Advanced Sulfur Control Concepts

Final Report

Work Performed Under
Contract No.: **DE- AC21-94MC31258**

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Submitted to

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ABSTRACT

Conventional sulfur removal in integrated gasification combined cycle (IGCC) power plants involves numerous steps: COS (carbonyl sulfide) hydrolysis, amine scrubbing / regeneration, Claus process, and tail-gas treatment. Advanced sulfur removal in IGCC systems involves typically the use of zinc oxide-based sorbents. The sulfided sorbent is regenerated using dilute air to produce a dilute SO_2 (sulfur dioxide) tail gas. Under previous contracts (DE-AC21-93MC30010, DE_AC21-90MC27224), RTI (Research Triangle Institute) and the U.S. Department of Energy / National Energy Technology Laboratory (DOE/NETL) have developed the highly effective first generation Direct Sulfur Recovery Process (DSRP) for catalytic reduction of this SO_2 tail gas to elemental sulfur. This process is currently undergoing field-testing.

In this project, advanced concepts were evaluated to reduce the number of unit operations in sulfur removal and recovery. Substantial effort was directed towards developing sorbents that could be directly regenerated to elemental sulfur in an Advanced Hot Gas Process (AHGP). Development of this process has been described in detail in Appendices **A-F**. RTI began the development of the Single-step Sulfur Recovery Process (SSRP) to eliminate the use of sorbents and multiple reactors in sulfur removal and recovery. This process showed promising preliminary results and thus further process development of AHGP was abandoned in favor of SSRP.

The SSRP is a direct Claus process that consists of injecting SO_2 directly into the quenched coal gas from a coal gasifier, and reacting the H_2S-SO_2 mixture over a selective catalyst to both remove and recover sulfur in a single step. The process is conducted at gasifier pressure and 125 to 160°C. The proposed commercial embodiment of the SSRP involves a liquid phase of molten sulfur with dispersed catalyst in a slurry bubble-column reactor (SBCR).

From micro fixed bed reactor experiments, a total sulfur conversion of 99% with 35 ppm COS formation was achieved. Increasing pressure had a positive effect on sulfur removal. The SSRP process concept was found to be feasible in liquid sulfur medium. The liquid sulfur was shown to be inactive for direct reaction with reducing gases in coal gas. The process was scaled up to 50 cc of catalyst dispersed in 400 cc of molten sulfur in a continuous stirred tank reactor (CSTR). Conversion, as expected, was lower (up to 97%) in the CSTR compared to the fixed-bed reactor. COS formation up to 500 ppm occurred, but it could be reduced to 75 ppm by increasing the total flow and steam concentration and reducing the operating temperature.

A preliminary economic evaluation of SSRP with amine-based sulfur removal process showed that SSRP had the potential of reducing the cost of electricity in a 400 MWe IGCC plant by about 5%. It is recommended that the SSRP be tested with actual coal gas to evaluate the effect of coal gas contaminants. Further work is needed to mitigate COS slip in SSRP, e.g. by using a Claus catalyst with COS hydrolysis functionality. Kinetics of the SSRP reactions should be evaluated and solubility of sulfur gases and major coal gas components in molten sulfur should be measured to enable modeling of the SBCR based commercial embodiment. Following development of dual function catalysts, the process should be scaled up to a pilot-scale SBCR.

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ABBREVIATIONS AND ACRONYMS

%	percent
°C	degree Celcius
°F	degree Farenheit
A	Feed Procedure: SO_2 followed by coal gas (no steam)
A'	Feed Procedure: coal gas followed by SO_2 (no steam)
AHGP	Advanced Hot-Gas Process
AII	Adjustment for Interest and Inflation
ASU	Air Separation Unit
B	Feed Procedure: steam addition after Procedure A
B'	Feed Procedure: steam addition after Procedure A'
BET	Brunauer-Emmett-Teller
C	Feed Procedure: SO_2 followed by steam and then by coal gas
C'	Feed Procedure: coal gas followed by steam and then by SO_2
cc, cm^3	cubic centimeter
CGCU	Cold Gas Cleanup Unit
Cl	Chlorine
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COE	Cost of Electricity
COR	Contracting Officer's Representative
COS	Carbonyl Sulfide
CSC	Convective Syngas Cooler
CSTR	Continuous Stirred Tank Reactor
D	Feed Procedure: steam followed by SO_2 and then by coal gas
D*	Feed Procedure: steam followed by simultaneous SO_2 & coal gas addition
D'	Feed Procedure: steam followed by coal gas and then by SO_2
DOE	Department of Energy
DSRP	Direct Sulfur Recovery Process
E-alumina	Engelhard alumina
Fe_2O_3	Iron Oxide
FPC	Fractional Process Contingency
G	Feed stream: H_2S-containing coal-derived synthesis gas
G'	Feed Procedure: coal gas followed by steam (no SO_2)
h, h^{-1}	hour, inverse hour
H_2	Hydrogen
H_2O	Water, steam
H_2S	Hydrogen Sulfide
Hg	Mercury
HGCU	Hot Gas Cleanup Unit
HGD	Hot Gas Desulfurization
HHV	high heating value
IC	Installed Cost
IGCC	Integrated Gasification Combined Cycle
L	liter
Lb	pound

