 | 0.09 | 0.13 |
| CO2 | | 0.11 | 0.12 | 0.06 | 0.19 |
| OCS | | 0.04 | 0.05 | 0.07 | 0.12 |
| O2/Ar | | 0.28 | 0.23 | 0.11 | 0.37 |
| N2 | | 1.64 | 3.10 | 5.05 | 10.26 |
| CO | | 97.86 | 96.43 | 94.62 | 88.94 |

Tests M161-164: Feed coal: -325 mesh Ill #6; Coal feed rate: 0.5-kg/hr; Fluidization gas: 100 percent CO; Pressure -- 450 kPa/50 psig
M161 -- 300°C/572°F reaction temp, 0.12 ft/s fluidization velocity
M162 -- 325°C/617°F reaction temp, 0.18 ft/s fluidization velocity
M163 -- 350°C/662°F reaction temp, 0.18 ft/s fluidization velocity
M164 -- 375°C/707°F reaction temp, 0.18 ft/s fluidization velocity

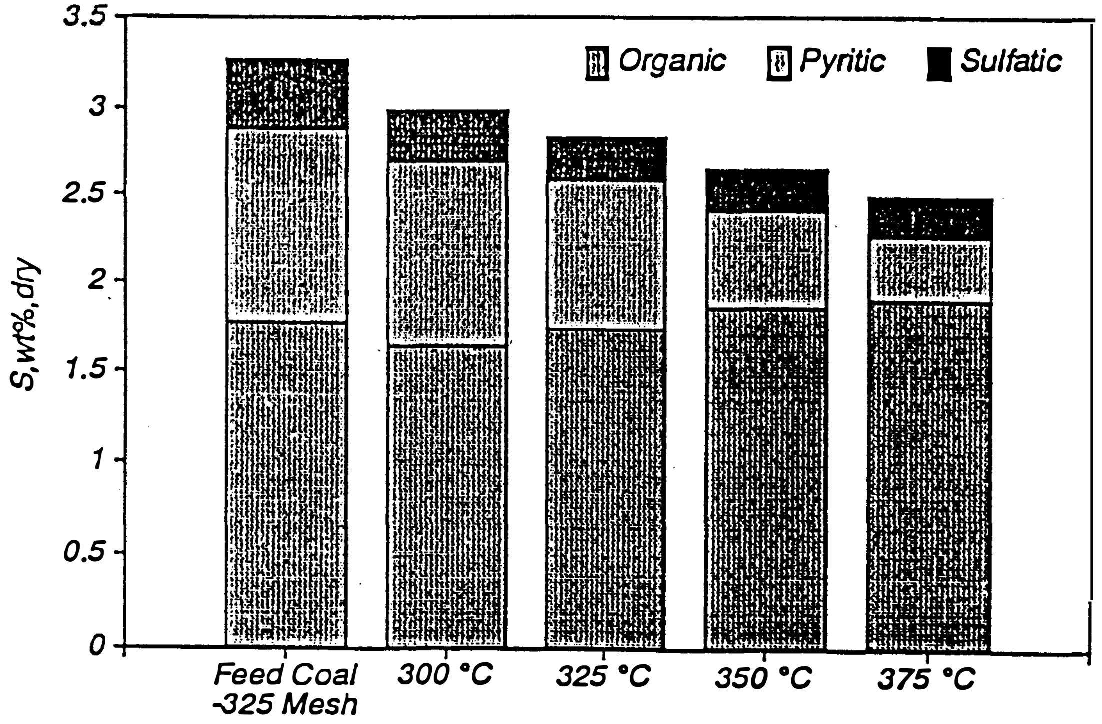


Figure 8. Temperature effects, 100 percent CO.

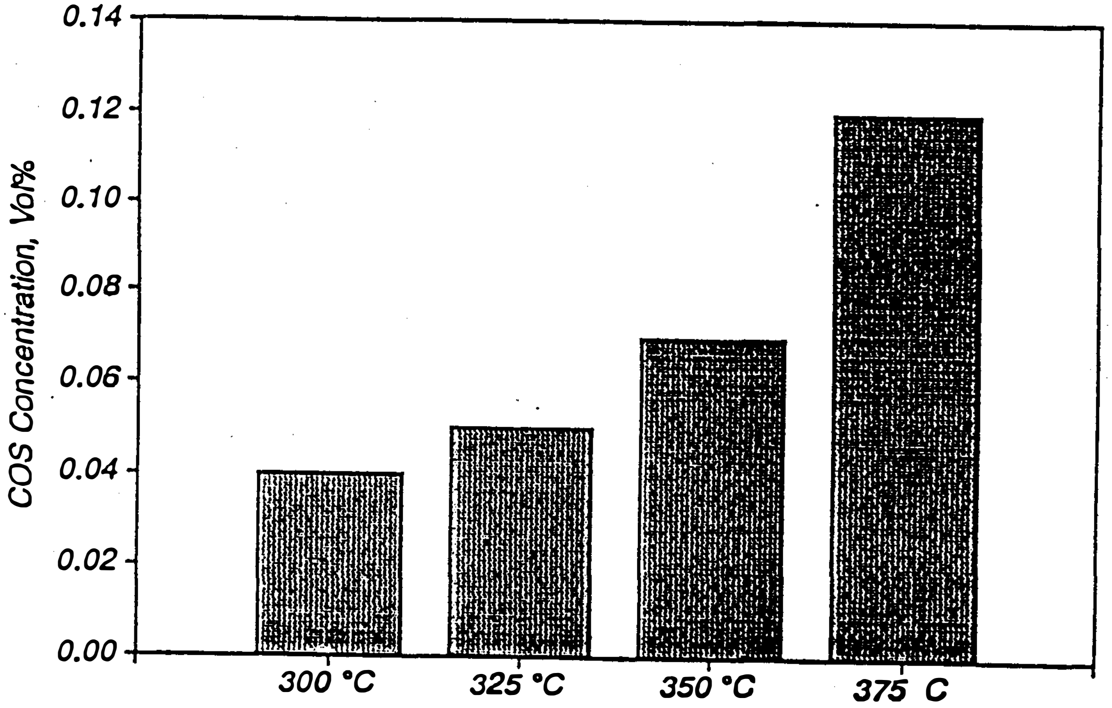


Figure 9. OCS with temperature.

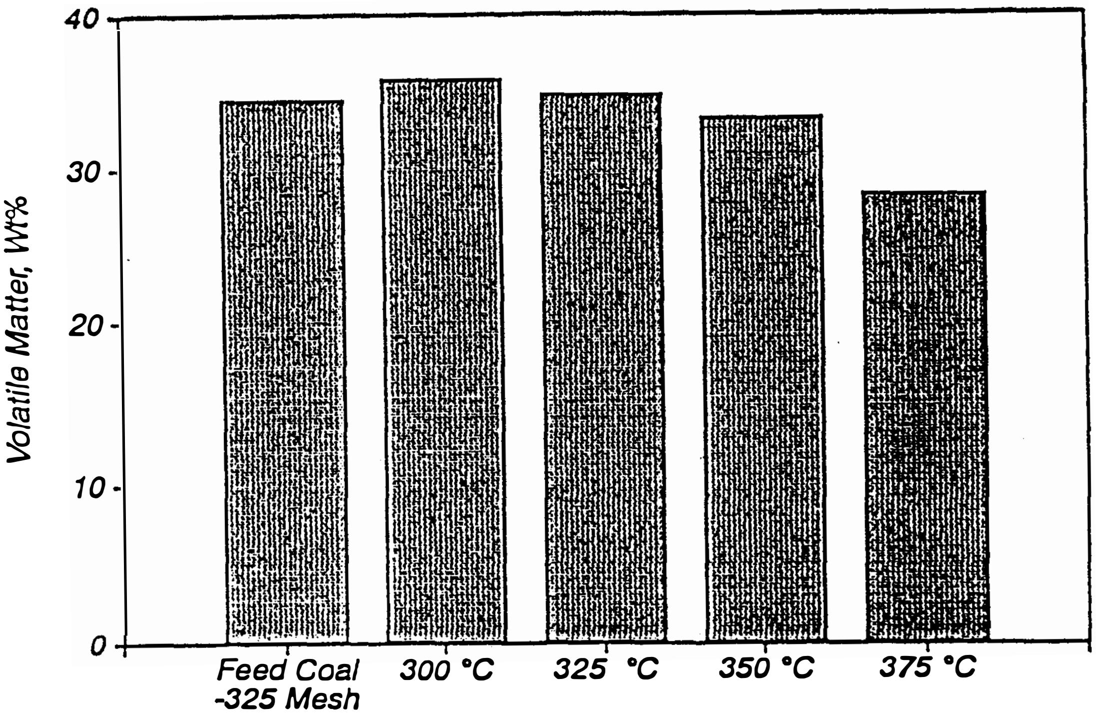


Figure 10. **Volatile Temperature effects, 100 percent CO.**

**Mössbauer Analysis Results**

Mössbauer analyses were performed by three different labs on three series of coal products. The results (Table 24) showed that the highest percentages of iron associated as pyrrhotite (50 and 62 percent) were found in coal products made under an atmosphere of 35 percent CO/65 percent nitrogen, at temperatures of 450 and 480°C (896°F), respectively. It should be noted that the feed coal used to produce these coal products had an abnormally high ash content of 20.75 weight percent (see Table 12, p. 40). Also, since analyses were performed by three labs, all of which presented data in a different form, comparison of results obtained at different labs may be inappropriate.

**Coal Devolatilization**

During thermal processing, coal undergoes devolatilization. To obtain information concerning the rate of devolatilization and the effects of rapid and slow heat-up rates, the coals used in Vycor tube tests and the CFU tests (discussed in the next sections) were analyzed using the thermogravimetric analysis (TGA) equipment. The weight loss with time observed when IBC-106 coal (9.5 wt percent moisture) followed by rapid heat-up to 350°, 375°, 400°, and 415°C (779°F) in separate TGA tests are shown in Figure 11. The data in Figure 12 includes an intermediate stage where moisture was first removed by heating to 121°C (250°F), and then rapidly heated to 375°, 400°, and 415°C (707°, 752°, and 779°F). The rapid heat-up data can be contrasted with the slow heat-up data for the same coal, shown in Figure 13. In the slow heat-up test, the weight loss was observed while staging the temperature in 20°C (68°F) increments of 8-10 minutes from 216° to 516°C (420°-960°F).

**Table 24.** **Mössbauer Analysis Results.**

| Reaction Sample[1] | Temp, °C/°F | Sulfur Gas[2] | wt%, mf | Fe Forms, % total Fe | | |
|---|---|---|---|---|---|---|
| | | | | $FeS_2$ | $Fe_{1-x}S$ | $FeSO_4$ |
| Feed Coal[3] | | | 4.55 | | | |
| M75,42 | 350/662 | 100% CO | 3.98 | 57 | 38 | 5 |
| M75,43 | 350/662 | 25% CO | 3.83 | 77 | 14 | 9 |
| M75,44 | 375/707 | 25% CO | 3.70 | 67 | 23 | 10 |
| M76,45[4] | 350/662 | 25% CO | 3.33 | 62 | 27 | 11 |
| Feed Coal | | | 5.01 | | | |
| M116 | 420/788 | 35% CO | 3.65 | 40 | 25 | 23 |
| M116 | 450/842 | 35% CO | 3.78 | 24 | 50 | 18 |
| M116 | 480/896 | 35% CO | 4.35 | 12 | 62 | 18 |
| M116 | 510/950 | 35% CO | 3.30 | 35 | 35 | 19 |
| Feed Coal | | | 3.38 | | | |
| M117,102 | 410/770 | 10% CO | 3.16 | 30 | 38 | 13 |
| M118,100 | 410/770 | 3% CO | 3.11 | 39 | 28 | 12 |
| M119,95-97 | 410/770 | 4% CO | 3.26 | 45 | 24 | 9 |
| M120,92 | 410/770 | 0% CO | 3.43 | 48 | 18 | 12 |
| Feed Coal | | | 3.38 | 60 | 9 | 7 |
| M114,105 | 410/770 | 25% CO | 3.19 | 37 | 30 | 15 |
| Feed Coal | | | 3.13 | | | |
| M146,194 | 420/788 | 50% CO<br>15% EtOH | 2.41 | 53 | 29 | 24 |
| M141,191 | 360/680 | 50% CO | 2.75 | 65 | 0 | 35 |
| M144,192 | 420/788 | 15% EtOH | 2.87 | 65 | 0 | 34 |

[1] Samples M75-76, M114-120 and feed coal for M114 analyzed by Dr. Peter DeBrunner, U. of Ill., Urbana-Champaign; Samples M141-146 analyzed by Mössbauer Spectroscopy Consultants, Burlington, MA; hence, data reduction techniques may vary

[2] All gas mixtures made up to 100 percent with nitrogen

[3] Each feed coal analysis refers to coal used to produce each series of coal products

[4] Coal feed rate was 0.25-kg/hr, while coal feed rate for M75,43 was 0.5-kg/hr

Wet coal initially rapidly devolatilized (losing mainly moisture at the lower temperature studied) for the first 10 to 20 minutes and then devolatilized slowly. Since the devolatilization was not due to any one species but a mixture of the loss of molecules either present initially in the coal or formed due to thermal fragmentation, it was unlikely to fit a simple decomposition equation. However, the moist coal data (Figure 11) did reasonably fit a two-term decomposition equation:

$$\text{wt\% Coal product at time (t)} = 100 - C_1(1-e^{-k1t}) - C_2(1-e^{-k2t})$$

where k1 equals 0.260 $min^{-1}$, k2 equals 0.0152 $min^{-1}$, and $C_1$ and $C_2$ vary according to the temperature of devolatilization:

| T°C/T°F | $C_1$ | $C_2$ |
|---|---|---|
| 350/662 | 11.9 | 4.0 |
| 375/707 | 14.0 | 8.9 |
| 400/752 | 15.5 | 8.9 |
| 415/779 | 22.5 | 8.9 |

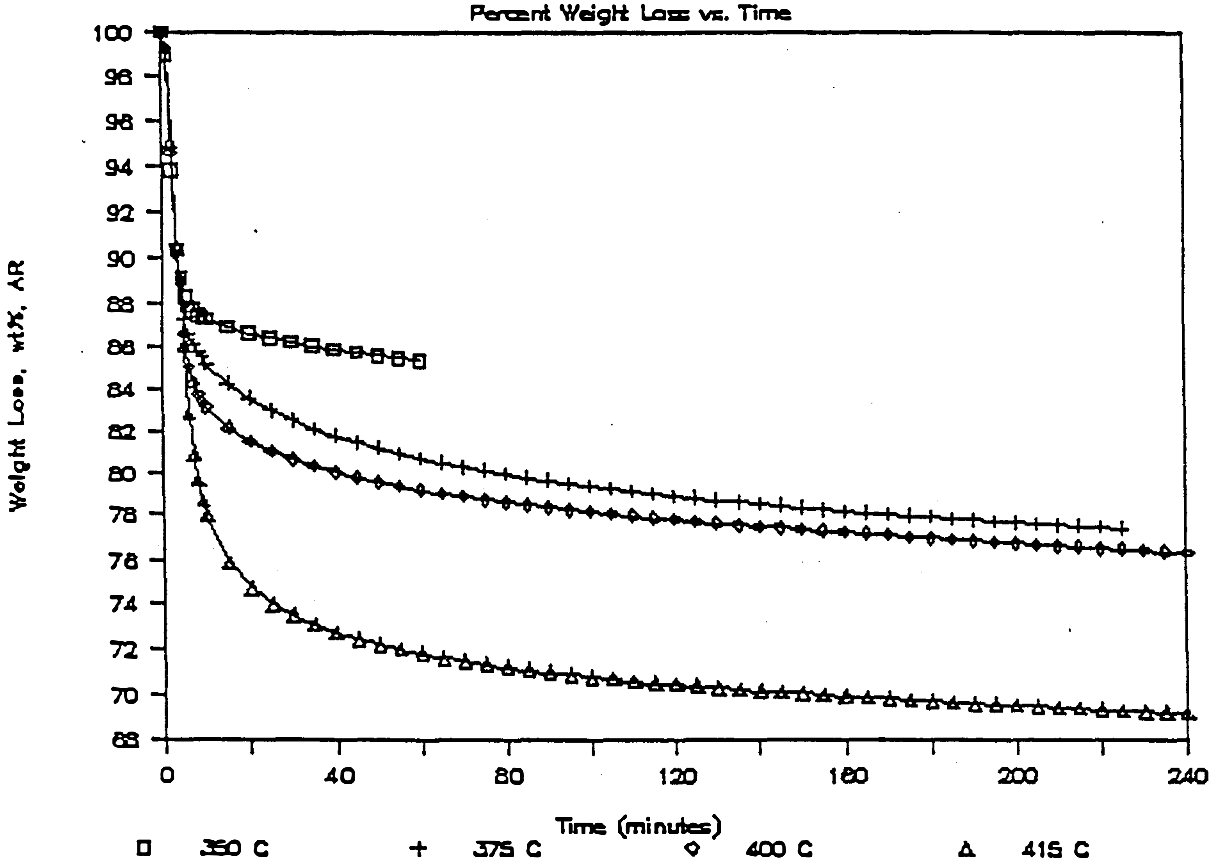


Figure 11. **Devolatilization at four temperatures.**

The high rate constant kl and variable $C_1$ value are important during the initial stages of devolatilization (initial 10 minutes) while the lower rate constant was important at longer reaction times. Devolatilization at the slow rate continues to occur even after 4 hours at temperature, indicating that it will be a factor in any thermal processing of the coal. The tests with coal that was dried prior to the application of higher temperatures (Figure 12) yielded similar results: an initial rapid devolatilization followed by a slow bleed. The staged data (Figure 13), where a higher final temperature was tested, indicates that even at 516°C (960°F) slow devolatilization occurs. The data indicates that the fastest rate of devolatilization in staged heating was at 415°C (779°F) after which prior

