



Project Summary

In-Process Control of Nitrogen and Sulfur in Entrained-Bed Gasifiers

E. F. Aul, Jr., R. C. Adams, R. A. McAllister, and S. V. Kulkarni

The objective was to evaluate the theoretical aspects and engineering considerations of in-process pollutant control of the entrained-bed slagging coal gasification process as applied to combined cycle operation or to the retrofit to existing boilers. The pollutants of concern are the nitrogen and sulfur oxides (NO_x and SO_x) which, without controls, are products of combustion of the gasifier product gas. A literature search and theoretical evaluation were conducted to identify the chemical/physical conditions and flow characteristics of entrained bed slagging gasification as they relate to in-process control of NO_x and SO_x precursors. A tentative scheme was postulated to maximize the conversion of fuel nitrogen species to elemental nitrogen by operating modifications and to remove H_2S and HCN with the slag by injecting alkaline metal oxides into the gasifier gas space. However, the degree of success of the suggested in-process controls could not be projected.

The applicability of potential in-process control was examined. It was concluded that in-process controls, if feasible, are applicable for reducing NO_x and SO_x precursors so that the capacities of downstream control devices can be reduced with subsequent cost savings.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This project evaluated the theoretical aspects and engineering considerations of in-process pollutant control of entrained-bed slagging coal gasification processes as applied to combined cycle operations or the retrofit to existing boilers. The pollutants of concern are the NO_x and SO_x which, without controls, are products of combustion of gasifier product gas. Therefore, the goal of the study is to examine the potential for control within the boundaries of the gasification process to reduce or eliminate NO_x and SO_x precursors (H_2S , NH_3 , HCN , etc.) that are formed in the gasifier. The target of such control is the elimination or reduction in scale of downstream cleanup devices and/or combustion stack gas cleanup controls.

Procedure

The project consists of two tasks: (1) Theoretical Evaluation — a literature search and theoretical evaluation of in-process control; and (2) Applicability — assessment of the effects of in-process control on gasification product gas streams and the associated impact on the downstream processes.

The objective of Task 1 was to evaluate the information available concerning chemical/physical conditions and flow characteristics of atmospheric and pressurized, high temperature, slagging gasification as related to in-process control of NO_x/SO_x precursors.

The results are based on an intensive literature review and close examination of the most applicable work that has been done in the areas of concern. Information on entrained-bed slagging

processes that are under development or commercialized was collected to define the chemical, physical, and flow conditions. Five processes (KBW, Saarberg-Otto, Shell, Texaco, and TRW) were selected to provide an approximate range of base case characteristics within which gasifier operation can be varied to achieve effective in-process control.

The objective of Task 2 was to examine the effects on utility and industrial users of providing a cleaner fuel gas by means of in-process gasifier controls. In particular, the effects on new combined cycle plants and on retrofit utility and industrial boilers were investigated.

Results and Discussion

Gasifier Operating Boundaries

Emission limitations for NO_x/SO_x define precursor levels which must be attained to eliminate downstream controls; particle loading of the gasifier exit gas must be controlled to protect the gas turbine. Operating conditions will play a dominant role in optimizing in-process control. The prominent control variables in the gasifier and the operating conditions which influence these variables are:

- Oxidant staging: depends on burner design.
- Temperature: depends on oxygen/coal ratio, steam/coal ratio, oxidant, feed stream temperatures, coal composition, and heat losses.
- Residence time in the gasifier/slagging zone: depends on reactor volume, gasification temperature, coal particle size, and flow rates for coal, steam, and oxidant.
- Temperature zones (gasifier and cooling): depend on reactor design (volume reactor geometry, wet or dry cooling, slag removal).

These gasifier operation and design considerations were examined as they relate to possible in-process controls. The tentative conclusions regarding the flexibility of gasification processes for the application of in-process controls are:

- Compatibility of oxidant feed for in-process controls with base case oxidant feed methods will need to be determined. At least one process employs staged oxidant feed for NO_x control.
- There is some latitude in manipulation of O_2 /coal and steam/coal ratios if needed for in-process control.
- There is considerable latitude in how much the CO/H_2 ratios can be varied and still produce an acceptable product gas.

- Compatibility of residence times and temperatures required for optimum in-process controls with base case residence times will need to be determined.

- Two temperature zones within the gasifier provide an opportunity for staged injection of capture materials that will avoid or minimize sintering.

Due to a paucity of reported data, a base case untreated gas composition was pieced together from several design and actual operation sources; this composition is believed to represent a base case reasonably well.

Control Theory and Experience

Of the several types of reactions that take place in an entrained bed gasifier, only coal devolatilization, combustion of volatiles, and combustion and gasification of resulting char play a significant role in the generation and fate of nitrogen and sulfur species. Studies at gasifier conditions are usually carried out for either nitrogen or sulfur species, but not both. Therefore as an initial step it was necessary to examine the reactions separately.