ABBREVIATIONS AND ACRONYMS (continued)

Lb/D	pounds per day
LHV	low heating value
LP	Mechanical and/or Electrical Power
MDEA	Methyl Diethanolamine
MWe	Mega Watt electric
NC	North Carolina
NETL	National Energy Technology Laboratory
NH_3	Ammonia
NOC	Net Operating Cost
O	Feed stream: O_2 in N_2
OX	Operating Expenses
P	pressure
P.O.	Post Office
PPC	Process Plant Cost
ppm	parts per million
PSDF	Power Systems Development Facility
psia, psig	pounds per square inch (absolute, gage)
RSC	Radiant Syngas Cooler
RTI	Research Triangle Institute
S	Feed stream: SO_2 in N_2
SBCR	Slurry Bubble Column Reactor
scc	standard cubic centimeter
SCOT	Shell Claus Offgas Treating
SLPM	standard liters per minute
SO_2	Sulfur Dioxide
SSRP	Single-step Sulfur Recovery Process
SV	space velocity
Syngas	synthesis gas
T	temperature, ton
T/D	ton per day
TCR	Total Capital Requirement
TGA	Thermogravimetric Analysis
TPC	Total Plant Cost
TPI	Total Plant Investment
U.S.	United States
W	Feed stream: water in the form of steam
WV	West Virginia
X	Conversion
ZnO	Zinc Oxide

ACKNOWLEDGEMENTS

EXECUTIVE SUMMARY

Background

Gasification of heavy feedstock (e.g. coal, petcoke, resid, biomass, and others) produces a raw syngas that must be cleaned before it can be used to produce electricity in a integrated gasification combined cycle (IGCC) power plant and/or synthetic liquid fuel using Fischer-Tropsch synthesis. The commercially proven process for gas cleaning involves quenching the gas to remove particulates and trace contaminants. Then a complex multi-step highly equipment intensive amine-based process consisting of an amine scrubber, regenerator, Claus plant, and tail-gas treatment plant to remove hydrogen sulfide (H_2S) and recover elemental sulfur follows. Also, conventional amine systems cannot effectively remove COS, and thus it needs to be hydrolyzed to H_2S first in a separate reactor.

To reduce the cost of electricity and increase efficiency of IGCC systems, research has been conducted on solid sorbent-based desulfurization systems for the past two decades. Advanced sulfur removal in IGCC systems involves typically the use of zinc oxide-based sorbents in a two-reactor system to reduce the H_2S and COS in syngas to below 10 ppmv:

$$ZnO + H_2S \text{ (or COS)} \rightarrow ZnS + H_2O \text{ (or } CO_2) \quad \text{(sulfidation)}$$

$$ZnS + 3/2\ O_2 \rightarrow ZnO + SO_2 \quad \text{(regeneration)}$$
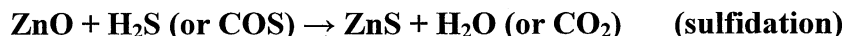
Due to the highly exothermic regeneration a dilute air stream is used. Unfortunately, this results in a problematic dilute SO_2 tail-gas that must be properly disposed. Conversion of this SO_2 to elemental sulfur is the most attractive disposal option. RTI has developed the highly effective first generation Direct Sulfur Recovery Process (DSRP) for catalytic reduction of the SO_2 tail-gas to elemental sulfur using a small slip stream of the syngas:

$$SO_2 + 2\ H_2 \text{ (or 2 CO)} \rightarrow 1/n\ S_n + 2\ H_2O \text{ (or 2 } CO_2)$$
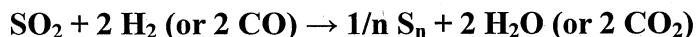
The combined sorbent / DSRP process is slated to begin undergoing field-testing in 2003 under a separate DOE contract (DE-AC26-99FT 40675).

