FINAL REPORT

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Development of an Integrated Multi-Contaminant Removal Process Applied to Warm Syngas Cleanup for Coal-Based Advanced Gasification Systems

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Abstract

This project met the objective to further the development of an integrated multi-contaminant removal process in which H_2S , NH_3 , HCl and heavy metals including Hg , As , Se and Cd present in the coal-derived syngas can be removed to specified levels in a single/integrated process step. The process supports the mission and goals of the Department of Energy's Gasification Technologies Program, namely to enhance the performance of gasification systems, thus enabling U.S. industry to improve the competitiveness of gasification-based processes. The gasification program will reduce equipment costs, improve process environmental performance, and increase process reliability and flexibility.

Two sulfur conversion concepts were tested in the laboratory under this project, i.e., the solvent-based, high-pressure University of California Sulfur Recovery Process – High Pressure (UCSRP-HP) and the catalytic-based, direct oxidation (DO) section of the CrystaSulf-DO process. Each process required a polishing unit to meet the ultra-clean sulfur content goals of <50 ppbv (parts per billion by volume) as may be necessary for fuel cells or chemical production applications. UCSRP-HP was also tested for the removal of trace, non-sulfur contaminants, including ammonia, hydrogen chloride, and heavy metals. A bench-scale unit was commissioned and limited testing was performed with simulated syngas. Aspen-Plus®-based computer simulation models were prepared and the economics of the UCSRP-HP and CrystaSulf-DO processes were evaluated for a nominal 500 MWe, coal-based, IGCC power plant with carbon capture. Section 1 of this report covers the progress on the UCSRP-HP technology development. The CrystaSulf-DO technology is covered in Section 2.

UCSRP-HP

A 1,000 hour solvent stability and materials of construction compatibility test that showed the catalyst was stable, carbon steel is an acceptable material of construction of the reactor/contactors, and that high quality sulfur (up to 99.2% elemental sulfur) was formed. Nine five percent mercury removal, to levels of less than 0.2 ppb, was observed. Preliminary selenium testing showed that the solubility of H_2Se was increased by the presence of an aqueous solution of DEG, ammonia, and chloride over water. Formation of carbonyl sulfide appears to be controllable by the excess of sulfur dioxide. Testing during this period indicated that 50% hydrogen selenide (H_2Se) and 33% arsine (AsH_3) removal was achieved during a 30 minute test. Ammonia and HCl solubility are dependent on the water content within the diethylene glycol (DEG) solvent. Experiments illustrated that when sulfur dioxide is added to the feed, both hydrogen sulfide and carbonyl sulfide are consumed. Ninety five percent of the carbonyl sulfide (from 490 to 35 ppm in a single stage reactor) was consumed and 99 percent of the hydrogen sulfide (from 10% to 70 ppm). Any COS that is not converted to H_2S within the reaction zone of the process will be absorbed into the lean diethylene glycol methyl ether (DGM) at the top of the column and brought back to react with the SO_2 and water. Further laboratory tests are required to determine the COS concentrations expected at the top of the reaction section of the column in order to size the DGM circulation rate.

Aspen Plus simulations were performed that indicate complete removal of ammonia (NH_3), hydrogen chloride (HCl) and hydrogen selenide (H_2Se) in the aqueous scrub step of the UCSRP-HP process. Thermodynamic considerations point to minimal formation of COS in the UCSRP-HP reactor for a CO_2 -rich-feed as compared to a CO -rich-feed gas stream.

An economic evaluation was performed that integrated the UCSRP-HP into a nominal 550 MWe Integrated Coal Gasification Combined Cycle (IGCC) facility gasifying Illinois coal. The results indicated that the cost of electricity (COE) could be reduced by about \$9.60/MWh (9.3%) compared to conventional IGCC technology with carbon capture, transportation, and

sequestration, estimated at \$103.00/MWh by DOE. The COE saving is mainly derived from a reduction in the overall capital expenses of about \$123 MM (December 2006 dollars). The UCSRP-HP design emits about 22 lb/h less SO₂; reducing the emissions to near zero would increase the capital by about \$10 MM and have a minimal effect on the COE. With these promising results, UCSRP-HP was integrated with advanced H₂/CO₂ separation technologies. With LANL/SRI's PBI membrane, UCSRP-HP decreased the COE from \$98.20 to \$94.70/MWh. With GTI/PoroGen's CarboLock membrane contactors, the COE decreased from \$93.40 to \$91.70/MWh. While replacing Selexol with the Advance H₂ Membrane decreased the COE with RTI Warm Gas Cleanup from \$101.60 to \$89.60/MWh, substituting UCSRP-HP for RTI resulted in an \$88.80/MWh COE.

The bench-scale test unit was fabricated and installed at GTI. It was delayed by third party construction issues under the cofunded DOE and GRI projects and impacted the performance of a number of tasks.

CrystaSulf-DO

This part of the project was undertaken to expand on work previously performed by CrystaTech and the Gas Technology Institute (GTI) with funding from various industrial clients in the area of hydrogen sulfide (H₂S) removal from coal gasification syngas streams. In that previous work, commercially available catalysts were tested for Direct Oxidation (DO) of H₂S to sulfur at pressure ranging from atmospheric to 800 psig and temperature from 250 °F to 600 °F. The equipment used for the project, the Catalyst Test Unit (CTU), is located in GTI's facilities in Des Plaines, IL and has been described in a previous publication.¹ Other operating parameters were also evaluated during the previous work. While much information was gathered and advancements were made, there was no clear catalyst or set of operating conditions that could be identified as acceptable for removal of large amounts (at least 70%) of H₂S in the syngas stream by converting it to sulfur. This current project sought to use the results of the previous work and identify a catalyst and operating conditions that would be more successful for converting H₂S to sulfur in coal gasification syngas streams.

CrystaTech and GTI discovered previously that many different catalysts could be used to convert H₂S into sulfur in gasification syngas streams, all with varying degrees of success. However, there were consistently two things generally common to all of the tests: first, was that when sulfur and carbon monoxide were present at high temperature (+ 250 °F) a significant amount of carbonyl sulfide (COS) was formed, and second, was that, as the temperature was increased, less H₂S was converted to sulfur. These observations and others were incorporated into the test plan for the current work under this project.

This section will provide a brief summary of the project test results; following sections will provide all of the detail by task. Based upon the data that was gathered during this testing program, the following conclusions have been made:

- When operating the DO reactor above the sulfur dewpoint temperature, i.e., above approximately 260 °F, the O₂ added to the process to react and convert H₂S into sulfur also reacts with and consumes CO and H₂, which is a significant drawback for a commercial unit.
- Based upon the above conclusion the majority of this work was conducted at sulfur sub-dewpoint temperature; at sub-dewpoint the sulfur accumulates on the catalyst rather than "dripping off". Because of the sulfur accumulation on the catalyst, the DO reactor should be operated in a multiple bed configuration, where one catalyst bed is in service at sulfur sub-dewpoint and the other is being regenerated at above sulfur dewpoint temperature
- Catalyst D was tested during September for 100 hours in a multiple bed configuration where H₂S was converted to sulfur and adsorbed for 6 hours followed by a 6 hour regeneration

step with nitrogen flowing at approximately 600 °F. However, the final cycle of the regeneration was not successful, indicating that a different regeneration approach is required, or that the catalyst has a very short lifetime. The vendor for Catalyst D was consulted for a different regeneration approach. The vendor successfully regenerated the catalyst at 572 °F in a flowing air stream for 2 hours.

- The long term test of Catalyst C in multiple bed operation was not successful.

Table of Contents

Disclaimer	i
Legal Notice	ii
Abstract.....	iii
Table of Contents.....	vi
Table of Figures	x
Table of Tables.....	xiv
SECTION 1: UCSRP-HP SULFUR RECOVERY	1
Disclaimer	3
Legal Notice	4
Abstract.....	5
Table of Contents.....	7
Table of Figures	12
Table of Tables.....	14
Executive Summary	16
Approach.....	22
Scope of Work.....	22
Tasks to be Performed	22
Task 1.0 – Bench-Scale UCRP-HP Reactor Setup Design, Construction and Commissioning:	22
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	22
Subtask 2.1 – UCSRP-HP Solvent Degradation and Corrosion	22
Subtask 2.2 – GTI Trace-Contaminant Removal	23
Subtask 2.3 – UCSRP-HP Sulfur Removal	23
Task 2.4 – CrystaSulf-DO Sulfur Removal.....	23
Subtask 2.5 – Syngas Component Effects on SO ₂ Formation	23
Subtask 2.6 -- UCSRP-HP Solvent Regeneration	23
Task 3.0 – Computer Simulation Model.....	24
Subtask 3.1 – Preliminary Aspen Model	24
Subtask 3.2 – Aspen Model	24
Task 4.0 – Economic Evaluation	24
Subtask 4.1 – Preliminary Economic Evaluation.....	24
Subtask 4.2 – Economic Evaluation.....	25
Task 5.0 –Bench-Scale Experiments.....	25

Subtask 5.1 – Reaction Kinetics	25
Subtask 5.2 – Trace Contaminants Removal.....	25
Subtask 5.3 – Hydrodynamics of the Gas-Liquid-Liquid Flow.....	25
Subtask 5.4 – Packed Bed Efficiency and Parameter Optimization.....	25
Task 8.0 – Project Management and Reporting	25
Introduction and Background	26
Treatment of Synthesis Gas from Coal Gasification	28
Reactor	28
NH ₃ and SO ₂ Removal.....	29
SO ₂ Generation.....	29
CO ₂ Capture	29
Syngas Temperature Recovery	30
Experimental Procedures.....	32
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	32
Solvent Degradation and Materials of Construction Experiment	32
Trace Contaminant Removal	35
Vapor-Liquid Equilibrium Experimentation.....	36
Heavy Metal Removal.....	38
Ammonia and Halogen Removal	39
Trace Sulfur Removal.....	41
Task 5.0 –Bench-Scale Experiments	46
Flooding	46
Mass Transfer Rates	47
Heat Transfer Rates	47
Column Limitation	47
Startup Permissives.....	47
Experimental Procedure	48
Gas Only Pressure Drop.....	48
Flooding Curve Testing.....	48
Operating Conditions (Liquid and Gas Flow Rates).....	49
Heat Transfer Coefficient.....	49
Mass Transfer Coefficient.....	49
Kinetic Testing	49
Results and Discussion.....	50

Task 1.0 – Bench-Scale UCRP-HP Reactor Setup Design, Construction and Commissioning:	50
Construction and Commissioning	51
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	58
Subtask 2.1 – UCSRP-HP Solvent Degradation and Corrosion	58
Subtask 2.2 – GTI Trace-Contaminant Removal	61
Ammonia and Halogen Removal	69
Regeneration of DEG	77
Subtask 2.3 – UCSRP-HP Sulfur Removal	81
Subtask 2.6 -- UCSRP-HP Solvent Regeneration	88
Task 3 – Computer Simulation Modeling and Economics	88
Subtask 3.1 – Preliminary Aspen Model	88
Subtask 3.2 – Aspen Model	91
Design Basis	92
Task 4.0 – Economic Evaluation	104
Subtask 4.1 – Preliminary Economic Evaluation	104
Subtask 4.2 – Economic Evaluation	108
Overall Material Balances	108
Equipment List	108
Total Installed Plant Cost Details	108
Energy/Utility Requirements, Plant Performance & Overall Sulfur Balances	111
DOE Case 2 vs. GTI UCSRP-HP Base Case	112
GTI UCSRP-HP Design Case 2: Achieve a H ₂ S Level in Product Syngas <50 ppbv	115
Economic Potential for the Integration of Key Membrane Technologies for the Removal of CO ₂ and H ₂ with the UCSRP-HP Sulfur Removal Process in IGCC Applications	116
Task 5.0 –Bench-Scale Experiments	121
Conclusions and Recommendations	124
LIST OF ACRONYMS AND ABBREVIATIONS	126
References	131
Acknowledgements	133
Appendix A – Bench-scale Unit Construction and Commissioning Activities	134
Construction Activities	134
Commissioning Activities	135
Appendix B – Brown and Root Braun's SO ₂ Generation Process	138
SECTION 2: CRYSTASULF-DO SULFUR RECOVERY	141

Disclaimer	143
Legal Notice	144
Abstract	145
Table of Contents.....	147
Table of Figures	149
Table of Tables.....	151
Approach.....	152
Scope of Work.....	152
Tasks to be Performed	152
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	152
Subtask 2.4 – CrystaSulf-DO Sulfur Removal	152
Subtask 2.5 – Syngas Component Effects on SO ₂ Formation	153
Task 3.0 – Computer Simulation Model.....	153
Subtask 3.1 – Preliminary Aspen Model	153
Subtask 3.2 – Aspen Model	153
Task 4.0 – Economic Evaluation	154
Subtask 4.1 – Preliminary Economic Evaluation.....	154
Subtask 4.2 – Economic Evaluation.....	154
Task 8.0 – Project Management and Reporting	154
Task Descriptions and Results	155
Task 2.4 CrystaSulf-DO Bench-scale Feasibility Tests for Multi-Contaminant Cleanup	155
Subtask 2.4.1 Catalyst Evaluation	155
Subtask 2.4.2 Operating Condition Optimization	177
Subtask 2.4.3 Long Term Testing.....	186
Subtask 2.4.4 Vapor-Liquid Equilibria Experiments.....	218
Subtask 2.5 Syngas Component Effects on SO ₂ Formation.	231
Task 3.0. Computer Simulation	240
CrystaSulf-DO Process Model.....	240
CrystaSulf-DO Process Description.....	240
Task 4.0. Economic Evaluation	247
Recommendations for Future Testing	257
References.....	258
List of Acronyms and Abbreviations.....	259
Biography.....	260

Table of Figures

SECTION 1: UCSRP-HP SULFUR RECOVERY

Figure 1 UCSRP-HP Block Diagram.....	31
Figure 2 UCSRP-HP Solvent Degradation and Corrosion Experimental Layout	34
Figure 3 Trace Contaminant Testing Apparatus	35
Figure 4 Mercury Permeation Tube	36
Figure 5 Mercury Vapor Sorption Apparatus	36
Figure 6 High Pressure Vapor Liquid Equilibrium Cell.....	36
Figure 7 Schematic of GTI Vapor-Liquid Equilibrium Cell.....	38
Figure 8 Trace Component Removal with Ammonia, Chloride, and Selenium	39
Figure 9 Trace Metal Experimental Schematic	40
Figure 10 Block Diagram of the Experimental Determination of Gas Solubility at Set Pressure.....	41
Figure 11 COS Experimental Set up.....	43
Figure 12 COS Test Equipment.....	44
Figure 13 Start Up Permissive for the Sulfur Mode	47
Figure 14 As-Designed Bench-Scale Unit P&ID	52
Figure 15 As-Built Bench-Scale Unit P&ID	53
Figure 16 Bench-Scale Unit Being Installed at GTI	54
Figure 17 Bench-Scale Unit.....	55
Figure 18 Bench-scale Unit Being Unloaded at GTI	56
Figure 19 Risk Matrix	57
Figure 20 Carbon Steel (left) and Stainless Steel (right) Coupon Photographs Before (top) and After (bottom) Clean up After 1,000 h in Solvent	61
Figure 21 Mercury Concentration in the Vapor Phase in the Presence of DEG	62
Figure 22 Mercury Concentration in the Vapor Phase with No Solvent.....	62
Figure 23 Trace Component Removal with Ammonia, Chloride, and Selenium	62
Figure 24 DEG After Exposure to H ₂ Se, NH ₃ , and Chloride	63
Figure 25 Sensitivity Analysis: Calculation of Distribution Ratio for the N ₂ -NH ₃ -Water System (30 °C).....	76
Figure 26 Equilibrium Distribution of Species using Aspen Plus (solvent: water).....	80
Figure 27 Effect of Trace Component Addition on the Distribution of Ammonia and Hydrogen Sulfide (Aspen simulation, T = 250°F, P = 800 psi, Base Gas Composition: Table 20), A. Ammonia B. Hydrogen sulfide	81
Figure 28 Illustration of Decreasing SO ₂ Concentration Being Delivered to the UCSRP-HP Reactor	85

Figure 29 Favorability of Reactions: Consumption and Formation of Trace Sulfur Components (COS, CS ₂).....	87
Figure 30 Aspen Plus Process Flow Diagram of Absorption Tower for UCSRP-HP	90
Figure 31 DOE Case 2 Process Flow Diagram, GEE IGCC with CO ₂ Capture (Total SO ₂ Emission: 56 lb/h)	95
Figure 32 Sulzer Mixer SMV with Stainless Steel Elements Dismantled.....	97
Figure 33 GTI UCSRP-HP Base Case IGCC with CO ₂ Capture (Total SO ₂ Emission: 34 lb/h)	98
Figure 34 Process Flow Diagram for E-Gas IGCC	107
Figure 35 Comparative Data for COE Using Multiple Technology Pathways and Integrations.....	120
Figure 36 Pressure Drop Measurements in the Bench-Scale Unit	121
Figure 37 Mass Transfer Dependence on Liquid Temperature	121
Figure 38 H ₂ S Solubility in DGM Solvent at 250 °F	122
Figure 39 Schematic for Submerged Sulfur/Oxygen Combustion Process	138
Figure 40 Submerged Sulfur Combustion and Viscosity of Liquid Sulfur	139
SECTION 2: CRYSTASULF-DO SULFUR RECOVERY	
Figure 41 Inlet and outlet gas composition of the CTU during a blank run, i.e., no catalyst	160
Figure 42 Inlet and outlet gas composition of the CTU during the test of Catalyst G	163
Figure 43 Inlet and outlet gas composition of the CTU during the repeat test of Catalyst G ...	165
Figure 44 Inlet and outlet gas composition of the CTU during the test of Catalyst D	167
Figure 45 Inlet and outlet gas composition of the CTU during the test of Catalyst	169
Figure 46 Inlet and outlet gas composition of the CTU during the test of Catalyst H	170
Figure 47 Inlet and outlet gas composition of the CTU during the test of Catalyst I	172
Figure 48 Inlet and outlet gas composition of the CTU during the test of Catalyst F	174
Figure 49 Inlet and outlet gas composition of the CTU during the test of Catalyst C	176
Figure 50 Inlet and outlet gas composition of the CTU during the test of Catalyst G	179
Figure 51 Inlet and outlet gas composition of the CTU during the test of Catalyst D	182
Figure 52 Inlet and outlet gas composition of the CTU during the above sulfur dewpoint test of regenerating the Catalyst D	184
Figure 53 Inlet and outlet gas composition of the CTU during the 30 hour test of Catalyst G .	187
Figure 54 Inlet and outlet gas composition of the CTU during the 46 hour test of Catalyst D .	191
Figure 55 Inlet and outlet gas composition of the CTU during the sulfur sub-dewpoint operation test of Catalyst D.....	192
Figure 56 Inlet and outlet gas composition of the CTU during the above sulfur dewpoint test of regenerating the Catalyst D	193
Figure 57 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst C long term test	199

Figure 58 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst C long term test	200
Figure 59 Inlet and outlet gas composition of the CTU during the third cycle of the Catalyst C long term test	201
Figure 60 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst D long term test	205
Figure 61 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst D long term test	206
Figure 62 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst D long term test	208
Figure 63 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst D long term test	209
Figure 64 Inlet and outlet gas composition of the CTU during the third cycle of the Catalyst D long term test	210
Figure 65 Inlet and outlet gas composition of the CTU during the fourth cycle of the Catalyst D long term test	211
Figure 66 Inlet and outlet gas composition of the CTU during the fifth cycle of the Catalyst D long term test	212
Figure 67 Inlet and outlet gas composition of the CTU during the sixth cycle of the Catalyst D long term test	213
Figure 68 Inlet and outlet gas composition of the CTU during the seventh cycle of the Catalyst D long term test.....	214
Figure 69 Inlet and outlet gas composition of the CTU during the eighth cycle of the Catalyst D long term test	215
Figure 70 Inlet and outlet gas composition of the CTU during the ninth cycle of the Catalyst D long term test	216
Figure 71 Solubility of hydrogen in RSC-103 solvent	221
Figure 72 Solubility of hydrogen in RSC-202 solvent	222
Figure 73 Solubility of hydrogen in RSC-312 solvent	223
Figure 74 Solubility of hydrogen in CrystaSulf solution.....	224
Figure 75 Solubility of carbon monoxide in RSC-103 solvent.....	226
Figure 76 Solubility of carbon monoxide in RSC-202 solvent.....	227
Figure 77 Solubility of carbon monoxide in RSC-312 solvent.....	228
Figure 78 Solubility of carbon monoxide in CrystaSulf solution	229
Figure 79 Comparison of Henry's Law Constants (m ³ kPa/mol) for Hydrogen and Carbon Monoxide for CrystaSulf Solution Components and CrystaSulf Solution with some Organic Solvents and Water. ²	230
Figure 80 Inlet and outlet gas composition of the CTU during the test of Catalyst A.....	232
Figure 81 Inlet and outlet gas composition of the CTU during the test of Catalyst A at 500 °F	233

Figure 82 Inlet and outlet gas composition of the CTU during the test of Catalyst A at 600 °F without H ₂ and CO addition.....	234
Figure 83 P&ID - DO Units.....	244
Figure 84 PFD CrystaSulf and Guard Bed Units	245
Figure 85 PFD - CrystaSulf Units Continued	246

Table of Tables

SECTION 1: UCSRP-HP SULFUR RECOVERY

Table 1	Experimental Plan for NH ₃ and HCl Solubility	42
Table 2	GC Minimum Detection Limits	44
Table 3	COS Experimental Gas Composition Used in March 2008 Experiments	46
Table 4	List of Major Components for Bench Scale Unit	50
Table 5	GC/MS Analysis of DGM Solvent Mixture Prior to Experiment Start	59
Table 6	Gas Chromatograph of the Vapor Stream in the 1,000 hour Degradation Experiment.	59
Table 7	Liquid Sample Impurities Found in Solvent Samples Throughout Solvent Stability Experiment.....	60
Table 8	Selenium Solubility Data	63
Table 9	Initial Conditions for COS Experiments.....	64
Table 10	GC Gas Outlet Results for Experiments	65
Table 11	Results of COS Experiments	67
Table 12	Trace Component Flows and Removal.....	70
Table 13	Analytical Results as per EPA Method 29	70
Table 14	Potential Glycol Ethers for Scrub Section	71
Table 15	Experimental and Literature Equilibrium Distribution Ratios for Ammonia-Gas-Water System	73
Table 16	Equilibrium Distribution of Species (Ammonia-Nitrogen-Water)	74
Table 17	Temperature and Pressure Measurements to Determine the Volume of Mixing Chamber	75
Table 18	Equilibrium Distribution Ratios for NH ₃ -Gas-Water System: Comparison of Experimental Results with Literature Values	75
Table 19	Ammonia Solubility: Equilibrium Distribution Ratios for NH ₃ -Gas-Solvent at 30°C.....	77
Table 20	Feed Gas Composition (after WGS reactor).....	78
Table 21	Experimental Results Conducted at 275°F and 400 psig	83
Table 22	Results of Experiments for the Evaluation of COS in UCSRP-HP	84
Table 23	Carbon Dioxide in Water Results	89
Table 24	Hydrogen Sulfide and Sulfur Dioxide Henry's Constant Coefficients.....	89
Table 25	Henry's Constant for Hydrogen Sulfide in DGM Results for Experimental Set 0	90
Table 26	Constants for Henry's Law Equation.....	90
Table 27	Stream Results from Aspen Plus of Absorption Tower at a Temperature of 104°F and 362.6 psi	91
Table 28	Design Targets for Contaminant Content	92
Table 29	GTI UCSRP-HP Base Case Design Stream.....	100

Table 30	Differential Analysis of UCSRP-HP into E-Gas Case	105
Table 31	Syngas Cleanup Equipment for Base Case.....	106
Table 32	Major Equipment List and Total Plant Costs (2009 \$) for Plant Area 5A	109
Table 33	Plant Performance Summary	111
Table 34	Sulfur Balances for DOE Case 2, UCSRP Base Case, and UCSRP Case 2	112
Table 35	Comparative Data on CAPEX: DOE Case 2 vs. UCSRP-HP Base Case.....	113
Table 36	UCSRP Base Case Initial and Annual Operating and Maintenance Costs.....	114
Table 37	Comparative Data on Power Production, Total CAPEX and Cost of Power	115
Table 38	Components of Levelized Cost of Electricity.....	115
Table 39	Comparative COE Data: DOE Case 2 vs. UCSRP-HP.....	118
Table 40	Comparative Data for COE (including CO ₂ capture, compression, transport, plus storage/monitoring)	119
Table 41	Heat Transfer Coefficient Testing Results	122
Table 42	Kinetics and Reactivity Data	123
SECTION 2: CRYSTASULF-DO SULFUR RECOVERY		
Table 43	Catalyst Evaluated in this Project	156
Table 44	Catalyst Evaluation Test Conditions	156
Table 45	Blank Test run with H ₂ S Check	158
Table 46	Verification of the concentrations and flow rates in the CTU	159
Table 47	Simulation of Multiple Bed Operation – Test Conditions for Long Term Testing	197
Table 48	Beginning, Final and Average H ₂ S Conversions for Each Cycle	217
Table 49	Solubility of Hydrogen in CrystaSulf Solution Components and in CrystaSulf Solution, Henry’s law constants	220
Table 50	Solubility of Carbon Monoxide in CrystaSulf Solution Components and in CrystaSulf Solution, Henry’s law constants	225
Table 51	Complete Results from Blank, Catalyst Screening and Long term Catalyst Tests ...	236
Table 52	Heat and Material Balance.....	243
Table 53	Cost Estimate Summary for CrystaSulf-DO by Unit.....	248

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- c. The results within this report relate only to the items tested.

