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Topics:
Coal pyrolysis
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Coal gasification

EPRI AP-5005
Project 2051-2
Final Report
January 1987

Pyrolysis of Coal for Production of Low-Sulfur Fuel

Prepared by
Westinghouse Electric Corporation
Pittsburgh, Pennsylvania

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NOTICE

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REPORT SUMMARY

SUBJECTS	Coal-derived gas / Coal-derived liquids / SO_X control / Coal preparation and analysis
TOPICS	Coal pyrolysis Coal desulfurization Fluidized-bed gasification Coal liquefaction Coal gasification
AUDIENCE	R&D managers and engineers

Pyrolysis of Coal for Production of Low-Sulfur Fuel

Fluidized-bed pyrolysis has potential as a process for producing clean burnable chars and liquid fuels from coal. Laboratory-scale pyrolysis experiments reduced SO_2 emissions from the product chars by 45% for Wyoming subbituminous coal and 68% for Illinois no. 6 coal.

BACKGROUND Pyrolysis is a simple, low-pressure process for segregating coal into a mixture of gaseous, liquid, and solid-fuel products. In previous work, EPRI has examined pyrolysis as a method of producing clean liquid and solid fuels for utility power plants (see EPRI reports AP-2603 and AP-3786). The process has not been applied commercially, however, partially because sulfur is distributed throughout the three product fuels, making all of them environmentally unacceptable.

OBJECTIVES

- To use coal pyrolysis to produce a low-sulfur solid fuel—or char—and to determine sulfur distribution in the solid, liquid, and gaseous pyrolysis products.
- To compare results of processing Illinois no. 6 and Wyoming subbituminous coal.

APPROACH In preliminary bench-scale experiments under EPRI project RP2051-1, the project team used a fixed-bed reactor for desulfurization of Illinois no. 6 coal (described in appendix A of the report). Subsequently, they extended this effort using a laboratory-sized fluidized-bed reactor (appendix B). The present project applied the fluidized-bed approach to Wyoming subbituminous coal. Analysts conducted four tests, varying temperature and fluidization gas composition during the course of the experiment to identify conditions for minimizing sulfur concentration in the char. They then determined the compositions of the gaseous, liquid, and solid pyrolysis products and calculated the anticipated SO_2 emissions from burning the char as a boiler fuel.

RESULTS Although the fluidized-bed pyrolysis process produced low-sulfur chars from both tested coals, sulfur levels were not low enough to meet New Source Performance Standards (NSPS). Calculated SO_2 emissions from burning the Wyoming subbituminous char were 0.4-lb $SO_2/10^6$ Btu, a 45% reduction from burning the feed coal. Burning the Illinois no. 6 char would result in a 68% reduction in SO_2 emissions. The NSPS would require a 70% reduction for the Wyoming-derived char and 90% for the Illinois-derived char.

EPRI PERSPECTIVE

In previous studies of coal pyrolysis, EPRI has encountered difficulties in upgrading tar to an acceptable liquid fuel and in using char as a boiler fuel. By reducing SO_2 emissions, this work made progress in addressing one of the difficulties associated with burning the char. Nevertheless, further laboratory work will be necessary before the pyrolysis method can produce an NSPS-compliant char from even a low-sulfur, low-pyrite young western coal.

PROJECT

RP2051-2
EPRI Project Manager: Robert W. Frischmuth
Advanced Power Systems Division
Contractor: Westinghouse Electric Corporation

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ABSTRACT

Various sulfur control strategies have been developed to meet existing federal regulations and potential future legislation. These include coal washing (physical cleaning), switching to low-sulfur coal, fluidized-bed combustion, coal gasification combined cycle, and flue gas desulfurization.

A fluidized-bed pyrolysis approach which selectively releases specific sulfur species while maintaining a significant portion of the heating value of the feed coal in the product char has been demonstrated on a laboratory scale at Westinghouse. This approach utilizes an alternate gas contacting sequence. The sequencing concept is based on a series of chemical reactions and transformations which are expected to occur within the organic and ash matrices of the coal. This report is a summary of three projects conducted at Westinghouse which identified process conditions that produce low sulfur char from Illinois No. 6 and Wyoming subbituminous coals.