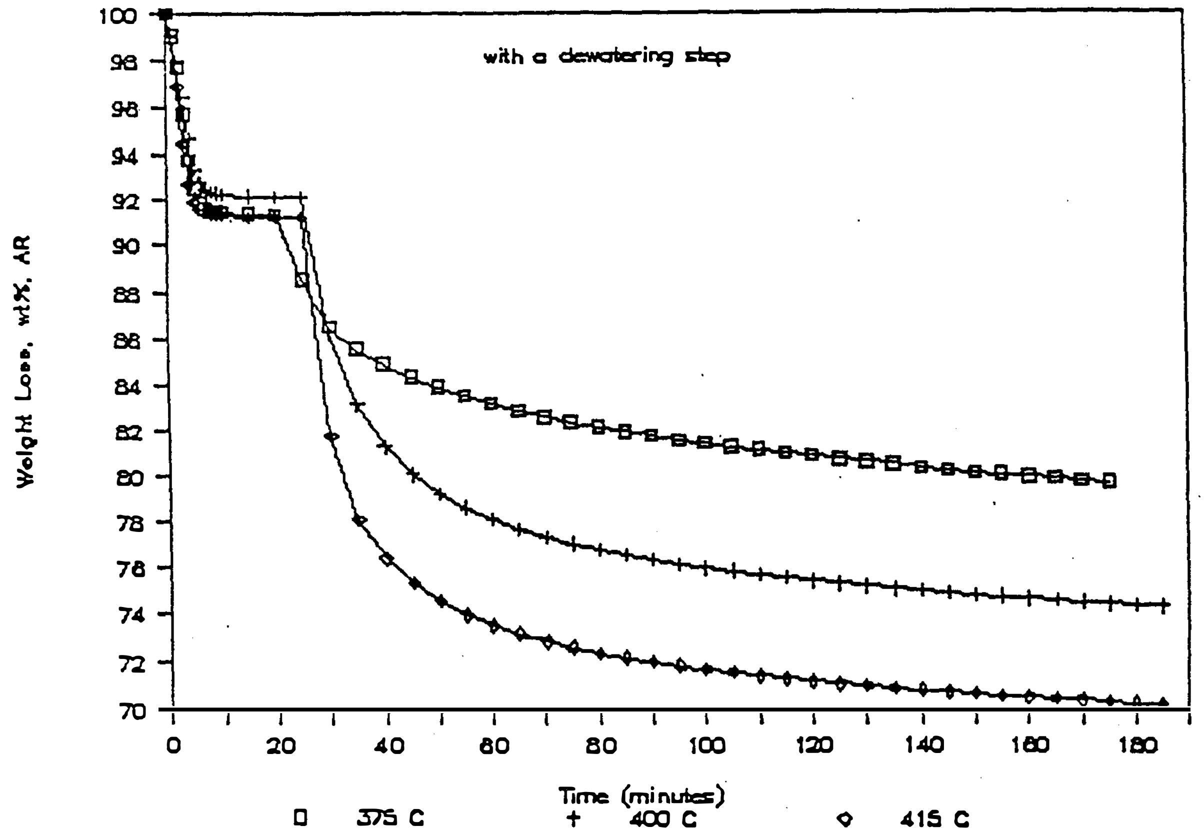


Figure 12. Devolatilization of IBC-105 coal.

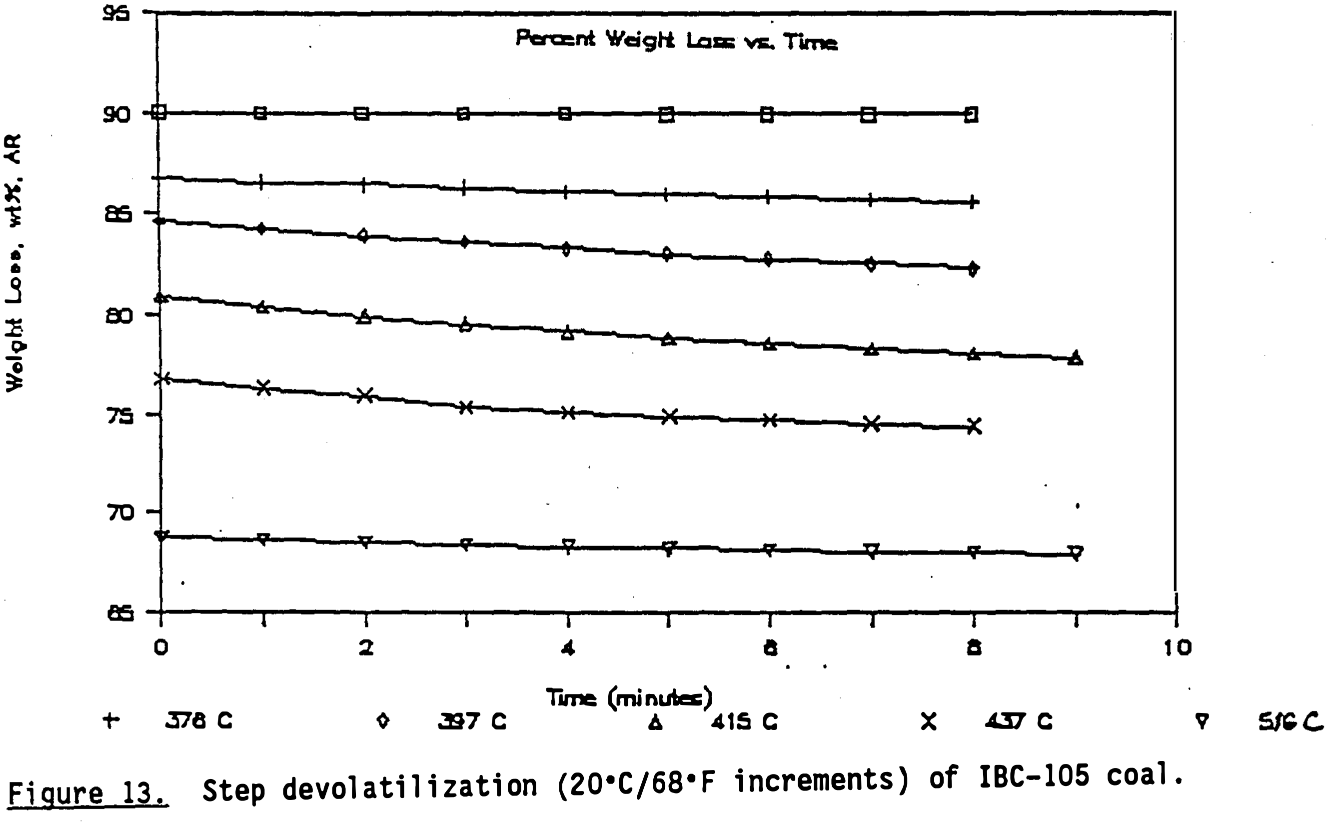


Figure 13. Step devolatilization (20•C/68•F increments) of IBC-105 coal.

volatile matter loss resulted in observing a lower rate. The AMAX Illinois #6 coal used in the CFU tests exhibited similar trends as the IBC-106 coal (Figure 14), but contained less total volatile matter.

## Lab-bench Scale Tests

Tests were performed using a static bed of coal in a Vycor glass tube in order to define:

The temperature-time relationships of the reactions.
The effect of slow heat-up.
Back reactions.
The effect of gas flow rate.

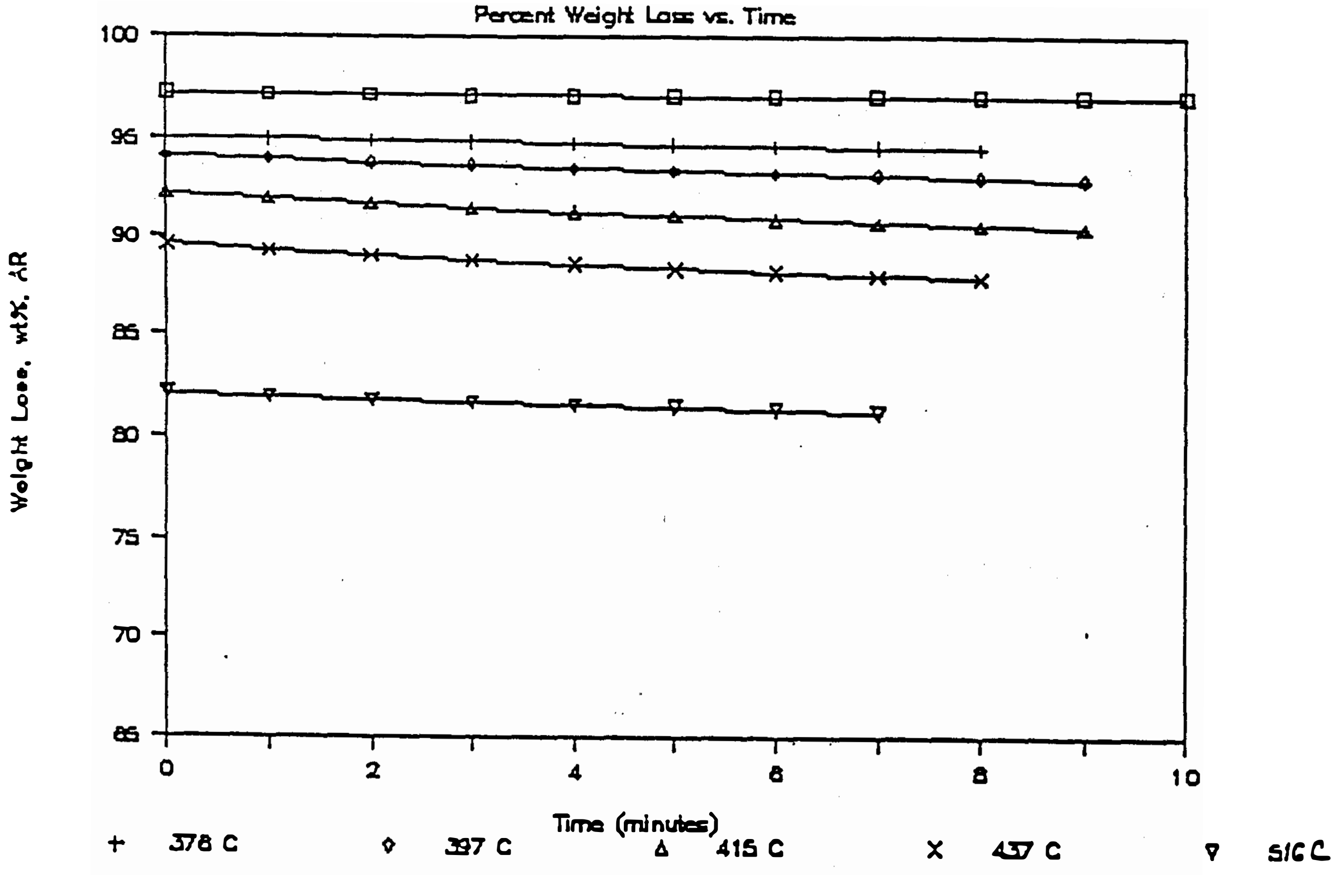


Figure 14. Step devolatilization of **AMAX** #6 coal.

The scope of the tests were limited to providing information concerning the operation of a continuous process unit (CPU); i.e., if a reaction was complete in 1 hour, a 3-hour residence time in a CPU would not be advisable. Test conditions were selected to enable observing changes of the OCS and $H_2S$ concentrations in the output gas stream as temperature and residence time were varied: 35 grams of AR coal (IBC-106), 35 mL/min (at room temperature) of CO gas (enough to react with all the sulfur in the coal in about 20 min), and 0.1 mL/min of absolute ethanol (again, enough to react with all the coal sulfur in about 20 minutes).

**Description of Bench-Scale Glass Tube Reactor System:** The bench-scale glass reactor system consisted of a 39-inch-long Vycor tube contained in a three-section Lindberg combustion tube furnace, and a Varian 3700 gas chromatograph. The three movable furnace sections were 4, 12, and 8 inches long. Coal was packed in the end of the Vycor tube and heated by the 8-inch furnace section (located at the exit end of the combustion tube). The 12- and 4-inch sections were used to preheat gas and liquid reactants prior to contact with the coal bed.

The Vycor combustion tube had an initial outside diameter (O.D.) of 2.1cm and tapered to a 7-mm O.D., with a 2-inch-long tip. Eight inches of the tapered end was packed with 35 to 40 grams (on an "as received" basis) of -60- mesh coal. A thermocouple was inserted into the coal from the tapered end of the Vycor tube and placed in the center of the coal bed. A cold trap containing dry ice and isopropanol was placed at the outlet end of the Vycor tube to condense volatiles out of the gas stream.

The gas stream passed through a six-port Teflon valve used to sample the gas stream for analysis by gas chromatography (GC). A 0.5-mL sample loop was used to inject the gas into the GC column. The Varian Model 3700 gas chromatograph was equipped with a flame photometer detector used to analyze the gas stream for carbonyl sulfide (OCS) and hydrogen sulfide ($H_2S$). Separation was achieved with an 8-ft-long, 1/8-inch O.D. Teflon column packed with Chromosil 310 (Supelco), maintained at a temperature of 50°C (122°F). Helium was used as the carrier gas. The detector output was handled by a Hewlett-Packard 3380A integrator.

Absolute ethanol was introduced through an Altex Model 110A liquid chromatography pump at a rate of 0.1 mL/min. All tubing connections and surfaces encountered by the gas stream after the coal bed were either glass, Teflon, Tygon, or rubber, to insure that the gas stream never contacted a metal surface that could adsorb or react with any of the sulfur gases produced.

For the tests, an 8-inch bed of coal was packed in the Vycor combustion tube with the aid of a vibrator. The packed tube was placed in the tube furnace and a carbon monoxide (CO) gas flow rate equal to 1.0 mL/min/g coal was established and allowed to purge for 30 minutes prior to heating. When the desired testing temperature was achieved, a 0.5-mL sample of the gas stream was injected directly into the GC column every 5 minutes for analysis. The chromatographic program was designed to analyze for OCS and $H_2S$ in less than 2 minutes. The temperature of the coal bed was monitored and controlled throughout the experiment.

VARIAN MODEL 3700 GAS CHROMATOGRAPH WITH TEFLON TUBING

| | |
|---|---|
| CARRIER GAS: | Helium |
| INJECTION PORT: | 6-port valve with sample loop; 0.5-mL sample injected every 5 minutes. |
| COLUMN: | Chromosil 310, 8 feet long, operated at 50°C (122°F) |
| DETECTOR: | Flame photometric (Sulfur specific) |
| RECORDER: | HP 3380A |

**Test Series:** A summary of the tests made to date in the tube reactor are as follows:

Test A-02: Slow-heat up with steps at 215°, 239°, and 262°C (419°, 462°, 504°F). The concentration of OCS in the off gas decreased if the temperature was not increased.

Test A-03: Slow heat-up to 403°C (757°F) over 500 minutes. The presence of OCS was detected in the off gas at 147°C (297°F) while $H_2S$ was detected at 201°C (394°F). At 384°C (723°F), the $H_2S$ concentration in the off gas decreased as temperature increased.