Abstract

This project met the objective to further the development of an integrated multi-contaminant removal process in which H_2S , NH_3 , HCl and heavy metals including Hg , As , Se and Cd present in the coal-derived syngas can be removed to specified levels in a single/integrated process step. The process supports the mission and goals of the Department of Energy's Gasification Technologies Program, namely to enhance the performance of gasification systems, thus enabling U.S. industry to improve the competitiveness of gasification-based processes. The gasification program will reduce equipment costs, improve process environmental performance, and increase process reliability and flexibility.

Two sulfur conversion concepts were tested in the laboratory under this project, i.e., the solvent-based, high-pressure University of California Sulfur Recovery Process – High Pressure (UCSRP-HP) and the catalytic-based, direct oxidation (DO) section of the CrystaSulf-DO process. Each process required a polishing unit to meet the ultra-clean sulfur content goals of <50 ppbv (parts per billion by volume) as may be necessary for fuel cells or chemical production applications. UCSRP-HP was also tested for the removal of trace, non-sulfur contaminants, including ammonia, hydrogen chloride, and heavy metals. A bench-scale unit was commissioned and limited testing was performed with simulated syngas. Aspen-Plus®-based computer simulation models were prepared and the economics of the UCSRP-HP and CrystaSulf-DO processes were evaluated for a nominal 500 MWe, coal-based, IGCC power plant with carbon capture. This report covers the progress on the UCSRP-HP technology development. The CrystaSulf-DO technology is covered in Volume 2.

A 1,000 hour solvent stability and materials of construction compatibility test that showed the catalyst was stable, carbon steel is an acceptable material of construction of the reactor/contacter, and that high quality sulfur (up to 99.2% elemental sulfur) was formed. Nine five percent mercury removal, to levels of less than 0.2 ppb, was observed. Preliminary selenium testing showed that the solubility of H_2Se was increased by the presence of an aqueous solution of DEG, ammonia, and chloride over water. Formation of carbonyl sulfide appears to be controllable by the excess of sulfur dioxide. Testing during this period indicated that 50% hydrogen selenide (H_2Se) and 33% arsine (AsH_3) removal was achieved during a 30 minute test. Ammonia and HCl solubility are dependent on the water content within the diethylene glycol (DEG) solvent. Experiments illustrated that when sulfur dioxide is added to the feed, both hydrogen sulfide and carbonyl sulfide are consumed. Ninety five percent of the carbonyl sulfide (from 490 to 35 ppm in a single stage reactor) was consumed and 99 percent of the hydrogen sulfide (from 10% to 70 ppm). Any COS that is not converted to H_2S within the reaction zone of the process will be absorbed into the lean diethylene glycol methyl ether (DGM) at the top of the column and brought back to react with the SO_2 and water. Further laboratory tests are required to determine the COS concentrations expected at the top of the reaction section of the column in order to size the DGM circulation rate.

Aspen Plus simulations were performed that indicate complete removal of ammonia (NH_3), hydrogen chloride (HCl) and hydrogen selenide (H_2Se) in the aqueous scrub step of the UCSRP-HP process. Thermodynamic considerations point to minimal formation of COS in the UCSRP-HP reactor for a CO_2 -rich-feed as compared to a CO-rich-feed gas stream.

An economic evaluation was performed that integrated the UCSRP-HP into a nominal 550 MWe Integrated Coal Gasification Combined Cycle (IGCC) facility gasifying Illinois coal. The results indicated that the cost of electricity (COE) could be reduced by about \$9.60/MWh (9.3%) compared to conventional IGCC technology with carbon capture, transportation, and sequestration, estimated at \$103.00/MWh by DOE. The COE saving is mainly derived from a

reduction in the overall capital expenses of about \$123 MM (December 2006 dollars). The UCSRP-HP design emits about 22 lb/h less SO₂; reducing the emissions to near zero would increase the capital by about \$10 MM and have a minimal effect on the COE. With these promising results, UCSRP-HP was integrated with advanced H₂/CO₂ separation technologies. With LANL/SRI's PBI membrane, UCSRP-HP decreased the COE from \$98.20 to \$94.70/MWh. With GTI/PoroGen's CarboLock membrane contactors, the COE decreased from \$93.40 to \$91.70/MWh. While replacing Selexol with the Advance H₂ Membrane decreased the COE with RTI Warm Gas Cleanup from \$101.60 to \$89.60/MWh, substituting UCSRP-HP for RTI resulted in an \$88.80/MWh COE.

The bench-scale test unit was fabricated and installed at GTI. It was delayed by third party construction issues under the cofunded DOE and GRI projects and impacted the performance of a number of tasks.

Table of Contents

Disclaimer	i
Legal Notice	ii
Abstract.....	iii
Table of Contents.....	vi
Table of Figures	x
Table of Tables.....	xiv
SECTION 1: UCSRP-HP SULFUR RECOVERY	1
Disclaimer	3
Legal Notice	4
Abstract.....	5
Table of Contents.....	7
Table of Figures	12
Table of Tables.....	14
Executive Summary	16
Approach.....	22
Scope of Work.....	22
Tasks to be Performed	22
Task 1.0 – Bench-Scale UCRP-HP Reactor Setup Design, Construction and Commissioning:	22
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	22
Subtask 2.1 – UCSRP-HP Solvent Degradation and Corrosion	22
Subtask 2.2 – GTI Trace-Contaminant Removal	23
Subtask 2.3 – UCSRP-HP Sulfur Removal	23
Task 2.4 – CrystaSulf-DO Sulfur Removal.....	23
Subtask 2.5 – Syngas Component Effects on SO ₂ Formation	23
Subtask 2.6 -- UCSRP-HP Solvent Regeneration	23
Task 3.0 – Computer Simulation Model.....	24
Subtask 3.1 – Preliminary Aspen Model	24
Subtask 3.2 – Aspen Model	24
Task 4.0 – Economic Evaluation	24
Subtask 4.1 – Preliminary Economic Evaluation.....	24
Subtask 4.2 – Economic Evaluation.....	25
Task 5.0 –Bench-Scale Experiments.....	25

Subtask 5.1 – Reaction Kinetics	25
Subtask 5.2 – Trace Contaminants Removal.....	25
Subtask 5.3 – Hydrodynamics of the Gas-Liquid-Liquid Flow.....	25
Subtask 5.4 – Packed Bed Efficiency and Parameter Optimization.....	25
Task 8.0 – Project Management and Reporting	25
Introduction and Background	26
Treatment of Synthesis Gas from Coal Gasification	28
Reactor	28
NH ₃ and SO ₂ Removal.....	29
SO ₂ Generation.....	29
CO ₂ Capture	29
Syngas Temperature Recovery	30
Experimental Procedures.....	32
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	32
Solvent Degradation and Materials of Construction Experiment	32
Trace Contaminant Removal	35
Vapor-Liquid Equilibrium Experimentation.....	36
Heavy Metal Removal.....	38
Ammonia and Halogen Removal	39
Trace Sulfur Removal.....	41
Task 5.0 –Bench-Scale Experiments	46
Flooding	46
Mass Transfer Rates	47
Heat Transfer Rates	47
Column Limitation	47
Startup Permissives.....	47
Experimental Procedure	48
Gas Only Pressure Drop.....	48
Flooding Curve Testing.....	48
Operating Conditions (Liquid and Gas Flow Rates).....	49
Heat Transfer Coefficient.....	49
Mass Transfer Coefficient.....	49
Kinetic Testing	49
Results and Discussion.....	50

Task 1.0 – Bench-Scale UCRP-HP Reactor Setup Design, Construction and Commissioning:	50
Construction and Commissioning	51
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	58
Subtask 2.1 – UCSRP-HP Solvent Degradation and Corrosion	58
Subtask 2.2 – GTI Trace-Contaminant Removal	61
Ammonia and Halogen Removal	69
Regeneration of DEG	77
Subtask 2.3 – UCSRP-HP Sulfur Removal	81
Subtask 2.6 -- UCSRP-HP Solvent Regeneration	88
Task 3 – Computer Simulation Modeling and Economics	88
Subtask 3.1 – Preliminary Aspen Model	88
Subtask 3.2 – Aspen Model	91
Design Basis	92
DOE Design Case 2	92
Gasification, Raw Gas Cooling/Particulate Removal	92
Quench and Syngas Scrubbing	93
Sour Water Gas Shift (SWGS) Unit	93
Acid Gas Removal (AGR)	93
Power Block	94
Air Separation Unit (ASU)	94
GTI UCSRP-HP IGCC Base Case (GTI Design Case 1): Total SO ₂ Emission at 34 lb/h	96
V-100: A Second High-pressure Water Scrubbing Unit	96
UCSRP Absorber/Sulfur Reactor	97
Scavenging (Sulfur Guard Bed) Unit	102
Single-stage Selexol Process for the Removal of CO ₂	102
DURCO Pressure Leaf Filter	103
Sulfur/Oxygen Submerged Combustion to Generate Liquid SO ₂	103
Special Hydrocyclone and Filter Units to Process a Slipstream of DGM Solvent Effluent from the Sulfur Reactor	103
Issues Related to Corrosion and Solvent Stability	103
Task 4.0 – Economic Evaluation	104
Subtask 4.1 – Preliminary Economic Evaluation	104

Subtask 4.2 – Economic Evaluation	108
Overall Material Balances	108
Equipment List	108
Total Installed Plant Cost Details	108
Energy/Utility Requirements, Plant Performance & Overall Sulfur Balances	111
Power requirements for various pumps and compressors: Base Case Design.....	111
Sulfur Balance	111
Solvent Make-up Rate: UCSRP-HP Base Case.....	112
DOE Case 2 vs. GTI UCSRP-HP Base Case	112
GTI UCSRP-HP Design Case 2: Achieve a H ₂ S Level in Product Syngas <50 ppbv	115
Economic Potential for the Integration of Key Membrane Technologies for the Removal of CO ₂ and H ₂ with the UCSRP-HP Sulfur Removal Process in IGCC Applications.....	116
Task 5.0 –Bench-Scale Experiments	121
Conclusions and Recommendations	124
LIST OF ACRONYMS AND ABBREVIATIONS	126
References.....	131
Acknowledgements.....	133
Appendix A – Bench-scale Unit Construction and Commissioning Activities	134
Construction Activities	134
Commissioning Activities.....	135
Appendix B – Brown and Root Braun's SO ₂ Generation Process	138
SECTION 2: CRYSTASULF-DO SULFUR RECOVERY	141
Disclaimer	143
Legal Notice	144
Abstract.....	145
Table of Contents.....	147
Table of Figures	149
Table of Tables.....	151
Approach.....	152
Scope of Work.....	152
Tasks to be Performed	152
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	152
Subtask 2.4 – CrystaSulf-DO Sulfur Removal	152
Subtask 2.5 – Syngas Component Effects on SO ₂ Formation	153

Task 3.0 – Computer Simulation Model.....	153
Subtask 3.1 – Preliminary Aspen Model	153
Subtask 3.2 – Aspen Model	153
Task 4.0 – Economic Evaluation	154
Subtask 4.1 – Preliminary Economic Evaluation.....	154
Subtask 4.2 – Economic Evaluation.....	154
Task 8.0 – Project Management and Reporting	154
Task Descriptions and Results	155
Task 2.4 CrystaSulf-DO Bench-scale Feasibility Tests for Multi-Contaminant Cleanup	155
Subtask 2.4.1 Catalyst Evaluation	155
Subtask 2.4.2 Operating Condition Optimization.....	177
Subtask 2.4.3 Long Term Testing.....	186
Subtask 2.4.4 Vapor-Liquid Equilibria Experiments.....	218
Subtask 2.5 Syngas Component Effects on SO ₂ Formation.	231
Task 3.0. Computer Simulation	240
CrystaSulf-DO Process Model.....	240
CrystaSulf-DO Process Description.....	240
Task 4.0. Economic Evaluation	247
Recommendations for Future Testing	257
References.....	258
List of Acronyms and Abbreviations.....	259
Biography.....	260

Table of Figures

Figure 1 UCSRP-HP Block Diagram.....	31
Figure 2 UCSRP-HP Solvent Degradation and Corrosion Experimental Layout	34
Figure 3 Trace Contaminant Testing Apparatus	35
Figure 4 Mercury Permeation Tube	36
Figure 5 Mercury Vapor Sorption Apparatus	36
Figure 6 High Pressure Vapor Liquid Equilibrium Cell.....	36
Figure 7 Schematic of GTI Vapor-Liquid Equilibrium Cell.....	38
Figure 8 Trace Component Removal with Ammonia, Chloride, and Selenium	39
Figure 9 Trace Metal Experimental Schematic	40
Figure 10 Block Diagram of the Experimental Determination of Gas Solubility at Set Pressure.....	41
Figure 11 COS Experimental Set up.....	43
Figure 12 COS Test Equipment.....	44
Figure 13 Start Up Permissive for the Sulfur Mode	47
Figure 14 As-Designed Bench-Scale Unit P&ID	52
Figure 15 As-Built Bench-Scale Unit P&ID	53
Figure 16 Bench-Scale Unit Being Installed at GTI	54
Figure 17 Bench-Scale Unit.....	55
Figure 18 Bench-scale Unit Being Unloaded at GTI	56
Figure 19 Risk Matrix	57
Figure 20 Carbon Steel (left) and Stainless Steel (right) Coupon Photographs Before (top) and After (bottom) Clean up After 1,000 h in Solvent	61
Figure 21 Mercury Concentration in the Vapor Phase in the Presence of DEG	62
Figure 22 Mercury Concentration in the Vapor Phase with No Solvent.....	62
Figure 23 Trace Component Removal with Ammonia, Chloride, and Selenium	62
Figure 24 DEG After Exposure to H ₂ Se, NH ₃ , and Chloride	63
Figure 25 Sensitivity Analysis: Calculation of Distribution Ratio for the N ₂ -NH ₃ -Water System (30 °C).....	76
Figure 26 Equilibrium Distribution of Species using Aspen Plus (solvent: water).....	80
Figure 27 Effect of Trace Component Addition on the Distribution of Ammonia and Hydrogen Sulfide (Aspen simulation, T = 250°F, P = 800 psi, Base Gas Composition: Table 20), A. Ammonia B. Hydrogen sulfide	81
Figure 28 Illustration of Decreasing SO ₂ Concentration Being Delivered to the UCSRP-HP Reactor	85
Figure 29 Favorability of Reactions: Consumption and Formation of Trace Sulfur Components (COS, CS ₂).....	87

Figure 30 Aspen Plus Process Flow Diagram of Absorption Tower for UCSRP-HP	90
Figure 31 DOE Case 2 Process Flow Diagram, GEE IGCC with CO ₂ Capture (Total SO ₂ Emission: 56 lb/h)	95
Figure 32 Sulzer Mixer SMV with Stainless Steel Elements Dismantled.	97
Figure 33 GTI UCSRP-HP Base Case IGCC with CO ₂ Capture (Total SO ₂ Emission: 34 lb/h) ..	98
Figure 34 Process Flow Diagram for E-Gas IGCC	107
Figure 35 Comparative Data for COE Using Multiple Technology Pathways and Integrations	120
Figure 36 Pressure Drop Measurements in the Bench-Scale Unit	121
Figure 37 Mass Transfer Dependence on Liquid Temperature	121
Figure 38 H ₂ S Solubility in DGM Solvent at 250 °F	122
Figure 39 Schematic for Submerged Sulfur/Oxygen Combustion Process	138
Figure 40 Submerged Sulfur Combustion and Viscosity of Liquid Sulfur	139

Table of Tables

Table 1	Experimental Plan for NH_3 and HCl Solubility	42
Table 2	GC Minimum Detection Limits	44
Table 3	COS Experimental Gas Composition Used in March 2008 Experiments	46
Table 4	List of Major Components for Bench Scale Unit	50
Table 5	GC/MS Analysis of DGM Solvent Mixture Prior to Experiment Start	59
Table 6	Gas Chromatograph of the Vapor Stream in the 1,000 hour Degradation Experiment.	59
Table 7	Liquid Sample Impurities Found in Solvent Samples Throughout Solvent Stability Experiment.....	60
Table 8	Selenium Solubility Data	63
Table 9	Initial Conditions for COS Experiments.....	64
Table 10	GC Gas Outlet Results for Experiments	65
Table 11	Results of COS Experiments	67
Table 12	Trace Component Flows and Removal.....	70
Table 13	Analytical Results as per EPA Method 29	70
Table 14	Potential Glycol Ethers for Scrub Section	71
Table 15	Experimental and Literature Equilibrium Distribution Ratios for Ammonia-Gas-Water System	73
Table 16	Equilibrium Distribution of Species (Ammonia-Nitrogen-Water)	74
Table 17	Temperature and Pressure Measurements to Determine the Volume of Mixing Chamber	75
Table 18	Equilibrium Distribution Ratios for NH_3 -Gas-Water System: Comparison of Experimental Results with Literature Values	75
Table 19	Ammonia Solubility: Equilibrium Distribution Ratios for NH_3 -Gas-Solvent at 30°C	77
Table 20	Feed Gas Composition (after WGS reactor).....	78
Table 21	Experimental Results Conducted at 275°F and 400 psig	83
Table 22	Results of Experiments for the Evaluation of COS in UCSRP-HP	84
Table 23	Carbon Dioxide in Water Results	89
Table 24	Hydrogen Sulfide and Sulfur Dioxide Henry's Constant Coefficients.....	89
Table 25	Henry's Constant for Hydrogen Sulfide in DGM Results for Experimental Set 0	90
Table 26	Constants for Henry's Law Equation.....	90
Table 27	Stream Results from Aspen Plus of Absorption Tower at a Temperature of 104°F and 362.6 psi	91
Table 28	Design Targets for Contaminant Content	92
Table 29	GTI UCSRP-HP Base Case Design Stream.....	100
Table 30	Differential Analysis of UCSRP-HP into E-Gas Case	105

Table 31 Syngas Cleanup Equipment for Base Case.....	106
Table 32 Major Equipment List and Total Plant Costs (2009 \$) for Plant Area 5A	109
Table 33 Plant Performance Summary	111
Table 34 Sulfur Balances for DOE Case 2, UCSRP Base Case, and UCSRP Case 2	112
Table 35 Comparative Data on CAPEX: DOE Case 2 vs. UCSRP-HP Base Case.....	113
Table 36 UCSRP Base Case Initial and Annual Operating and Maintenance Costs.....	114
Table 37 Comparative Data on Power Production, Total CAPEX and Cost of Power	115
Table 38 Components of Levelized Cost of Electricity.....	115
Table 39 Comparative COE Data: DOE Case 2 vs. UCSRP-HP.....	118
Table 40 Comparative Data for COE (including CO ₂ capture, compression, transport, plus storage/monitoring)	119
Table 41 Heat Transfer Coefficient Testing Results	122
Table 42 Kinetics and Reactivity Data	123

Executive Summary

Advanced gasification systems are planned to provide synthesis gas feed for advanced, combined cycle power plants; for separation systems for hydrogen production or for separating CO₂ for sequestration purposes; or for chemical conversion plants. All of these advanced applications require that any sulfur-containing species, as well as other contaminants, be reduced to parts-per-million (ppm) or in some cases parts-per-billion (ppb) levels. For acid-gas and trace contaminant removal, technologies that are either currently available or under development include: low-temperature or refrigerated solvent-based scrubbing systems using amines, such as MDEA, or physical solvents, such as Rectisol, Selexol, Sulfinol, or high temperature sorbents, such as RTI's HTDP and DSRP (high-temperature desulfurization process and direct sulfur recovery process). Sulfur recovery is performed by a gas-phase, catalytic Claus process or sulfuric acid production followed by a tail gas recovery process, such as SCOT. Varieties of processes are required to remove trace components, such as ammonia, hydrogen chloride, and heavy metals. These processes are capital and energy intensive, with minimal reference plants due to the small number of Integrated Coal Gasification Combined Cycle (IGCC) facilities operating worldwide.