The coal devolatilizes rapidly at gasifier temperature to form char and a gas fraction consisting primarily of CO , H_2 , CO_2 , and CH_4 . Significant quantities of HCN and NH_3 are also often reported. The quantity of volatiles produced has been shown to be a function of particle size, heating rate, pressure, and coal type.

Most workers in the field generally believe that HCN is the primary nitrogenous intermediate formed during pyrolysis of fuel nitrogen compounds. Subsequently, HCN reacts with other gaseous species to form NH_3 , NO , and N_2 .

Since both HCN and NH_3 in gasifier exit gas will be converted to NO_x by subsequent combustion of that gas, the objective of in-process control in the gasifier will be to convert a maximum fraction of fuel nitrogen to N_2 . Several studies have been conducted involving fuel-rich combustion of coal in which these same phenomena have been examined.

For the sulfur species case, as with nitrogen coal devolatilization, combustion of volatiles and combustion and gasification of the resulting char also play a dominant role in identifying the fate of coal sulfur. Sulfur is present in coal in three forms: organic, inorganic, and elemental. Review of work on the kinetic and thermodynamic relationships affecting sulfur species reactions at high temperatures reveals the following major expected effects:

- Pyrolysis of coal in the fuel-rich reducing atmosphere leads to devolatilization of sulfur compounds which readily are reduced to produce H_2S through the hydrodesulfurization mechanism. The reaction rate is very fast.

- COS and CS_2 are formed in the gasifier due to the reactions of devolatilized sulfur in the gas phase with carbon and the reaction of H_2S with CO_2 . COS is detected in gasifier effluents in small amounts, but CS_2 is usually not reported.

- Some of the H_2S is expected to react with the available basic oxides of the ash and thus be retained in the slag.

The use of metal oxides other than calcium as desulfurization media has been examined by the Morgantown Energy Research Center (MERC) for possible application as a hot gas contaminant control in the gasifier product stream. On the basis of thermodynamic studies, there are indications that the oxides of barium and strontium (and perhaps manganese) have potential as in-process sorbents. However, thermodynamic analyses do not address the physical phenomena, such as desurfacing, which may occur to solid sorbents at high temperature, and little information was found on physical effects work for metal oxides other than CaO .

Combined Effort for Control of NO_x and SO_x Precursors

The literature appears to address the issue of either SO_x control or NO_x control. Very few attempts to consider the effect of alkali oxides on gasifier intermediates such as HCN have been noted.

If CaO is added to the gasifier, competing reactions between CaO and HCN would significantly affect the concentration of HCN . Acidic HCN and basic CaO are expected to undergo a neutralization reaction that results in calcium cyanamide (CaNCN) as the reaction product. One would expect that the rate of absorption of HCN with CaO would parallel the rate of absorption of H_2S by CaO since both HCN and H_2S are acidic gases. During the absorption of H_2S by lime, the rate of reaction is found to depend on the reaction temperature and the desurfacing of CaO . Surface activity depends on temperature and plays an important role in the absorption of the acid gas. Probably such a phenomenon is important in the $\text{CaO} + \text{HCN}$ reaction also. Absorption of HCN by CaO will proportionately reduce the amount of NH_3 , NO , and N_2 in the gasifier exit gas.

It is expected that the sulfur and nitrogen compounds captured by the added CaO will be removed from the reactor with the slag. For H₂S absorption, the rate limiting step appears to be the internal particle diffusion process. Although diffusion itself is not strongly temperature dependent, desulfurizing will have a dramatic effect on the diffusion coefficient. Experimental observations suggest that CaO should be added to the gasifier at lower temperatures. The coal conversion requirements for an efficient gasifier demand that it be operated at higher temperatures. A possible compromise for maximum absorption activity and minimum desulfurizing activity for lime may be to add lime in the regions of lower temperature away from the flame. Probably a staged addition of lime will have to be adopted to facilitate removal of NO_x and SO_x precursors. Part of the CaO may be added with the coal slurry to capture H₂S/HCN released in the initial devolatilization, whereas the major portion of the lime may be added in the temperature regions of 800-1000°C. These temperatures correspond to the cooling zone of the gasifier.

Model Concept Development

The preceding discussion indicates potential means of reducing NO_x/SO_x precursor concentrations through in-process control. Without an available theoretical model that has been validated with actual results, the specific effects on product gas quality and precursor concentrations cannot be projected. The literature surveyed revealed that several models exist for entrained-bed slagging gasifiers. However, none of these models apply to control of nitrogen and sulfur species in the gasifier.

The feasibility of adopting an existing model for the prediction of nitrogen and sulfur species control effects was investigated. A model that was verified from Texaco pilot plant data was chosen.