ACKNOWLEDGMENTS

We wish to acknowledge the support and guidance of Mr. Robert Frischmuth, who served as our EPRI program officer under Contract No. RP 2051-02, and the continuing suppport of Mr. Neville Holt at EPRI. We also wish to acknowledge the efforts and contributions of the following Westinghouse Research and Development Center personnel: Mr. A. Carr for his excellent assistance in performing the fluidized-bed reactor test program; Mr. G. R. Marshall and Mr. R. D. Straw for their outstanding commitments in providing the gas chromatograph and elemental analyses; and Mr. A. L. Wolfe and Mr. R. E. Diss for their efforts in the ash characterizations. Expressed thanks are also extended to Mr. T. W. Bergstresser of the Geochemical Testing Laboratory for conducting sulfur distribution analyses, and to Mr. J. R. Pilling for providing the initial coal samples and analyses.

SUMMARY

This study, conducted under EPRI Contract No. RP 2051-02, produced low-sulfur chars from Wyoming subbituminous coal using a laboratory fluidized-bed process. The effort was a continuation of Contract No. RP 2051-01 in which 45 bench-scale, gas composition/temperature sequencing, fixed-bed reactor tests were performed with Illinois No. 6 coal. The relatively low desulfurization (57 percent total sulfur volatilization) which resulted in the fixed-bed reactor was attributed to poor contact between the reactant gas and the Illinois No. 6 coal sample which agglomerated during processing. In an extension to this effort, Westinghouse continued to explore the desulfurization approach with Illinois No. 6 coal in a fluidized-bed reactor unit. Fluidization enhanced the gas-solid contact, increasing the total desulfurization capacity of Illinois No. 6 coal to 87 percent.

Unrestrained combustion of Illinois No. 6 coal is projected to emit 4.08 lb $SO_2/10^6$ Btu. Under the New Source Performance Standard (NSPS), 90 percent sulfur removal would be required for Eastern coals, restricting SO_2 emissions from Illinois No. 6 coal to 0.4 lb $SO_2/10^6$ Btu. The preliminary test data demonstrate that a maximum sulfur dioxide emission reduction of 68 percent can be achieved for Illinois No. 6 coal in a fluidized-bed reactor system in the presence of steam, corresponding to an emission level of 1.29 lb $SO_2/10^6$ Btu.

The present work extended the fluidized-bed gas composition/temperature sequencing desulfurization approach to Western coals. Wyoming subbituminous coal was selected on the basis of its low ash content, low calcia and magnesia content, high organic and total sulfur content relative to other Western coals, and readily marketable reserves.

Four fluidized-bed tests were conducted with Wyoming subbituminous coal. The first test exposed -50 +60 mesh Wyoming subbituminous coal particles to low temperature (300°C), partially reducing gases in order to release inorganic pyritic and sulfatic sulfur. The fluidized-bed reactor temperature was then increased to 550°C in order to release sulfur from the various coal organic sulfur constituents. In the

presence of steam and temperatures ranging between 550° and 600°C, sulfidic sulfur was expected to undergo conversion to an oxide. Continued exposure to the elevated temperature was expected to promote maximum desulfurization of the aromatic and thiophenic sulfur constituents, resulting in a low sulfur processed char. Under these conditions, 35 percent of the coal's carbon content, and 70 percent of the coal's sulfur content were released during processing. Anticipated sulfur dioxide emission from burning the low sulfur char was calculated to be about 0.44 lb $SO_2/10^6$ Btu, corresponding to 41 percent removal.

Alternately, processing at high temperature (600°C) in the presence of steam in the second fluidized-bed test was considered to directly promote release from the organic sulfur complexes, with limited sulfur recapture within the ash constituents. Both inorganic and organic sulfur species were expected to undergo decomposition simultaneously. A maximum sulfur release of 76 percent was achieved under these process parameters; however, release of carbon from the coal increased to 43 percent. Anticipated sulfur dioxide emission from burning the low sulfur char was calculated to be about 0.41 lb $SO_2/10^6$ Btu, corresponding to 45 percent removal.