GTI is in the process of developing the UCSRP-HP¹⁹ (University of California Sulfur Recovery Process-High-Pressure), an integrated multi-contaminant removal process whereby coal-derived syngas is sent to an absorbing column where chlorides and ammonia, as well as trace heavy metals (mercury, selenium, arsenic, and cadmium) are removed from the gas stream. The partially cleaned gas then passes to a reactor column at a temperature above the melting point (247°F) and below the polymerization temperature (310°F) of elemental sulfur and a gasification pressure of 400 psig (or any higher pressure). Hydrogen sulfide in the syngas, together with injected sulfur dioxide, dissolves in a solvent that is circulated co-currently or counter-currently in the column. The Claus reaction is carried out in the liquid phase. Sulfur is only sparingly soluble in the solvent and so forms a separate liquid phase. The solvent contains a homogeneous liquid catalyst (less than 1% by weight of the solution). The catalyst is a commonly available and inexpensive material that does not degrade nor dissolve in the sulfur. One-third of the recovered sulfur product is burned with oxygen (if an oxygen-blown gasifier is involved this would be a fraction of the oxygen requirement for the process), and fed to the reactor column. The process is ideal for syngas desulfurization at 285 to 300°F, at any given pressure (higher the better) and offers a tighter integration with the process for removal of trace contaminants and heavy metals. This process is projected to be significantly lower in capital and operating cost compared to conventionally applied amine or physical solvent-based acid-gas removal process followed by Claus/SCOT process plus systems to remove other contaminants or warm gas cleanup systems now in development.

This project was a laboratory program to obtain critical process data for the treatment of syngas derived from Illinois basin coals. The ultimate application of this process will favor high sulfur coals, such as Illinois #6, by reducing the cleanup costs and providing an environmentally benign facility to utilize economically these coals. The specific objectives of the project includes laboratory- and bench-scale work on the removal of hydrogen sulfide, heavy metals, ammonia, halogens, and carbonyl sulfide and the development of an Aspen-Plus®-based computer simulation model used to perform a techno-economic evaluation of the process applied to syngas cleanup for a 500 MWe coal-based IGCC power plant. This project was co-funded by the U.S. DOE through National Energy Technology Laboratory (NETL) under their funding opportunity announcement number DE-PS26-04NT42249. The funding received from ICCI was used to conduct work under each task using test conditions and gas compositions representative of Illinois # 6 coal.

A long-term, 1,000 hour test was performed with a synthetic syngas mixture in a four liter, jacketed, stainless steel pressure vessel at 400 psig and 275°F to study solution stability and materials of construction issues. Mixtures of H₂S, syngas, and SO₂ flowed through the solvent and out through a scavenging system to assure there was no sulfur releases from our vent streams. The solution was periodically analyzed for the solvent and catalyst concentration to determine stability. Corrosion coupons were exposed in the gas and liquid phases in the vessel and analyzed for metal loss, pitting, and other corrosion issues.

The results from this test showed good stability for the solvent and catalyst. Approximately 2.3% of DGM solvent degraded to tetraglyme. Tetraglyme is a potential substitute for DGM since it is less volatile and has a higher H₂S solubility than DGM. However, tetraglyme is more viscous. Therefore conversion of the solvent is not a significant issue. Approximately 25% of catalyst at 0.2% by weight of solution broke down to 3-methylpyridine and 4-formylpyridine. These pyridines are also active catalyst and did not appear to affect reactivity. During the testing with high CO levels, COS was formed. This became an issue that was addressed later. Without any washing or other preparation techniques, the sulfur that was formed during this test was 99.2% pure. The target for commercial purity is greater than 99.5% sulfur.

Metal Samples Inc. provided the standard corrosion coupons and independent analysis of these coupons after exposure of 1,000 hour. The coupon results for corrosion showed no pitting or etching. Weight losses for uncoated 1010 carbon steel and stainless steel samples in the chamber were 0.02 and 0.008 g, respectively. The corrosion rates were 0.52 mils/year and 0.23 mils/year over the 1,000 hour period; below 2 mils/year is considered excellent corrosion inhibition. The coupons in the gas and in the liquid phase showed essentially the same weight loss and corrosion rate. These tests verified the use of carbon steel as an acceptable material of construction for the process.

GTI's Vapor-Liquid Equilibrium (VLE) unit was modified to obtain mass transfer and kinetic measurements. This required sampling of not only the gas and liquid phases in the VLE cell, but also of the continuous running phase. In a typical experiment, the reactor is filled with the desired amount of liquid, and the system is allowed to equilibrate to the desired temperature. Next, the gas flow to the cell is set to the desired rate or pressure, and passed directly to the cell. The GC is able to measure the reactor inlet concentration. The stirrer is switched to the desired rate, and the flow is led through the reactor until the achievement of a pseudo steady state, as indicated by a constant concentration reading from the GC or pressure reading, marking the end of the experiment.

Trace contaminant removal testing was conducted under a number of different conditions. Mercury and selenium removal testing were carried out at atmospheric pressure in quartz reactors. Elemental mercury was introduced into the system through a permeation tube and analyzed by an Ohio Lumex instrument. Selenium was introduced as H₂Se in nitrogen through a cylinder mixture along with cylinder supplies of anhydrous ammonia and anhydrous hydrogen chloride. Samples were sent to GTI's Analytical Department for analysis. Carbonyl sulfide formation was studied at pressures up to 500 psia. Gas chromatographs were used to measure input and outlet sulfur compounds.

The mercury concentration in the vapor phase was brought down from 44,300 ng/m³ to 1,900 ng/m³, achieving 95.7% mercury removal. This concentration is equivalent of 0.2 ppb by weight in the product stream. This is well within the DOE target of less than 5 ppb in the outlet gas. Selenium removal is based on the solubility of H₂Se into DEG. Preliminary testing showed that its solubility is positively affected by the presence of ammonium chloride. The solubility increased at least three fold by the presence on the ammonium chloride at 275°F. EPA Method 29 was used to analyze the inlet and outlet streams to determine the overall removal of

selenium and arsenic during a 30-minute run. We achieved about 50% removal of the H_2Se and 33% of the AsH_3 during the test. Precipitated solids were collected and serve as an indication that filtration can be used to collect the removed metals. Further testing is required to determine the operating conditions to achieve the 0.2 ppm concentration target in the product gas.

Carbonyl sulfide adds to the sulfur targets for the product gas. COS is formed in the gasifier, but will be shifted to H_2S if a sour water gas shift (WGS) catalyst is used prior to the UCSRP-HP process. Potential chemical formation pathways were identified and studied. Preliminary results have shown that an excess of SO_2 will mitigate any COS from forming and will promote the COS reaction to form H_2S . Experiments illustrated that when sulfur dioxide is added to the feed, both hydrogen sulfide and carbonyl sulfide are consumed. Ninety five percent of the carbonyl sulfide (from 490 to 35 ppm in a single stage reactor) was consumed and 99 percent of the hydrogen sulfide (from 10% to 70 ppm). COS formation should also be mitigated by the lower CO concentrations downstream of WGS.

VLE equipment was used to determine the Henry's Law constant for H_2S and SO_2 in DGM. This is needed to determine the solubility of these compounds within the Aspen Plus® simulation model. The results showed that calculated Murphree tray efficiencies are in good agreement with experimental data and therefore validating our model for calculating reasonable high pressure and temperature tray efficiencies. Aspen Plus models have been completed for all the major process steps, including H_2S and SO_2 absorption in DGM, the sulfur furnace, and the absorption of ammonia, chloride, and H_2Se in DEG.

An initial, differential techno-economic analysis was performed. This identified the areas in the base case E-Gas Gasifier IGCC facility with Illinois #6 coal that are impacted by the UCSRP-HP process. Qualitatively, the UCSRP-HP continues to offers great potential as an integrated sulfur and trace component removal technology to lower significantly the cost of electricity or chemicals from coal-derived gasification processes.

The Aspen Plus® model was used to integrate the UCSRP-HP process into an IGCC plant with carbon capture using Illinois #6 coal. DOE economic studies were used to determine the potential impact of the technology compared to the current gas cleanup technology as well integrated with future technologies. For the base UCSRP-HP case, the process was introduced just downstream of the first heat exchanger (HP Steam) in the Gas Cooling, BFW Heating & Knockout block where the syngas feed is at ~772 psia and 450°F. This is downstream of the Quench and Scrubber Section and the Water Gas Shift Reactors. The DOE Case 2 is rejoined at the feed to the CO_2 removal section of the dual stage Selexol unit. This design replaces or eliminates the Mercury Removal, H_2S -removal section of the dual-stage Selexol unit, the Claus Plant, and Hydrogenation Reactor and Gas Cooler Section. At the request of DOE, two levels of sulfur removal were studied. One case was for a conventional IGCC where the feed to the turbine would be ~8ppm and the other case was where the feed to the turbine or a chemical application would be <50 ppb.

The raw syngas is further cooled within the UCSRP-HP to 165°F and then processed in a high-pressure, co-current, down-flow Water Contactor unit to separate a large fraction of water present in the gas along with much of the NH_3 and essentially all of the halogens and heavy metals, as sulfides or water-soluble salts. Following this step, the gas is preheated to about 250°F prior to its processing in the UCSRP-HP reactor.

The UCSRP-HP reactors are co-current, down-flow contactors. At the operating conditions of ~750 psia and 250-300°F, the sulfur forms as a liquid, essentially immiscible in DGM/catalyst solvent and over twice as dense. This overcomes the equilibrium limitations that occur in conventional gas-phase Claus reactor systems. The sulfur is separated, filtered by a DURCO

sulfur filter, and sent to a sulfur pit or to a commercial-design O₂/sulfur submerged combustion furnace, as needed to generate the required liquid SO₂ for reaction with H₂S in the UCSRP-HP reactors. Solvent and reaction water are recovered by cooling and the cleaned syngas is transferred to the CO₂ removal section of the dual-stage Selexol unit and the power island.

To achieve the <50 ppb sulfur target, a COS hydrolysis unit was introduced within the UCSRP-HP block to produce a syngas containing about 7.6 ppm H₂S and 0.4 ppm COS. Further experimentation is required to establish if the hydrolysis unit will be required. A zinc oxide guard bed is also added downstream of the high-pressure separator to reduce the total sulfur level to <50 ppb in the effluent gas.

The cost analysis of a nominal 550 MWe IGCC plant with carbon capture was conducted following DOE economic evaluation guidelines to calculate capital expenditures (CAPEX), operating and maintenance costs (OPEX), and the levelized cost of electricity (COE). The results compared to conventional cold-gas cleanup are shown in Table ES-I.

Table ES-I. Comparative COE Data: DOE Case 2 vs. UCSRP-HP

	DOE Case 2	GTI UCSRP-HP Base Case	GTI UCSRP-HP Chemical case
Coal Feed Rate, dry, lb/h	444,737	444,737	444,737
SO ₂ Emissions (lb/h)	56	34	~0
Gas Turbine, MWe	464.0	464.0	464.0
Sweet Gas Expander, MWe	6.3	6.3	5.8
Steam Turbine, MWe	274.7	287.5	287.5
Total Auxiliaries, MWe	<u>-189.3</u>	<u>-184.5</u>	<u>-184.5</u>
Net Power for Sale, MWe	555.7	573.3	572.8
Thermal Efficiency, % (HHV)	32.5	33.5	33.4
Total CAPEX, \$MM (Y-2006 \$)	1,328	1,205	1,215
Cost of Power, \$/MWh (or, mills/kWh)**	103.0	93.4	95.2

These results show:

- A net CAPEX savings of about \$123 MM (December 2006 dollars) based on the conservative design and ± 30% cost estimate basis;

- The overall thermal efficiency (HHV basis) would increase from about 32.5% for the DOE Case 2 to about 33.5% for the UCSRP-HP design;
- An increase of about 17.6 MW (~3.2 %) in net power sale;
- A reduction of about \$9.60/MWh (~9.3%) in the cost of power production with carbon capture, CO₂ compression plus transport/storage/monitoring; and
- A reduction in total SO₂ emission of about 22 lb/h;
- Preparing the syngas for a chemical application that requires <50 ppb sulfur in the syngas would increase the required CAPEX by about \$10.1MM over the base case, and would result in a subsequent increase of \$1.80/MWh in COE if the syngas were to be used for power generation in a near zero SO₂ discharge IGCC plant.

With these promising results, UCSRP-HP was integrated with developing technologies, identified in DOE's Current and Future Technologies: A Pathway Study Focused on Non-carbon Capture Advanced Power Systems R&D using Bituminous Coal- Volume 1 and 2. These included (1) the LANL/SRI's PBI (polybenzimidazole), high-temperature (~250-450°C), polymeric CO₂-removal membrane, (2) the GTI/PoroGen's CarboLock Membrane for CO₂ removal, and (3) an advanced H₂-separation membrane that would meet specific year-2015 performance targets assumed by DOE/Noblis LLC were also examined. These cases were compared to the published data on RTI's warm gas cleanup (WGC) process and can be seen in Table ES-II.

Table ES-II. Comparative Data for COE (including CO₂ capture, compression, transport, plus storage/monitoring)

Design Case	H ₂ S Removal Option	CO ₂ Removal Option	COE, \$/MWh	COE Differential, %
DOE-1	Selexol	None	77.8	Base
DOE-2	Selexol	Selexol	103.0	32.4
A	UCSRP-HP	Selexol	93.4	20.1
B	UCSRP-HP	GTI/ PoroGen CarboLock Membrane Contactor w/Selexol	91.7	17.9
C	Selexol	LANL/ SRI PBI Membrane	98.2	26.2
D	UCSRP-HP	LANL/ SRI PBI Membrane	94.7	21.7
E	RTI	Selexol	101.6	30.6
F	RTI	Advanced H ₂ Membrane	89.6	15.2
G	UCSRP-HP	Advanced H ₂ Membrane	88.8	14.2

Approach

Scope of Work

The objective of this project is to develop an integrated multi-contaminant removal process in which H_2S , NH_3 , HCl and heavy metals including Hg , As , Se and Cd present in the coal-derived syngas can be removed to specified levels in a single/integrated process step.

Tasks to be Performed

The specific objectives of this project include:

1. Testing the feasibility of sulfur removal concepts at lab scale. Two sulfur conversion concepts will be tested: (1) The solvent-based high pressure University of California Sulfur Recovery Process - High Pressure (UCSRP-HP), and (2) the catalyst-based direct oxidation (DO) section of the CrystaSulf-DO process. It is anticipated that each process may need a polishing unit to meet the cooperative agreement maximum sulfur goal (50 ppbv), and that the CrystaSulf process will be used in concert with the CrystaSulf-DO process to obtain these ultra-clean levels.
2. Testing the GTI trace-contaminant process feasibility at lab scale.
3. Exposing the UCSRP-HP solvent and CrystaSulf catalysts to syngas with typical contaminants that may be present in the feed to a syngas cleanup reactor.
4. Investigation of long-term solvent and catalyst stability.
5. Testing the UCSRP-HP bench-scale unit with up to 20 lb/day sulfur production capacity to gather data for further verification of the process concept, measuring contaminant removal efficiencies, determining reaction kinetics and optimizing the process parameters for designing a pilot-scale demonstration unit for Phase-II study.
6. Development of Aspen-Plus based computer simulation models.
7. Evaluating the economics of the UCSRP-HP and CrystaSulf processes, each combined with the GTI trace-contaminant cleanup process, applied to syngas cleanup for a nominal 500 MWe coal-based IGCC power plant with carbon capture.

Task 1.0 – Bench-Scale UCSRP-HP Reactor Setup Design, Construction and Commissioning:

GTI will design and construct a bench-scale UCSRP-HP reactor with an associated solvent recirculation to handle a simulated syngas flow of nominally 10 scfm. The minimum suite of contaminants to be measured is H_2S , COS , SO_2 , NH_3 , HCl , Hg , As , Se and Cd .

Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup

Subtask 2.1 – UCSRP-HP Solvent Degradation and Corrosion

Subject the UCSRP-HP solvent to a long-term solvent stability test by exposing it to simulated syngas inside a batch autoclave reactor for around 1000 hours at 300°F and 350 psig. During this test small liquid samples will be withdrawn from the reactor periodically and analyzed for degradation product(s) using gas chromatography. Metal coupons will be placed inside the reactor to measure corrosion rates.

Subtask 2.2 – GTI Trace-Contaminant Removal

Screen two or three possible solvents and identify the most suitable solvent for effective removal of NH₃, HCl, Hg, As, Se and Cd. Demonstrate the potential for the GTI cleanup concept to be able to remove the listed contaminants at conditions as representative as practical of the anticipated commercial unit and investigate various ways to regenerate the solvent as required. The removal goals for these contaminants are:

Contaminant	Maximum After Cleanup
NH ₃	0.1 vol%
HCl	1 ppm
Hg	5 ppbv
Se	0.2 ppm
As	5 ppb
Cd	30 ppb

Subtask 2.3 – UCSRP-HP Sulfur Removal

Demonstrate the potential for the UCSRP-HP concept to be able to remove sulfur (SO₂, H₂S and COS) at conditions as representative as practical of the anticipated commercial unit. Determine the effect of temperature and pressure and other process variables on the total sulfur removal, and gather the data needed to determine the optimum amount of sulfur that can be removed using the UCSRP-HP.

Task 2.4 – CrystaSulf-DO Sulfur Removal

Demonstrate the potential for the CrystaSulf-DO concept to be able to remove sulfur (SO₂, H₂S and COS) at conditions as representative as practical of the anticipated commercial unit. Establish the equilibrium solubility of hydrogen and carbon monoxide in CrystaSulf solution. Determine the effect of temperature and pressure and other process variables on the total sulfur removal, and gather the data needed to determine the optimum amount of sulfur that can be removed using the CrystaSulf-DO process. The goal is 80-90% H₂S conversion at 400 psi without significant loss of fuel value (i.e., minimal conversion of H₂ or CO). If H₂S conversions are sufficiently high and H₂ and CO conversions are sufficiently low, conduct a long-term test to observe any deactivation of the catalyst.

Subtask 2.5 – Syngas Component Effects on SO₂ Formation

Conduct SO₂ formation catalyst tests at pressure and temperature conditions to determine operating conditions for conversion of a portion of the H₂S to SO₂, as needed for the Claus reaction, without significant loss of fuel value.

Subtask 2.6 -- UCSRP-HP Solvent Regeneration

Conduct regeneration tests on the UCSRP-HP solvents as needed so that a credible

economic analysis can be performed on the overall process.

Task 3.0 – Computer Simulation Model

Subtask 3.1 – Preliminary Aspen Model

Based on the data gathered during Task 2, develop Aspen-Plus based computer simulation models that will be used to design the bench-scale test plan, and for process optimization and economic analysis of the UCSRP-HP and CrystaSulf-DO sulfur removal processes, each in combination with the GTI trace contaminant removal system. Include any needed syngas polishing units in the model. Syngas purity after all cleanup processes must be at the levels shown below:

Contaminant	Maximum After Cleanup
H ₂ S	50 ppbv
NH ₃	0.1 vol%
HCl	1 ppm
Hg	5 ppbv
Se	0.2 ppm
As	5 ppb
Cd	30 ppb

Subtask 3.2 – Aspen Model

Based on the data gathered during Tasks 2 and 5, develop an Aspen-Plus based computer simulation model that will be used for process optimization, economic analysis, and planning and designing a pilot-scale unit for Phase 2. Include any needed syngas polishing units in the model. Syngas purity after the cleanup must be at the levels shown in the Subtask 3.1 chart.

Task 4.0 – Economic Evaluation

All analysis will be consistent with the most recent version of NETL’s “Quality Guidelines for Energy System Studies”. Comparison evaluations will utilize NETL system reports as the basis where possible.

Subtask 4.1 – Preliminary Economic Evaluation

Based on the results of Subtasks 2.1, 2.2, 2.3 and 3.1, compare the economic potential of the following: (1) UCSRP-HP with the GTI trace-contaminant cleanup process, (2) CrystaSulf-DO with the GTI trace-contaminant cleanup process, and (3) conventional processes. For the hydrogen production case, assume the water-gas-shift reaction is performed on dirty syngas, with the cleanup occurring on the shifted syngas. Determine the optimum sulfur removal split between the UCSRP-HP and a polishing bed, and among the DO, CrystaSulf and a polishing processes. Syngas

purity, after all cleanup processes, must be at the levels shown in the Subtask 3.1 chart. Perform the analysis including the creation of sequestration-ready CO₂.

Subtask 4.2 – Economic Evaluation

Based on the results of Subtasks 2.1, 2.2, 2.3, 2.5, 4.1, and Tasks 3.0 and 5.0, compare the economic potential of the following: (1) UCSRP-HP with the GTI trace-contaminant cleanup process and (2) conventional processes. For item (1), determine the optimum sulfur removal split (if any) between the developing processes and a polishing bed. Determine if it is more cost effective to reuse the trace contaminant solvent or not. Syngas purity, after all cleanup processes, must be at the levels shown in the Subtask 3.1 chart. Perform the analysis on a nominal 500 MWe, coal-based IGCC power plant with carbon capture.

Task 5.0 –Bench-Scale Experiments

Subtask 5.1 – Reaction Kinetics

GTI shall measure the reaction rate constant for the reaction between H₂S, COS and SO₂ to produce elemental sulfur in the UCSRP-HP solvent to develop a method to accurately estimate packed bed efficiencies for column design using a reactive mass transfer model.

Subtask 5.2 – Trace Contaminants Removal

GTI shall conduct experiments designed to predict the removal efficiencies and total removal potential of the trace contaminants (NH₃ and HCl) in an industrial setting.

Subtask 5.3 – Hydrodynamics of the Gas-Liquid-Liquid Flow

GTI shall measure column hydrodynamics to the extent necessary to size equipment for the modeling and economic efforts of Tasks 3 and 4 and to design an integrated pilot plant unit for Phase II.

Subtask 5.4 – Packed Bed Efficiency and Parameter Optimization

GTI shall conduct experiments designed to predict overall packed bed efficiency based on the estimated point efficiency using the column at different operating conditions and use this information to design a pilot-scale demonstration reactor column.

Task 8.0 – Project Management and Reporting

GTI shall provide overall project management to include, as a minimum, technical status and administrative reports as required under terms and conditions of the Agreement with DOE. Project management activities shall also include supplying periodic information to the COR for the DOE-NETL metrics, planning and progress reporting programs.

Introduction and Background

When coal is gasified, the syngas produced may contain not only H_2S , but also NH_3 and HCl and heavy metals, such as As, Cd, Hg, and Se. Before this syngas is used as fuel for a gas turbine or further processing to methane, liquid hydrocarbons, or hydrogen, all of the above should be reduced to very low values.

In advanced gasification applications where a low-temperature absorption process such as Rectisol or Selexol is employed to scrub the gas and remove the sulfur compounds, the sulfur-containing species such as H_2S and COS are recovered as an acid gas, which then requires a sulfur-recovery process. The modified Claus process coupled with a tail gas treatment (TGT) process such as SCOT are typically used to recover elemental sulfur and produce a dischargeable plant tail gas. Some plant designs produce sulfuric acid rather than elemental sulfur. Mercury removal is achieved by chemisorption with sulfur-impregnated carbon.