Project Goal

The ultimate goal of this project is to develop a simple economically attractive process to remove and recover elemental sulfur from raw syngas that can be easily integrated with the gasifier. To this end advanced concepts were evaluated to reduce the complexity of conventional and advanced sulfur removal/recovery process.

Advanced Hot Gas Process (AHGP)

The problematic dilute SO_2 tail gas produced by air regeneration not only needs disposal but also consumes 2 mol of valuable reducing component in syngas for every mol of SO_2 that is

converted to elemental sulfur. To alleviate this problem, substantial effort was directed towards an Advanced Hot Gas Process (AHGP) that uses a bimetallic zinc-iron sorbent. It aimed to eliminate the problematic SO_2 tail-gas using a two-stage regeneration reactor in which the sulfided sorbent flows down counter current to a regenerating gas containing SO_2 and O_2. The iron sulfide portion of the sorbent is regenerated by SO_2 in the upper stage whereas the zinc sulfide portion of the sorbent is regenerated by O_2 in the lower stage to provide heat and SO_2 for the upper stage:

$$FeS + \tfrac{1}{2} SO_2 \rightarrow FeO + \tfrac{3}{4} S_2 \text{ (upper stage)}$$

$$ZnS + \tfrac{1}{2} O_2 \rightarrow ZnO + SO_2 \text{ (lower stage)}$$
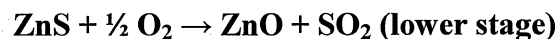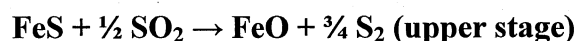
The effluent SO_2 and S_2 mixture is cooled to condense elemental sulfur, and the SO_2 is recycled. Following lab-scale feasibility studies, multi-cycle bench-scale tests were conducted at high-temperature, high-pressure conditions, to demonstrate quantitative elemental sulfur recovery. Preparations were made for a field test of the process at Southern Company Services Power Systems Development Facilities in early 2000. However, research emphasis had shifted toward lower temperature desulfurization due to the difficulty of trace containment (NH_3, Cl, Hg) removal at high temperature.

RTI began the development of a lower temperature Single Step Sulfur Recovery Process (SSRP). This process showed promising preliminary results and thus further process development of AHGP was abandoned in favor of SSRP. Complete details of the AHGP work are provided in Appendices **A-F** and the rest of this summary is dedicated to SSRP.

Single-Step Sulfur Recovery Process (SSRP)

Process Description

Unlike the amine-based process, the SSRP is a direct Claus process consisting of injecting SO_2 directly into the syngas to oxidize H_2S selectively on a suitable catalyst to both remove and recover sulfur in a single step.

$$2 H_2S + SO_2 \rightarrow 3/n\, S_n + 2 H_2O \qquad \text{(Claus Reaction)}$$
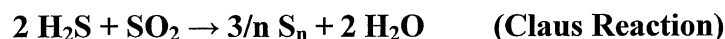
The key differences between SSRP and the traditional Claus process are: a) in SSRP the catalytic oxidation of H_2S by SO_2 (Claus reaction) occurs selectively in a highly reducing atmosphere containing the highly reactive H_2 and CO fuel gas components, and b) the reaction is carried out at the pressure of the fuel gas (300-1200 psig). Higher pressures favor conversion due to more favorable thermodynamics. The temperature of the SSRP reactor is between 125°C (257°F, where sulfur liquefies) and 160°C (320°F, where liquid sulfur viscosity starts to increase rapidly). The SSRP uses a catalyst that is highly selective for the oxidation of H_2S as opposed to the undesirable oxidation of H_2 and CO that is present in great excess in the syngas.

Commercial Embodiment

The proposed commercial embodiment of the SSRP involves a liquid phase of molten sulfur with dispersed catalyst in a slurry bubble-column reactor (SBCR) as shown in Figure ES-1; it is currently under development. The advantages of this embodiment are: a) ease of scale-up and excellent temperature control; and b) the potential to eliminate the Claus plant, amine regenerator, and COS hydrolyzer, by removing COS in addition to H_2S in a single step.

Furthermore, the molten sulfur can act to:

- Moderate the reaction, minimize side reactions, and control the temperature; and
- Dissolve sulfur formed on the catalyst surface, thereby achieving recovery of product as well as a potential shift in thermodynamic limitations on sulfur formation.