Test A-05: Heated to 300°C (572°F) and held for 200 minutes, and then heated to 400°C (752°F). OCS and $H_2S$ concentrations in the off gas decreased as the temperature stabilized at 300°C (572°F). When the temperature was again increased, OCS and $H_2S$ concentrations again increased rapidly with increasing temperature until the $H_2S$ concentration began decreasing at 378°C (712°F).

Test A-06: Heated to 360°C (680°F) and held for 245 minutes. The concentration of OCS in the off gas maximized at 285°C (545°F). The $H_2S$ concentration reached a maximum when the temperature stabilized and decreased over the next 150 minutes.

Test A-07: Heated to 360°C (680°F) and held for 140 minutes. Absolute ethanol was started at a rate of 0.1 mL/min and the temperature was increased to 503°C (937°F). $H_2S$ appeared in the off gas and increased in concentration rapidly until the temperature reached 400°C (752°F) before flattening out. At 475°C (887°F) the temperature became sporadic and the concentration of $H_2S$ in the off gas decreased rapidly. The coal product was agglomerated.

Test A-08: A duplicate of test A-07 except the final temperature was to be 460°C (860°F). However, the coal agglomerated at 438°C (820°F), plugging the system.

Test A-09: Heated to 400°C (752°F) and held for 150 minutes, heated to 415°C (779°F) and held for 40 minutes, and then cooled to 400°C (752°F) and held for 40 minutes. This test used an inclined bed rather than a horizontal bed. The $H_2S$ maxima observed when the temperature reached 386°C (727°F) was 1.5 times higher indicating the slanted bed resulted in better stripping of $H_2S$ than the horizontal bed.

Test A-10: Absolute ethanol was pumped after the temperature had been raised above 78°C (172°F). The temperature was stepped as in test A-09. Plots of OCS and $H_2S$ concentrations in the off gas were similar in shape to test A-09, except at lower concentrations. Ethanol or ethanol byproducts may have escaped the cold trap and diluted the off gas.

Test A-11: The product from test A-10 was kept in the reactor over night under a nitrogen purge. It was re-reacted using the conditions of test A-10. $H_2S$ was observed in the off gas only at very low concentrations.

Test A-12: A number of changes were made during the heating to 400°C (752°F), as well as during the 60 minutes at 400°C (752°F). At 105 minutes, water flow was started at 0.1 mL/min, at 190 minutes the CO flow rate was increased, at 205 minutes, the water was stopped (the system was approaching 400°C/752°F) and ethanol was pumped at 0.1 mL/min, and at 235 minutes, the ethanol flow rate was increased to 0.2 mL/min. Finally, after 60 minutes at 400°C (752°F) the temperature was increased to 438°C (820°F). The concentration profiles of OCS and $H_2S$ were similar to those of test A-09, except for a decrease in $H_2S$ concentration when the CO flow rate was increased.

**Table 25. Feed coal and product coal TGA proximate data[a].**

| | | AR | ----- | Moisture Free | -------- | |
|---|---|---|---|---|---|---|
| | Test | Moist | VM | FC | Ash | Total |
| Feed Coal | A-06 | 7.32 | 39.64 | 51.56 | 8.79 | 100.00 |
| Coal Product | A-03 | 1.31 | 28.25 | 62.34 | 9.41 | 100.00 |
| Coal Product | A-05 | 2.21 | 28.07 | 62.20 | 9.72 | 100.00 |
| Coal Product | A-06 | 3.36 | 32.42 | 58.28 | 9.30 | 100.00 |
| Coal Product | A-07 | 1.41 | 21.37 | 68.33 | 10.30 | 100.00 |
| Coal Product | A-09 | 1.48 | 27.24 | 63.35 | 9.41 | 100.00 |
| Coal Product | A-11 | 1.09 | 23.42 | 66.62 | 9.97 | 100.00 |
| Coal Product | A-12 | 0.97 | 24.66 | 65.13 | 10.21 | 100.00 |
| 700°C (1292°F) LTGA CLP[b] | | | | | | |
| of Coal | A-06 | 0.78 | 7.51 | 79.81 | 12.68 | 100.00 |
| of Coal Product | A-05 | 0.76 | 7.63 | 80.03 | 12.34 | 100.00 |
| of Coal Product | A-06 | 0.80 | 6.62 | 80.73 | 12.65 | 100.00 |
| of Coal Product | A-07 | 0.73 | 6.54 | 80.86 | 12.60 | 100.00 |

a) AR = as received; VM = volatile matter; and FC = fixed carbon.
b) Coal-like product was prepared using the large-scale TGA equipment.

Table 26. **Feed coal and product coal ultimate analysis.**

| | Moisture | Moisture Free, wt% | | | | | |
|---|---|---|---|---|---|---|---|
| | AR | C | H | N | S | ASH | NAW-S[a] |
| Feed Coals: | | | | | | | |
| A-03 | 8.26 | 73.15 | 5.04 | 1.50 | 3.47 | --- | 1.28 |
| A-05 | 9.58 | 73.11 | 4.87 | 1.49 | 3.46 | --- | 1.29 |
| A-06 | 9.70 | 74.17 | 4.72 | 1.57 | 3.36 | --- | --- |
| A-07 | 9.77 | 74.42 | 4.67 | 1.61 | 3.45 | --- | --- |
| A-09 | 9.57 | 72.48 | 4.90 | 1.51 | 3.34 | --- | 1.12 |
| A-11 | 9.57 | 72.66 | 4.83 | 1.47 | 3.32 | --- | 1.14 |
| A-12 | 9.62 | 72.65 | --- | 1.47 | 3.30 | --- | --- |
| Product Coals: | | | | | | | |
| A-03 | 0.24 | 74.33 | 4.33 | 1.60 | 2.47 | 9.76 | 1.23 |
| A-05 | 1.86 | 75.10 | 4.38 | 1.57 | 2.49 | 9.80 | 1.49 |
| A-06 | 4.12 | 74.88 | 4.61 | 1.55 | 2.63 | 9.42 | 1.70 |
| A-07 | 0.48 | 77.42 | 3.65 | 1.72 | 2.22 | 10.47 | 1.69 |
| A-09 | --- | 74.91 | 4.39 | 1.65 | 2.40 | 9.93 | 1.28 |
| A-11 | --- | 77.38 | 4.13 | 1.70 | 2.20 | 10.16 | 1.36 |
| A-12 | 0.50 | --- | --- | --- | 2.18 | 7.92 | 1.77 |

a) NAW-S is the sulfur content determined after washing with nitric acid.

Proximate and ultimate analysis data for the feed coal and products from the tests are listed in Tables 25 and 26. Fixed carbon content (mf feed basis) had a relatively narrow range of 55 to 59 wt percent for most of the samples (feed coal fixed carbon content was 51.6 wt percent), while volatile matter content ranged from 5 to 31 wt percent.

In all the tests OCS was first observed at 120° to 160°C (248°-320°F, at 0.1 mol percent concentration), while $H_2S$ was first observed in the product gas at around 200° to 220°C (392°-428°F). Molar concentrations of over 5 percent $H_2S$ (at 400°C/752°F) and over 3 percent OCS (at 200°C/392°F) were observed in the product gas, indicating that high concentrations could exist in the presence of coal. When temperature was held isothermal with CO gas flowing at 215°, 240°, 265°, 300°, and 360°C (419°, 464°, 509°, 572°, and 680°F), the amount of OCS and $H_2S$ observed in the product gas started decreasing within 5 minutes. When the temperature was again increased, the amount of OCS and $H_2S$ observed in the product gas recovered (after an incubation period) to the values observed in other runs where temperature was steadily ramped. The total amount of sulfur removed from the coal was dependent mainly on the final reaction temperature, and to a lesser extent on residence time (up to about 1 hour) at that temperature. Decreasing the heat-up time to reach 360°C (680°F, from 400 minutes to 150 minutes) resulted in slightly lower sulfur removals. Total sulfur content of the product increased ~5 percent, while organic sulfur content increased by 10-20 percent.

## Liquid Products

Liquid products were analyzed in a number of tests to determine the ethanol conversion. The total liquid products were collected in a cold trap. The major product was diethylacetal, $CH_3CH(OC_2H_5)_2$, which was expected in a water deficient reaction. Ethanol would react to form acetaldehyde, $CH_3CHO$, which in a water deficient system would react with additional ethanol to form the diethylacetal. If hydrolyzed with water, acetaldehyde and ethanol would reform. The lowest concentration of diethylacetal was seen in test A-07, where ethanol was present at temperatures of 360° to 500°C (680°-932°F, see Table 27). The liquid products in test A-10, where ethanol was pumped throughout the test from 93° to 400°C (199°-752°F), contained 9.3 percent diethylacetal. In test A-11, the cooled coal product from test A-10 was reheated in the presence of ethanol and CO gas to 435°C (815°F), and the liquid product contained 20.8 percent diethylacetal. This showed that: a) diethylacetal was preferentially formed when CO and absolute ethanol were reacted with dry coal, b) that the highest production of diethylacetal was with previously devolatilized dry coal, c) that even at the low flow rates used in these tests (0.1 mL of liquid ethanol/minute for 35 grams of AR coal), the ethanol was not fully converted to other products, and d) that the presence of ethanol reduced the sulfur content of the coal product by 10 to 20 percent compared to tests where only CO was present.

Table 27. **Products of ethanol and coal reactions.**

| Test | Ethanol | Diethyl-acetal | Acetaldehyde | Unidentified Small Peaks |
|---|---|---|---|---|
| A-07 | 87% | 1.2% | ~1 % | 10.8% |
| A-10 | 86 | 9.3 | 1.8 | 2.9 |
| A-11 | 75 | 20.8 | 0.4 | 3.8 |

## Back Reactions

At the end of test A-11, the 8-inch product coal bed was removed in sections and each was analyzed to determine sulfur contents (Table 28). The weighted average of the total sulfur content of the four sections agrees well with the total sulfur content of the combined sections (2.20 and 2.25 wt percent). The first two sections (58 percent of the coal bed) nearest the gas inlet contained only 2.1 wt percent total sulfur. The next two contained 2.2 and 2.8 wt percent, indicating a build-up of sulfur in Section 4 (Table 28). The coal product acid-wash data indicates that the additional sulfur was organic in nature. Since this product had a relatively severe processing history (reacted once with CO and ethanol and then again with CO and ethanol), further testing would be required to determine under what conditions the sulfur build-up in Section 4 occurred.

The success of the sectioning method indicated it was a good way to determine the extent of back reactions. Further work is required to improve the acid washing method to obtain data where the "sum of the parts" equals the combined value.

**Table 28.** **Back reaction data, Test A-11.**

| Section | Weight | Total Sulfur | NAW[a] Sulfur |
|---|---|---|---|
| 1[b] | 10.7g | 2.07 wt% | 1.52 wt% |
| 2 | 4.8 | 2.06 | 1.42 |
| 3 | 4.9 | 2.18 | 1.36 |
| 4 | 6.5 | 2.76 | 1.98 |
| Total | 26.9 | 2.25[c] | —[d] |
| Combined Product[e] | -- | 2.20 | 1.36 |
| Feed Coal, mf | -- | 3.32 | 1.14 |

a- Nitric acid washed -- the samples were washed with hot dilute nitric acid and analyzed for sulfur content.
b- The section nearest the gas inlet.
c- The weighted average of the four sections.
d- The weighted average value would be high.
e- Sections 1-4 were mixed and analyzed.

## TGA Thermal Desulfurization

The degree of sulfur removal from coal and coal products due to thermal effects was determined using large pan TGA equipment. About 5 grams of coal in a 316 SS screen basket was heated in 40 minutes to 700°C (1292°F) and held there for 20 minutes with an argon gas purge of the chamber at 300 mL/min. The data in Table 29 indicates that the product of coal heated at 700°C (1292°F) in an inert atmosphere contains only slightly more sulfur than the coal product made in the Vycor tube tests under similar conditions, but at the expense of most of the volatile matter. Treating the Vycor tube product at 700°C (1292°F) decreased the sulfur content of the product an additional 5-15 percent, but again at the expense of volatile matter.

**Table 29.** **Thermal desulfurization of IBC-106 coal[a].**

| Sample | Before --------- | | After[b] ---------- | |
|---|---|---|---|---|
| Coal Feed | VM[c] | Sulfur | VM | Sulfur |
| A-03 | .[d] | 3.49 | . | 2.59 |
| A-05 | . | 3.46 | . | 2.52 |
| A-06 | 39.64 | 3.36 | 7.45 | 2.39 |
| A-07 | . | 3.41 | . | 2.41 |
| Coal Products from Vycor tube tests | | | | |
| A-03 (400°) | 27.88 | 2.47 | . | 2.24 |
| A-05 (400°) | 27.54 | 2.49 | 7.57 | 2.36 |
| A-06 (360°) | 31.33 | 2.63 | 6.57 | 2.32 |
| A-07 (503°) | 21.07 | 2.22 | 6.49 | 2.13 |

---

a - All values expressed as wt percent of moisture-free sample.
b - "After" refers to after treating the sample at 700°C (1292°F).
c - Volatile matter (VM) was determined by TGA.
d - Not analyzed.

## Results and Discussion of Vycor Tube Tests

The Vycor tube test data indicated that the concentrations of OCS and $H_2S$ in the off gas were most related to temperature for the conditions tested with the IBC-106 coal. Figure 15 depicts the concentration profiles (in detector counts) for test A-07 with time. The detector was approximately twice as sensitive to $H_2S$ as to OCS. Figure 16 depicts the concentration profile of tests A-06 and A-07 with temperature. The OCS and $H_2S$ concentrations in the off gas were essentially the same (the maximum temperature of test A-06 was 360°C (680°F) while in test A-07 it was 500°C (932°F). Overlaying the cumulative $H_2S$ data from a number of tests indicates the strong dependence on temperature for the total sulfur removed, and the secondary dependence of time, at a given temperature. In Figure 17, the cumulative data for tests A-03, A-05, A-06, and A-07 is depicted. Data from tests A-03 and A-05 overlay each other at under 300°C (572°F) and from 340° to 400°C (644°-752°F). In test A-03, the temperature was steadily increased to 400°C (752°F) while in test A-05, the temperature was held for 245 minutes at 300°C (572°F) before increasing it to 400°C (752°F). Test A-06 overlays the previous data to 360°C (680°F), the maximum temperature for this test. Test A-07 overlays the data to 360°C (680°F) where the temperature was held 140 minutes, and upon a further increase in temperature to 400°C (752°F), the total $H_2S$ produced recovered to the amount produced in tests A-03 and A-05. At 400°C (752°F), ethanol pumping was started and temperature was increased. The total $H_2S$ produced increased to a higher value. OCS data exhibited similar repeatability trends.

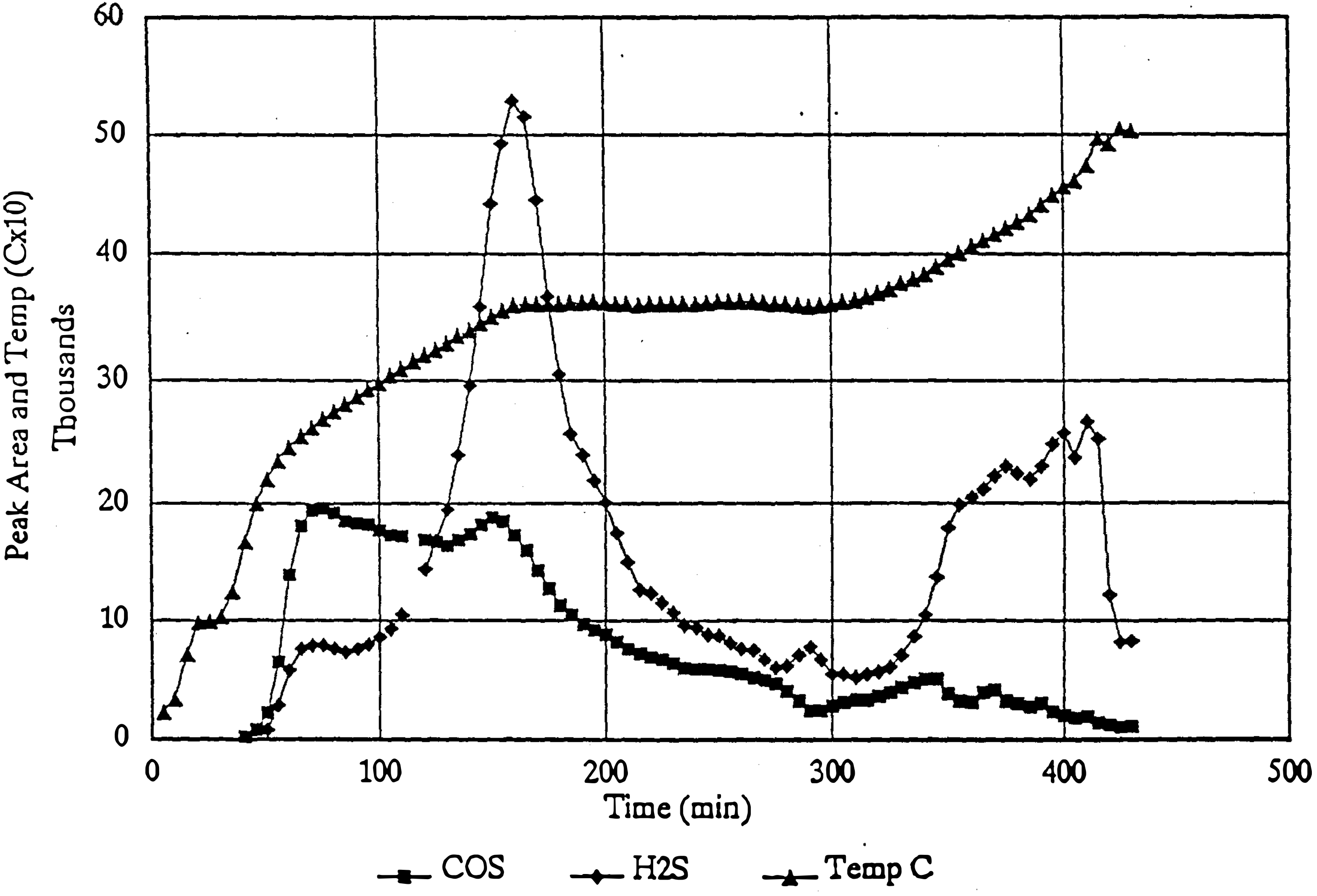


Figure 15. Run A-07.