Research at the University of California, Berkeley (UCB), coupled with experimental work at Gas Technology Institute (GTI), is leading to the development of an integrated multi-contaminant removal process whereby syngas is sent to a reactor column at a temperature above the melting point (247°F) and below the polymerization temperature (310°F) of elemental sulfur, at a gasification pressure of 400 psig or higher. Details of the UCSRP-HP have been presented previously.¹

H_2S in the syngas, together with injected SO_2 , dissolves in a solvent that is circulated in the column. The Claus reaction where H_2S reacts with SO_2 to form sulfur and water occurs in the liquid phase. The sulfur formed is only sparingly soluble in the solvent and therefore forms a separate liquid phase. The solvent contains 3-Pyridinemethanol, a homogeneous liquid catalyst at less than 1% by weight of the solution. This catalyst is a commonly available and inexpensive material that does not degrade nor dissolve in the sulfur. One-third of the sulfur product is burned with oxygen (if an oxygen-blown gasifier is involved this would be a fraction of the oxygen requirement for the process), and recycled to the reactor column as the SO_2 source. The remaining sulfur product is sent to the sulfur pit for export. Means are also provided to remove COS , HCl , NH_3 , and trace heavy metals. The treated gas leaving the system is expected to meet the strict specifications set for H_2S and the other contaminants for turbines, fuel cells, and catalytic processes.

The process is ideal for syngas desulfurization at 285 to 300°F and at any given pressure (the higher the better) and offers a tighter integration with the process for removal of trace contaminants and heavy metals. It is expected to be significantly lower in capital and operating cost compared to conventionally applied amine or physical solvent-based acid-gas removal process followed by Claus/SCOT process. Testing done at GTI has shown negligible chemical consumption (including catalyst), unlike typical chemicals costs of \$300 - \$1000 per ton sulfur removed found in competing processes. There is much less need for stainless steels in the process, and no apparent cut-off point in terms of sulfur handling at which Claus/SCOT becomes more economical.

This process differs from liquid redox processes in important ways. There is no need for filtering a solid sulfur paste with attendant handling problems and loss of solvent. The sulfur quality can be as good as Claus sulfur due to the low solubility of the solvent in the liquid sulfur, and to the large density difference and ease of liquid/liquid separation in the process. The process can operate at significantly higher temperatures than the liquid redox or CrystaSulf processes, which is of value in IGCC applications. No foaming of the solution occurs since the solvent is non-

aqueous and has no surfactant properties. No sticky or solid sulfur is present anywhere in the system so the problems of liquid redox plugging and pump wear would not be present.

Although there is no minimum (or maximum) pressure at which the process can operate, the flow of solvent is reduced and reaction rates are increased at higher pressures. This permits the use of smaller equipment and lowers operating costs; hence, the process is projected to be attractive for the treatment of H₂S-containing gases at high pressure. This technology offers great advantages for Illinois basin coals. The ability to reduce the cost for sulfur and other coal impurities will lead to a greater usage of the high sulfur Illinois coals that are not currently competitive for power generation.

Research at the University of California, Berkeley (UCB), coupled with experimental work at Gas Technology Institute (GTI), is leading to the development of an integrated multi-contaminant removal process whereby syngas is sent to a reactor column at a temperature above the melting point (247°F) and below the polymerization temperature (310°F) of elemental sulfur and a gasification pressure of 400 psig or higher. H₂S in the syngas, together with injected SO₂, dissolves in a solvent that is circulated in the column. The Claus reaction is carried out in the liquid phase. Sulfur is only sparingly soluble in the solvent and therefore forms a separate liquid phase. The solvent contains 3-Pyridinemethanol, a homogeneous liquid catalyst at less than 1% by weight of the solution. This catalyst is a commonly available and inexpensive material that does not degrade nor dissolve in the sulfur. The water formed in the Claus reaction vaporizes and forms part of the syngas. One-third of the sulfur product is burned with oxygen (if an oxygen-blown gasifier is involved this would be a fraction of the oxygen requirement for the process), and fed to the reactor column. Means are also provided to remove COS, HCl, NH₃, and trace heavy metals. The treated gas leaving the reactor column will meet the strict specifications set for H₂S and the other contaminants for turbines, fuel cells, and catalytic processes.

The process is ideal for syngas desulfurization at 285 to 300°F and at any given pressure (the higher the better) and offers a tighter integration with the process for removal of trace contaminants and heavy metals. It is expected to be significantly lower in capital and operating cost compared to conventionally applied amine or physical solvent-based acid-gas removal process followed by Claus/SCOT process. Testing done at GTI has shown negligible chemical consumption (including catalyst), unlike typical chemicals costs of \$300 - \$1000 per ton sulfur removed found in competing processes. There is much less need for stainless steels in the process, and no apparent cut-off point in terms of sulfur handling at which Claus/SCOT becomes more economical.

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the organic liquid solvent contains a homogeneous catalyst that promotes the liquid-phase reaction

the temperature in the reactor column is above the melting point of sulfur, and the SO_2 is fed in stoichiometric excess to the H_2S .

Although there is no minimum (or maximum) pressure at which the process can operate, the flow of solvent is reduced and reaction rates are increased at higher pressures. This permits the use of smaller equipment and lowers operating costs; hence the process will be most attractive for the treatment of H_2S -containing gases at high pressure.

Treatment of Synthesis Gas from Coal Gasification

When coal is gasified, the syngas produced may contain not only H_2S , but also NH_3 and HCl and heavy metals, such as As, Cd, Hg, and Se. Before the syngas is used as fuel for a gas turbine or further processing to methane, liquid hydrocarbons, or hydrogen, all of the above should be reduced to very low values. A process flow diagram demonstrating one application of UCSRP to this problem is shown in Figure 1.

Reactor

The countercurrent reactor column is divided into two sections: the scrub section and the reactor section. The sour gas feed enters scrub section, 2A, where it is contacted with a stream of diethylene glycol (DEG) or other glycol ether. At the pressure, temperature and water content of the syngas, the DEG will have a steady-state water content of about 10 to 20 wt%. It will also have substantially smaller, but significant, steady-state contents of NH_3 and H_2S . As a result, the HCl content of the feed gas will be absorbed very effectively to form highly soluble NH_4Cl . A small but significant concentration of NH_4HS will also be present in the liquid phase, and the heavy metals As, Cd and Hg will be absorbed to form their respective, very insoluble sulfides. Selenium will be present in the syngas as H_2Se and will be absorbed to form highly soluble $(\text{NH}_4)_2\text{Se}$ under these conditions. At the bottom of the scrub section, the DEG stream is withdrawn and circulated by pump back to the top. A small slipstream of the DEG stream may be withdrawn, perhaps intermittently, for filtration and other treatment to remove the accumulated impurities, and then returned. The gas stream leaving the scrub section passes into the reactor section through a chimney that effectively prevents the mixing of the solvent in the two sections.

In the operation of the reactor column, 2B, a stream of glycol ether, such as diethylene glycol methyl ether (DGM) is circulated from the bottom of Stripper 1 to the top of the reactor section. The temperature of this stream may be increased or decreased by the heater-cooler, depending on the heat balance in the reactor section. This lean solvent stream, depleted of COS , SO_2 and NH_3 , effectively absorbs those components from the gas stream flowing upward in the reactor section. NH_3 passes through the reactor section without being oxidized but is absorbed as an ammonium salt through its reaction with SO_2 . The solvent has a water content that is essentially in equilibrium with the syngas. A stream of liquid SO_2 is injected into the reactor section at one or more points below the entry of the solvent stream, and is mixed with the solvent flow within the column. The quantity of SO_2 fed into the column exceeds that required to react with the H_2S and COS in the feed stream by an amount between 0.5 and 1 mole per mole of NH_3 in the feed stream. The solvent catalyzes the reaction between H_2S and SO_2 . The water formed by the reaction remains in the vapor phase. The sulfur forms a second liquid phase. The two liquids flow from the bottom of the reactor section to a liquid/liquid separator. The solvent stream then flows to Stripper 1, STR1, by way of HX2. The liquid sulfur stream flows to the furnace.

NH₃ and SO₂ Removal

The gas stream leaving the reactor section of the reactor column has passed through a section in which the gas has been contacted with a solvent stream that is depleted in NH₃ and SO₂, but has a water content that is in near equilibrium with the gas. Depending on the water content of the solvent, NH₃ and SO₂ will be absorbed as the separate compounds, as the ion pair or as ammonium sulfite and/or bisulfate. The treated gas leaving the process has a temperature, water, and CO₂ content that are little changed from those of the feed stream but is substantially free of H₂S, NH₃, HCl, SO₂ and heavy metals. The solvent stream that exits the reactor section of the reactor column exchanges heat with the bottoms stream as it flows to Stripper 1, which operates at near-ambient pressure. The overhead vapor from Stripper 1 is condensed to form a solution of ammonium sulfite and bisulfate. The water stream entering the condenser is provided to insure that no solid salts are formed. As was noted above, the flow of SO₂ to the reactor column is regulated so that the molar ratio of SO₂ to NH₃ stripped out of the fat solvent stream fed to Stripper 1 is between 0.5 and 1. Both can therefore be absorbed in the water stream (plus the water from the condensed overhead vapor) and pumped as a solution to the furnace to moderate the combustion temperature, destroying the NH₃ and recovering the SO₂.

SO₂ Generation

The stream of liquid sulfur leaving the reactor column flows directly to the furnace, where, when time-averaged, exactly one-third of it is burned with a stream of oxygen to form the SO₂ required for the process. The high pressure in the reactor column, about 10 bar absolute, makes it advantageous to use oxygen for the combustion, so that the SO₂ formed may readily be condensed and pumped as a liquid to reactor pressure. The aqueous solution from Stripper 1 is used to moderate the temperature of combustion in the furnace. The high temperature that would result when one-third of the sulfur combusted reacts with oxygen could damage the materials in the furnace if such moderation were not provided. The NH₃ content of the aqueous stream is converted to N₂ and H₂O as it passes through the furnace. The presence of S₂ vapor prevents any NO_x formation. The combustion gas raises steam in the boiler and then passes through the condenser, where liquid sulfur is collected. The wet SO₂ gas then flows to a cooler, where liquid water, saturated with dissolved SO₂, is condensed. The SO₂ stream leaving the cooler is converted to liquid in another condenser, and then pressurized to the pressure of the reactor column by a pump as shown. This pump must also be able to handle the small amounts of N₂ and CO₂ that will be present.

CO₂ Capture

An option for non-IGCC facilities would be to capture the CO₂ for sequestration. Here, the gas stream leaving the reactor column is cooled to near-ambient temperature in the heat exchanger(s) before entering a dryer column, where it is contacted with a part of the physical solvent stream, such as Morphosorb or Selexol, from a CO₂ column. The solvent absorbs H₂O together with some CO₂ and syngas components. The dissolved CO₂ tends to desorb from the solvent as H₂O is absorbed, which reduces the temperature rise that might otherwise occur. The reboiler at the bottom of column heats the solvent sufficiently to strip out a large fraction of the CO₂, and syngas dissolved in it while retaining substantially all of the H₂O. The solvent stream then flows to the H₂O stripper.

The gas stream leaving the dryer column flows to the CO₂ column and is contacted with freshly stripped, cooled solvent. A major fraction of the CO₂ in the natural gas stream is absorbed. The reboiler at the bottom of the CO₂ column heats the rich solvent sufficiently to strip out a large fraction of the syngas while retaining substantially all of the CO₂. The reboiler serves also to cool the stream leaving the solvent strippers. The product gas leaving the CO₂ column will have

a CO₂ content of 1 vol % or less and will be dried to a dew point of 0°C or to meet process specifications. The CO₂-rich solvent then flows to the CO₂ stripper, which operates near ambient pressure and removes most of the CO₂ from the solvent. The solvent contains about 1 wt% water, so that most of the stripping vapor in the reboiler of the CO₂ stripper is H₂O and the temperature is low enough to prevent thermal degradation of the solvent. No water is removed from the system in the CO₂ stripper; the water vapor condensed at the top is returned as a reflux that prevents loss of solvent vapor. The captured CO₂ can then be compressed for transfer to a sequestration facility.

Syngas Temperature Recovery

To maximize thermal efficiency, it is preferable to minimize the temperature drop during sulfur removal. This process is preferably operated above the melting point (247°F) and below the polymerization temperature (310°F) of elemental sulfur. Therefore, if the temperature of the sour syngas feed to the reactor is above this range, stream 1 will be passed through a gas-gas heat exchanger, HX1. The feed gas temperature will be reduced to about 280 to 300°F by exchange with the treated syngas stream 5. This way we expect that almost all heat will be recovered and the maximum temperature differential between sour feed gas and treated sweet gas will be around 30 to 40°F.

This technology offers great advantages for Illinois basin coals. The ability to reduce the cost for sulfur and other coal impurities will lead to a greater usage of the high sulfur Illinois coals that are not currently competitive for power generation.

Experimental Procedures

The overall approach taken in this project is to use simulated coal-derived syngas for laboratory testing of the UCSRP-HP process, with supporting computer simulations. The gas mixtures are complex, consisting of a number of components down to the parts per million (ppm) level. Therefore, modeling results have been used to design experiments, simplify gas mixtures used in the experiments, and capture the important aspects of the process.

Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup

Solvent Degradation and Materials of Construction Experiment

A 1,000 hour test was conducted to study solvent stability and the corrosivity of the system on potential reactor materials of construction. As noted previously, the reactor section of the process will have SO_2 and H_2S being converted to molten, elemental sulfur in a DGM solvent contains a homogeneous liquid catalyst. It is important to verify that the catalyst and solvent remain stable and active, as well as verifying that carbon steel vessels will be acceptable to prevent the expense of requiring stainless steels.

Figure 2 shows the schematic diagram of the apparatus that was used. It was run at 400 psi and 275°F with an average outlet flow rate of 0.2 L/min. It mainly consists of a 4L jacketed, cylindrical, stainless steel vessel with a stainless steel top and bottom plate equipped with a variable speed stirrer, and bottom drain valves to periodically remove sulfur produced and the sample during the reaction. All the surfaces exposed to the chemicals are stainless steel or Teflon to withstand temperature and the corrosive conditions within the reaction vessel. The inlet gases are heated using heating tape and the wall is electrically heated. Temperature of the reaction medium is measured with a K-type thermocouple and controlled using PID type temperature controller. H_2S /syngas and SO_2 inlet pipes and exit gas pipe from the reactor were heated to avoid the plugging of flow lines. Flow rates of the feed gas were controlled manually by means of precession needle valves and monitored by separate mass flow meters. The exit gas stream passed through the gas-washing bottle to condense water produced in the reaction, which was then sent to a second gas-washing bottle filled with 50% sodium hydroxide (NaOH) solution to consume all the unreacted H_2S before it was vented. H_2S and SO_2 leak detectors were placed near the setup to detect any leaks. 2200 ml of 94.5% diethylene glycol methyl ether (DGM), 5% water (H_2O) and 0.5% 3-pyridyl carbinol (3-HP) was taken into the reaction vessel. The solution was stirred well and heated to 135°C. After the desired temperature was achieved, SO_2 and H_2S /syngas were introduced into the reactor.

The flow rates of H_2S and SO_2 were controlled manually by means of precession needle valves (outlets) and by separate mass flow meters (inlets) to maintain a constant reactor pressure of 400 psia. The outlet flow was measured with a bubble flow meter and the total outlet flow was 0.2 slpm. The ratio of inlet flows was kept at 1.8% SO_2 to 0.9% H_2S during the experiment.

The experiment was conducted at 400 psia and 275°F for 1,000 hours. Small liquid samples (5-10 mL) were withdrawn from the reactor at regular intervals and analyzed by GC/MS. An initial analysis of the solvent was performed to be able to identify any degradation products during the experiment.

To study the corrosive nature of the reaction mixture, four, pre-weighed, photographed, 1" × 1" × 1/16" metal coupons (2 uncoated carbon steel Grade 1010 and 2 stainless steel Grade 304) were mounted on two diffuser shafts at two different location such that one was half way submerged and the other was always fully submerged in the solution for each metal. Grade 304 was chosen because it is the "standard 18/8 stainless"; it is the most versatile and most widely

used stainless steel. At the end of the 1,000 hour experiment, these coupons were carefully dismantled, and sent for analysis to determine the type and rate of corrosion in the units of mills per year (mpy). Metal Samples Inc. provided the standard corrosion coupons and independent analysis of these coupons after exposure of 1,000 hour.

Figure 2 UCSRP-HP Solvent Degradation and Corrosion Experimental Layout

Trace Contaminant Removal

Laboratory units for testing the absorption and conversion of trace contaminants in coal-derived syngas were prepared. Separate tests with mercury as elemental mercury, selenium as H_2Se , chloride as HCl , and ammonia as NH_3 were initiated with diethylene glycol (DEG) as the solvent. A permeability tube was used to introduce the mercury into the gas stream. H_2Se , HCl , and NH_3 were added as separate gases from prepared cylinders.

Figure 3 illustrates the schematic diagram and Figure 5 is a photograph of the mercury vapor adsorption apparatus. The Hg source was a mercury permeation tube (VICI Metronics, Inc., CA) as seen in Figure 4. A bath maintained the required stable temperature. The carrier gas was high purity grade nitrogen gas. The reactor temperature was regulated by an electrical jacket fitted around it. Teflon and stainless tubing was selected as connecting materials. A bubble flow meter measured the inlet, intermediate and outlet flows from the reactor. The tubing and valving were such that the selection of which flow rate to be measured could be made during the experiment with the same bubble flow meter.

An Ohio Lumex analytical instrument was employed for measuring the mercury concentrations. Initially, straight through “blank” experiments were performed to measure the Hg^0 concentration in the inlet gas to the reactor. The main limitation of inlet Hg^0 concentration is the measurement maximum of the Ohio Lumex Instrument, which can measure Hg^0 concentration up to $200\mu\text{g}/\text{m}^3$ (STP). Thus, if the concentrated mercury vapor needed to be diluted for measurement purposes, a bypass line was installed with nitrogen gas before being introduced into the reactor. This was not necessary for these runs because the average inlet mercury concentration tested was $44.3 \pm 0.4 \mu\text{g}/\text{m}^3$. We also observed that the concentration of mercury decreased as the nitrogen flow rate over the permeation tube increased, as expected.

Figure 3 Trace Contaminant Testing Apparatus

Figure 4 Mercury Permeation Tube

Figure 5 Mercury Vapor Sorption Apparatus

Vapor-Liquid Equilibrium Experimentation

The experimental set-up for mass transfer and kinetic measurements was build around a stirred cell reactor, see Figure 6 and Figure 7. The equilibrium cell is made of nonmagnetic stainless steel 9 1/8 in. in length and 3in. inside diameter. The feed system allows up to three gas sources/cylinders to be used at a time; pre-blended gas mixtures are employed to increase the number of components tested. The gases are blended by means of partial pressure, utilizing a high-precision pressure gauge and then added to the test cell by means of system pressure. Liquid is drawn into the test cell by vacuum.

Figure 6 High Pressure Vapor Liquid Equilibrium Cell

The equilibrium vessel has a nominal volume of one liter and is rated for operation up to 5,000 psig. This vessel is contained in an environmental chamber, so that temperatures can be

controlled between -85°F to 350°F. The vapor-liquid system is mixed thoroughly by a magnetically-driven agitator that is supplied with a hollow shaft for gas circulation and is extended so that the agitator drive can be located outside the environmental chamber.

A Hewlett-Packard PLC-based control system is provided to assure reliable and repeatable operation. Data are logged regularly from the control system into a dedicated computer for permanent storage and with flexible capabilities for displaying parameter trends during and after the experiments. The unit has an ambient gas monitor for H₂S, CO, and SO₂ and alarms to notify operators of levels above OSHA PEL-TWA. All process and relief vents are collected into a single stream and scrubbed in a caustic solution prior to entering the building vent system.

This arrangement allowed the Vapor-Liquid Equilibrium Unit to be run in the batch phase for both the liquid and gas phase only with no sampling. This is adequate for furnishing vapor-liquid equilibrium information from P-V-T measurements, with no need for sampling or analysis of either phase when the assumption that the vapor contains essentially none of the nonvolatile components is valid or the vapor consist of a pure gas. However, when dealing with a more volatile liquid phase or when more complex static equilibrium studies are necessary, such as reaction kinetics, not only must gas and liquid sampling be performed, but the consideration of a continuous running phase must be included. Two gas chromatographs, with a range of detector options, analyze the vapor and liquid samples in these cases.

In a typical experiment, the reactor is filled from vacuum with the desired amount of liquid, and the system, is allowed to equilibrate to the desired temperature. Next, the gas flow to the cell is set to the desired rate or pressure, and passed directly to the cell. The GC measures the reactor inlet concentration. The stirrer is switched to the desired rate, and the flow is led through the reactor until the achievement of a pseudo steady state, as indicated by a constant concentration reading from the GC reading or pressure reading, marking the end of the experiment.

The liquid phase mass transfer coefficients was determined by monitoring the pressure drop during the absorption of CO₂ in water, while operating both gas and liquid phases in batch mode. The variation of the CO₂ partial pressure with time, obtained from molar balances for CO₂ over both phases is given by

$$N_y = K_g (y^{bulk} - Hx^{bulk})$$

$$N_x = K_l \left(\frac{y^{bulk}}{H} - x^{bulk} \right)$$

for a dynamic solution of the liquid mass transfer coefficient directly from the initial and time dependent concentration readings. Pressure readings at the initial and equilibrium points can then directly be used to obtain Henry's coefficient as follows which is the solubility multiplied by RT.

Figure 7 Schematic of GTI Vapor-Liquid Equilibrium Cell

Heavy Metal Removal

Figure 9 shows the schematic and Figure 8 shows a photograph of apparatus that was used to conduct the investigation of heavy metals removal from coal-derived syngas. The apparatus consists of the following main components:

- three rotameter (3) (6) (9) systems to blend an inlet gas from three gas cylinders;
- a 3000 ml Pyrex glass reactor vessel (21) fitted with a variable speed stirrer and a drain valve for liquid sample acquisitions;
- a heating jacket around the glass reactor to heat the DEG solvent to 135°C (not shown);
- a Water Knock-Out (12), Caustic Trap (19), and Drierite Trap (16);
- a rotameter (17) to measure the outlet gas rate;
- two 3-way valves (10) (14) to divert either inlet or outlet gases for sampling;
- 3-way valve (18) to divert inlet for bubble meter flow rate verification (bubble meter is temporary device);
- two gas sample trains (11) (13) consisting of two wash bottles in a water bath.