Experimental

The SSRP was studied in a 5-cc micro fixed-bed reactor, a 1-cc molten sulfur bubbler and a 2.0-liter continuous stirred tank reactor containing up to 50 cc of catalyst and 400 cc of sulfur. Most of the experiments were conducted using an Engelhard alumina catalyst. Blank reactors and molten sulfur without catalyst were also evaluated.
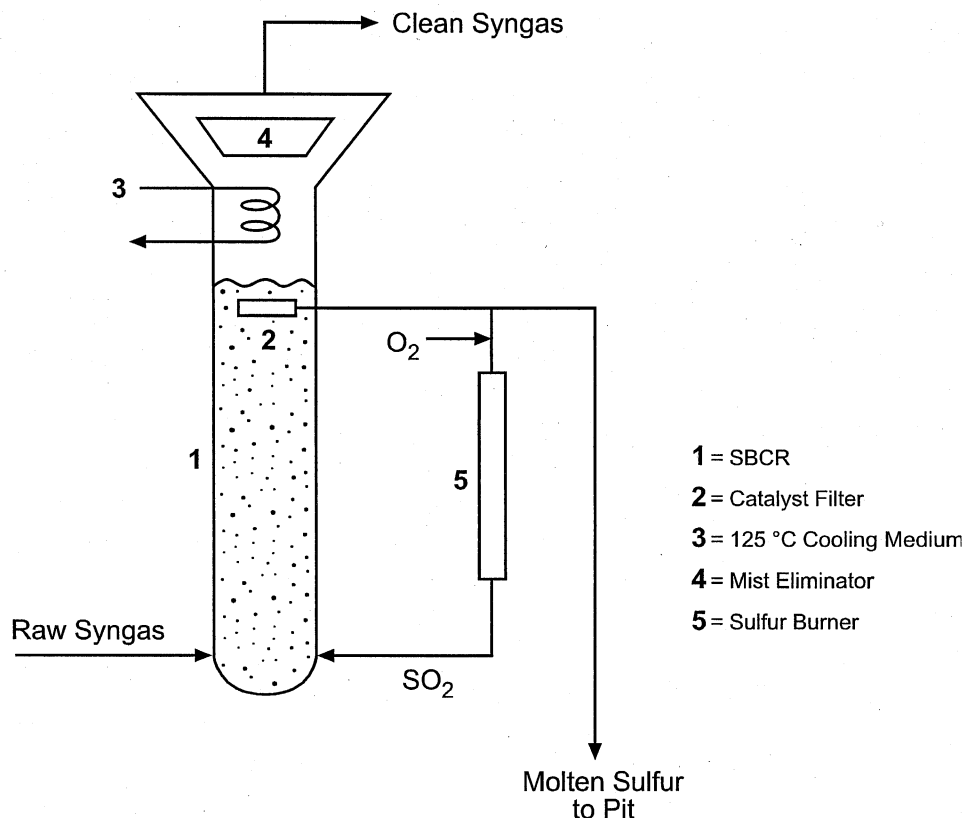

Figure ES-1. Proposed commercial embodiment of the Single-step Sulfur Recovery Process (SSRP)

Results and Accomplishments

- From micro fixed-bed reactor experiments, a total sulfur conversion of 99% with 35 ppm COS formation was achieved.

- The SSRP concept was shown to be feasible in the liquid sulfur medium.

- The process was scaled up to 50 cc of catalyst dispersed in 400 cc of molten sulfur in a continuous stirred tank reactor (CSTR).

- The liquid sulfur was shown to be inactive for direct reaction with reducing gases (H_2 and CO) in coal gas, but was shown to be active for the Claus reaction.

- Conversion, as expected, was lower in the CSTR (up to 97%) compared to fixed-bed reactor (up to 99%).

- COS formation up to 500 ppm occurred in the CSTR, but it could be reduced to 75 ppm by increasing the total feed flow and steam inlet concentration and reducing the reaction temperature.

- Runs over 100 hours duration demonstrated no deactivation of the catalyst. This suggested that the sulfur formed on the catalyst surface dissolved into the molten sulfur medium.

- A patent was filed on the process and papers were presented at the Pittsburgh Coal Conference (September 2002) and AIChE Meeting (November 2002).

- A preliminary economic comparison of the SSRP with a conventional amine-based process showed the potential to reduce the installation cost, operating cost, and cost of electricity of a 400 MWe IGCC plant by about 5%.

Recommendations for Future Work

Further work is needed to minimize COS formation in SSRP by (1) preventing COS formation during SSRP and (2) promoting COS hydrolysis and hydrogenation during SSRP. Fundamental research is needed to develop proper catalysts by combining Claus and COS conversion functionalities. Kinetics of the SSRP reactions should be evaluated. The solubility of sulfur gases and major coal gas components in molten sulfur should be measured to enable modeling of the SBCR commercial embodiment. The process should be scaled up to a pilot-scale SBCR.