Gas chromatographic analyses of the initial tests indicated that the maximum concentration of sulfur released from Wyoming subbituminous coal occurred between 500° and 550°C. The third fluidized-bed test was therefore conducted at 530°C. A mixture of nitrogen and hydrogen was used to reduce the inorganic pyritic sulfur complexes and aliphatic and aromatic sulfides, and to limit carbon release. Later, steam was added to the H_2/N_2 fluidization gases. The purpose of the steam was to continue to remove sulfur from the inorganic constituents and to release sulfur bound within the aryl and thiophenic complexes. Although carbon release was minimized, the total sulfur release was also reduced. Anticipated sulfur dioxide emission from burning this char was calculated as 0.52 lb $SO_2/10^6$ Btu, corresponding to 31 percent removal.

The final fluidized-bed test conducted in this program was performed at 500°C, exposing Wyoming subbituminous coal initially to partially reducing (H_2/N_2) reactant gases, and subsequently to partially oxidizing (steam in H_2/N_2) reactant gases. The lower processing temperature was selected in an attempt to further minimize carbon loss during desulfurization. A final temperature increase to 560°C in the H_2/steam/N_2 environment was included to promote further conversion and desulfurization. The total desulfurization capacity under these conditions was marginally increased over the previous test (66 percent vs 65 percent, respectively); however, both tests were below the desulfurization levels achieved in either the low temperature/partially reducing, high temperature/partially oxidizing (Test 1), or high temperature steam (Test 2) exposure. Anticipated sulfur dioxide emission from burning Test 4 char was calculated to be 0.53 lb $SO_2/10^6$ Btu, corresponding to 29 percent removal.

The NSPS requires sulfur emission reductions of 70 percent for Western coals and 90 percent for Eastern coals. The preliminary desulfurization data indicate that when Wyoming subbituminous and Illinois No. 6 coals were exposed to 600°C temperatures in the fluidized steam/N_2 environment, the processed chars would achieve sulfur dioxide emission reductions of 45 percent and 68 percent, respectively. In order to meet the NSPS, further work on this approach is required. Alternately, utilization of the chars produced by gas sequencing for utility or industrial-sized boiler applications would require the use of additional gas desulfurization technologies in order to comply with the existing NSPS.

Recommendations for further work include: (1) additional laboratory work to refine this technique; (2) economic evaluation to determine if further work is justified; (3) identification of an overall flow-sheet to generate electricity which includes this approach.

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Section 1

INTRODUCTION

Coal used in utility and industrial-sized boilers accounts for approximately 20 percent of the total energy use in the United States. This use of coal, especially high sulfur coal, is currently limited by regulatory constraints on the emissions of sulfur oxides, nitrogen oxides, and particulates. To increase coal use in an environmentally acceptable manner with improved thermal efficiency and economics, three alternative routes -- namely, gasification, liquefaction, and fluidized-bed combustion -- have been emphasized during the last 10 years. Conventional gasification and liquefaction processes are generally designed to produce a single marketable fuel product, either gas or liquid. The supply and price of natural gas and petroleum crude, therefore, greatly influence the economic attractiveness of conventional gasification and liquefaction processes.

Westinghouse has conducted several experimental studies, developing a pyrolysis process for coal which produces a mix of gaseous, liquid, and solid fuel products that can be utilized in an environmentally acceptable manner. In comparison with conventional gasification and liquefaction processes, relatively less severe conditions of temperature, pressure, gas and solid residence times, and reactant gas composition can be employed to produce a mix of fuel products.

The concept behind these studies is that a low sulfur char material can be formed from coal under specific pyrolysis, hydropyrolysis, or gasification conditions at various temperatures, pressures, and gas contacting times, while maintaining a high heating value in the resulting char. By this means, the chars can be produced for use in conventional boilers without the necessity of stack gas cleaning systems for SO_2 removal.

In comparison with the single fuel production approach, the attractiveness of the Westinghouse pyrolysis process depends on the quality and quantity, as well as the market for the various fuel products -- low sulfur char, liquid crude, and fuel gas. The process design and operating conditions can be manipulated technically to produce either one or more of these fuels as primary products.