The selenium, ammonia, and chloride sources are high pressure cylinders containing 15% H_2Se in nitrogen, 99%+ anhydrous ammonia, 99%+ HCl , respectively. The carrier gas was high purity grade nitrogen gas. The arsine, hydrogen selenide, and ammonia gas cylinders were installed in a safety chamber that vents into the safety hood. A face mask with a regulator specific for NH_3 and HCl , and personal protection monitors were obtained for use. The inlet gas flow rates were calculated for a desired composition in the feed gas and, once verified by bubble meter measurements, were maintained during experimentation by the rotameters, designated as (3), (6) and (9) in the Figure 9. The exit gas stream passed through a wash bottle containing sodium hydroxide (caustic - NaOH) for excess H_2S removal after the trace metals were collected in inlet or outlet sample trains. The hydrogen-sulfide-free outlet gas flow rate was measured by a rotameter (17).

The trace metal, As and Se, components in the inlet and outlet streams were first captured by the sample trains (11) or (13) in Figure 9 using EPA Method 29¹ for loading and timing of sampling, approximately 15 minutes of collection for the inlet samples and 30 minutes for the outlet samples. The remaining exit gas stream was passed through a wash bottle containing sodium hydroxide (NaOH) for excess H₂S removal. The method is designed to specifically absorb each of the metals in an aqueous acidic solution of hydrogen peroxide for analysis of all metals. These samples were then sent to the GTI Analytical Lab for elemental analysis for As and Se by inductively coupled argon plasma emission spectroscopy (ICAP). Samples were also taken of the reactor solvent (2146 g of solvent) and of various solids that were found in the system.

Ammonia and Halogen Removal

Aqueous solutions of weak electrolyte gases (like ammonia) and strong electrolytes (hydrogen chloride) have to be treated in many processes (e.g., in coal gasification). Reliable models for the thermodynamic properties of such complex, chemical reacting mixtures are required to design and optimize those processes. In particular, the basic design of the absorption equipment requires experimental information on the equilibrium properties (basically vapor–liquid equilibrium data). The equilibrium speciation of the liquid mixtures must be known reliably in order to describe not only the equilibrium properties, but also the kinetic processes, as the driving force for any kinetic process results from the deviation from equilibrium.

The experimentation plans focused on ammonia and halogen removal from the syngas in the bottom section of the column by examining the solubility of NH₃ and HCl in diethylene glycol (DEG) solvent.

Figure 8 Trace Component Removal with Ammonia, Chloride, and Selenium

Figure 9 Trace Metal Experimental Schematic

Gas solubility can be measured experimentally using several instruments working based on pressure–volume–temperature–composition (p , V , T , x) determinations. The available techniques were reviewed, taking into account different characteristics of the solvents studied (vapor pressure, viscosity, surface tension, etc.) and the levels of precision and accuracy on the gas solubility. We studied three potential experimental techniques, namely an extraction technique, isobaric saturation, and isochoric saturation methods and selected the isochoric saturation method as the most viable technique for the $\text{NH}_3\text{-HCl-H}_2\text{O-DEG}$ system.

The isochoric saturation method has been used to measure gas solubility in a number of systems, requiring even smaller volumes of solvent when compared to the isobaric method and having no mobile parts². In this case, known amounts of dry gas, determined by a (p , V , T) measurement, and liquid solvent, determined gravimetrically, are put in contact at constant temperature. The equilibrium pressure is in direct relation with the gas solubility, provided the saturation properties of the pure solvent are known. The temperature can very easily be changed, and a new state point is obtained when a constant pressure value is attained (indicating that thermodynamic equilibrium at the new temperature is reached). Equilibration times are longer than in the isobaric method, especially with volatile solvents, for an uncertainty that is similarly below 1%. This technique can be easily extended to the study of mixtures of solvents. In this case, the vapor pressure of the mixture needs to be determined before the gas is put in contact with the liquids and the gas/liquid equilibrium has been attained.

The solubility testing was performed in GTI's high-pressure vapor-liquid equilibrium (VLE) unit. The experimental arrangement has been used previously with success at GTI. The experimental set-up for mass transfer and kinetic measurements was build around a stirred cell reactor as described previously.

A block diagram, Figure 10, describes the general procedure of the technique used for gas solubility experiments in this type of V-L-E equipment. The uncertainty in solubility, expressed as Henry's law constant, has been found to be lower than 5 % for several aqueous solutions previously reported for CO₂ in water.

Figure 10 Block Diagram of the Experimental Determination of Gas Solubility at Set Pressure

A safety procedure that includes PPE usage and alarms was written and distributed to personnel working with these toxic gases. The preliminary experimental plan is shown in Table 1.

Trace Sulfur Removal

The fate of COS in the process is a critical issue for the success of the process. The mechanism for COS either forming or being consumed under our operating conditions is being studied. The test system is shown schematically in Figure 11 and as a photograph in Figure 12.

Table 1 Experimental Plan for NH₃ and HCl Solubility

Test	Solvent	Solvent volume, ml	Test gas	Temp, °C	N ₂ partial pressure, psia	Gas partial pressure, psia
1	Water	270	NH ₃	27	100	73.5
2	DEG	270	NH ₃	27	100	73.5
3	DEG	270	NH ₃	40	100	73.5
4	DEG	270	NH ₃	60	100	73.5
5	DEG	270	HCl	22	100	10.0
6	DEG	270	HCl	40	100	10.0
7	DEG	270	HCl	60	100	10.0
8	DEG + 5% H ₂ O	270	HCl	22	100	10.0
9	DEG + 5% H ₂ O	270	HCl	40	100	10.0
10	DEG + 5% H ₂ O	270	HCl	60	100	10.0

The apparatus consisted of a 4 L steel reaction vessel equipped with a variable speed stirrer. The vessel was also equipped with a bottom drain valve that was used to remove periodically sulfur produced during a side reaction. The reaction vessel was designed to be operated from 120-160°C at pressures up to 500 psia. The exit gas stream passed through the gas-washing bottle to condense water produced in the reaction and then to a second gas-washing bottle filled with 50% sodium hydroxide (NaOH) solution to consume all the untreated H₂S before it is sent to vent. H₂S and SO₂ leak detectors were placed near the setup to detect any leaks.

The flow rates of H₂S and SO₂ were controlled by using two Brooks Mass Flow Controllers (MFC) and a back pressure regulator was used to maintain a constant reactor pressure of 400 psia. The outlet flow was measured with a bubble flow meter.

The gas streams were analyzed using a Varian CP-4900 Micro Gas Chromatograph. It is equipped with a Thermal Conductivity Detector (TCD) and calibrated with known gas standards. To minimize noise and small baseline changes that could be interpreted as real peaks, a minimum peak area threshold value is selected to reject all peaks that are below the threshold. A mathematical formula is then established to determine the concentration of the components of interest. The entire peak area scan is maintained so that the total peak areas can be examined if required. The threshold concentration for these experiments is approximately 7-10 ppmv. Based on our previous experience with the detector at low ppm levels, the standard deviation in

the peak area results is quite high and the precision is not good. Table 2 shows the minimum detection limit for the GC without using special methods and procedures.

Figure 11 COS Experimental Set up

Figure 12 COS Test Equipment

Table 2 GC Minimum Detection Limits

Component	mol%	ppm
H ₂ S	1.55E-03	15.5
COS	1.13E-03	11.3
N ₂	8.20E-04	8.20
H ₂	9.89E-05	0.99
SO ₂	1.28E-03	12.8
CO	7.88E-04	7.88
CO ₂	1.25E-03	12.5

The outlet flow is measured with a bubble flow meter, but the flow rate is measured before the knock-out pot rather than after the knock-out pot as shown in the diagram.

The following chemical reactions are still believed to be the major contributors to the formation and consumption of COS:

Reaction (2) has an equilibrium constant in the reverse direction of $K_p = 579$ at 500°F (260°C). The reverse reaction becomes less favorable at higher temperatures with $K_p = 304$ at 600°F . This may indicate that no COS is likely to form by way of Reaction (2) at 300°F and below, and possibly the reverse reaction dominates.

Reaction (3) is analogous to the Water Gas Shift reaction for making H_2 from CO and H_2O , with H_2S replacing the H_2O in that reaction. The WGS reaction requires catalysis below about 600°F , and becomes highly favorable at 300°F , where K_p is 783. Reaction (3), in contrast, has a $K_p = 9.68$ in the reverse direction at 600°F and $K_p = 7.96$ in the reverse direction at 500°F . It becomes slightly less unfavorable at lower temperatures. If these kinetics are found to be slow, and if the partial pressure of H_2S is also low, COS should not be found under our experimental conditions.

Reaction (4) has a log K_p of 7.79 in the forward direction at 300°F , so it is highly favorable. Factors that may mitigate this COS forming reaction are the very low partial pressure of S in the gas phase and the low solubility of CO in the liquid phase. In addition, if the rate of Reaction (2) is much faster than the reverse Reaction (4), any COS formed could be consumed.

Earlier investigations of the reaction with H_2S and SO_2 performed in this equipment showed the possibility of COS production through these side reactions. The blend gas composition, hereinafter referred to as “the blend gas”, is presented in Table 3. SO_2 is introduced to the reactor from a cylinder with nitrogen as the carrier gas. The reaction of the gases then takes place in a calorimetric-type 4 L reactor. The solution is heated to the required operating temperature of 275°F and pressurized to 400 psig before the gases were introduced into the reactor. The inlet and outlet liquid flow rates are measured by a bubble meter and the temperature is controlled with an electric heater. The blend gas and 1% to 5% sulfur dioxide in nitrogen are fed to the reactor in flow rates controlled by Brooks mass flow controllers. Gas rates varied between 0.25 and 1.3 slpm and are bubbled into the reactor into solvent at the operating temperature.

Table 3 COS Experimental Gas Composition Used in March 2008 Experiments

Component	Target Volume Percent ³	Measured Volume Percent (used by GTI)
Blend Gas		
CO	40	41.6
H₂	30	30
CO₂	16	10.8
COS	0.01	0
H₂O	10	0
N₂	3.49	16.82
H₂S	5000 ppmv	7764 ppmv
SO₂ Gas		
SO₂	3	3.01
N₂	97	96.99

Task 5.0 –Bench-Scale Experiments

Flooding

In determining the column diameter, the limiting (maximum) gas velocity that can be used must be known. This is because the higher the gas velocity, the greater the resistance that will be encountered by the down-flowing liquid and the higher the pressure drop across the packings. Too high a gas velocity will lead to a condition known as flooding whereby the liquid filled the entire column and the operation became difficult to carry out. High pressure will crush and damage the packings in the column. Typically, an absorption column is operated at about 70-80% of the flooding point.

To determine the flooding point, the nitrogen gas flow rate will first be kept constant and the liquid water flow rate will be varied, in order to measure the pressure drop increase with an increase in the liquid flow rate. This occurs because as the liquid fills the voids in the column, the cross-sectional area available for gas flow is reduced. Up to the loading point, the pressure drop at a constant liquid rate show slopes that are fairly linear and approximately equal to that of a dry run. Above the loading point, an increase in slope occurs, indicating a more rapidly increasing pressure drop. Finally, at the flooding point, the slope becomes exponential; liquid will build up on top of the packing and/or spray out of the column. At this point, the drag force of the gas bubbling through the downcoming liquid is the predominate cause of the pressure drop (ΔP_{flood}) across the column.

Mass Transfer Rates

To perform the mass transfer testing, carbon dioxide will be used in nitrogen as the gas stream and sodium hydroxide in water as the liquid stream. Gas sampling will determine the transfer of carbon dioxide from the gas phase to the liquid phase. HETP values will be calculated and graphed against liquid mass flux at a given gas mass flux. HETP values generally increase as liquid mass flux is increased. As liquid mass flux increases, mass transfer decreases; therefore, HETP values increase to reflect the lower mass-transfer efficiency. A plot for water against a known gas will be used to calibrate the validity of the above equations to those reported for the packing.

Heat Transfer Rates

To perform the heat transfer testing, DGM will be used as the liquid phase and nitrogen as the gas phase. The liquid temperatures and flowrates will be varied and the temperatures of both phases in and out of the column will be measured.

Column Limitation

The packing height of the absorber column, V-100, is very short. The same overall mass and heat transfer are not expected to be achieved in the Bench Scale Unit as expected in a full commercial column where some 20 theoretical stages may be needed to complete the reactions and absorption. Therefore, the Unit results cannot be used for direct verification the simulation performance of absorption processes. Rather, the column must be tested as if it represents one segment within the column. Testing will be repeated to represent conditions at the bottom, middle, and top of the column, as necessary to provide sufficient data to model the entire column.

Startup Permissives

Prior to startup for any test, the control system has a number of safety and process conditions that must be met. These are shown as the Permissives screen capture as shown in Figure 13.

Figure 13 Start Up Permissive for the Sulfur Mode

Experimental Procedure

- Manipulated (Independent) Variables
 - Gas flowrate 0.19-0.4 SCFD
 - Liquid flowrate TBD gal/h
- Ranges of Dependent Variables
 - Pressure drop: 0 ~ 5 psi
 - Temperature: 240-280°F and -40°F to ambient

Gas Only Pressure Drop

If the packing is wet, dry by blowing nitrogen through the column.

1. Set the nitrogen flowrate to lowest value.
2. Record the flow rate reading and pressure drop across the column. The pressure drop is measured in inches of water.
3. Record the nitrogen temperature and nitrogen pressure in line with the air flowmeter.
4. Repeat the procedure for 20% opening increases in compressor controller.

The flowmeter measures the flows at standard temperatures and pressures. The flow readings must be corrected for operating pressure P_o (psia) and operating temperature T_o (R):

$$\text{acfm} = \text{scfm} \frac{(P_s T_o)}{(P_o T_s)}$$

P_s = Standard pressure, 14.7 psia

T_s = Standard temperature, 70°F or 530R

Flooding Curve Testing

1. Select a gas flowrate and choose five liquid flowrates in increasing order to collect data. For each flowrate of liquid, record the pressure drop until the column floods.
2. Once liquid holdup in the column is observed, take data at very tiny increments in gas flow rate in order to record flooding data. Patience is needed to obtain accurate steady-state readings especially in the holdup/flooding region. At a given liquid and gas flowrate in the vicinity of flooding, the pressure across the packed bed should rise slowly until the liquid holdup in the column reaches its maximum, but the pressure readings will probably oscillate.
3. Record data when the pressure drop across the column is more or less constant.
 - a) Good data in the curved region between loading and flooding are difficult to obtain.
4. Record the observed value of DP_{flood} , and include notes documenting flooding observations on data sheet.
5. After flooding, decrease the liquid flowrate and gas flowrate slowly. Do not have the operating water level increase too rapidly as the nitrogen flowrate is decreased.

6. After all readings have been taken for each desired data point, shut down the unit.

Operating Conditions (Liquid and Gas Flow Rates)

1. Determine operating gas velocity by multiplying superficial gas velocity at flooding by 0.7 (70% flooding)
2. Calculate all operating flow rates from superficial gas velocities at 70% of flooding.

Heat Transfer Coefficient

1. With the liquid (water, or DGM) and gas (nitrogen) flow rates from above, measure both inlet and outlet gas water vapor content as well as liquid concentrations
2. Record inlet and outlet temperatures for both gas and liquid streams
3. Record outlet stream temperatures for different inlet stream temperatures.

Mass Transfer Coefficient

1. Make up a solution of sodium hydroxide and water to be used as the liquid. Use the same liquid rates as above.
2. Blend CO₂ into the feed nitrogen stream.
3. Measure inlet and outlet gas concentrations for all operating flow rates obtained above.

Kinetic Testing

1. A GC will record inlet gas composition of H₂S and SO₂. Be sure to mark the data with the corresponding operating conditions.
2. A plot of concentration versus liquid flow rate at each condition will be plotted. This will provide an empirical correlation of absorption to liquid flow.

Results and Discussion

Task 1.0 – Bench-Scale UCRP-HP Reactor Setup Design, Construction and Commissioning:

The design of the bench-scale unit was completed and NATCO completed fabrication of the pressure vessels and procurement of other equipment according to the process and instrumentation diagram presented in Figure 14 as designed and Figure 15 as built. The installed equipment in GTI's gas processing laboratory can be seen in Figure 16 and Figure 17. Table 4 list the major process equipment for the UCSRP-HP bench-scale unit.

Table 4 List of Major Components for Bench Scale Unit

Nomenclature	Description
H-200	Feed/Recycle Liquid Heater
H-300	Feed Gas Heater
P-100	Liquid Feed Pump
P-101	Liquid Recycle Pump
P-102	Quench Water Pump
P-105	Heater/Chiller-2 Auxiliary Pump
V-100	Absorber/Contact Tower
V-101	High Pressure Flush
V-102	Three Phase Separator
V-104	Liquid Knock Out
V-105	Off Gas Scrubber
V-106	Knockout Pot
V-200	Quench Water Tank

The bench scale unit consists mainly of a reactor/absorption tower, V-100 packed with Sulzer Mellapak 250Y; a three phase separation tank, V-102, for removal of liquid sulfur from the DGM solvent before re-circulation back to V-100; gas-liquid separator, V-104; gas scrubber, V-105, equipped with a pH probe ; and two Chromalox heaters, H300 and H200, for gas and liquid heating. To minimize heat losses most of the plant has been insulated with some lines/tubes having heat tracing to prevent sulfur condensation and plugging. A Neslab Model 85 heater/chiller was purchased and installed with an auxiliary pump, P-104, to provide high temperature heat transfer fluid to the jackets on V-100, V-101, and V-102. A quench vessel, V-

200, and pump P-102 were added to add quench water to the top of V-100 to prevent equipment damage and a decrease in absorption efficient due to heat of reaction and adsorption as the gas moves up the absorption tower. Liquid feed and recycle pumps, P-100 and P-101, were installed.

As can be seen from in the figure, the main unit where absorption and reaction will take place is in the absorber. It is a 4-inch-outer-diameter by 36-inch-high bench-scale packed bed reactor. The simulated feed gas used in these experiments will contain synthesis gas components including hydrogen sulfide, sulfur dioxide, and nitrogen. The flow rate of simulated feed gas through the packed bed was set to be between 20-100 scfh. The operating condition ranges for the bench-scale packed bed reactor is from ambient temperature to 300°F and pressures from atmospheric to 1000 psig.

Heat is generated as a result of the exothermal chemical reaction between hydrogen sulfide and sulfur dioxide. Heat may also be generated when large amounts of solute are absorbed into the liquid phase, due to the heat of solution. The resulting change in temperature along the height of the absorber column may damage equipment and reduce absorption efficiency. This problem can be avoided by adding cooling coils to the column or by adding quench water as shown for this small vessel. The evaporation of water will cause a substantial cooling within the absorber to offset the heat generated if it deemed necessary for temperature control. Heat losses in the small column may be sufficient to control temperature. A thermocouple, as shown in the diagram, will regulate the addition of water to the system as necessary.

A once-through caustic scrubber was chosen as a simple and effective system to remove any H₂S and SO₂ remaining at the end of the process before venting to our internal compressor system. Other scrubber systems including lime/limestone systems were looked at, but many have other prohibitive restrictions, e.g. limestone systems are typically limited to fairly weak gases of SO₂ and can be adversely affected by rapid changes in concentration. This is true because the pH decreases as the SO₂ concentration increases via SO₃⁻² and HSO₃⁻¹ concentrations. Thus, for a laboratory-scale system, the caustic scrubber is both economical and efficient, which are not as sensitive to these fluctuations because the following SO₂ absorption chemistry that holds in a caustic scrubber:

Construction and Commissioning

The bench-scale unit was delivered to GTI from NATCO in the first quarter of 2007. See Figure 18. Assembly started and continued as the remaining components were received.

For safe operations with toxic gases, such as H₂S and SO₂, the bench-scale unit was contained in a Plexiglas enclosure. The ventilation system within the enclosure maintains a lower pressure than the rest of the room and ensures that any leaks are not released to the remainder of the laboratory, but are properly handled. H₂S and LEL monitors were mounted to test stand and in the compressor room to warn operators of any leaks. A GTI-owned compressor was then connected to the bench scale unit for gas circulation and flow rate control.

Figure 14 As-Designed Bench-Scale Unit P&ID

Figure 16 Bench-Scale Unit Being Installed at GTI

Figure 17 Bench-Scale Unit

Figure 18 Bench-scale Unit Being Unloaded at GTI

As part of GTI's and industrial safe operating practices, a comprehensive Hazard and Operability study (HAZOP) scheduled on the unit as NATCO continued assembly. Since NATCO could not provide any of the required documents to conduct a HAZOP, GTI and Vector House undertook the task of making all detailed PI&D and electrical drawings. The HAZOP study was performed using Dyadem's PHA-Pro 7 Software. The four day session was facilitated by a Director of Packer Engineering and six senior GTI engineers. Five nodes were selected for analysis, namely CH-1 Heating/Cooling Loop, CH-2 Cooling Loop, Gas Feed, Contacting, and Waste Treating. Overall there were 87 recommendations set forward. A breakdown of the HAZOP risk matrix is shown in Figure 19. GTI brought the unit up to safe and operable engineering standards concentrating first on those items with highest frequency and highest severity, that is, those items with the greatest number of consequences (most likely to occur with the greatest impact on personnel and equipment). After construction and assembly of the bench scale unit, GTI then initiated the commissioning of the plant. A listing of the construction and commissioning activities performed is included in Appendix A.

Figure 19 Risk Matrix

Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup

Subtask 2.1 – UCSRP-HP Solvent Degradation and Corrosion

The fresh solvent was analyzed by the GTI Analytical Laboratory in order to identify any degradation of the solvent during the test. The results of the GC/MS of the fresh solvent are presented in Table 7. DGM is not listed as a component because the system is set up to “bypass” DGM as it is a major component in such high concentration that it will cause the GC/MS to shut down as a safety measure, or if the safety does not activate in time, it would blow out a filament. The catalyst, 3-pyridinemethanol, appears to diminish in concentration during the experiment, but comes back when the gases and reaction are stopped as indicated in the 7/12 measurement. This would be expected as the catalyst partakes in the reaction, but is not itself consumed. The results from this test showed good stability for the solvent and catalyst. Approximately 2.3% of DGM solvent degraded to tetraglyme. Tetraglyme is a potential substitute for DGM since it is less volatile and has a higher H₂S solubility than DGM. However, tetraglyme is more viscous. Therefore conversion of the solvent is not a significant issue. Approximately 25% of catalyst at 0.2% by weight of solution broke down to 3-methylpyridine and 4-formylpyridine. These pyridines are also active catalyst and did not appear to affect reactivity.

The gas analysis indicates that COS is created by reaction of carbon dioxide with the sulfur that is formed with the high CO levels. Table 6 shows that possibly up to 30 ppmv may have formed via this reaction pathway. These levels are at the limit of the gas chromatograph accuracy and may not actually be forming any carbonyl sulfide. COS is in the Wabash River gasifier syngas at about 700 ppm. However if carbonyl sulfide has formed, it is in equilibrium with the reverse reaction of carbonyl sulfide combining with sulfur dioxide to reform carbon dioxide and sulfur. Therefore, withdrawal of sulfur from the reactor should further minimize carbonyl sulfide formation. Further testing of COS was initiated as explained later in this report.