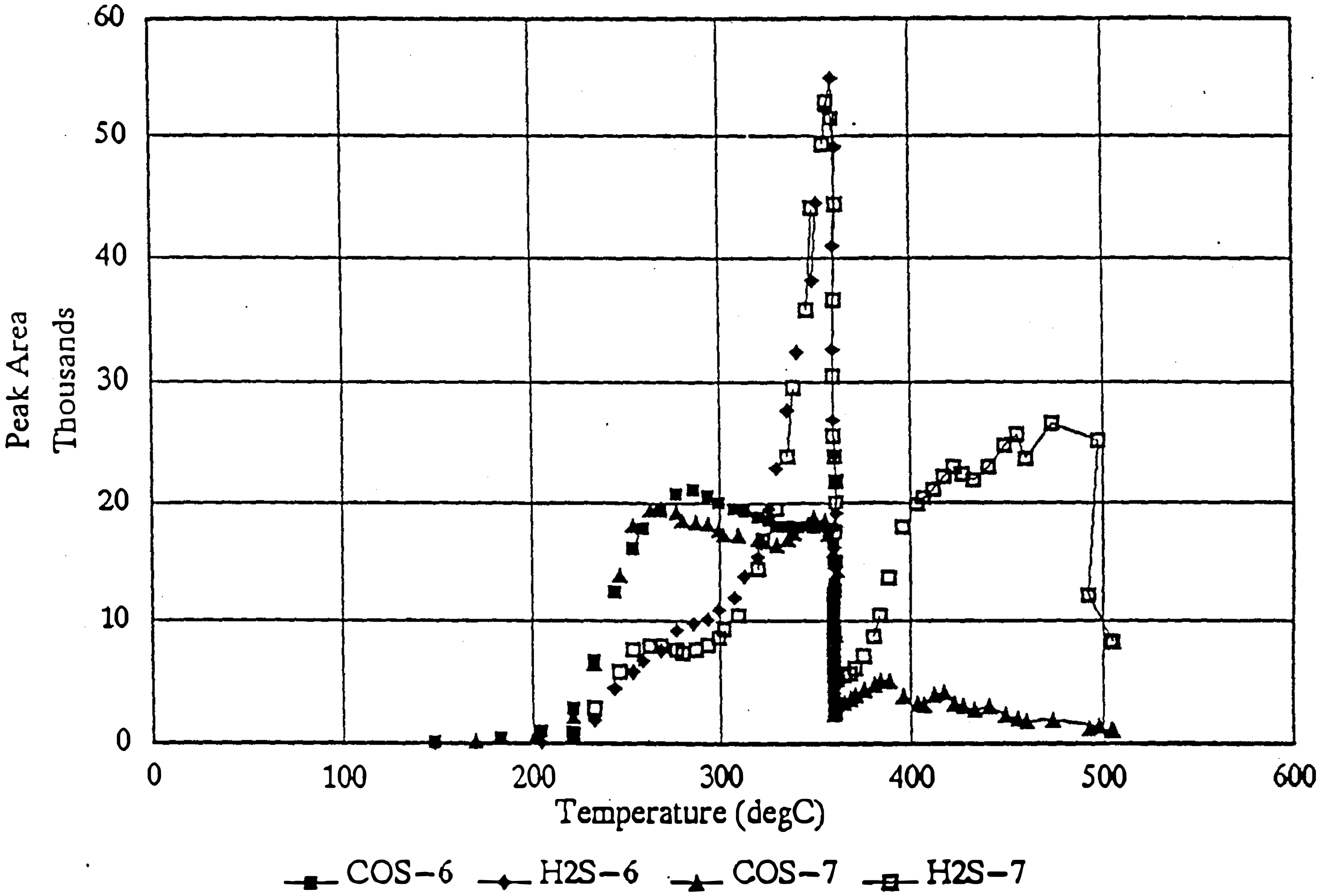


Figure 16. Runs A-06 and A-07.

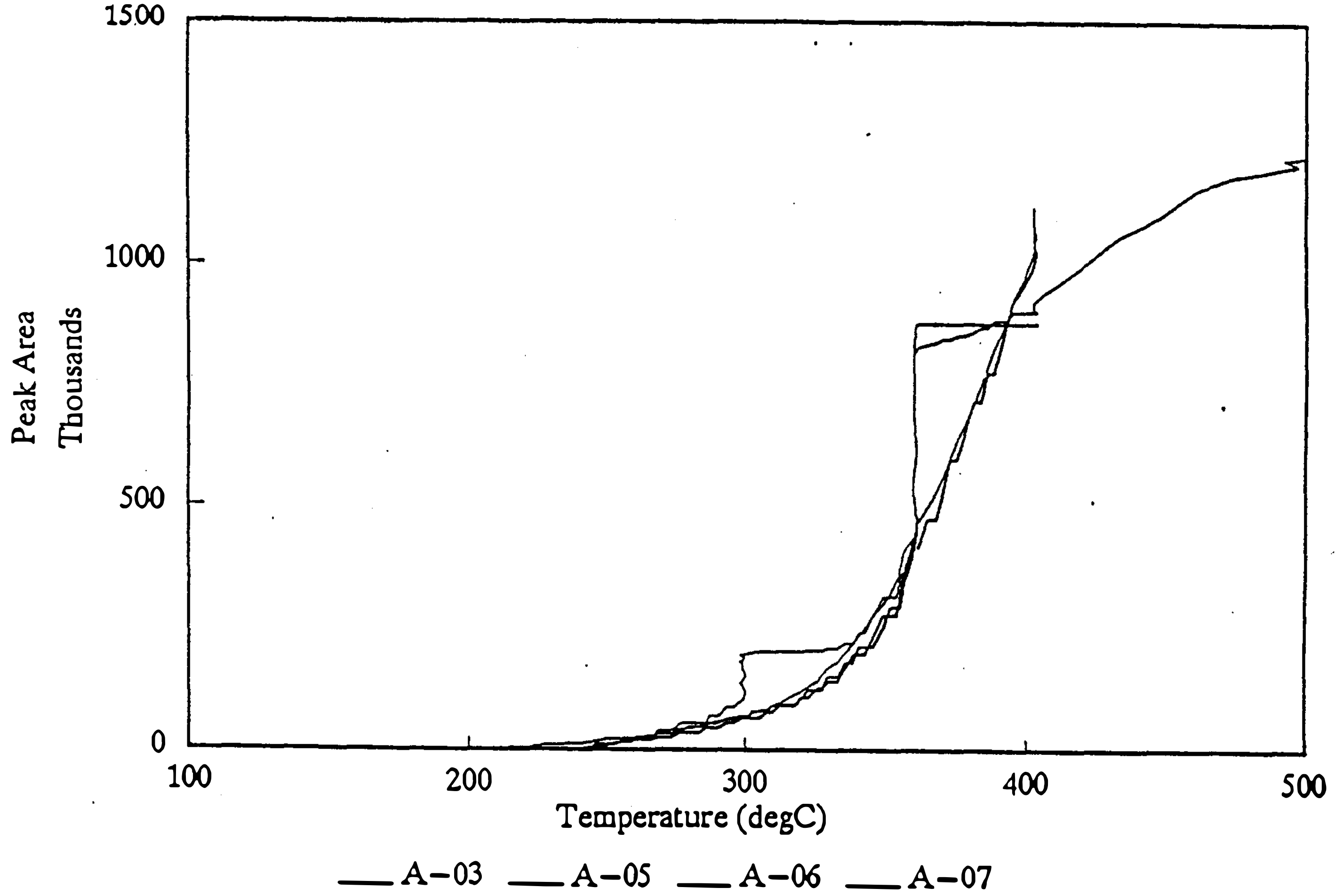


Figure 17. $H_2S$-cumulative, A-03,05,06,07.

Product sulfur contents were related inversely to the total OCS and $H_2S$ produced. The feed coal contained 3.4 wt percent mf sulfur. A-06 product contained 2.63 wt percent sulfur and was reacted at the lowest temperature. A-07 product which had the lowest sulfur content of 2.22 wt percent, and saw the highest temperature, 500°C (932°F), and was reacted with ethanol. The organic sulfur content of the products was in general somewhat higher than in the feed coal (see Table 26). The lowest organic sulfur contents were achieved with the extremely slow heat-up test (A-03 and test A-09). The extended residence time tests (A-10, continued in A-11) resulted in the lowest total sulfur content of 2.20 wt percent (2.06 wt percent for the initial 55 percent of the coal bed). However, the total organic sulfur content was 1.36 wt percent.

Assigning the sulfur removed to the amount of pyrite converted results in Figure 18. In test A-07, enough sulfur was produced to account for the removal of one sulfur atom from almost all (95 percent) of the pyrite in the feed coal. The total amounts of sulfur removed as OCS and $H_2S$ are essentially the same. A calculation which takes into account the volatile matter loss indicates that essentially 50 percent of the pyritic sulfur and 20 percent of the organic sulfur was removed from the coal in test A-07.

In these tests, it appears that an effective troilite catalyst was not produced from the pyrite, or that the reactant mix was not conducive to enabling ethanol to effectively reduce the organic sulfur content of the coal. It was possible to remove half the pyritic and some organic sulfur while minimizing the back reaction to form organic sulfur.

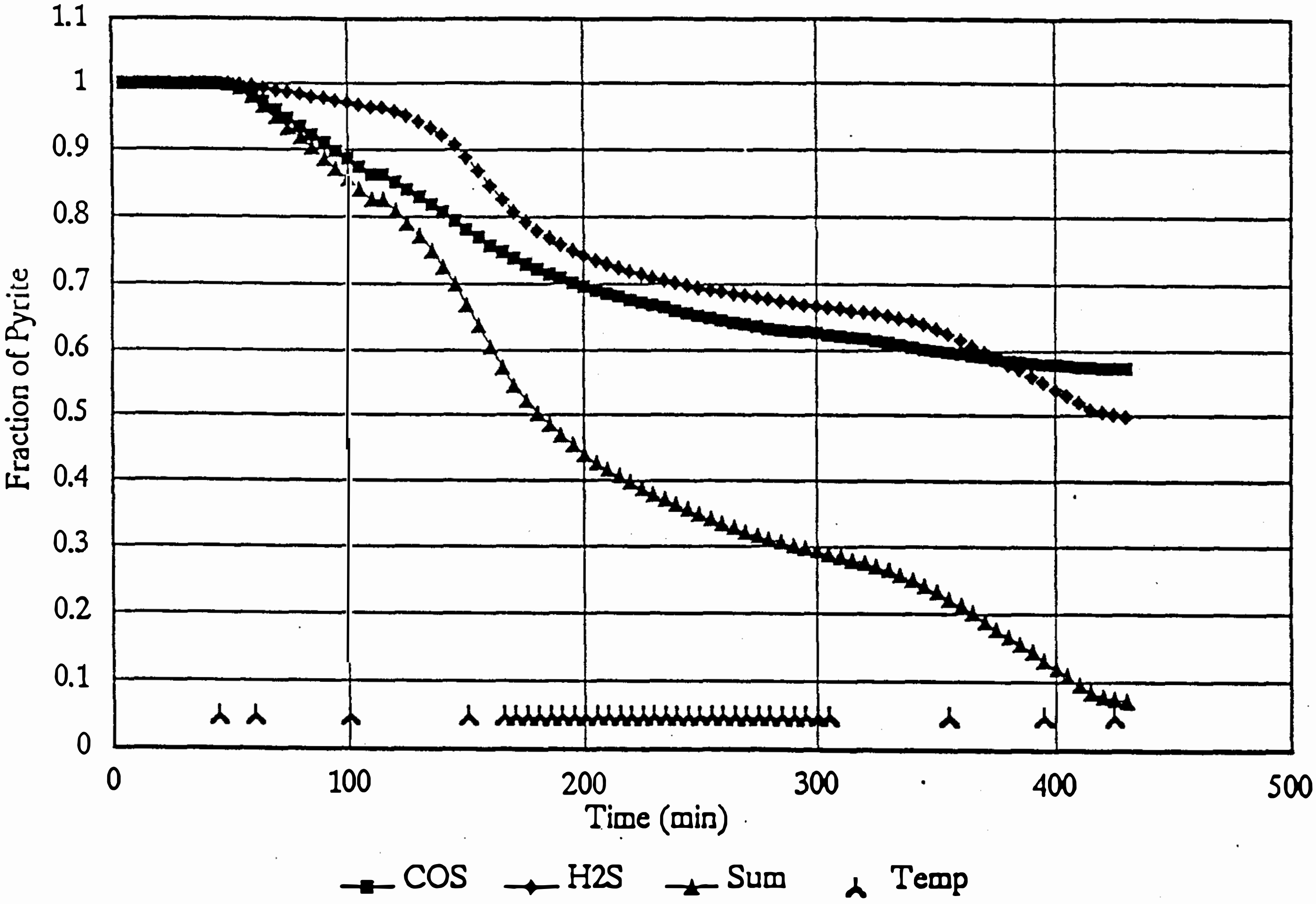


Figure 18. Run A-07d.

## CFU PROJECT CONCLUSIONS

The coal devolatilization tests, Vycor tube tests, and CFU tests added information concerning the temperature and residence time requirements of the three-step CO/Ethanol Process to desulfurize bituminous coal. Above 375°C, coal devolatilization was rapid during the initial 10 to 20 minutes after the coal reached reaction temperature. Even after this time the coal steadily loses volatile matter over a period of hours. This volatile matter issuing out of the coal would interfere in the penetration of reactant gaseous molecules such as CO and ethanol.

The Vycor tube test data indicated that the initial reactions that result in desulfurization are primarily temperature dependent (the higher the temperature the more inorganic sulfur removed). The back reactions of $H_2S$ and OCS did not seem important in these slow heat-up tests in that high concentrations (5 mol percent of $H_2S$) could exist in the off gas. However, in tests where absolute ethanol was present, no sustained production of OCS or $H_2S$ gases was observed, nor was there any significant reduction in organic sulfur content of the product. The Vycor tube tests were made at a pressure of one atmosphere.

Ultimately, the CFU tests yielded mixed results. Coal was successfully fed to and products were recovered from 0.5- and 2-kg/hr continuous fluidized bed reactor systems. A modification (the addition of a side leg) enabled operation at 450 kPa (50 psig) with less fluidizing gases. Initial tests indicated varying degrees of pyrite conversion to pyrrhotite depending on operating parameters. However, there tended to be an increased conversion of pyritic sulfur to organic (or elemental) sulfur with operating temperature, which resulted in only nominal total sulfur reductions. Troilite was not observed.

Based on the available data, it does not appear that a single fluidized bed reaction system can effectively prevent back reactions due to the rapid heat-up inherent in such a system. A multiple-staged fluid bed system may be more effective. However, further continuous-mode tests of the 3-step process are not recommended until the coal can be shown to be reactive in smaller scale equipment.