The pyrolysis process concept in Figure 1-1 shows the low sulfur char ("compliance" solid fuel[a]) as the primary product and demonstrates that the following events selectively release specific sulfur phases with minimal effect on the coal matrix (heating value) to produce a compliance solid fuel from coal:

- Exposure of coal particles to an inert gas or a reducing gas containing hydrogen at a temperature below 400°C which converts the FeS_2 to FeS, releasing sulfur as H_2S.

- Contacting the coal particles with a slightly oxidizing gas (mixture of oxygen and/or steam in an inert gas) which converts the sulfide(s) of iron into oxide(s) of iron, and also releases a portion of organic sulfur in vapor-gas products.

- If needed, exposing the partically desulfurized coal particles to a steam, or steam-hydrogen mixture in an inert gas at a higher temperature (< 600°C) which further releases organic sulfur, as well as any inorganic sulfur (in reduced form) remaining in the solid fuel.

The process concept as described above assumes that a reactor design and processing conditions (i.e, temperature(s); gas and solid residence times; various reaction environments (inert, reducing, oxidizing); composition of reactant gases (partial pressures of H_2, steam, O_2); operating pressure; and coal particle size) can be selected to produce a compliance solid fuel with minimal release of volatiles (carbon) from coal. Figure 1-1 indicates that under ideal conditions, the inorganic sulfur containing species and the organic sulfur containing structures in coal release sulfur independently via irreversible reactions. In actual practice (under nonideal conditions) there is a possibility that the released organic sulfur can be captured by the desulfurized iron, calcium, or magnesium species in the coal particles. The extent to which this can happen, and can be minimized, is currently under investigation.

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[a]Compliance Solid Fuel: $$\frac{\text{lb } SO_2}{10^6 \text{ Btu in Solid Fuel}} \leq 10\% \frac{\text{lb } SO_2}{10^6 \text{ Btu in Coal}}$$