The sulfur that was formed during this test was analyzed for sulfur purity. Without any washing or other preparation techniques, the sulfur was 99.2% pure. The commercial target for sulfur purity is greater than 99.5%.

Metal Samples Inc. provided four standard uncoated carbon steel Grade 1010 and stainless steel Grade 304 corrosion coupons and an independent analysis of these coupons after exposure of 1,000 hour. The coupon results for corrosion showed no pitting or etching as shown on Figure 20. Weight losses for uncoated 1010 carbon steel and stainless steel samples in the chamber were 0.02 and 0.008 g, respectively. The corrosion rates were 0.52 mils/year and 0.23 mils/year over the 1,000 hour period; below 2 mils/year is considered excellent corrosion inhibition. The coupons in the gas and in the liquid phase showed essentially the same weight loss and corrosion rate.

These tests verified the use of carbon steel as an acceptable material of construction for the process.

Table 5 GC/MS Analysis of DGM Solvent Mixture Prior to Experiment Start

061286-001 DGM 5/31/06			
Compound Name	CAS #	Match Quality	Est. Conc. $\mu\text{g/mL}$
Water	7732-18-5	-	1470
Ethylene glycol methyl ether	109-86-4	90	4.4
3-Pyridinemethanol	100-55-0	-	2920 *
Triethylene glycol methyl ether	112-35-6	83	77.2
Hexanedioic acid, dimethyl ester	627-93-0	86	2.4
2,6-Di-tert-butyl-4-methylphenol	128-37-0	96	18.6
A phthalate, possibly 2-Methyl-butyl-phthalate or Cyclohexyl butyl phthalate	17851-53-5 / 84-64-0	80 / 78	14.3

Table 6 Gas Chromatograph of the Vapor Stream in the 1,000 hour Degradation Experiment

Matheson certification:		
CO	41.54 %	+/-2%
CO2	11.00 %	+/-2%
H2	29.87 %	+/-2%
H2S	7651 ppmv	+/-2%
N2	16.82 %	+/-2%
COS	N/A	

MicroGC analysis:	Initial	Experimental Average
CO	N/A	
CO2	9.037 % v/v	
H2	N/A	
H2S	8333 ppmv	232.5 ppmv
N2	N/A	
COS	12 ppmv	34.5 ppmv
SO2	100.00	1691 ppmv

Table 7 Liquid Sample Impurities Found in Solvent Samples Throughout Solvent Stability Experiment

Compound Name	Measured Concentration, µg/mL					
	5/31	6/8	6/12	6/14	6/20	7/12
3-Pyridinemethanol	2920	1200	1090	888	540	2160
Sulfur Dioxide		356	61.6	128	56.1	21.1
Water	1470	42.2	295	274	258	489
1,4-Dioxane		13.5	27.1	44.4	222	694
2,6-Di-tert-butyl-4-methylphenol	18.6	19	17.9	17.7	15.8	27.5
2-Methyl-1,3-dioxolane					4	
3-Formylpyridine or 4-Formylpyridine		33.6	90.9	67.9	11.9	
3-Methylpyridine						563
4,4'-(1,2-ethanediyl) bis-pyridine						102
A phthalate, possibly 2-Methyl-butyl-phthalate or Cyclohexyl butyl phthalate	14.3	13.7	11.8	12.7	10.6	26
Diethylene glycol ethyl ether		23.3	21.2	29.2	5.1	
Ethylene glycol dimethyl ether					2.5	
Ethylene glycol methyl ether	4.4	10.9	14.2	17.3	62.2	557
Long-chain glycol, possibly Hexaethylene glycol dimethyl ether						125
Long-chain glycol, possibly Pentaethylene glycol dimethyl ether		24.8	23.1	21	17.4	
Long-chain glycol, possibly Tetraethylene glycol dimethyl ether		65.3	142	227	1190	22900
Long-chain glycol, possibly Triethylene glycol dimethyl ether		4.3	7.5	11.8	64	116
Tetraethylene glycol						133
Triethylene glycol						1540
Triethylene glycol methyl ether	77.2	95.5	103	105	232	3050
Unidentified, M.W. > 087		6.5	4.5	3.7	11.3	
Unidentified, M.W.> 108		4.7				
Unidentified, M.W.> 187		5.5				

Unidentified, M.W. > 152			9.8	9.9	14.7	
Unidentified, M.W. > 213			8.8	8.1	11.1	
Unidentified, M.W. ≥ 090						29.9
Unidentified, M.W. ≥ 107						133
Unidentified, M.W. ≥ 117						189
Unidentified, M.W. ≥ 152						174
Unidentified, M.W. ≥ 168						93.8
Unidentified, M.W. ≥ 171						64

Figure 20 Carbon Steel (left) and Stainless Steel (right) Coupon Photographs Before (top) and After (bottom) Clean up After 1,000 h in Solvent

Subtask 2.2 – GTI Trace-Contaminant Removal

Mercury vapor phase concentration curves in the presence of DEG are presented in Figure 21. The spike at about 4400 seconds resulted from bypassing the reaction vessel to ensure that mercury was still flowing. DEG improved the extent of the reaction of Hg with hydrogen sulfide over that observed in a vapor phase reaction; i.e., 95% of the mercury reacted with the hydrogen sulfide in the presence of DEG, while only 58% reacted in the vapor phase, as can be seen Figure 22. This is important because it is desired to bring the mercury concentration down to ppb levels in the gas, which was indeed accomplished in the presence of DEG. The final mercury concentration in the vapor phase was 0.2 ppb (1,900 ng/m³) when the solvent was present for absorption and reaction to take place.

Figure 21 Mercury Concentration in the Vapor Phase in the Presence of DEG

Figure 22 Mercury Concentration in the Vapor Phase with No Solvent

A series of tests were conducted to study the solubility of H_2Se . The qualitative results showed H_2Se solubility as indicated by the bright red color shown in Figure 24. A solution of 85 wt% DEG and 15 wt% H_2O was prepared, but found to boil at 131.5°C , which is lower than the temperature set point for the experiment of 135°C . Subsequently, the temperature set point had to be lowered to 129.3°C to avoid boiling. This was accomplished by a simple calculation using the boiling point elevation equation and finding that 13 wt% H_2O (353 ml H_2O in 2L of DEG) would raise the boiling point of water to 135°C . Solution in the tank turned from clear to reddish-pink which later turned to grey-black on cooling.

The analytical results for the total selenium content in solution are presented in Table 8. At this point, the higher temperature resulted in lower physical solubility, but, in the presence of ammonium chloride in the solution, the solubility appeared to have increased. Further testing was delayed due to a reverse air flow from inside the hood into the laboratory space. For safety reasons, the testing was deferred until proper ventilation could be assured while working with these hazardous gases.

Figure 23 Trace Component Removal with Ammonia, Chloride, and Selenium

Table 8 Selenium Solubility Data

<u>Sample Number</u>	<u>Sample Description</u>	<u>Se, mg/l</u>	<u>Notes</u>
0071026-001	NH ₄ Cl + DEG + water + H ₂ Se	20	grey color
0071026-002	275°F - water + H ₂ Se	7	red color
0071026-003	75°F - water + H ₂ Se	438	grey color

Figure 24 DEG After Exposure to H₂Se, NH₃, and Chloride

The fate of COS in the UCSRP-HP process was raised as an issue during a project review meeting with DOE. The solubility of COS in DGM was measured at 275°F. The high solubility measured indicates that any unreacted COS in the top section of the reactor column will be absorbed into the lean DGM and carried back into the reaction zone.

Carbon monoxide and hydrogen sulfide were fed to the reactor to study the production of COS in a gas phase only and in a liquid phase. Finally, tests with CO, H₂S, and SO₂ in gas phase were completed. Tests were conducted with CO, H₂S, and SO₂ in DGM; CO with sulfur-saturated DGM, and SO₂ and COS in DGM. The initial test conditions are seen in Table 9 and the composition of the outlet gases are seen in Table 10.

Table 9 Initial Conditions for COS Experiments

Test Plan #	Components	Mass of Solvent (g)		Water Content (wt%)		Initial Sulfur Charge (g)	Reactor Conditions		Inlet Gas Flow Rates (slpm)				Inlet Gas Concentrations (mole%)			
		Before	After	Before	After		Temp (C)	Pressure (psig)	CO	H ₂ S	SO ₂	COS	CO	H ₂ S	SO ₂	COS
2a	CO, H ₂ S	n/a	n/a	n/a	n/a	-	135	400	0.58	0.72	n/a		p	10.229	n/a	
2b	CO, H ₂ S, 95% DGM, 4.5% H ₂ O, 0.5% 3-HP	2346.04	2342.4	4.77	3L	-	135	400	0.58	0.72	n/a		10	10.229	n/a	
3	SO ₂ , CO, H ₂ S	n/a	n/a	n/a			135	400	0.23	0.235	2.468		p	10.229	1.062	
1a	COS, 94.62% DGM, 4.85% H ₂ O, 0.53% 3-HP	2194.84	2190.6	5.52	4L	0	135	Atmospheric	n/a	n/a	n/a	0.5		n/a	n/a	2.941
	CO, 90.83% DGM, 4.65% H ₂ O, 0.52% 3-HP, 4% S	2268.38	2274.9		5L	91.45	135	400	0.235	n/a	n/a	n/a	10	0	0	0
3c	CO, H ₂ S, SO ₂ , 94.61% DGM, 4.85% H ₂ O, 0.54% 3-HP	2194.81	1772	5.16	3.945	0	135	400	0.235	0.235	2.468					
repeated 3c	CO, H ₂ S, SO ₂ , 94.56% DGM, 4.856% H ₂ O, 0.548% 3-HP	2190.53	2023.6	5.19	3.55	0	135	400	0.235	0.235	2.468			10.229	1.062	
3d	CO, H ₂ S, 120% SO ₂ , 95% DGM, 4.74% H ₂ O, 0.5% 3-HP	2346.15		4.77	7.5	0	135	400	0.23	0.235	2.82					
3d-1	CO, H ₂ S, 100% SO ₂ , 94.59% DGM, 4.88% H ₂ O, 0.537% 3-HP	2195.61	1997.8	5.55	3.77	0	135	400	0.23	0.235	2.35			10.229		

Table 10 GC Gas Outlet Results for Experiments

Test Plan #	Components	Total Outlet Flow (splm)	Outlet Gas Concentration (mole%)					
			CO	H ₂ S	SO ₂	COS	CO ₂	COS
2a	CO, H ₂ S	1.32	3.05	2.76	-	0.018	0.24	0.056
2b	CO, H ₂ S, 95% DGM, 4.5% H ₂ O, 0.5% 3-HP	2.37	3.56	3.42	-	0.01	0.04	< 0.01
3	SO ₂ , CO, H ₂ S	2.9	0.072	0.362	0.41	0.007	0.0053	
1a	COS, 94.62% DGM, 4.85% H ₂ O, 0.53% 3-HP	0.49	0	1.248	0	1.531	1.2035	
	CO, 90.83% DGM, 4.65% H ₂ O, 0.52% 3-HP, 4% S	0.24	2.59	0.004	-	-	0.0048	
3c	CO, H ₂ S, SO ₂ , 94.61% DGM, 4.85% H ₂ O, 0.54% 3-HP	1.77		0.021	0.0237	0.0027		
repeated 3c	CO, H ₂ S, SO ₂ , 94.56% DGM, 4.856% H ₂ O, 0.548% 3-HP	2.62	0.01	0.007	0.17	0.0035	0.0054	
3d	CO, H ₂ S, 120% SO ₂ , 95% DGM, 4.74% H ₂ O, 0.5% 3-HP	2.75		0.007	0.128	0.0054	0.0144	
3d-1	CO, H ₂ S, 100% SO ₂ , 94.59% DGM, 4.88% H ₂ O, 0.537% 3-HP	1.82	4.32	0.008	0.0812	0.0042	0.0085	

In Table 11, we have found negligible COS production from this reaction. This could be because either the kinetics are slow or the partial pressure of H_2S is low. This is further illustrated by test plan CO + S, where all of the COS produced is immediately converted to hydrogen sulfide and carbon dioxide.

After this was realized, different concentrations of SO_2 were introduced keeping all other conditions uniform. COS was produced unless an excess of SO_2 was used. Once an excess of SO_2 was used, CO_2 was produced, indicating that either the reverse of Reaction (2) was taking place or that COS was being hydrolyzed. Further testing is needed to verify these pathways.

Heavy metals that can be in the syngas stream include selenium, mercury, cadmium, and arsenic. Selenium is expected to be in the form of H_2Se while mercury is expected in the metallic form. The earlier testing showed the increased solubility of H_2Se in DEG with the presence of ammonia chloride. Mercury removal was shown down to 0.2 ppb levels through a reaction with sulfur. In this subtask, GTI investigated means to increase the heavy metal solubility and/or reactivity at 275-300°F and pressures from atmospheric to 400 psi. Means to regenerate the loaded solvent was also to be investigated.

The results from the chemical analyses are presented in Table 12.

The molar flows for each element were calculated by two methods. The feed flow rates (ml/min) and the gas cylinder contents (volume %) were used to calculate the Inlet Flow molar rate. The analytical results in Table 13 were used to calculate the “Analytical Results” molar rates presented in Table 12. This was performed by adding the mass of each metal in the two sets of wash bottles, converting the mass to moles and dividing by the sampling time. The last column on Table 12 shows a 97% correspondence between the two methods for H_2Se , but only 40% for AsH_3 . In addition, Table 12 shows that we achieved about 50% removal of the H_2Se and 33% of the AsH_3 during the 30 minute test.

Table 11 Results of COS Experiments

		Reactor_out
Experiments	Moles/h Consumed (in-out)	Output_Matl. Streams
		bal: N2
2a	0.04624	CO
CO, H ₂ S	-0.02365	H ₂ S
RXN: CO + H ₂ S -->COS + H ₂	-0.00061	COS
	-0.00089	CO ₂
2b	0.04696	CO
CO; H ₂ S; +Solvent	0.08267	H ₂ S
RXN: CO + H ₂ S + Solvent -->COS + H ₂	0.00060	COS
	-0.00123	CO ₂
3	0.01000	CO
SO ₂ , CO, H ₂ S	0.03839	SO ₂ (B)
RXN: SO ₂ + CO + H ₂ S -->	0.03630	H ₂ S
	-0.00023	COS
	0.00026	CO ₂
	0.04313	S
1a	0.01869	COS
COS; +Solvent	-0.01632	CO ₂
RXN: COS + Solvent --> H ₂ S + CO ₂	-0.01692	H ₂ S
CO; +Solvent	0.05139	CO
RXN: CO + Solvent + S ---->	-0.00002	H ₂ S
	-0.00001	CO ₂
	0.00000	COS

	0.01188	S
3c	0.06604	CO
CO,H2S, SO2, +Solvent	0.06846	SO2
	0.06286	H2S
	0.00388	COS
	0.15325	S
repeated 3c	0.06527	CO
CO,H2S, SO2, +Solvent	0.05406	SO2
	0.06394	H2S
	0.00004	COS
	-0.00036	CO2
	0.12028	S
3d *	0.06604	CO
CO, H2S, 120%SO2, +Solvent	0.06567	SO2
	0.06387	H2S
	0.00031	COS
	-0.00119	CO2
	0.06359	S
3d-1	-0.26644	CO
CO, H2S, 100%SO2, +Solvent	0.05769	SO2
	0.06386	H2S
	-0.00001	COS
	-0.00060	CO2
	0.106	S

DEG was initially identified as a likely solvent for the scrub section. The major reason for using DEG as the scrubbing liquid instead of plain water is to minimize the water vapor in the gas leaving that section and the NH_4Cl in plain water would be much more corrosive than it would be in DEG containing only 5 wt% or so water. DEG is not necessarily the best glycol ether to use for this service. One that is more hydrophobic and lower in volatility might be better - some experimentation will be required after the solubility of ammonia and chloride in DEG/water mixtures is determined. Several alternative glycol ethers are shown in Table 14.

Ammonia and Halogen Removal

The purpose of this subtask is to understand the effect of water content and ammonia solubility on formation of NH_4Cl as assumed for the removal of chlorides. The ammonia solubility may also affect the solubility of the heavy metals in the removal solvent system.

The preliminary experimental results for the $\text{NH}_3 - \text{HCl} - \text{H}_2\text{O} - \text{DEG}$ system as per the testing plan shown in Table 1, are given in Table 15. Although the results obtained were consistent in a qualitative manner, the error was large for the equilibrium distribution ratios. The numerical values for the gas solubilities are very low with the distribution parameter being an order of magnitude higher than literature values as shown in Table 18.

The literature data for NH_3 -Air-Water system was for 1 atm pressure. However, the effect of pressure on the distribution ratio (or equivalently Henry's Law constant) is weak. The effect of pressure on gas solubility is given by the Krischevsky-Kasarnovsky equation.⁴ For ammonia, the partial molar volume in dilute aqueous solution is $v_{\text{NH}_3}^\infty = \sim 30 \text{ cm}^3/\text{mol}$ at 30°C . Initial and final total pressures for the runs were 173.5 psia (11.8 atm) and 129.5 psia (8.8 atm). Using these numbers and the following equation, the pressure effect can be neglected. The weak dependence can be attributed to the linear dependence of pressure on the logarithm of Henry's Law constant at any given temperature.

$$\ln(H^P) = \ln(H^{Ps}) + \frac{v_{\text{NH}_3}^\infty(P - P^s)}{RT}$$

Table 12 Trace Component Flows and Removal

Element	Gas Inlet # in Fig.	Gas Cylinder Content	Feed Flow Rates, ml/min	Flow Rate Inlet, mol/min	Analytical Results		Percent Removal		Compare Inlet Flow vs. Analytical, (mol/min)/(mol/min)
					Inlet, mol/min	Outlet, mol/min	Based on Analytical Results	Based on Flow Rates	
Se	Gas 2	15% H_2Se / N_2	196.5	9.4E-04	9.1E-04	4.8E-04	47%	49%	97%
As	Gas 3	1% AsH_3 / N_2	318.4	1.0E-04	4.1E-05	2.7E-05	34%	73%	41%

Table 13 Analytical Results as per EPA Method 29

Sample Description	Inlet wash bottle #1, mg	Inlet wash bottle #2, mg	Outlet wash bottle #3, mg	Outlet wash bottle #4, mg	Reactor Solvent, $\mu\text{g/g}$	Inlet wash bottle #1, red particulates, wt %	Outlet wash bottle #3, red particulates, wt %
Arsenic, mg	46	3	61	4	20	0.2	0.04
Selenium, mg	1106	0.4	1592	0.3	290	3.7	1.8
Total wt. of solids in Sample Solution, g					2250	0.027	0.154

Table 14 Potential Glycol Ethers for Scrub Section

Glycol Ethers ⁵	Empirical Formula	Mol. Wt.	Boiling point	Molar volume	Density (20°C)	Viscosity (20°C)	Vapor Pressure (25°C)	CAS-Reg. No.
		(g/mol)	(°C)	(cm ³ /mol)	(g/cm ³)	(cP or mPa s)	(Pa)	
Diethylene glycol	C ₄ H ₁₀ O ₃	106.14	245	94.9	1.120	38.5	1	111-46-6
Dipropylene glycol (a)	C ₆ H ₁₄ O ₃	134.18	224	130.9	1.025	107	4.25	25265-71-8
Dipropylene glycol (isomer) (a)	C ₆ H ₁₄ O ₃	134.18	225.7	142	1.023		1.6	110-98-5
H (of -OH) substituted by ALKYL GROUP at one end of diethylene glycol								
Diethylene glycol monomethyl ether	C ₅ H ₁₂ O ₃	120.17	193	118	1.017 (@ 25°C)	3.48 (@ 25°C)	24	111-77-3
Diethylene glycol monoethyl ether (isomer) (a)	C ₆ H ₁₄ O ₃	134.2	202	130.9	0.984 (@ 25°C)	3.85 (@ 25°C)	17	111-90-0
Diethylene glycol monobutyl ether (isomer) (b)	C ₈ H ₁₈ O ₃	162.26	225.5	170.6	0.953	5.83	3	112-34-5
Diethylene glycol isobutyl ether (isomer) (b)	C ₈ H ₁₈ O ₃	162.26	217		0.950			18912-80-6
Diethylene glycol n-hexyl ether	C ₁₀ H ₂₂ O ₃	190.28	259	204.3	0.936		1.3 (@ 20°C)	112-59-4
H (of -OH) substituted by ALKYL GROUP at both ends of diethylene glycol								

Diethylene glycol dimethyl ether (isomer) (a)	C ₆ H ₁₄ O ₃	134.2	162		0.938 (@ 25°C)	0.989 (@ 25°C)	394	111-96-6
Diethylene glycol diethyl ether (isomer) (b)	C ₈ H ₁₈ O ₃	162.26	188.9	179.8	0.906	1.40	50 (@ 20°C)	112-36-7
Diethylene glycol dibutyl ether	C ₁₂ H ₂₆ O ₃	218.38	256	248.1	0.890	2.39	1.33 (@ 20°C)	112-73-2
Related Esters								
Diethylene glycol monomethyl ether acetate	C ₇ H ₁₄ O ₄	162.21	209.1		1.040		16 (@ 20°C)	629-38-9
Diethylene glycol monoethyl ether acetate	C ₈ H ₁₆ O ₄	176.24	217.4	175.5	1.009	2.80	1 (@ 20°C)	112-15-2
Diethylene glycol monobutyl ether acetate	C ₁₀ H ₂₀ O ₄	204.3	245	208.2	0.980	3.02 (@ 25°C)	5.3 (@ 20°C)	124-17-4

Table 15 Experimental and Literature Equilibrium Distribution Ratios for Ammonia-Gas-Water System

System	NH ₃ -N ₂ -Water	NH ₃ -Air-Water ⁵			NH ₃ -Air-Water ⁷	
T, °C	26.7	20	26.7	30	20	30
Equilibrium Ratio, $y_{\text{NH}_3}/x_{\text{NH}_3}$ ¹	29.0	0.69	0.97	1.15	0.77	1.14

It was determined that a change in experimental set up would have to be made for studying systems where gas components are absorbed rapidly into the solvent phase. The initial number of moles in the system was estimated using the pressure reading from the VLE cell (together with known VLE cell headspace volume and temperature). However, for a fast absorbing system, the initial pressure reading is only indicative of the moles of gas remaining in the headspace volume after rapid absorption. The amount of gas transferred to the VLE cell can be calculated using the mixing chamber conditions (P,V,T) as well. Using the initial and final pressures in the mixing chamber, together with the mixing chamber volume, the number of moles admitted to the VLE cell can be readily estimated.