## FUTURE WORK

The Ethanol Coal Desulfurization project continued to pursue two separate methods to produce a cleaner coal product. The first method, known as the 3-Step process, has been described herein at length. In the second method, known as the 1-Step process, ground coal is heated and treated with ethanol in the presence of a "reaction accelerator." This latter technology has been patented with ownership assigned to the Illinois State Geological Survey and the Board of Trustees, Southern Illinois University.

This project was scheduled to complete demonstration at the process-development unit (PDU) reactor level (15- to 50-kg/hr) by August 1991. The work was being supported the Illinois Department of Commerce and Community Affairs (DCCA), Illinois Corn Marketing Board, Ohio Corn Growers Association, and USDOE through the University of North Dakota Energy and Environmental Research Center (UNDEERC).

The results to date with the 3-Step process will be balanced against the batch and CFU work on the 1-Step process currently being conducted with Ohio University. Preliminary batch results have achieved a 96 percent total sulfur removal at 420°C (788°F) with, perhaps more importantly, 78 percent total sulfur reduction achieved at only 200°C (392°F). Work was underway to transfer the 1-

Step technology to UNDEERC, scale-up that process to 2-kg/hr, compare the two processes, and advance the best technology into the PDU reactor by the end of the new contract period (31 August 1991).

## ACKNOWLEDGEMENTS

This research was supported in part by the Illinois Coal Development Board, the Illinois Center for Research on Sulfur in Coal, the Southern Illinois University Coal Extraction and Utilization Research Center, the Illinois Corn Marketing Board, and the Illinois State Geological Survey. We would like to thank Drs. Herbert D. Glass and Randall E. Hughes, ISGS, for interpreting XRD traces and searching the literature for articles on iron sulfides. Mössbauer analyses were performed and analyzed in part by Dr. Peter DeBrunner, Department of Physics, University of Illinois, Urbana-Champaign. Microwave research was supervised by Dr. Ravi Varma, formerly of Argonne National Laboratory. Chemical engineering consulting was provided by Lindal Mark, Dr. Stanley Walas, Lane Harold, and Tom Rogers of C.W.Nofsinger, Co., Kansas City, Missouri, and Dr. Lyle Albright, Purdue University.

We are indebted to Richard H. Shiley, Lawrence Wu, John R. Webster, Robin L. Warren, William T. Nelson, Rose Popp, Patricia L. Fox, John M. Fox, Henry P. Ehrlinger III, Melissa M.-I. Chou, JoAnn Amber, Somenath Mitra, Donald E. Cogswell, Douglas K. Cowin, Pamela K. Foster, and Kenneth L. Konopka of the ISGS; Tomasz Wiltowski, Teresa Wiltowska, Daniel W. Ellison, and Ruth E. Walker of SIU-C; Daniel C. Cleaveland, Cindy L. Ludwig, and Linda C. Warfel of EIU; Gerald Groenewold, Warrack Willson, Annette Wilke, Arthur Ruud, Ronald Timpe, Ronald Kulas, Diane Rindt, Peter Behling, Edwin Olson, and Ames Grisanti of UNDEERC for their many outstanding contributions to this work.

# REFERENCES

1. Webster, J. R., R. H. Shiley, R. E. Hughes, C. C. Hinckley, G. V. Smith, and T. Wiltowski. Development of the Carbon Monoxide-Ethanol Desulfurization Process, in: Third Annual Pittsburgh Coal Conference Proceedings, September 8 - 12, 1986, Pittsburgh, Pennsylvania, pp. 101-114.

2. Warren, R. L., R. H. Shiley, R. E. Hughes, J. R. Webster, L. Wu, C. C. Hinckley, G. V. Smith, and T. Wiltowski. Development of the Carbon Monoxide/Ethanol Desulfurization Process, in: Y. P. Chugh and R. D. Caudle (Eds.), Processing and Utilization of High Sulfur Coals II, Proceedings of the Second International Conference on Processing and Utilization of High Sulfur Coals, September 28 - October 1, 1987, Carbondale, Illinois, pp. 235-244.

3. Analysis of Acid Rain Control Alternatives, prepared by D. Baker and J. Bishop, Illinois Department of Energy and Natural Resources, ILENR/RE-PA-87/17, October, 1987, 107 p.

4. Cost and Quality of Fuels for Electric Utility Plants -- 1988. Energy Information Administration, DOE/EIA-0191(88).

5. Coal Production 1988. Energy Information Agency, DOE/EIA-0118(88).

6. McMahan, R. L. and K. Knutson. 1989. "Acid rain: a needle in the smokestack." Coal, May, p. 43-44.

7. Smith, G. V., C. C. Hinckley, M. Saporoschenko, and R. H. Shiley. 1982. Comment on the Nature of Iron Sulfides During Catalytic Reactions. J. Catalysis, v. 78, p. 262-263.

8. Snow, R. D. 1932. Industrial Engineering Chem., v. 24, p. 903.

9. Eliot, R. C., ed. 1978. Coal Desulfurization Prior to Combustion, Noyes Data Corp., Park Ridge, NJ.

10. Yan, T. Y. 1977. U.S. Patent 4 052 170.

11. Schroder, C. W. 1975. U.S. Patent 3 909 212.

12. Sinke, G. V. 1978. U.S. Patent 4 071 328.

13. Longanbach, J. R. 1977. U.S. Patent 4 054 420.

14. Diaz, A. F. and E. D. Guth. 1975. U.S. Patent 3 909 211.

15. Whitten, C. M., V. Mansfield, L. J. Petrovik, and J. C. Agarwal. 1973. U.S. Patent 3 759 673.

16. Stambaugh, E. P. and G. F. Sachsel. 1977. U.S. Patent 4 055 400.

17. Sanders, R. N. 1977. U.S. Patent 3 909 213.

18. Meyers, R. A. 1973. U.S. Patent 3 768 988.

19. Ruchfuss, T. 1984. Illinois Coal Research Board Second Annual Contractor's Technical Meeting, Round Barn Center, Champaign, IL, 30 October.

20. Keller, L. J. 1977. U.S. Patent 4 045 093.

21. Kalvinskas, J. J., N. Vasilakos, W. H. Corcoran, K. Grohmann, and N. K. Rahatgi. 1982. U.S. Patent 4 325 707.

22. Research-Cottrell, Inc., Report DOE/PC/3014T. 1980.

23. Dugan, P. R. and W. A. Apel. 1984. U.S. Patent 4 456 688.

24. Zavitsanos, P. D., J. A. Golden, and K. W. Blieler. 1982. Report DOE/PC/30142-T4.

25. Mesher, J. A. and E. E. Peterson. 1979. Coal Desulfurization Via Chemical Leaching with Aqueous Solutions of Sodium Sulfide and Polysulfide, Thesis, University of California, Berkeley, 88 p.

26. Friedman, S. and B. R. Utz. 1985. Chemistry of Fused Caustic Desulfurization of Coal. Proceeding of the Second Annual Pittsburgh Coal Conference. p. 111, Pittsburgh, PA, 16 September.

27. Wu, M. M. and R. A. Winschel. 1985. Coal Desulfurization and Coal Conversion with Formates. Proceedings of the Third Annual Pittsburgh Coal Conference. p. 115, Pittsburgh, PA, 16 September.

28. Lin, K. L., D. C. Liu, and R. Markuszewsku. 1985. Chemical Desulfurization of Coal with Caro's Acid. Proceedings of the Third Annual Pittsburgh Coal Conference. p. 127, Pittsburgh, PA, 16 September.

29. Meyers, R. A., L. C. Liu, and R. Markuszewsku. 1985. Development of the TRW Gravimelt Process. Proceedings of the Second Annual Pittsburgh Coal Conference. p. 112, Pittsburgh, PA, 16 September.

30. Guy, D. and E. N. Given. 1982. Ind. Eng. Chem. Process Des. Der., v. 21, p. 113.

31. Stohl, F. V. and B. Granoff. 1981. Sandia National Laboratory, Report SAND-80-2361C, 24 pp.

32. Webster, J. R., R. H. Shiley, R. E. Hughes, P. L. Lapish, D. K. Cowin, G. V. Smith, C. C. Hinckley, T. Nishizawa, N. Yoshida, T. Wiltowski, Y. Wada, and M. Saporoschenko. 1985. Desulfurization of Illinois Coal by in situ Preparation of Iron Sulfide Catalysts. Proceedings of the Second Annual Pittsburgh Coal Conference. p. 138, Pittsburgh, PA, 16 September.

33. Shiley, R. H., R. E. Hughes, K. L. Konopka, C. C. Hinckley, G. V. Smith, T. Nishizawa, N. Yoshida, and M. Saporoschenko. 1985. Design Principles for a Coal Desulfurization Process with Iron Sulfides as In-Situ Catalysts. Environmental Geology Note no. 114.

34. Wrathall, J., T. Vermeulen, and S. Ergun. 1979. Coal Desulfurization Prior to Combustion, Univ. of California, Berkeley, DOE Report LBL-1011, 20 pp.

35. Smith, G. V., C. C. Hinckley, T. Nishizawa, N. Yoshida, M. Saporoschenko, R. H. Shiley and K. L. Konopka. 1984. Structure Sensitive Catalytic Dehydrogenation and Desulfurization Over Iron Sulfides: Effect of Catalyst Stoichiometry on the Reactions. Eighth International Congress on Catalysis, Berlin (West). 2 July 1984. Sensitivity of Dehydrogenation, Dehydration and Desulfurization of Surface Stoichiometry and Structure of Iron Sulfides. Proceedings, IV, 439.

36. Mineral Effects in Coal Conversion. 1983. IEA Coal Research, NTIS# PB83-15911.

37. Kor, G. J. W. and T. D. Wheelock (Editors). Desulfurization and Sulfation of Coal and Coal Desulfurization, Chemical and Physical Methods, A. C. S. Symposium Series 64 (1977), Ch. 13, p. 221.

38. Boodman, N. S., T. R. Johnson, and K. C. Krupinski. Fluid Bed Carbonization/Desulfurization of Illinois Coal by the Clean Coke Process: PDU Studies, in G. J. W. Kor and T. D. Wheelock (Eds.), Coal Desulfurization, Chemical and Physical Methods, A.C.S. Symposium Series 64 (1977) Ch. 19, p. 248.

39. Attar, A. 1978. Chemistry and Thermodynamics and Kinetics of Reactions of Sulfur in Coal. Fuel, v. 57, p. 201.

40. Webster, J. R., R. H. Shiley, R. E. Hughes, C. C. Hinckley, G. V. Smith, and T. Wiltowski. 1986. Development of the Carbon Monoxide-Ethanol Desulfurization Process. Third Annual Pittsburgh Coal Conference Proceedings. pp. 101-114.

41. "Faith, Keyes and Clarks Industrial Chemicals." 1975. Acetic Acid, John Wiley and Sons.

42. Aguilo, A., Hobbs, C. C., Zey, E. G. 1985. "Ullman's Encyclopedia of Industrial Chemistry", Acetic Acid.

43. Hydrocarbon Processing, 1985. November, p. 116.

44. Brown, A. S. 1984. "Technology Shift Tightens Acetic Acid Market", Chemical Business, November.

45. "Facts and Figures for the Chemical Industry", 1988. Chemical and Engineering News, June 20.

46. "Acetic, VAM Supplies Tighten Up", 1987. Chemical Marketing Reporter, June 1.

47. "Celanese Planning to Rebuild Damaged Plant in Pampa, Texas", 1987. Chemical Marketing Reporter, December 21.

48. "Acetic Shortfalls Are Squeezing VAM As Export Mart Rises", 1987. Chemical Marketing Reporter, September 28.

49. "Chemical Profiles: Acetaldehyde." 1986/1985/1979. Chemical Marketing Reporter. May 12, 1986; May 30, 1985; January 11, 1982; March 5, 1979.

50. Boice, L. P. 1986. "CMA: An Alternative to Road Salt?", Environment, Jan.-Feb. p. 5.

51. "The Great Salt Debate", 1987. Better Roads, June, p. 30.

52. Salcedo, R. N. and Jensen, W. N. 1987. "Corrosivity Tests Pit Salt vs. CMA", Public Works, November. p. 58.

53. Schultz, F. 1987. "Mild winter limits road-salt substitute test; more needed", The Capital Times, Madison, Wisconsin, April 13.

54. Bodle, W. W. and Huebler, J. 1981. "Coal Handbook", Coal Gasification, Marcel Dekker Inc. p. 668.

55. 1988 Gas Process Handbook, Hydrocarbon Processing, April.

56. "Sulfuric Acid Versus Elemental Sulfur as By-products", 1978. United States Department of Energy and Gas Research Institute, January.

57. "Chemical Origins and Markets", 1975. Stanford Research Institute.

58. "Kirk-Othmer Encyclopedia of Chemical Technology." 1983. Sulfur Compounds: Hydrogen Sulfide, Third Edition, v. 1, John Wiley and Sons.

59. Morse, D. E. 1988. "Mineral Commodity Summaries 1988", Sulfur, U.S. Department of the Interior, Bureau of Mines, p. 156.

60. Eckert Jr., G. F. 1988. "Sulphur, Demand Improves Slowly", Engineering and Mining Journal, April.

61. Rivoire, J. 1987. "Sulfur is set for another upward swing", Chemical Week, August 26, p. 44.

62. Lumpkin, R. E. 1988. "Recent Progress in the Direct Liquefaction of Coal", Science, v. 238, February, p. 873.

# <u>APPENDIX A.</u>

# ECONOMIC EVALUATION OF CO-PRODUCT MARKETS

A preliminary study was conducted in order to determine market conditions and predict future market conditions for the current co-products of the CO/Ethanol Desulfurization process. This study included an extensive literature review covering a wide range of books, journals and government reports as well as discussions with members of industry. The results of the study can be summarized as follows:

* Acetaldehyde, the dehydrogenation product of ethanol, may be a marketable co-product if it can be priced low enough to compete with methanol carbonylation for the production of acetic acid (demand for which was growing steadily in 1989). Prospects for the use of acetaldehyde in the production of an environmentally and economically viable alternative to road salt appear to be rising.

* Hydrogen sulfide and carbonyl sulfide are not marketable co-products and should be converted to elemental sulfur.

* At this point it is premature to try to estimate the market value of the co-product oil. More information about the oil must be known, specifically boiling point range, hydrogen content, and heteroatom content (particularly nitrogen and oxygen).

## Acetaldehyde

The economics of commercial processes for the manufacture of acetaldehyde depend largely upon prices and availability of the feedstocks used. Acetaldehyde is produced commercially by the oxidation of ethylene, the oxidation or dehydrogenation of ethanol, the hydration of acetylene, and from the oxidation of butane. Since 1960, the liquid phase oxidation of ethylene has been the process of choice.

A major problem with these processes are the high reaction temperatures required which may lead to material and maintenance problems. There are also safety considerations due to the addition of air at high temperatures to an organic material and the handling of the co-product hydrogen. The major problem with ethanol-based processes for acetaldehyde production is economic and due to the high price of ethanol.

**Supply and demand:** In the United States, there are currently only two major producers of acetaldehyde, Texas Eastman and Hoechst-Celanese (see Table 30) with a current combined capacity of approximately 700 million pounds per year. Union Carbide closed a 200 million pound plant at Institute, West Virginia in March of 1978 and Celanese closed a 450 million pound plant at Clear Lake, Texas in 1981.

Table 30. **Acetaldehyde Producers and Capacities**

| Producer | Capacity(million lb./yr.) |
|---|---|
| Hoechst-Celanese, Bay City, Tex. | 225 |
| Eastman, Longview, Tex. | 475 |
| Total | 700 |

**Production:** Estimating the amount of acetaldehyde produced in one year is extremely difficult. The vast majority of acetaldehyde produced (estimated at

95 percent (Faith, Keyes and Clarks Industrial Chemicals, 1975 [41]) is consumed internally by the manufacturer. Most of the acetaldehyde derivatives can be, and in fact are, produced from starting materials other than acetaldehyde. Both major U.S. acetaldehyde producers would not release any specific information regarding current acetaldehyde production. A source from Hoechst-Celanese stated that they had no plans for shutting down their remaining acetaldehyde plant. He also stated that Hoechst-Celanese does not produce acetic acid from the acetaldehyde it currently produces. The acetaldehyde is used for the production of polyols (polyhydric alcohols). A source from Eastman said that the outlook for acetaldehyde is negative due to the switch from acetaldehyde-based production of acetic acid to methanol-based production. He also stated that within the next few years virtually all acetic acid will be produced from methanol.