$$\text{and} \leq 1.2 \frac{\text{lb } SO_2}{10^6 \text{ Btu}}$$

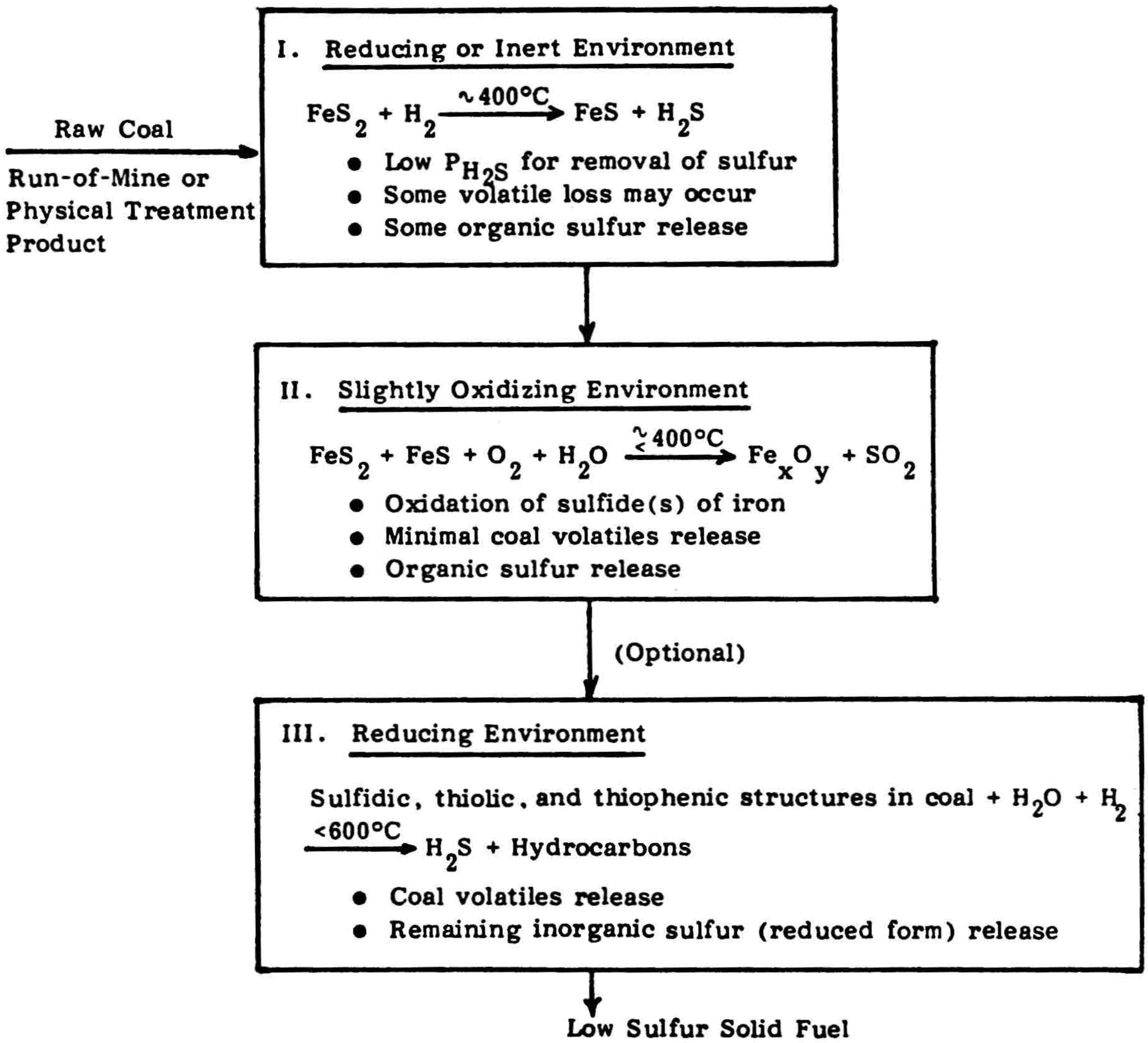

Figure 1-1. Westinghouse Coal Pyrolysis Process Concept

In order to demonstrate the feasibility of the pyrolysis concept, Westinghouse began by conducting an experimental program under EPRI Contract No. RP 2051-01 using a fixed-bed reactor system for the desulfurization of the high sulfur, agglomerating Illinois No. 6 coal. From the 45 bench-scale tests which were performed, a maximum of 57 percent desulfurization of the -20 +40 mesh Illinois No. 6 coal was achieved. Desulfurization principally occurred through the release of pyritic and sulfatic sulfur, with an observable increase in the char's combined sulfidic and organic sulfur content. The degree of organic sulfur release could not be assessed in this study since the analytical methods used did not differentiate between the sulfidic and organic sulfur constituents. This work is presented in its entirety in Appendix A.

Westinghouse-supported efforts continued to develop the gas composition/temperature sequencing desulfurization process, and demonstrated the effective use of a fluidized-bed reactor design for achieving a maximum of 87 percent desulfurization of -50 +60 mesh Illinois No. 6 coal. The summary report of this effort is presented in Appendix B. Higher desulfurization was attributed mainly to better contacting of the reactant gas with the fluidized Illinois No. 6 coal particles.

In the Illinois No. 6 coal fluidized-bed studies, the relative ease of sulfur release from the pyritic coal structure, and the conversion of pyritic sulfur into sulfidic sulfur were shown to have occurred under both partially reducing and/or oxidizing environments. Release of organically bound sulfur was most effectively demonstrated in the presence of a steam environment.

In comparison with the Eastern coals, Western coals and lignites contain a relatively lower total sulfur concentration, but higher organic sulfur concentration relative to their total sulfur content. Desulfurization of the Western coals and lignites was considered to require processing which not only selectively releases sulfur from both the inorganic and organic species, but which also focuses additional processing specifically on the decomposition of the organic sulfur complexes.

Westinghouse has undertaken the current study in an effort to demonstrate the application of fluidized-bed pyrolysis for desulfurization of Western coals or lignites; to gain insight into the optimization of gas composition/temperature sequencing desulfurization process conditions; and to provide fundamental