This required that an additional pressure transducer be connected to read the pressure changes in the mixing chamber. The test plan was revised to calibrate the volumes and pressures along the entire tubing path leading to the VLE cell and then monitoring the pressure changes in the mixing chamber during the filling of the VLE cell. Table 17 lists the data used to determine the volume of the mixing chamber and the previously measured volume of the VLE cell. The manufacturer supplied nominal size of the mixing chamber is 1 gallon (3.79 L), so the resulting average error in the volume measurements is approximately 3%.

¹ Equilibrium ratio is given by $y_{\text{NH}_3}/x_{\text{NH}_3} = 0.10 \cdot \exp(0.0284T)$ where T is between 32 and 140°F.

Table 16 Equilibrium Distribution of Species (Ammonia-Nitrogen-Water)

System	VLE Cell							Distribution - ratio, NH ₃
	T (°C)	p _{NH3} , psia		Vapor phase conc., NH ₃		Liquid phase conc., NH ₃		
		initial	final	y _i , NH ₃	y _f , NH ₃	x, NH ₃	mol/L (M)	
NH ₃ -N ₂ - H ₂ O	26.7	73	29.8	0.42	0.23	7.93E-03	0.44	29
NH ₃ -N ₂ - DEG	26.7	73	26.6	0.42	0.21	8.34E-03	0.46	25.2
NH ₃ -N ₂ - DEG	40	71.6	31.2	0.42	0.24	6.72E-03	0.37	35.7
NH ₃ -N ₂ - DEG	60	71.6	32.9	0.42	0.24	6.87E-03	0.38	34.9
NH ₃ -N ₂ - DEG	135	71.6	52.3	0.42	0.29	5.25E-03	0.29	55.2

New solubility measurements were then made for the $\text{NH}_3\text{-N}_2\text{-H}_2\text{O}$ system to verify the procedure. The distribution ratios and the associated errors are given in Table 18. Although the new experimental values are of the same order of magnitude as the literature values, the errors are still large.

Table 17 Temperature and Pressure Measurements to Determine the Volume of Mixing Chamber

VLE CELL					MIXING CHAMBER				
P _i , psia	P _f , psia	V, L	T, °F	Moles, n	P _i , psia	P _f , psia	T, °F	Moles, n	V, L
0.29	172.24	1.29	76.0	0.619	413.64	357.18	75.2	0.619	3.91
0.29	170.33	1.29	76.0	0.612	357.18	301.30	75.2	0.612	3.91
0.29	170.33	1.29	75.9	0.612	301.30	246.49	75.2	0.612	3.99
0.37	124.07	1.29	76.3	0.445	419.41	377.72	75.2	0.445	3.80
0.29	122.92	1.29	76.4	0.441	377.72	337.30	75.2	0.441	3.89

Table 18 Equilibrium Distribution Ratios for NH₃-Gas-Water System: Comparison of Experimental Results with Literature Values

T (°C)	Distribution ratio ($y_{\text{NH}_3}/x_{\text{NH}_3}$)		% Error
	Experimental	Literature values (NH ₃ +Air+Water)	
26.8	1.32 ± 0.17	0.98 ⁵	25.8 %
30.1	0.82	1.16 ⁵ , 1.15 ⁷ (30°C)	-40.2 %
59.3	2.37	5.14 ⁵	-116.9 %

A sensitivity analysis was performed for the distribution ratio calculation to identify the sources of error (Figure 25). It can be seen that uncertainty in the calculated composition and pressure readings of the mixing chamber has a huge effect on the value of the final equilibrium distribution ratio. The equilibrium value is also significantly impacted by the pressure measurements in the VLE cell.

Figure 25 Sensitivity Analysis: Calculation of Distribution Ratio for the N₂-NH₃-Water System (30 °C)

A modified procedure was established where the order of contacting fluids is reversed with the VLE cell itself acting as the “mixing chamber”. The liquid solvent is now contacted with the gas mixture in the VLE cell.

A gas mixture having the desired concentration is made in the VLE cell by method of partial pressures. It may be noted that the objective is to determine accurately the moles of various gas constituents admitted into the VLE cell initially (the initial state). In the present set up, the number of moles input is calculated using an equation of state, the measured initial VLE conditions (temperature and pressure), and the known VLE cell volume. The number of gas moles input may be calculated using accurate weight measurements as well (weight of source gas tank prior to and after filling).

The VLE cell is filled with the component gases under ambient temperature conditions. In other words, the source gas tanks and the VLE cell are all at ambient temperature. The required amount of solvent is then slowly pumped into the VLE cell and contacted with the gas mixture. The mass of solvent transferred is recorded by a weighing balance. Now, the system (VLE cell with the gas and solvent) can be isolated and taken to any desired temperature. The gas solubility is subsequently calculated using an equation of state, the equilibrium VLE temperature and pressure (final state), gas headspace and solvent volumes, and initial gas composition (initial state).

Table 19 Ammonia Solubility: Equilibrium Distribution Ratios for NH₃-Gas-Solvent at 30°C

Solvent	Distribution ratio ($y_{\text{NH}_3}/x_{\text{NH}_3}$)
Water	1.10
Diethylene glycol (DEG)	4.73
5 wt. % water in DEG	4.40

The equilibrium distribution ratios are given in Table 19. The experimental errors are considerably reduced by the modified procedure for solubility measurements. The obtained distribution value (1.10) compares well with the literature values (1.15-1.16) at 30°C. Ammonia is also seen to be less soluble in DEG than in water. However, the equilibrium distribution ratio is of the same order of magnitude.

Regeneration of DEG

In this subtask, the clean up system/chemistry for the DEG was studied. Loadings were determined in order to determine a reasonable regeneration scheme. Since the coal gas will contain H₂S and more NH₃ than HCl, all of the heavy metals will be present as insoluble sulfides. That may also be the case even in the entering gas as well as in the liquid being used to scrub it. The insoluble sulfides could be easily filtered out of water, DEG or other glycol ethers unless the particle size is too small. NH₄Cl is extremely soluble in water. When we determine its solubility in 95 wt% DEG, if its solubility is not too high, then filtration could be used to remove it also. Otherwise, the regeneration system could adjust the pH to precipitate it out of solution.

In the UCSRP-HP process one of the key steps is the conversion of raw syngas (at 400-800 psia and 400°F) from the Quench/Scrubber section to a H₂ (+ CO₂) rich gas in a WGS (Water Gas Shift) reactor using sour shift catalyst. Heat is recovered and a major portion of the residual water vapor is removed from the effluent gas from the WGS reactor. The various contaminants [e.g., H₂S, NH₃, HCl, As (AsH₃), Se (H₂Se), Hg, HCN] in the syngas are also removed along with the water stream.

Phase equilibrium calculations for the system using Aspen Plus (v. 7.1, Aspen Tech) have been performed for establishing a theoretical basis for the separation. The property method used was the electrolyte NRTL (eNRTL) suitable for electrolyte systems. The feed for the calculations is the stream after the sour gas shift reactor. Equilibrium distribution of species for various temperatures and pressures of interest have been calculated using the process simulators. Additionally, the distribution of species in the solvents (water and DGM) has been calculated at the Claus reactor conditions where H₂S is reacted with SO₂ in the catalyzed DGM solvent.

The feed gas composition used in the simulation studies is given in Table 20. It can be considered as a base case scenario with no minor contaminants present (e.g., H₂Se, HCl, Hg, AsH₃, HCN).

Table 20 Feed Gas Composition (after WGS reactor)

COMPONENTS	Formula	Volume %
Ammonia	NH ₃	0.11
Hydrogen sulfide	H ₂ S	0.48
Nitrogen	N ₂	2.05
Carbon dioxide	CO ₂	31.13
Hydrogen	H ₂	43.06
Water	H ₂ O	23.17
Total = 100		

The various reactions in aqueous phase that were taken into account in the simulation are given below:

Dissociation of water

Dissociation of hydrogen sulfide

Dissociation of ammonia

Formation of ammonium bisulfide and ammonium sulfide

HCl addition

H₂Se addition

Hg addition

AsH₃ addition

The equilibrium distribution of species (H₂S, NH₃, H₂O) at various temperatures and pressures in water are given in Figure 26. As seen, H₂S is mostly present in the vapor phase unlike ammonia that is largely dissolved in aqueous phase. Effect of pressure and temperature on the equilibrium distribution is as expected. Increase in pressure increases the gas solubility and an increase in temperature decreases the gas solubility.

The effect of the addition of contaminants (H₂Se, HCl, Hg, and AsH₃) on the distribution of ammonia and hydrogen sulfide is considered next. The contaminants are introduced one at a time to the base gas mixture in the simulation. The temperature and pressure conditions chosen were respectively 250°F and 800 psi. Two cases are considered for each contaminant, one is the addition of one tenth the volume percentage of ammonia and the other is an addition equal to the amount of ammonia present in the mixture. In other words, the volume percentage of the contaminant were 0.011% and 0.11% for the simulation runs. It may be noted that the actual concentrations of these contaminants are much less (of the order of one fiftieth the concentration of ammonia).

It can be seen from Figure 27A that HCl and H₂Se addition greatly reduces the amount of ammonia in the vapor phase. The enhanced distribution in the aqueous phase is simply due to the acid-base chemistry involved between ammonia (base) and the various hydric acids present (e.g., HCl, H₂S, H₂Se). It may be noted that H₂S and H₂Se are the hydric acids of Group VI elements (S, Se) with H₂Se being a stronger acid. In other words, increased solubility for H₂Se in the aqueous phase can be expected. Equilibrium speciation results predict the formation of bisulfide (HS⁻) and selenide (HSe⁻) in the aqueous phase.

In the case of hydrogen sulfide (Figure 27B), the effect of the contaminant addition on the equilibrium distribution is seen to be minimal. The reactions considered do not include the precipitation of heavy metals (mercury and arsenic), as sulfides. Both mercury and arsenic can form sulfides. The consideration of these precipitation reactions will alter the distribution of H₂S in the vapor phase.

It may be pointed that in the case of arsine (AsH₃), the proton affinity is very low (compared to ammonia) and the tendency to form the onium ions MH₄⁺ (M = N, As) is very little resulting lower solubility. NH₃ and AsH₃ are the trihydrides of Group V elements nitrogen (N) and arsenic (As).

Figure 26 Equilibrium Distribution of Species using Aspen Plus (solvent: water)

It needs to be mentioned that the equilibrium calculations (Figure 26 and Figure 27) did not take into consideration the effect of reactions due to ammonia and carbon dioxide. The various reactions can be given as follows:

The major effect of CO_2 addition is on the distribution of ammonia (NH_3). The calculations show the formation of a solid phase (ammonium carbamate) resulting in the removal of the contaminant from the solvent phase.

Figure 27 Effect of Trace Component Addition on the Distribution of Ammonia and Hydrogen Sulfide (Aspen simulation, T = 250°F, P = 800 psi, Base Gas Composition: Table 20), A. Ammonia B. Hydrogen sulfide

Subtask 2.3 – UCSRP-HP Sulfur Removal

The objective of this subtask is to complete the previous COS studies to estimate the ultimate cost of removal/converting COS from the feed gas. The earlier results showed that by

controlling the various reaction pathways, COS formation can be minimized. This may require additional water within the reactor to promote the WGS equivalent reaction to minimize the amount of COS in the product gas.

These experiments illustrated that when sulfur dioxide is added to the feed, both hydrogen sulfide and carbonyl sulfide are consumed. Ninety five percent of the carbonyl sulfide (from 490 to 35 ppm in a single stage reactor) was consumed and 99 percent of the hydrogen sulfide (from 10% to 70 ppm). Any COS that is not converted to H_2S and then elemental sulfur will be absorbed into the lean DGM at the top of the column. Further laboratory tests are required to determine the COS concentrations expected at the top of the reaction section of the column in order to size the DGM circulation rate.

The following experiments were performed to determine the influence of the solvent at conditions of 275°F (135°C) and reactor pressure of 400 psia. Figure 11 shows the experimental set-up.

Experiment 2a – July 9, 2008 – With 0.2 standard liters per minute (slpm) CO (in N_2) to quantify its solubility in solvent at 135°C.

Experiment 1 – July 18, 2008 – Slowly flow 0.2 slpm COS (in N_2) to quantify its solubility in solvent; this test was to compare solubility to previously reported tests in pure DGM and DGM with 3-HP, at 135°C.

Experiment 2c – September 14, 2008 – Slowly flow CO and CO_2 through the system with elemental sulfur present to study Equation 4, $\text{CO} + \text{S} = \text{COS}$. This showed that this reaction contributes very little towards COS formation.

Blend Gas – September 19, 2008 – Here the feed gas contained a typical syngas composition without any SO_2 added to provide a baseline measurement. It showed a significant increase in the number of COS moles.

Experiment 5d – April 23, 2008 – This older test is shown to illustrate the effect of excess SO_2 on H_2S and COS conversion. Two streams are being blended as the feed gas, one containing SO_2 and CO in N_2 and the other H_2S , COS, and CO_2 in nitrogen. The amount of nitrogen from the two streams is counted separately in the inlet streams. There is only one outlet stream so all of the nitrogen is reported on one line.

Table 21 shows the results of these experiments. Column one in Table 21 refers to the experiment number and date. Column two identifies the compounds for the gas streams in and out of the reactor. Columns 3 and 4 show the gas input to the reactor, and 5 and 6 the gas output. The last column summarizes the difference between the input and output, and shows whether each specific compound was absorbed or released by the solvent. When making a check on the nitrogen flow, the product gases entering the bubble meter were above room temperature. The correction factors that were applied were based on assuming the gas was at the reactor outlet temperature. This may contribute to a slight error due of the decrease in temperature on the gas traveling to the bubble meter, but is not considered significant. Moving the measurement downstream of the water knockout did not help the nitrogen balance. After rechecking the calibration on the feed gas flow controllers, it was found that the deviation within the mass flow controllers accounted for some of the gain in nitrogen at the exit, but not in the losses. Experiments were conducted to reduce the error in the material balance, including minimization of solvent losses to the vapor.

The last two experiments in this table illustrate the point that when sulfur dioxide is added to the feed, both hydrogen sulfide and carbonyl sulfide are consumed. Ninety five percent of the carbonyl sulfide was consumed and 99 percent of the hydrogen sulfide. Additional testing will be

needed to confirm the consumption of these compounds to below the required levels by using the actual field levels as in the blend gas composition along with a 2:1 ratio of hydrogen sulfide to sulfur dioxide in the next batch of upcoming experiments. To meet the DOE specifications for sulfur content of the product gas, a scavenger guard bed will be required. The data to date indicate that the guard bed can be decreased in size and cost by the bulk removal occurring in the UCSRP-HP process. This tradeoff between the degree of removal between UCSRP-HP and the guard bed was addressed in the economic evaluation.

Table 21 Experimental Results Conducted at 275°F and 400 psig

Experiments	Compound	Input, %mole	Input, mol/min	Outlet, %mole	Output, mol/min	Produced, mol/min
2a, July 9	N ₂	89.2000	26.9000	89.9000	28.9000	1.9700
	CO	10.8000	3.2400	9.9900	3.2100	-0.0346
	CO ₂	0.0054	0.0016	0.0095	0.0031	0.0014
	COS	0.0000	0.0000	0.0780	0.0250	0.0250
	H ₂ S	0.0000	0.0000	0.0041	0.0013	0.0013
1, July 18	N ₂	98.5300	29.7000	97.1000	34.0000	4.2600
	COS	1.4600	0.4410	2.7600	0.9640	0.5220
	H ₂ S	0.0033	0.0010	0.0178	0.0062	0.0052
	CO ₂	0.0000	0.0000	0.0713	0.0249	0.0249
	CO	0.0000	0.0000	0.0304	0.0106	0.0106
2c, Sept. 14	N ₂	89.9000	40.6000	89.5000	35.5000	-5.1800
	CO	10.1000	4.5700	10.0000	3.9600	-0.6060
	CO ₂	0.0103	0.0047	0.0473	0.0187	0.0141
	COS	0.0000	0.0000	0.0184	0.0073	0.0073
	H ₂ S	0.0000	0.0000	0.4650	0.1840	0.1840
	Sulfur	91.42g			90.78g	
Blend Gas, Sept. 19	N ₂	17.8000	5.3600	16.7000	4.1500	-1.2000
	CO	40.1000	12.1000	40.9000	10.2000	-1.9100
	H ₂ S	0.8560	0.2580	0.4780	0.1190	-0.1390
	CO ₂	10.1000	3.0300	9.1700	2.2800	-0.7480
	H ₂	31.2000	9.4100	32.3000	8.0300	-1.3800
	COS	0.0093	0.0028	0.4380	0.1090	0.1060
5d, April 23	N ₂	98.2000	176.394	99.8000	199.0000	8.0000
	CO	0.9130	1.6400	0.0100	0.0199	-1.6201
	SO ₂	0.9280	1.7500	0.1700	0.3380	-1.4120
	N ₂	89.7000	14.1585	*	*	*
	H ₂ S	10.2000	1.6100	0.0070	0.0139	-1.5961
	COS	0.0492	0.0077	0.0035	0.0070	-0.0008
	CO ₂	0.0006	0.0001	0.0054	0.0107	0.0106

The test conditions are shown in Table 22. The flow rates for the two feed gases, blend gas and SO₂ gas were varied to achieve targeted molar H₂S/SO₂ ratios in accordance with the equations above. A GC was online to measure and record the effluent stream for H₂S, COS and SO₂. The first tests to evaluate the underlying cause for no SO₂ or COS in the effluent began with the 2:1

stoichiometric molar ratio for H₂S reacting with SO₂ in Experiment C. No SO₂ was expected or measured. However, we also did not detect H₂S. We proceeded to increase the inlet H₂S stream flow rate until we had excess H₂S with 3:1 molar ratio. These results are reported as Experiment B of Table 22 and are not in agreement with the expected effluent H₂S concentration of zero. Therefore, we ran the test under H₂S deficient condition (1.2:1) as presented Experiment A. After 12 hours of operation, a trace level of COS with no SO₂ or H₂S was identified in the effluent so the mole ratio of H₂S to SO₂ was further reduced to 0.5:1 in the next experiment to force some H₂S reading. Experiment D, in Table 22, again supported a problem with the SO₂ recording. No SO₂ or H₂S were identified in the outlet stream although SO₂ was expected.

Table 22 Results of Experiments for the Evaluation of COS in UCSRP-HP

Experiment ID		inlet gas concentration mol%	outlet gas concentration mol%	Inlet mol/min (10 ⁻³)	outlet mol/min (10 ⁻³)
A	N2	17.99	35.07	12.86	29.53
	CO	40.26	30.93	28.80	26.05
	CO2	10.09	7.95	7.22	6.70
	H2S	0.88	0.00	0.63	0.00
	H2	30.77	25.57	22.01	21.53
	COS	0.00	0.47	0.00	0.39
	N2	96.99	0.00	16.44	0.00
	SO2	3.01	0.00	0.51	0.00
B	N2	17.99	25.71	12.94	17.95
	CO	40.26	35.55	28.97	24.82
	CO2	10.09	9.31	7.26	6.50
	H2S	0.88	0.01	0.64	0.01
	H2	30.77	28.93	22.14	20.20
	COS	0.00	0.50	0.00	0.35
	N2	96.99	0.00	6.57	0.00
	SO2	3.01	0.00	0.20	0.00
C	N2	17.99	30.16	8.37	15.06
	CO	40.26	33.48	18.74	16.72
	CO2	10.09	8.55	4.70	4.27
	H2S	0.88	0.00	0.41	0.00
	H2	30.77	27.36	14.33	13.66
	COS	0.00	0.43	0.00	0.22
	N2	96.99	0.00	6.57	0.00
	SO2	3.01	0.00	0.20	0.00
D	N2	17.99	52.62	5.25	23.38
	CO	40.26	22.28	11.76	9.90
	CO2	10.09	5.59	2.95	0.00
	H2S	0.88	0.00	0.26	0.00
	H2	30.77	19.18	8.99	8.52
	COS	0.00	0.34	0.00	0.15
	N2	96.99	0.00	16.44	0.00
	SO2	3.01	0.00	0.51	0.00

The configuration of the inlet was changed to accommodate measurement of the total combined inlet stream with a bypass to either the GC or the reactor. With known flow rates for both the blend gas and SO₂, the inlet concentration were calculated and compared to those given by the GC. The reported inlet SO₂ concentration by the GC continued to be zero SO₂. We tested the Mass Flow Controller and found the filter had been plugged up. We exchanged this and reran the test with only SO₂ in the inlet stream. The GC continued to report zero levels of SO₂. We

placed the GC inlet to measure the gas directly from the cylinder. At first it recorded SO₂ at the correct level, but after 10 minutes the inlet SO₂ concentration began to gradually decrease until it could not be detected anymore. Figure 28 illustrates this. Based on this test, the problem could not be the first probable cause. This leaves the last two causes: the column itself leading to a faulty signal/response or the GC mathematical method for converting the signal to concentration. (A GC mathematical method describes the equation that best fits the column/detector response to the component. This is non-linear and requires at least three calibration points to obtain a valid calibration curve for the component. A new curve must be created whenever the detector response changes due to the absorption of contaminants or other column/gas interactions.)

Figure 28 Illustration of Decreasing SO₂ Concentration Being Delivered to the UCSRP-HP Reactor

The GC mathematical method was modified to enhance the signal by creating a new curve. This did not improve the error, however. SO₂ concentrations of zero continued to be reported after several minutes. The decreasing SO₂ signal pointed to a problem with the GC column itself. To overcome the decrease in SO₂ absorption, a new mathematical method was implemented after the column was cleaned out by the chemist. The new recordings of SO₂ are now stable along with the other gas components. The experiment was ready to go into a series of tests to verify mass flow balance and answer the question of COS production by the reaction under our operating conditions.

In the reactor section of the UCSRP-HP process, hydrogen sulfide reacts with sulfur dioxide to form water and liquid sulfur. The reaction proceeds in the liquid phase (DGM solvent) containing a homogeneously dissolved catalyst. Under these conditions, there are paths where trace sulfur components such as carbonyl sulfide (COS) and carbon disulfide could form. The fate of trace sulfur components is of critical importance to the success of the UCSRP-HP scheme. The various reactions involving the trace sulfur components are given below.

Formation and consumption reactions for carbonyl sulfide (COS)

Presence of hydrocarbons (e.g., methane) and formation of carbon disulfide (CS₂)

Figure 29 shows the equilibrium constants (log K) of the various reactions at 135°C. The thermodynamic quantity is a good indicator of the favorability or feasibility of a reaction although it gives no information on the kinetics. It can be seen that thermodynamic considerations point to COS formation is unfavorable for a CO₂ rich feed as compared to a CO rich gas stream. On a relative basis, the most favorable reactions are the ones where COS is consumed. Further, presence of hydrocarbons, such as methane, would have to be present for the formation of yet another sulfur component (CS₂).