**Table 31. Acetaldehyde Demand (millions of pounds) (From: Chemical Marketing Reporter)**

| Year | Demand |
|---|---|
| 1978 | 1300 |
| 1979 | 1350 |
| 1980 | 950 |
| 1981 | 900 |
| 1982 | 900 |
| 1983 | 900 |
| 1984 | N.A. |
| 1985 | 650 |
| 1986 | 650 |

The Chemical Marketing Reporter (May 12, 1986) estimated demand for acetaldehyde at 650 million pounds per year for 1986 and expected "demand" to remain constant through 1990. Acetaldehyde demand over the period 1978 through 1986 is presented in Table 31. One can assume that "demand" is referring to consumption. If there is no addition to or reduction of acetaldehyde stocks, then consumption, and therefore "demand", is equal to production. Therefore, the current annual production of acetaldehyde is approximately 650 million pounds per year.

**Table 32. Acetaldehyde Uses (from Chemical Marketing Reporter)**

| | |
|---|---|
| Acetic Acid | 50% |
| Exports | 14% |
| Miscellaneous including lactic acid and crotonaldehyde | 13% |
| Pyridine and pyridine bases | 8% |
| Pentaerythritol | 7% |
| Peracetic Acid | 6% |
| 1,3 Butylene glycol | 2% |
| Total | 100% |

**Consumption:** Acetaldehyde is produced commercially as an intermediate for the production of other organic chemicals. Traditionally, the majority of acetaldehyde has been used for the production of acetic acid. For a breakdown of the uses of acetaldehyde see Table 32.

The acetic acid market has gone through a transition from ethylene- (via acetaldehyde) based production to methanol-based production of acetic acid. According to a source from Hoechst-Celanese, in the past up to 70 percent of the acetaldehyde produced was used for the manufacture of acetic acid. In 1968, Monsanto discovered a new iodide-promoted rhodium catalyst with remarkable activity and selectivity for methanol carbonylation to form acetic acid. Methanol could be carbonylated at atmospheric pressure with yields of 99 percent on methanol and 90 percent on carbon monoxide. The process was commercialized by Monsanto in 1970 (Aguilo, et al, 1985 [42]).

One method for the production of acetic acid is from the oxidation of acetaldehyde. The raw material and utility requirements for this process are presented in Table 33. This was the process of choice before the development of methanol carbonylation. During this process acetaldehyde is oxidized into acetic acid by oxygen in the presence of a manganese acetate catalyst. The reaction takes place at normal pressure and at a temperature of 60°C (140°F). The reaction is exothermic and the heat of reaction is removed by a cooling system. The crude acetic acid is separated from the off-gases and distilled in three columns under normal pressure (<u>Hydrocarbon Processing</u>, 1985 [43]).

Like acetaldehyde, acetic acid is also an intermediate in the production of other organic chemicals. Half of all acetic acid output is used for the production of vinyl acetate monomer (VAM). VAM is an intermediate used to produce adhesives, paints and paper and textile sizing (Brown, 1984 [44]). Over the last ten years, the market for VAM has been growing at an annual rate of 5 to 6 percent (Chemical and Engineering News, 20 June 1988 [45]). Another 25 percent of acetic acid is used in the production of cellulose acetate, which is used in the production of cigarette filter tow and textiles. Since 1977, cellulose acetate production has been growing at a rate of 8 percent per year. The majority of acetic acid produced in the U.S. is used captively by the manufacturer. According to a November 1984 issue of Chemical Week, about 2.2 billion pounds of acetic acid are used captively each year. Another 400 million pounds are accounted for by special agreements between large producers and large consumers. This leaves approximately 400 million pounds, or between 10 and 15 percent, of acetic acid available for the merchant market.

**Table 33. Raw Materials and Utilities for Acetic Acid Production from Acetaldehyde (per 1000 kg acetic acid)**

| | |
|---|---|
| Acetaldehyde(100%), kg | 764 |
| Oxygen(100%), Nm$^3$ | 205 |
| Cooling water(30°C/86°F), m$^3$ | 160 |
| Cooling agent(0°C/32°F), kJ | 12,560 |
| Steam, kg | 700 |
| Electric power, kWh | 6 |
| Nitrogen, Nm$^3$ | 4 |

Over the last 10 years, acetic acid production has been growing at a rate of 2 percent annually. Acetic acid production reached 3.2 billion pounds in 1987, an 18 percent increase from the previous year (Chemical and Engineering News, 20

June 1988 [45]). This large increase occurred despite production problems throughout the year at acetic acid plants (Chemical Marketing Reporter, 1 June 1987 [46]) and an explosion and fire which shut down 15 percent of U.S. acetic acid capacity. The Celanese plant at Pampa, Texas is schedule to be completely rebuilt and should be back in operation in late 1988 and completed by the end of 1989 (Chemical Marketing Reporter, 21 December 1987 [47]). Much of the increase in production was due to acetic acid manufacturers taking advantage of a high export price for VAM, which was selling at a price of $0.32 to $0.33 per pound compared to a domestic price of $0.28 to $0.30 per pound (Chemical Marketing Reporter, 28 September 1987 [48]).

The major producers of acetic acid in the United States are Air Products, Hoechst-Celanese, Eastman, Monsanto, and U.S.I. Since 1980, new plants have pushed marginal producers (high cost producers) out of business. Among those that closed plants between 1980 and 1984 include Bordeen, which closed a 150 million pound high-pressure methanol plant, and Union Carbide, which closed a 600 million pound butane based plant. During that time, Celanese closed two ethylene-based plants with a combined capacity of over 600 million pounds per year (Chemical Marketing Reporter, 1 June 1987 [46]).

**Price:** Since 1972, the list price of acetaldehyde has risen from $0.09 per pound to $0.37 per pound, where it has remained over the last four years. The real price of acetaldehyde, in terms of 1986 dollars, has risen from $0.26 per pound to $0.37 per pound. Since most of the acetaldehyde produced in the United States is used internally by the manufacturers, this list price may not be very significant. The price increase probably reflects the increase in the price of ethylene, which has risen from $0.0325 per pound in 1972 to $0.285 per pound in 1988 (Chemical Marketing Reporter, 12 May 1986/30 May 1985/11 January 1982/5 March 1979 [49]).

**Sources of new demand - calcium magnesium acetate:** One possible source of new demand for acetaldehyde is for the production of calcium magnesium acetate (CMA). CMA is a road and bridge deicer being developed which is much less corrosive than salt. CMA is a metal organic salt that is usually produced by reacting lime or limestone with acetic acid. Acetic acid can be produced by the oxidation of acetaldehyde.

Each year approximately 10 million pounds of salt will be used for road deicing. The price of salt ranges from $24 to $40 per ton (1.2 to 2 cents/lb), depending on how far it must be shipped. But according to various studies, the actual cost to society is many times the price of salt. In 1979, the National Cooperative Highway Research Program estimated that the cost of automobile corrosion, due to the use of salt for deicing, ranged from $800 million to $2 billion per year. An estimate for damages to bridges found an annual cost due to corrosion of $1.6 billion per year. Including the cost of salt along with the costs of automobile and bridge corrosion, the real cost of salt was approximately $3.1 billion per year or $310 per ton of salt (15.5 cents/lb). This is a conservative estimate since the study was done several years ago and cars as well as road construction are much more expensive today. In a 1976 study by the Environmental Protection Agency, salt damage was estimated at more than $5 billion annually. This study concluded that salt also impairs public health, water supplies, and utilities. Throughout the northeastern part of the United States the use of salt has caused contamination of wells used for drinking water. Over 90 wells in Massachusetts and 30 wells in Connecticut located near roadways have sodium contents greater than the maximum recommended for persons on a low sodium diet. Since these studies were conducted, the general salt price level in the United States has risen 55 to 75 percent, making salt alternatives economically quite attractive.

An alternative to the use of salt for deicing is the use of CMA. If CMA is processed correctly, it is less corrosive to metals than salt, does not harm drinking water and may be beneficial to soils. The Washington State Department of Transportation performed a field test of CMA and compared it to salt for deicing. It was found that if CMA was applied at the beginning of a snowstorm, there was much less snow compaction. This resulted in less snow plowing being required than if salt was used. CMA was also able to break the bond between ice and the road surface at a temperature of -13°C (9°F), which is similar to results for salt. Problems with the use of CMA include that it is slower to react than salt and may be sticky after absorbing moisture, which may tend to clog equipment. These minor problems would probably be overcome as crews adjust from the use of salt to CMA or with the help of small amounts of additives, such as sand.

The current problem for the implementation of CMA as a road deicer is its cost because CMA is being compared with the salt alone instead of the total cost including damage caused by salt. Chevron Chemical Corporation is currently the only domestic manufacturer of CMA. It currently charges $0.25 per pound ($500 per ton). Chevron has completed the construction of a CMA plant in Fort Madison, Iowa. The plant, which is expected to be in operation by the summer of 1989, is expected produce 140 million pounds of CMA per year within 5 years (Boice, 1986 [50]; Better Roads, June 1987 [51]; Salcedo and Jensen, 1987 [52]; and Schultz, 1987 [53]).

**Conclusions:** Acetaldehyde production in the United States has been cut in half over the last ten years, due to the replacement of acetaldehyde-based production of acetic acid by methanol-based production. Acetic acid production has traditionally consumed the majority of acetaldehyde produced in the U.S. Production of acetic acid continues to grow at a steady rate, thus maintaining a good potential market for acetaldehyde, provided it can compete with methanol on price. When acetic acid is produced from acetaldehyde, the costs of the acetic acid include all of the upstream costs associated with the production of acetaldehyde. If the acetaldehyde was produced as a co-product, it could be priced low enough so that acetic acid produced from acetaldehyde would be cheaper than acetic acid produced by methanol carbonylation.

The acetic acid market is currently much larger than the acetaldehyde market and is growing steadily, at about 2 percent per year. If all of the acetic acid produced in the U.S. last year was produced from acetaldehyde, it would have required 2.4 billion pounds of acetaldehyde, over 3.5 times the amount that is currently produced in the U.S. Therefore, there would be a much larger market for acetaldehyde if it could be priced low enough to compete with other methods for the production of acetic acid. The current price of methanol is $0.09 per pound ($0.60 per gallon) and 0.54 pounds of methanol are required to produce one pound of acetic acid. Therefore, approximately $0.05 worth of methanol are needed to produce one pound of acetic acid. Along with the methanol, approximately 0.52 pounds of carbon monoxide are required per pound of acetic acid, based on a 90 percent yield. Future work may include a determination of the cost of carbon monoxide production and other costs associated with methanol carbonylation. With this information, the price of acetaldehyde, which would make production of acetic acid from acetaldehyde competitive with methanol carbonylation, could be determined. The exact price that one could charge for the acetaldehyde would depend on such things as the concentration and purity of the co-product acetaldehyde as well as the location of a plant or plants that would consume the acetaldehyde. These items must be determined before one can set a price that one could charge for the acetaldehyde.

### Hydrogen Sulfide

Hydrogen sulfide is produced as a co-product of many industrial processes. Hydrogen sulfide is the major contributing component of "sour" natural gas. In order to market sour gas the hydrogen sulfide must be removed. Hydrogen sulfide is also produced as a co-product during the refining of crude oil.

The vast majority of hydrogen sulfide, produced as either a co-product from an industrial process or from sour natural gas, is converted to elemental sulfur by the Claus process. By 1981, over 200 plants using the Claus process were built in the United States, Japan and 24 other countries. A typical Claus plant will recover 95 to 97 percent of the sulfur feed. Because this is not sufficient to meet current emission standards, the Claus tail gas must also be treated.

Environmental regulations may require sulfur recoveries in excess of 99 percent. Therefore, the Claus tail gas must be treated to remove much of the remaining $H_2S$. The tail gas may also contain $SO_2$, $S_8$, entrained liquid sulfur, $N_2$, $CO_2$, CO,$H_2$, OCS and $CS_2$. If the Claus plant is of the split-flow type, the tail gas may also contain any impurities that were present in the bypassed acid gas. Available processes to treat the tail gas can be divided into two categories, low and high efficiency. Low efficiency processes will result in 99 to 99.5 percent overall sulfur recovery. Low efficiency processes include the MODOP and the Sulfureen process. High efficiency processes require much more energy input per unit of sulfur recovered, but may reduce the $H_2S$ concentration to less than 10 ppm. Examples of high efficiency units include Beavon Sulfur Recovery/MDEA, Clauspol 1500 and Sulften (Bodle and Huebler, 1981 [54] and 1988 Gas Process Handbook, Hydrocarbon Processing, April [55]).

If there is an assured market for sulfuric acid, it may be more attractive to produce sulfuric acid than sulfur as a co-product. The capital cost is higher for a plant to produce sulfur and the product value per unit of contained sulfur is lower. Many factors enter into the price of sulfur and of sulfuric acid. If there is a close market available for sulfuric acid, then the prices and transportation costs should be looked into in order to determine which co-product should be produced ("Sulfuric Acid Versus Elemental Sulfur as By-products", United States Department of Energy and Gas Research Institute, January 1978 [56]). Hydrogen sulfide is also used for the production of alkyl mercaptans, which may be used in for the production of agricultural chemical, pharmaceuticals and jet fuel additives. Various inorganic sulfides, such as sodium sulfide and sodium hydrosulfide, may be prepared from hydrogen sulfide and used for the manufacture of dyes, rubber chemical, pesticides, polymers, plastic additives and dyes ("Chemical Origins and Markets", Stanford Research Institute, 1975 [57] and "Kirk-Othmer Encyclopedia of Chemical Technology." 1983 [58]).

### Carbonyl Sulfide

There appears to be no large scale production of carbonyl sulfide. It is available in 97 percent min. purity cylinders and is mainly used for small scale synthesis and experiments. Carbonyl sulfide is also produced as a co-product in the manufacture of carbon disulfide and is an impurity in some natural gases, in manufactured fuel gases and refinery gases, and in combustion products of sulfur containing fuels. Because very little carbonyl sulfide is produced in the United States, little information is available about its manufacture. Less than 1000 pounds of carbonyl sulfide were commercially produced in the U.S. in 1973. Carbonyl sulfide may be produced by the reaction of carbon monoxide with sulfur, reduction of sulfur dioxide with carbon, or hydrolysis of carbon dioxide.

There does not appear to be any market that would be able to absorb the large scale production of carbonyl sulfide. Technology has been developed for hydrolysis of carbonyl sulfide in gas streams, which would permit the ready removal of the sulfur content as hydrogen sulfide. When carbonyl sulfide remains in Claus unit tail gas, it may be removed by the Beavon process. The sulfur compounds, including carbonyl sulfide and carbon disulfide, are converted to hydrogen sulfide by a process that involves hydrolysis and hydrogenation over a cobalt molybdate catalyst. The process for removing sulfur compounds from gas streams and recovering elemental sulfur is a widespread activity in the United States. The use of carbonyl sulfide as a feedstock for chemical manufacturing has been proposed, but does not appear to occur on a large scale at this time.

## Sulfur

One of the most important methods of sulfur production is the Frasch process, which has been used in the United States since 1894. The Frasch process uses superheated water pumped down through wells into deposits of native sulfur. The heat from the water melts the sulfur, which, being more dense than water, accumulates at the bottom of the well. The molten sulfur is then blown to the surface where it is ponded and the water removed.

**Consumption:** Sulfur is different from other major minerals in that it is used as a chemical reagent rather than as a component of a finished product. It is usually converted to an intermediate chemical to be reacted with other minerals and chemicals. The sulfur component is often not retained in the final product and discarded as a waste product. By far the largest of these intermediate chemicals is sulfuric acid. In 1987, about 87 percent of sulfur consumed was converted to or directly produced in this form (Morse, 1988 [59]). Sulfuric acid plants using elemental sulfur are normally located close to plants which consume the sulfuric acid, because the cost is lower to ship sulfur than sulfuric acid. Approximately 70 percent of the sulfur consumed in the U.S. is used for the production of agricultural chemicals.

**Supply and demand:** In 1987, approximately 10.6 million metric tons of sulfur were produced in the United States with a total shipment value of nearly $1 billion. Slightly more than half of the sulfur produced in the U.S. came from Texas and Louisiana. Recovered elemental sulfur was produced as a co-product at petroleum refineries and natural gas processing plants by 56 companies with 157 individual plants in the U.S. The major changes in the sulfur market from the previous year were a fall in Frasch production and an increase in sulfur demand. All three U.S. Frasch producers reduced production and withdrew from stocks. Frasch production has been cut by 30 percent over the last three years and is expected to continue to decline. Recovered elemental sulfur reached and all time high of 6.1 million metric tons in 1987 with nearly all the increase over the previous year coming from natural gas processing plants. Over the last 10 to 15 years, sulfur supply has switched from mainly Frasch production to recovered elemental sulfur.