Applicability of In-Process Controls

The applicability of in-process controls was examined in relation to the limitations imposed by the design specifications of the gas turbine of a new combined cycle plant and imposed by the emission limits of the gas turbine. Emission limitations were considered for the retrofit applications of utility and industrial boilers.

It appears that a modest reduction in gasifier NH₃ and HCN emissions by in-

process controls would result in compliance with NSPS for NO_x emissions from low-Btu gas-fed turbines. It would perhaps also eliminate the need for the downstream ammonia scrubber. However, medium-Btu gas would require in excess of 50 percent reduction of nitrogen species from the gasifier because thermal NO_x is a significant contributor to total NO_x emissions when medium-Btu gas is the fuel. Therefore, it is likely that NH₃ scrubbing or hot gas cleanup would still be required with in-process controls for gas turbine applications.

Assuming current and proposed SO₂ emission limitations for boilers that are based on heat input to the coal gasifier, gasifiers without in-process controls require substantial control device capacity downstream of either the gasifier or the boiler. Removal efficiency will vary depending on industrial- or utility-boiler applications, on air-blown (producing low-Btu gas) or oxygen-blown (producing medium-Btu gas) operation, or on coal sulfur content. In-process controls would limit control device capacity requirements.

For the gas turbine application, sulfur species concentrations are restricted by NSPS limits for sulfur in the fuel gas, SO₂ emissions in the gas turbine exhaust, and turbine design specifications to limit turbine blade corrosion. It appears unlikely that in-process controls for sulfur species can achieve the level of sulfur control required. Therefore, as with boiler applications, the primary benefit would be a reduction of the burden on downstream control devices.

Particulate matter (PM) control of gasifier product gas for gas turbine and boiler applications is substantially influenced by design specifications to avoid turbine blade erosion and protect gas burners from erosion and plugging. These design restrictions mandate that PM controls precede combustion. The use of dry sorbent injection for in-process sulfur control will increase the PM loading of the gasifier product, putting further demands on PM control devices.

Conclusions and Recommendations

On the basis of theoretical evaluations to understand nitrogen and sulfur species reaction mechanisms in entrained-bed gasifiers, some tentative conclusions have been formulated.

For the nitrogen case, the following process parameter changes are suggested as a way to increase the conversion of

fuel nitrogen to N₂ in an entrained-bed gasifier:

- Operate at higher O₂/coal ratios and hence higher temperatures.
- Decrease the particle size of feed coal.
- Inject a small amount of oxygen 50-100 msec downstream of the gasifier flame zone.

Under normal entrained-bed gasifier conditions, 85 to 90 percent of the fuel nitrogen which enters the gasifier is converted to N₂; the remainder exits as NH₃ and HCN. The objective of the process changes described above would be to raise this N₂ conversion to 95 percent or greater in order to combust the fuel gas in a new gas turbine and meet NSPS limitations without additional NO_x control. It is not possible, at this time, to project the N₂ conversion that would result from the recommended changes due to the complex interactions of process parameters and their effect on gas composition.

For the sulfur species case, some of the H₂S formed during gasification is expected to react with the available basic oxides of the ash and be removed with the slag. Further H₂S would have to be removed by reactions of metal oxides with H₂S. Experimental studies have shown that CaO will absorb H₂S, but significant surface area is lost above 1000°C as a result of sintering. Consideration of other materials (e.g., alkaline cement kiln dust, alkaline fly ash, and metal oxides being investigated in hot gas cleanup studies) is recommended.

It was concluded that the model that was verified from Texaco pilot plant data could be adopted as needed. Added assumptions would need to be made about the reaction surface area of CaO. The voidage fraction of CaO particles would need to be reduced from any measured values at ambient temperature to account for sintering at temperatures to be found in the entrained-bed gasifier.

If feasible, in-process controls are applicable for reducing the amount of NO_x and SO_x precursors to combined cycle gas turbines and to boiler retrofits so that the capacities of downstream control devices can be reduced (with subsequent cost savings), while still meeting emissions requirements and design specifications.

R. C. Adams, E. F. Aul, S. Kulkarni, R. A. McAllister, and S. Margerum are with Radian Corporation, Research Triangle Park, NC 27709.

Chester A. Vogel is the EPA Project Officer (see below).

The complete report, entitled "In-Process Control of Nitrogen and Sulfur in Entrained-Bed Gasifiers," (Order No. PB 87-141 032/AS; Cost: \$18.95, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Air and Energy Engineering Research Laboratory

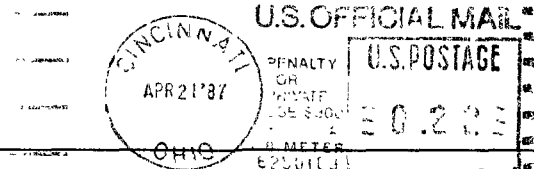
U.S. Environmental Protection Agency

Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use \$300
EPA/600/S7-86/051



0000329 PS

U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604