Sulfur consumption in the U.S. rose 8 percent in 1987 to 11.3 million metric tons due to an increase in demand for sulfur used by phosphate fertilizer producers. Agricultural chemicals accounted for 70 percent of sulfur demand, followed by 11 percent for chemicals, 7 percent for petroleum refining, and 12 percent for a variety of manufacturing industries.

The critical short term issue for sulfur continues to be the level of demand. The amount of sulfur consumption over the next few years will be determined mainly by phosphate fertilizer consumption and inventory accumulation of finished phosphates. For U.S. sulfur demand to remain strong, both the farmers and domestic fertilizer manufacturers must continue to be able to compete successfully in the international marketplace. For the long term, supply factors become more important to the sulfur market. Reductions in U.S. Frasch production may be offset by an increase in imports or recovered elemental sulfur. One of the major problems with the sulfur supply is that recovered sulfur is non-discretionary and production is not adjusted for sulfur demand. The combination of non-discretionary supply and variable demand, which is largely dependent on the uncertain agricultural industry, may lead to periodic swings from oversupply to shortage (Morse, 1988 [59]; Eckert, 1988 [60]; and Rivoire, 1987 [61]).

### Recommendations for Hydrogen Sulfide and Carbonyl Sulfide

From economic considerations, both hydrogen sulfide and carbonyl sulfide reaction co-products should be converted to elemental sulfur. Hydrogen sulfide is toxic and corrosive, which would lead to serious problems with handling and storage. When industry is faced with the production of hydrogen sulfide as a co-product, it is normally converted to elemental sulfur by the Claus process. There also does not appear to be any market for large scale consumption of carbonyl sulfide. Elemental sulfur is the preferred form of sulfur. It is easily handled and stored and readily converted to sulfuric acid.

### Oil

There has been much research done on the production of "syncrudes" or synthetic crude oil derived from coal. These oils are similar to petroleum but may require different processing steps before they can be used as fuels. Coal derived oils typically contain high heteroatom contents, particularly nitrogen and oxygen, and also have lower hydrogen contents than petroleum. The oil may also contain a larger portion of distillates in the high boiling point range, which makes it more difficult, and therefore more expensive, to refine.

In studies sponsored by the U.S. Department of Energy, Chevron has been doing research on hydroprocessing of various coal derived liquids. These coal liquids were produced by coal liquefaction processes including SRC-II (Solvent Refined Coal), H-Coal, EDS (Exxon Donor Solvent), and ITSL(Integrated Two Stage Liquefaction). Chevron considered two refining plans. The first plan has target products of gasoline and mid-distillates (diesel and/or jet fuel), while the second refining plan has only gasoline as a target product. Estimated refining costs for a 50,000 barrel per day refinery ranged from $14 to $23.50 per barrel for the first plan and from $16 to $20.50 per barrel for the second plan. There are several factors that one must consider before attempting to apply these figures. It is unlikely that any new refineries will be built in the near future strictly for refining coal liquids. Coal liquefaction has been technically possible for many years, but it has not been economically attractive. Recent progress in direct coal liquefaction has led to a decrease in cost to approximately $35 per barrel. But with crude oil recently below $20 per barrel, coal liquefaction is not likely to become a commercial process in the near future. Unless there is a permanent rise in the price of crude oil, large scale refineries specifically for processing coal derived oils will not be built in the near future (Lumpkin, 1988 [62]). More likely, coal derived oils will be refined along with petroleum in existing refineries.

Before any specific upgrading process can be selected, for the co-product oil, various properties of the oil must be known. These include boiling point range, hydrogen level and heteroatom content, particularly nitrogen and oxygen. It would be premature at this point to consider any upgrading or refining process before these properties are known. Only after an upgrading process is then selected and its cost determined could an appropriate credit for the co-product oil be determined.

* * * * *

# APPENDIX B.

## QUESTIONS CONCERNING THE ECONOMICS OF DESULFURIZATION OF ILLINOIS COAL

Subhash B. Bhagwat
Mineral Economist
Illinois State Geological Survey

1) Are the economics of the process favorable to continue the project ?

The economics of the 1-Step Ethanol Desulfurization process have not been assessed as yet. A meaningful economic assessment must be based on experimental results from a 1- to 10-lb/hour continuously operating laboratory unit. The 1-Step process offers some conceptual advantages over the 3-Step process which increase the potential of the desulfurization effort to be economical. The main differences between the 1-Step and the 3-Step process are highlighted later in this section.

An attempt was made in 1988/89 to estimate the economic feasibility of a 3-Step process conceptual plant to desulfurize coal using carbon monoxide and ethanol. It is important to stress that the estimates were based on a "concept" of how the plant would be configured. Experimental data, especially on input-output mass balance, was too preliminary to be relied upon. However, economic estimates were made because the main purpose--desulfurization of coal--appeared to be successfully achieved in the laboratory.

The 1988/89 economic estimates of a conceptual 3-Step process plant to desulfurize Illinois coal were based on the following critical assumptions:

- desulfurization occurred in 3 stages;
- reaction time for desulfurization was about 20-25 minutes;
- safety precautions to handle carbon monoxide and hydrogen sulfide, both highly toxic gases, were needed; and
- the process byproducts would be acetaldehyde and elemental sulfur.

Under the above assumptions the conceptual 3-Step process plant would not have been economical without a 50 to 60 percent reduction in initial capital investments. The 1988/89 study recommended process simplifications to reduce the required investments.

The current approach to desulfurization differs significantly from the one on which the 1988/89 economic estimates were based. The current approach includes the following:

- a one-step process desulfurization instead of three-step process;
- a reaction time of 6-8 minutes in the 1-Step process instead of 20-25 minutes in the 3-Step process;
- elimination of the toxic carbon monoxide gas; and
- operation at lower temperatures and pressures.

The differences noted between the 3-Step and the 1-Step processes appear to be in the right direction in order to reduce investment costs:

1. The 1-Step process approach reduces the number of reactors with their accessories, piping and other cost factors.
2. The 2/3 reduction in reaction time increases plant capacity 3 fold or reduces the plant investments by approximately 50 percent. This is the largest single economic benefit of the 1-Step process over the 3-Step process.

3. Elimination of carbon monoxide and operation at lower temperatures and pressures further save investments because some safety features can be simplified or eliminated.

The previously stated cost saving potentials should be studied in the next stage of the project.

2) What are the byproducts? What is their value? Are there projected disposal problems?

The experimental data available to-date indicate that the 3-Step process will produce a very low-sulfur coal-like product, acetaldehyde and sulfur. Data from the 1-Step process are not sufficient to ascertain if the byproducts will be different from those of the 3-Step process. It is also realized that the byproduct stream will have to be carefully monitored for toxic substances in both 3-Step and 1-Step approaches to desulfurization.

The byproduct values will ultimately be determined by the demand/supply situation in the market at the time of project commercialization. Major new supply sources such as the coal desulfurization plants could alter markets radically. Under the currently prevailing circumstances, which are not expected to change until a substantial number of new plants are built commercially, the acetaldehyde is valued at about 50 cents per pound and elemental sulfur at about $90 per ton.

The low-sulfur coal-like product must be compared with its competing fuels in the market. Such a comparison requires a segmented approach as follows:

- In electric utility plants built before the initial clean air act became effective in 1971, the new desulfurized fuel from the proposed plant must compete with low sulfur western coals which currently cost about $3.00 per million Btu delivered in Illinois compared with about $1.50 per million Btu delivered cost of Illinois coal today. Under this scenario the ethanol desulfurization process has a maximum margin of $1.50 per million Btu in terms of net cost addition. This is the maximum margin because it must be expected that prices of western coal will be reduced when faced with competition. (It is assumed that pre-1971 plants will not consider retrofitting with "scrubbers" for compliance purposes).

- Plants built between 1971 and 1978, which used low-sulfur coals for compliance reasons, must be won back as customers. To do this, the clean coal-like product must be sold at a competitive price. Currently in Illinois, that price is determined by the low-sulfur western coal delivered to Illinois utilities at $ 3.00 per million Btu.

- Plants built after 1978 i.e. after the revised Clean Air Act became effective, must reduce pollution potential of the fuel they use by 70 to 90 percent. This virtually mandates the use of "scrubbers" regardless of what coal they use. The plants that we are concerned about will be those built after the commercialization of the Ethanol Desulfurization process. The "Ethanol Desulfurization" can, under the 1977 Clean Air Act amendments, serve as a substitute for scrubbers in attaining the mandatory 70-90 percent reduction in $SO_2$ emission potential. This leads to the following preliminary comparison of costs for an Illinois based electric utility (per million Btu).

| | Western Coal with scrubber | Illinois Coal with scrubber | Low Sulfur coal like product |
|---|---|---|---|
| Cost of coal delivered | \$2.00-\$3.00 | \$1.50 | ? |
| Scrubber cost | \$1.00-\$1.25 | \$1.50 | none |
| Total cost | \$3.00-\$4.25 | \$3.00 | \$3.00 or under |

The coal-like product with very low sulfur content must therefore aim to remain under \$3.00 per million Btu. If the product has a Btu value of 11,000 to 12,000 per pound, the delivered cost would have to be under \$66 to \$72 per ton.

The waste disposal issue involves a) generation of wastes and b) plant location. Sufficient data are not available to estimate what waste products will be generated in the desulfurization process. At this stage the main waste disposal issues to be concerned about are: the waste from conventional coal cleaning, which is near the mine, and the waste from burning the fuel, which is at the generating station.

It is expected that less waste will be generated by the electricity generating plants because the coal-like fuel will contain less than 1/10 of the original sulfur. This should lower waste disposal costs. If advanced conventional coal cleaning could reduce the ash content of coal delivered to the desulfurization plant, it would further reduce the waste disposal costs at the generating station.

3) How does the project timetable compare with the goals of the Clean Air Act? If work will not be commercial until the year 2000, and industry actively adds scrubbers, won't it be too late for this technology?

The Acid Rain bills passed by the two houses of the Congress require a reduction in $SO_2$ emissions by 10 million tons from the 1980 levels in two phases by the year 2000. In phase I, the emissions from coal burning power plants must be lowered to under 2.5 lbs $SO_2$ per million Btu consumed. In phase II, the emissions must be further reduced to 1.2 lbs $SO_2$ per million Btu. These two requirements will affect the older power plants, built primarily before 1971, because the newer plants are already required to meet the 1.2 lbs. emission limit. An important provision of the Acid Rain bills is a nationwide cap on emissions after the year 2000. Such a cap will mean that new plants could only be built if the emissions they cause are offset by further emission reductions from existing plants. If existing plant emissions cannot be reduced any further, the only alternative available would be to build plants free of emissions or to trade emission rights with other companies. An extremely low-sulfur fuel would find a good market under the anticipated post-2000 situation.

The acid rain bills do not mandate the use of any particular technology because the legislators do not wish to hinder development of new competitive technology. If scrubbers were considered as the only desirable technology there would be no need for any research programs except those intended to improve scrubbers. Apart from this basic free-market, pro-development consideration, there are good reasons to look forward to markets past the year 2000. The main reason for such a long-term approach is that the acid rain legislation is primarily intended to clean the pollution from existing non-compliance plants. (The new or recently built plants are covered by the Clean Air Act as amended in 1977). Coal burning electric utility plants will continue to be built after the year 2000 and they all will have to comply with very strict emission limits, especially if the acid rain act puts a cap on total emissions. Thus not only will this technology be timely in the year 2000, but there will be scope for many other technologies as well because the applicability of technologies often varies from plant to plant.

* * * * *

# APPENDIX C.

## SUMMARY REPORT - Design and Layout of Pilot-Size Continuous-Processing Unit for Demonstrating ISGS Coal Desulfurization Process

Lindal Mark, P.E.
C.W.Nofsinger Company
Engineering Consultants

# SUMMARY REPORT

Design and Layout of Pilot Size Continuous Processing Unit for Demonstrating I.S.G.S. Coal Desulfurization Process.

## EXECUTIVE SUMMARY

A Task Group assembled by I.S.G.S. administrative personnel has evaluated literature, experimental data, and seminar presentations to amass sufficient information from which the C.W. Nofsinger Co. was instructed to design a Pilot Unit. The process used was a novel one developed by I.S.G.S. and University of Illinois (U.I., S.I.U., and E.I.U.) investigators using a combination of carbon monoxide (CO) and ethanol treatment followed by chemical or magnetic separation of final iron sulfide troilite/pyrrhotite. Such a process is expected to produce compliance fuel coal from typical high-sulfur Illinois sources currently being under utilized.

Using information and conclusions from the Task Group, Nofsinger personnel have developed a preliminary design and equipment layout using available space in Room 203 of the Applied Research Lab at the Illinois State Geological Survey (I.S.G.S.) facilities. The Unit should process 1-10 kg/hour of high-sulfur coal in a continuous flow mode featuring mild pretreatment to prevent agglomeration, followed by a subsequent two-reactor environment using flowing treatment gases to produce a low-sulfur coal-like product. Advantages and disadvantages of the current layout are described, as well as a preliminary description of major processing equipment. No further design work has been done pending the outcome of recent I.S.G.S. fluidized-bed pilot work.

## I. INFORMATION AVAILABLE FROM I.S.G.S. SOURCES

It was necessary initially for the key Illinois Task Group personnel to familiarize members of the C.W. Nofsinger team (Lindal Mark, Dr. Stanley Walas, and Lane Harold) with the process concept and current state of development. This was accomplished in several conference phone conversations and in several visits to either Champaign, Kansas City or Lawrence, KS. This sequence took place during 1987 and the first half of 1988.

In addition, several key process and data transmittal documents were sent or given to Nofsinger personnel. These were as follows:

Project Proposal to Illinois Department of Energy and Natural Resources, "Carbon Monoxide-Ethanol Desulfurization of Illinois High Sulfur Coal: Demonstration."

ACS Symposium Series 64, Paper 19; "Fluid Bed Carbonization/Desulfurization of Illinois Coal by Clean Coke Process: PDU Studies"; pp. 248-266, Thomas D. Wheelock, editor, 1977.

ACS Symposium Series 64, Paper 20; "Hydrodesulfurization of Coals"; pp. 267-279, Thomas D. Wheelock, editor, 1977.

Process Description Sheet, "Carbon Monoxide-Ethanol Coal Desulfurization Process", Richard Shiley, Randall Hughes and Conrad Hinckley, no date.

Evaluation of Four Patents on Methacoal Development, John R. Webster, Consultant. (Patents 4,030,893; 4,045,092; 4,146,366; and 4,192,651).

Quarterly Report, "Carbon Monoxide-Ethanol Desulfurization of Coal," Conrad Hinckley, November, 13, 1987.

Quarterly Report, "Results of Coal Desulfurization Reactions", Conrad Hinckley, February 22, 1988.

Quarterly Report, "Carbon Monoxide-Ethanol Desulfurization of Illinois High-Sulfur Coal: Demonstration," Morris W. Leighton and co-workers, March 31, 1988.

Letter, Lawrence Wu to Dr. Stanley Walas, July 20, 1987.

Meeting Report, Dr. Lyle Albright to Henry Ehrlinger III, April 19, 1988.

Meeting Report, Dr. Lyle Albright to Henry Ehrlinger III, June 22, 1988.

Letter, Henry Ehrlinger III to Lindal Mark, May 19, 1988.

Phone Instructions taken by Lindal Mark, regarding Pressure, Temperature, and Organic Sulfur Basis Desired, no date.

Guideline FAX Letter, Lawrence Wu to Lindal Mark, December 23, 1987.

From these pieces of information gradually emerged the requested design basis for the Process Flow Diagram and for the preliminary design/configuration of major equipment pieces and layout. Please refer to Drawing No. 1010-D1 (Figure A), for a graphical depiction of major process equipment pieces and their flow relationship.

## II. INSTRUCTIONS GIVEN TO NOFSINGER FOR DESIGN

Room 203 in the Applied Research Lab was assigned to be used, even though it was only 3.4-3.7m high. The spacial advantages of a single reactor Pilot Unit were discussed, but this limitation would have necessitated performing the CO treatment in one run, storing the partially desulfurized, hot product, then making a subsequent run with ethanol to complete the in-reactor desulfurization. This limitation was felt to be overly restrictive, and Nofsinger was instructed to design two reactors in series. After discussing the data available, Nofsinger personnel were concerned that caking would present a problem as the coal was heated vigorously in the Charge Tank and metered through the first feeder into the first reactor. Accordingly, Nofsinger recommended sending the coal through these reactors once under mild conditions using flue gas to effect a minimum pretreatment so as to avoid subsequent caking. The pretreated coal would be recycled or stored and then passed through the reactors again, using flowing CO in the first reactor and flowing ethanol (and oxidant if necessary) in the second reactor. The continuous gas flow would sweep out product gases and avoid an incomplete desulfurization because of equilibrium considerations.

Heating would be provided in each reactor and the Charge Tank so that high-temperature processing could be achieved. Different temperatures could be achieved in each reactor, if required. Although some lab data indicated no need

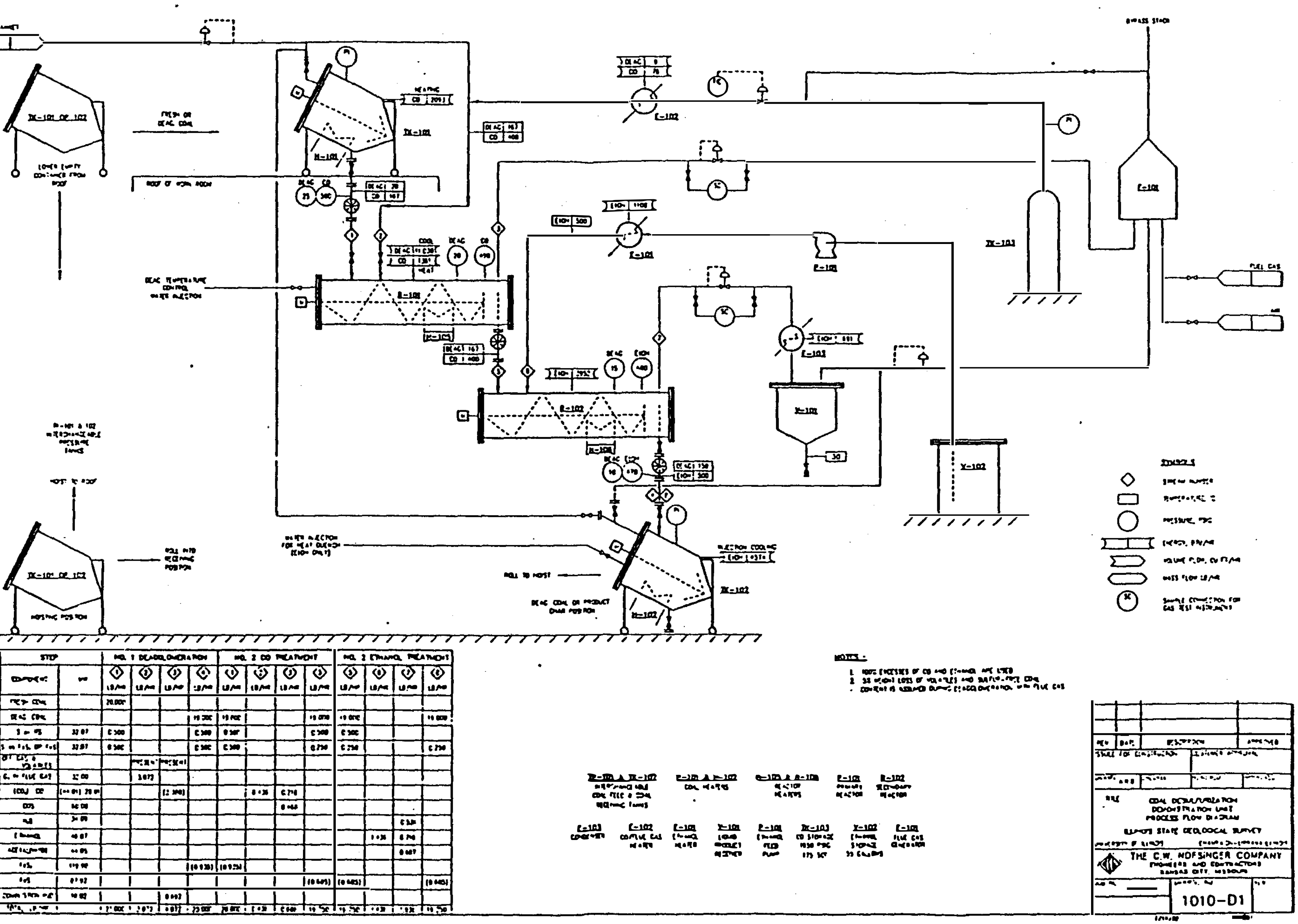


Figure A. Process Flow Diagram (1010-D1).

for pressures higher than 450 to 790 kPa (50-100 psig), the lack of complete experimental data (at that time) caused the Task Group to instruct Nofsinger to design for 3550 kPa (500 psig) and 500°C (932°F), in the reactors. The hope was that before final design and construction these parameters could be reduced somewhat.

Several reactor types were discussed and some literature reviewed. These included vertical stirred reactors, horizontal stirred reactors, and vertical fluidized-bed reactors. The Task Group selected the horizontal stirred reactor because of its ease of fabrication in high-pressure construction, its plug flow characteristic and its adaptation to once-thru flowing gas conditions. An adjustable weir design was agreed upon as sufficient to vary holdup time within desired limits in each reactor.

The Charge Vessel was sized to contain enough coal (or pretreated coal) to permit at least 12 hours of continuous operation. Since the scheme agreed upon called for two passes through the reactor system, it would be necessary to move pretreated coal from floor level back to the roof. No particular method of doing this was specified. The Task Group was unwilling to accept the hazard of containment of the hot char product at 250° to 500°C (482°-932°F) in a sealed pressure vessel for 20-60 hours before it cooled by natural conduction and convection. Nofsinger was instructed to design a rapid cooling method so that the vessel could be cooled enough to be made non-reactive before personnel left for the night. Since the two Charge Vessels are interchangeable, this meant that both should be fitted with heating and cooling capabilities.

Synfuels literature and information available from Stanley Walas indicated an operational limitation with lock hoppers above about 2860 kPa (400 psig). The decision was made to design with pressure rotary feeders although it was realized that our very low feed rates of 1-10 kg/hour would present a design challenge with the feeders operating at the extreme lower end of their capabilities.

Because the final separation of magnetic iron pyrrhotite ($Fe_7S_8$) had not been optimized and may require either innovative magnetic removal or further chemical treatment elements, Nofsinger was instructed to eliminate this final step in the present design. It was felt that it could be added successfully at a later date, even after construction, when definitive test data should be available.

## III. DESIGN CALCULATION CONSIDERATIONS

Initial consideration was given to both horizontal stirred reactors and to fluidized-bed reactors. Both had certain advantages for a desulfurization process. The need for providing high pressure and high temperature processing, and for providing two different reactor environments (one for contact with CO and one for contact with ethanol/oxidant) became increasingly desirable. Thus, subsequent preliminary calculations were built around a pair of horizontal, stirred pressure reactors piped in series and processing Illinois coal of 60-200 mesh size continuously. Consultant Dr. Stanley M. Walas of University of Kansas provided necessary design calculations.

By using appropriately heavy pipe and flanged ends, a suitable pair of pressure reactors could be constructed, and stirred with an adjustable speed ribbon mixer. The required maximum heat transfer coefficient of about 30 Btu/hr-ft$^2$-°F seemed reasonable, as fluidized bed reactors attain typically about 60 Btu/hr-ft$^2$-°F.

Various values of coal preheat from none to complete (500°C/932°F) preheat required heat transfer coefficient (U) values of 17-3 (same units). All of these seemed attainable with the reactors specified.

Caking of the coal was a possibility which, if it occurred to any appreciable extent, could foul the reactor's inner surfaces, worsen the coefficients and eventually plug the equipment. A wise precaution seemed to be to pretreat the coal by passing it through both reactors in series using low oxygen flue gas and mild conditions of 167°C (333°F) and 100 to 140 kPa (15-20 psia). The reactors can provide a wide range of holdup times (8.5-340 minutes) but a target of 68 minutes total for pretreatment (both reactors) was shown on the Process Flow Diagram. This pretreatment should protect reactors, rotary feeders and charge tanks from fouling excessively.

The holdup time for subsequent chemical treatment can be varied over wide limits but a target value of 34 minutes in each reactor will result from conditions shown on the Process Flow Diagram and using a 40 percent coal volume in each reactor. Adjustable weirs should permit holdup volumes between 10 percent and 40 percent.

The Charge Vessel TK-101 provides a way to get 125 kg of coal feed to the roof, enables storage and complete pressurization under a nitrogen blanket, and provides preheat for the coal feed to 167°C (333°F). This moderate level of preheat was specified by the Task Group because of safety considerations. Higher levels of preheat can be achieved by oversizing the heating panels.

The Receiving Vessel TK-102 provides; a) hot deagglomerated coal receiving (or hot product char receiving) at full pressurization under nitrogen blanket; b) controlled depressurization to the Flue Gas Furnace F-101 for safe destruction of residual toxic or flammable gases; and c) for the hot char product a controlled cooling to the range of 200° to 250°C (392°-482°F) by measured addition of deionized quench water. The deagglomerated coal can be stored overnight under nitrogen without unloading and lifted back to the roof for reprocessing.

No surge tank for coal between reactors is provided. Therefore, the feeder rates to both reactors must be very closely synchronized. Space in Room 203 does not permit a surge vessel. Rotary feeders will have a turndown rate such that feedrates of 1-10 kg/hour are possible. Such low rates require modification of small feeders for ultralow speed gearing and extra shallow buckets.

## IV. PARAMETERS FINALLY SELECTED FOR CONTINUOUS PILOT UNIT PRELIMINARY DESIGN (SEE DRAWING NO.1010-D1)

The Pilot Unit has been designed to handle 1-10 kg/hour of coal feed. Stated reason for such a low-end feed rate was to conserve coal at times when certain variables were being investigated. The high-end feed rate was needed to fulfill contractual obligations to sponsoring state agencies which called for a sustained feed rate of 10 kg/hour over 8-12 continuous hours.

Although the Task Group originally hoped to keep pilot pressures below 790 kPa (100 psig) and temperatures below 350°C (662°F), considerably higher maximum capabilities were finally specified to cover the uncertainty of yet-to-be-obtained (as of July 1988) laboratory data. Accordingly, the Pilot Unit was designed preliminarily for 3550 kPa (500 psig) and 500°C (932°F) operation at the reactors. Because of needed flange size and height, this decision resulted in the reactors being considerably larger and heavier than initially visualized. Our preliminary design thinking had been to construct the reactors of schedule 120 stainless pipe of 20cm nominal diameter and about 60cm long inside. Flanges would need to be at least 300kg rating. Estimated reactor weight including insulation would be about 450kg, exclusive of agitator weight. With coal occupying 40 percent of the internal volume, such a reactor would allow a residence time of about 35 minutes at the maximum feed rate of 10kg per hour. These reactor details are preliminary only, as final design was not done, but they are illustrative of the complexity into which the selected design conditions translate.

These reactors would be interchangeable and would be agitated slowly with end-mounted agitators. They would contain an adjustable (during shutdown) internal baffle which would control coal bed depth and thus residence time. Rotary feeders would be positioned above and below each of these reactors to meter the various coal flows and prevent surging or bridging.

The manufacturer makes the point that these units are machined to very close tolerances and are designed for very specific temperature/pressure ranges. Since the processing conditions for deagglomeration are much less severe than for CO/ethanol treating, it will probably be necessary to have at least two sets of these feeders available. One set will be bolted into the flow line while the others will be on standby and easily moved into position. A monorail system might be helpful in carrying these heavy units and holding the spare units alongside.

Available headroom in Room 203 of the Applied Research Lab is very limited. Our preliminary idea was to tightly stack feeders, reactors and floor-positioned Receiving Tank TK-102. Such space considerations required that Charge Tank TK-101 be placed on the roof of the building, with the first rotary valve located inside the building in the gallery or ridge ventilator area. The ultimate spacial feasibility of this scheme will await final design and specification of equipment pieces. Tanks TK-101 and TK-102 are interchangeable and have to be hoisted to the roof area. This scheme safely contains the fresh deagglomerated coal and avoids having to bag it off, carry it up, and redump it on the roof.

However, if the desired mode of operation should change and it is decided to deagglomerate a large supply of coal in one extended run, it would be possible to eliminate the need to lift and interchange these heavy vessels. Each would be permanently positioned in its place and the need for a heavy lifting hoist would be avoided. In this case the deagglomerated coal or char product would have to be bagged off after cooling.

In the deagglomeration scheme the coal is dumped into Tank TK-101 on the roof and pressurized to 170 kPa (25 psia) with nitrogen. Pretreatment is accomplished in both reactors sequentially under mild conditions of 167°C (333°F) and 140 kPa (20 psia) using on-site manufactured flue gas. Treated coal is received in TK-102 and hoisted back to the roof where the vessel is reconnected and heated under nitrogen to 167°C (333°F). CO treatment is accomplished in R-101 by heating to 400°C (752°F) and using CO gas from high-purity gas cylinders. Semi-treated material is then sent to reactor R-102 where the temperature is increased to 500°C (932°F) and the vessel flushed with heated ethanol vapors. Final char product is metered into Receiving Tank TK-102 where it will be cooled if desired to a safe overnight storage temperature by careful, controlled water injection. With this scheme, all vessels can serve a dual function but must be designed for the most stringent service.

## V. PREPARATION OF THE PROCESS FLOW DIAGRAM

The two reactors R-101 and R-102 are placed in sequence so each can have a separate gaseous environment and temperature if required. The need for heating in TK-101 and cooling in TK-102 is solved by providing heating panels and a water connection on each tank. Operating parameters are shown for each processing mode on the same drawing as noted.

Many different experimental results were available but did not always agree. The equipment called for will have a wide tolerance of operating capabilities. On a moisture-free basis we chose a 4.8 percent weight loss for mass balance in deagglomeration and a further 3.5 percent weight loss in CO/ethanol treatment. All sulfur was shown lost from the latter steps, but in practice some sulfur will likely be lost in each process step. Lower feed rates than the maximum 10 kg/hour shown for the illustrative material balance will likely result in higher residence times and correspondingly greater coal weight losses.

## VI. POSSIBLE PROBLEMS WITH CPU AS CURRENTLY LAID OUT

The most serious potential problem appears to be the physical size and constraints of Room 203 in the Applied Research Lab. Only about 3.4-3.7m of headroom is available. A comfortable equipment layout, with a monorail located above the reactors, would require about 4.6m of headroom, even with the Charge Tank TK-101 located on the roof. By compressing the assembly and placing the top rotary valve up in the ridge ventilator (skylight) area, we can get the height required to about 3.7-4.0m. Thus we are very marginal on having enough height, and a final verification of operability must await final design and selection of major equipment. Periodic changeout of rotary valves will be required and will be difficult in such compressed space.

The widely different operating conditions being requested between deagglomeration and actual chemical treatment present a problem for the rotary feeder manufacturer. These feeders are very carefully machined for tight clearances and do not adapt satisfactorily to pressures and temperatures greatly different from their design ratings. This means that at least two complete sets will be required. If experimental conditions of chemical treatment are varied widely (temperature and pressure), even more sets may be required. Consultation with the manufacturer on this problem is suggested.

Another task required because of the limited headroom available is to hoist Charge Tank TK-101 to the building roof and return it periodically. This vessel, built to withstand the operating conditions and insulated and loaded with coal, is expected to weigh 2000-2250 kg. An existing hoist is available, but may not be heavy enough and does not go all the way up to the roof. Hence, it will have to be modified or replaced to make possible these routine switches of the two charge tanks from the floor to the roof.

Lastly, the severe operating conditions so far required translate into bulky, heavy equipment pieces heavily insulated. Those pieces of equipment having to be moved or opened regularly will present the greatest problem. These are the rotary feeders and the two reactors. The feeders with gearmotor and insulation are expected to weigh 250-500 kg each, and the two reactors have been calculated to weigh about 500 kg each with agitator and insulation. Thus a monorail hoist is felt to be essential to permit two workers to roll these assemblies into place and support them while they are being bolted up.

Our conclusions on the size, weight, and operability of high-pressure rotary feeders have been derived from literature and comments supplied by Ms. Judith Stelian of Beaumont-Birch Co. of Pennsauken, N.J. Other feeders are possible, but it is doubtful they will be smaller or lighter than the 5cm model offered by Beaumont-Birch Co. A larger workspace or less severe operating conditions (temperature and pressure) would relieve many of these envisioned problems.

* * * * *