Simulation results predict high solubility for CO₂ in DGM solvent compared to water. The equilibrium distribution ratios (y_{eq}/x_{eq}) at the reactor conditions (T = 270°F, P = 770 psi) in DGM and water are respectively about 5 and 140. The high CO₂ solubility has the potential to form COS through reaction with H₂S. However with low CO levels and SO₂ presence in the solvent, the $2CO_{2(g)} + 3S_{(l)} \Leftrightarrow 2COS_{(g)} + SO_{2(g)}$ reaction is expected to be driven to the left, consuming any COS formed. Experimentation is required to quantify COS formation.

Figure 29 Favorability of Reactions: Consumption and Formation of Trace Sulfur Components (COS, CS₂)

Subtask 2.6 -- UCSRP-HP Solvent Regeneration

No meaningful results were obtained on this task. Regeneration schemes were addressed in Tasks 3 and 4.

Task 3 – Computer Simulation Modeling and Economics

Subtask 3.1 – Preliminary Aspen Model

To confirm the accuracy of our test equipment and our simulation model, CO₂ solubility in water at 25°C was measured and compared to literature values. The vapor-liquid mixture was kept in the equilibrium cell which is temperature and pressure controlled. The magnetic stirring device was used to enhance the attainment of equilibrium. The influence of the stirrer speed and the pressure was evaluated. Table 23 presents the results of the CO₂ in water experiments. The pressure was kept low to study the effects of the stirrer, because it has been previously published that at pressures above 9 atm the interactions of the gas phase with the liquid phase changes the gas phase hydrodynamics too much. With increasing pressures, the deviation from the true Henry's constant increased, as seen in Table 23. This is to be expected, as Henry's Law accounts for a region that is not accounted for by Raoult's Law. Raoult's Law only works over the whole concentration range when the two compounds are almost identical; it generally also works well for the solvent in the region where the concentration of solute is low and the pressure is low. Although no thorough investigation was carried out, it is quite clear that the gas phase hydrodynamics change with pressure (density) as was also found by Versteeg. Through the experimental, as shown in Table 23, decreasing the pressure and increasing the stirrer rate was found to provide reproducible results closer to the fitted published data presented in Versteeg.

A temperature dependant Henry's Law constant for hydrogen sulfide and sulfur dioxide in diethylene glycol methyl ether (DGM) is given in literature and the values are presented in Table 24. Hydrogen sulfide solubility in DGM was measured and compared to the published results in Table 24. Agreement of hydrogen sulfide solubility in DGM to the experimental results of Scott Lynn at 25°C confirms our experimental and theoretical techniques. Modifications to the published equation for Henry's constant of a pure gas to a binary gas mixture equation were made to the form of Henry's constant as a function of temperature used in Aspen Plus. Aspen's Henry's constant equation form is

$$\ln H_{i,j} = A+B/T+C \ln(T)+D (T).$$

Where i = solute or non-condensable component

j = solvent or condensable component

H_{ij}= Henry's coefficient between i and j [kPa]

A = coefficient entered as a_{ij} in the Aspen parameter matrix [cal/gmole]

B = coefficient entered as b_{ji} in the Aspen parameter matrix [cal/gmole]

C = coefficient entered as c_{ij} in the Aspen parameter matrix [cal/gmole]

D = coefficient entered as d_{ji} in the Aspen parameter matrix [cal/gmole]

T = temperature in degrees K.

The variables C and D were set to zero to which the experimental data was fitted as represented in Table 26. The comparison between Aspen Plus results and Scott Lynn's

experiment at 40°C and 122 kPa is presented in Table 25. The inlet gas concentration was taken to be 4500 ppmv for H₂S with liquid and gas flows at 3.55 mol/min and 8.57 mol/min, respectively. The Murphree tray efficiency from experiment was determined to be 0.16±0.09 under these conditions, and in our simulation the efficiency was found to be 0.08, falling within the acceptable limit of the published experimental result. The good agreement with the measured efficiency provides encouragement for using the model to provide high-pressure and temperature tray efficiencies.

Aspen Plus models of the H₂S and SO₂ absorption in DGM, as shown in Table 27 and Figure 30 for absorption without the reaction mechanism, the sulfur furnace, and the absorption of ammonia, chloride, and H₂Se in DEG have been completed. The integrated model was not completed in this period because the lack of bench-scale data.

Table 23 Carbon Dioxide in Water Results

Stirrer Rate	T _{cell} , (K)	P _{init} (psia)	P _{final} (psia)	Henry's Coefficient Experimental (m ³ Pa/mol)	Henry's Coefficient Published (m ³ Pa/mol)	Deviation from Published Values
0%	298.13	214.50	199.2	3992.9	2968.7	34%
15%	298.39	204.20	189.9	4079.6	2986.7	37%
15%	298.32	204.66	183.6	4096.9	2982.2	37%
25%	298.45	208.60	188.2	3589.8	2991.2	20%
25%	298.38	202.90	169.7	3589.8	2986.3	20%
25%	298.38	59.31	49.0	3284.9	2986.3	10%
25%	298.39	59.21	48.8	3258.8	2986.7	9%
25%	298.26	23.59	19.7	3389.4	2977.6	14%
25%	298.26	24.10	20.1	3323.9	2977.6	12%

Table 24 Hydrogen Sulfide and Sulfur Dioxide Henry's Constant Coefficients

Gases	H ^o ₂₁ kPa/m.f.	H _{soln} kJ/mol	R kJ/mol K	H ₂₁ at 130 C kPa/m.f.	Solubility at 25 C mol/Kg Mpa	Solubility at 130 C mol/Kg MPa
H ₂ S	843.4	-16.16	0.008314	4614.03	9.87	1.80
SO ₂	31.15	-37.13	0.008314	1546.07	267.19	5.38

Table 25 Henry's Constant for Hydrogen Sulfide in DGM Results for Experimental Set 0

Gas	Temp (K)	P _i (psia)	P _f (psia)	H _{exp} (m ³ Pa/mol)	H (Lynn@ 25°C, 1 atm) (m ³ Pa/mol)
H ₂ S(10%)/N ₂	298.19	29.0	23.5	109	101
H ₂ S(10%)/N ₂	298.19	25.2	22.6	104	101

Table 26 Constants for Henry's Law Equation

Gas	Temperature (K)	A	B	Aspen H(kPa)	Published Lynn
H ₂ S	408	13.28	1948.74	4917.29	4894.65
SO ₂	408	18.47	4477.52	1789.58	1770.70

Figure 30 Aspen Plus Process Flow Diagram of Absorption Tower for UCSRP-HP

Table 27 Stream Results from Aspen Plus of Absorption Tower at a Temperature of 104°F and 362.6 psi

	FEED	PROD-GAS	PROD-LIQ	SOLVENT
Temperature, °F	104.0	104.1	104.1	104.0
Pressure, psi	362.6	362.6	362.6	362.6
Vapor Frac,	1.0	1.0	0.0	0.0
Mole Flow, lbmol/h	1.1	1.1	0.5	0.5
Mass Flow, lb/h	31.8	31.6	56.6	56.4
Volume Flow, cuft/h	19.0	18.9	1.1	1.1
Enthalpy, MMBtu/h	0.0	0.0	-0.1	-0.1
Mass Flow, lb/h				
H ₂ O	0.0	0.0	0.0	0.0
H ₂ S	0.1	0.1	0.0	0.0
N ₂	31.7	31.5	0.1	0.0
SULFU-01	0.0	0.0	0.0	0.0
DGM	0.0	0.0	56.4	56.4

Subtask 3.2 – Aspen Model

The UCSRP-HP Aspen Plus® model was completed. The computer model was used for process optimization and economic analysis. The model will also be used for designing and planning of pilot-scale unit for later phases.

The process design for the evaluation of UCSRP-HP (Case A) was based on DOE Case 2 of “Cost and Performance Baseline for Fossil Energy Plants”⁵ for an IGCC plant with a net nominal 550-MW power generation. This is the GE gasifier for Illinois coal in IGCC with carbon capture. At the request of DOE, a “Chemicals” application (with a more stringent cleanup required to protect fuel cells or conversion catalysts from being poisoned) was also prepared as Design Case A-1. Table 28 shows the contaminant targets for the two cases. The UCSRP-HP cases were designed for the Chemicals specifications in both cases except for the H₂S level. In the IGCC case, Design Case A, the H₂S concentration in the feed gas to the gas turbine was ~8 ppm. In the Chemical case, Design Case A-1, it was <50 ppb. The low level may require the addition of a COS hydrolysis reactor in addition to a guard bed added to the IGCC case as noted later. With a H₂S level of ~50 ppbv in the syngas product to power generation, the SO₂ emission will be near zero.

Table 28 Design Targets for Contaminant Content

Contaminant	Maximum after Cleanup	
Application	IGCC	Chemicals
Case	A	A-1
H ₂ S	0.0128 lb SO ₂ /MM Btu	50 ppbv
NH ₃		0.1 vol%
HCl		1 ppm
Hg	>90% Capture	5 ppbv
Se		0.2 ppm
As		5 ppb
Cd		30 ppb

Design Basis

DOE Design Case 2

A block-flow diagram with stream numbers identified for the DOE IGCC design scheme used in Case 2² is shown in Figure 31. This DOE design study involves:

Illinois #6 Dry Coal Feed Rate	lb/h	444,737
Net Power Output for Sale	MWe	555.7
Total Plant SO₂ Emission	lb/h	56
Total CO₂ emissions*	lb/h	114,476

* DOE/IGCC Case 1 without CO₂ capture emission rate was 1,123,781 lb/h.

Gasification, Raw Gas Cooling/Particulate Removal

This plant utilizes two gasification trains of GE Energy slurry gasifier with Illinois No. 6 coal. The syngas from the gasifier is cooled from about 2,400°F to about 1,100°F in the radiant syngas cooler (Stream 8) and is directed downwards by a dip tube into a water sump. Most of the entrained solids are separated from the syngas at the bottom of the dip tube as the gas goes

upwards through the water. The slag handling system removes solids from the gasification process.

Quench and Syngas Scrubbing

Syngas exiting the water-quench passes to a syngas scrubber where a water wash is used to remove remaining chlorides and particulates. The syngas exits the scrubber at ~ 410°F. A sour-water stripper removes ammonia, SO₂ and other impurities from the scrubber. The stripper consists of a sour drum that accumulates sour water from the scrubber and syngas coolers. The sour water then flows to a stripper tower which consists of a packed column with a steam heated reboiler. The sour gas will be processed in the sulfur recovery (Claus) unit. The remaining water is sent to wastewater treatment.

Sour Water Gas Shift (SWGS) Unit

The effluent syngas (Stream 9) is mixed with some steam (Stream 10) to adjust the steam/CO molar ratio to 2:1 prior to the SWGS step. The hot syngas from the first stage of SWGS is used to generate some steam for addition to Stream 10. A second stage of SWGS results in 96% overall conversion of the CO to CO₂. The effluent stream (#11: at 777 psia and 519°F) from the second stage of the SWGS unit is further cooled to about 450°F to raise IP steam that is sent to the reheater in the HRSG. The SWGS catalyst also serves to hydrolyze COS thus, eliminating the need for a separate COS hydrolysis reactor. Following the second SWGS reactor, the syngas is further cooled to about 103°F prior to the mercury removal beds.

Acid Gas Removal (AGR)

The AGR process in the DOE Case 2 is a two stage Selexol process where H₂S is removed in the first stage and CO₂ in the second stage of absorption. The acid gas from the first stage is routed to the Claus plant. The process results in three product streams: the clean syngas, a CO₂-rich stream, and an acid-gas feed to the Claus plant. The CO₂ stream from the 2nd stage of the Selexol plant is generated at three pressure levels. The LP stream is compressed from about 22 psia to 160 psia and is then combined with the MP stream. The HP stream is combined between compressor stages at about 300 psia. The combined stream is compressed from 300 psia to about 2,215 psia using a multi-stage, intercooled compressor. During compression, the CO₂ stream is dehydrated to a dew-point of about minus 40°F with triethylene glycol. The pure CO₂ (Stream 16) is transported to the plant fence line and is sequestration ready.

The H₂S-rich stream (Stream 17) from the first-stage stripper of the Selexol unit is routed to the Claus plant. This contains about 41 percent H₂S and 45 percent CO₂ with the balance primarily N₂.

The Claus plant partially oxidizes the H₂S to elemental sulfur. The acid gas from the Selexol unit is preheated to 450°F for processing in the Claus furnace along with oxygen from the ASU unit. In the furnace, H₂S is catalytically oxidized to SO₂ at a furnace temperature greater than 2,450°F. Following the thermal stage and condensation of sulfur, two reheaters and two sulfur converters are used to obtain a per-pass H₂S conversion of about 99.7 percent. The Claus plant tail gas is hydrogenated and recycled back to the Selexol process. No information is given on the source of hydrogen for this step, although the material balance shows additional hydrogen recycled to the Selexol unit with the tail gas. In the furnace waste heat boiler, medium-pressure steam (at 525 psia) is produced to meet all Claus process preheating and reheating requirements.

The oxygen (95 mol% purity) requirement for Claus plant in the DOE Case 2 design is about 6,904 lb/h (~ 214 lbmole/h).

Power Block

Clean syngas from the AGR plant is heated to about 465°F using HP boiler feed water before passing through an expansion turbine. The clean syngas (Stream 15) is diluted with nitrogen from the ASU unit (Stream 4) before combustion in the gas turbine burner. The exhaust gas (Stream 21) exits the gas turbine at about 1050°F and enters the HRSG unit where additional heat is recovered to raise HP steam (at about 1800 psig) for power generation in a commercially available steam turbine. The flue gas exits the HRSG at about 270°F for discharge through the plant stack.

Air Separation Unit (ASU)

For this DOE Case, the ASU produces about 4,635 tonnes/day of 95 mol% oxygen and 13,070 tonnes/day of nitrogen. There is no integration between the ASU and the gas turbine other than the nitrogen stream (Stream 4).

About of 98.4 wt% of the oxygen from the ASU is used in the coal gasifiers; the rest is sent to the Claus plant.

GTI UCSRP-HP IGCC Base Case (GTI Design Case 1): Total SO₂ Emission at 34 lb/h

A block flow diagram of the GTI UCSRP-HP Base Case IGCC design is shown in Figure 33 and the stream material balances are shown in Table 29. This conceptual flow scheme has been developed with significant feedback from Prof. Scott Lynn of the University of California, Berkeley. The mass and energy balances have been developed using Aspen HYSYS® based on the data presented in the DOE Case 2 mentioned above. The UCSRP-HP Design Case A keeps the DOE Case 2 design up through the first heat exchanger (HP Steam) in the Gas Cooling, BFW Heating & Knockout block where the syngas feed is at ~772 psia and 450°F. This is downstream of the Quench and Scrubber Section and the Water Gas Shift Reactors. The DOE Case 2 is rejoined at the feed to the CO₂ removal section of the dual-stage Selexol unit. This design replaces or eliminates the Mercury Removal, H₂S-removal section of the dual stage Selexol unit, the Claus Plant, and Hydrogenation Reactor and Gas Cooler Section. For these designs, the total SO₂ emission from the UCSRP-HP IGCC power plant is about 34 lb/h vs. 56 lb/h specified in the DOE Case 2.

The process steps are essentially the same as the DOE Base Case through gasification, quench and syngas scrubbing and SWGS above, with the exception that the effluent from the second SWGS reactor is cooled to about 103°F prior to the mercury removal beds whereas the gas is being cool to only 165°F in the UCSRP case. Key process steps included in this design are mentioned below:

V-100: A Second High-pressure Water Scrubbing Unit

This step is used as a second water-scrubbing step (besides the Quench/Scrubbing step, integrated with a sour-water stripper, used prior to the Sour Water Gas Shift Reactor: SWGS) to remove a large fraction of water present in the gas along with much of the NH₃ and essentially all of the halogens and heavy metals, as sulfides or water-soluble salts that could be present in the syngas effluent from the SWGS. The use of syngas cooling to 165°F and the V-100 (integrated with a low pressure separator) reduces the water vapor content from about 23 mol% (at the outlet of SWGS reactor) to about 1 mol% in the syngas feed to the UCSRP-HP reactor.

To enhance removal of various precipitated metal salts, including AsS, HgS, and CdS, a relatively large quantity of water would be recycled to the top section of the down-flow, concurrent, V-100 contactor. At the pressure, temperature, and water content of the syngas, the circulating water will have a steady-state content of NH₃ and H₂S. As a result, the HCl content of the feed gas will be absorbed very effectively to form highly soluble NH₄Cl. A small but significant concentration of NH₄HS will also be present in the liquid phase and the heavy metals As, Cd and Hg will be absorbed to form their respective, insoluble sulfides. Selenium will be present in the syngas as H₂Se and will be absorbed to form highly soluble (NH₄)₂Se under these conditions. To be conservative, there are three means to collect the heavy metals in the process. One is primarily by using these water filters in the Water Removal unit. The other two backup means involve the use of DURCO liquid sulfur filter, and hydrocyclone/precipitation filters to process a slip-stream of the recycle DGM solvent from the UCSRP-reactor. If further experimentation shows that all of the heavy metals are collected in the Water Removal unit as solid sulfides, the backup means can be eliminated.

At the bottom of the scrub contactor, the water stream is withdrawn and circulated by pump back to the top after dissolved gases are flashed and returned to the feed gas stream. The net water flow from this unit would be first filtered in a specific filter to remove water-insoluble metal salts and the filtrate would be processed in the stripper unit included in the DOE Design Case 2 for treating water from the Quench/Scrubber unit. The gas is preheated to about 250°F prior to

its processing in the UCSRP-HP reactor. The key objective for the removal of a large fraction of the water prior to the UCSRP-HP reactor is to minimize the cost of separation of water from DGM solvent used in the reactor.

UCSRP Absorber/Sulfur Reactor

The Aspen Plus® simulation UCSRP-HP model was prepared to identify a co-current, down-flow contactor reactor design that is simple and less expensive to build compared to the original counter-current designs. At the operating conditions of ~750 psia and 250-300°F, the sulfur forms as a liquid, essentially immiscible in DGM/catalyst solvent and over twice as dense. This, along with the lower operating temperatures, overcomes the equilibrium limitations that occur in conventional gas-phase Claus reactor systems. The $\text{H}_2\text{S}/\text{SO}_2$ reaction is run at about 10% excess to drive the reaction to completion for the other component. To be conservative, the design cases assume that some COS is formed within the UCSRP-HP reactor system.

In this absorber/reactor design, Sulzer SMV™ type co-current contactor systems (shown below in Figure 32) was used to obtain high mass transfer rates and relatively low pressure drops.

Figure 32 Sulzer Mixer SMV with Stainless Steel Elements Dismantled.

Figure 33 GTI UCSRP-HP Base Case IGCC with CO₂ Capture (Total SO₂ Emission: 34 lb/h)

Table 29 GTI UCSRP-HP Base Case Design Stream

Stream Description	1 Air to ASU	2 Vent gas from ASU	3 O ₂ to sulfur furnace	4 N ₂ Diluent	5 Oxygen to Gasifier	6 Coal Slurry	7 Slag	8 Gasifier Effluent to Quench & Scrubber	9 Syngas Feed to Sour-Shift Reactor	10 Steam to Shift Reactor
Mol%										
CH ₄					--			0.10	0.08	
CO								34.42	26.66	
CO ₂	0.03	0.23						15.11	11.66	
H ₂								33.49	25.94	
H ₂ O	1.08	8.31				100		14.29	33.65	100
H ₂ S								0.73	0.56	
COS								0.02	0.01	
N ₂	77.19	83.72	1.4	99.22	1.8			0.88	0.69	
NH ₃								0.17	0.13	
SO ₂					--			0.00	0.00	
Ar	0.94	0.94	3.6	0.24	3.2			0.79	0.62	
O ₂	20.76	6.80	95.0	0.54	95.0			0.00	0.00	
DGM		--						--		
Sulfur										
V-L										
Flowrate, lb-mole/h	64,331	8,332	204.	42,780	13,015	14,511	--	52,422	67,674	13,313
Lb/h	1,855,930	229,942	6,581	1,200,560	418,847	261,198	--	1,069,860	1,343,900	239,846
Solids										
Flow, lb/h	0	0	0	0	0	444,737	54,925	0	0	0
Temp., °F	232	60	90	385	206	141	410	1,100	410	615
Pressure, psia	190.6	16.4	145	460	980	1,050	798	799.7	797.7	875

Please refer to Figure 33 for the corresponding process flow diagram to these stream numbers.

Table 29 GTI UCSRP-HP Base Case Design Stream (continued)

Stream Description	11 Syngas Product from for the Shift Reactor	12 Syngas Feed to the UCSRP Plant	13 Syngas Feed to the CO ₂ Removal Unit	14 Clean Syngas from the CO ₂ Removal Unit	15 Syngas from Expander	16 Total CO ₂ Product	20 Ambient Air	21 Flue Gas	22 Stack Gas
Mol%									
CH ₄	0.06	0.06	0.08	0.13	0.13				
CO	0.90	0.90	1.18	1.90	1.90				
CO ₂	31.14	31.14	40.73	4.46	4.46	100.0	0.03	0.85	0.85
H ₂	43.05	43.05	56.31	91.00	91.00			--	--
H ₂ O	23.17	23.17	0.15	0.00	0.00		1.08	12.26	12.26
H ₂ S	0.48	0.48	4 ppm	6.5 ppm	6.5 ppm		0.00		
COS			4.1 ppm	6.6 ppm	6.6 ppm		0.00		
N ₂	0.58	0.58	0.78	1.26	1.26		77.19	75.27	75.27
NH ₃	0.11	0.11	0.11	0.17	0.17				
SO ₂	--	--			0.00			--	
Sulfur	--	--			--				
Ar	0.51	0.51	0.66	1.08	1.08		0.94	0.92	0.92
Oxygen	--	--					--20.76	10.71	10.71
DGM	--	--	10 ppm	--	--				
Total Flow, lb-mole/h	80,987	80,987	61,918	38,315	38,315	23,510	243,972	307,285	307,285
Lb/h	1,583,740	1,583,740	1,234,233	197,664	197,664	1,034,675	7,038,470	8,438,010	8,438,010
Temp., °F	519	165	90	95	386	155	59	1,052	270
Pressure, psia	777.2	745	710	695	460	2,214.7	14.7	15.2	15.2

The NTU (number of transfer units) requirements can be estimated based on the following equation:

$$\text{NTU} = \ln(C_i/C_o), \text{ where } C_i \text{ and } C_o \text{ are inlet and outlet H}_2\text{S concentrations (in ppmv).}$$

Based on Sulzer Inc. literature, as an example, for a 6-inch diameter by 6-feet long SMVTM contactor, the height of a transfer unit (HTU) is typically about 0.4 NTU/feet. GTI oversized the design by 30% relative to Sulzer's criteria. Sulzer has had experience building large diameter mixers for gas/liquid contacting applications. During 2009, Sulzer fabricated three 117" diameter SMV's for an EDC (ethylene dichloride) project.²¹

In the Sulfur reactor section, the H₂S from the feed gas along with the SO₂ from the sulfur/oxygen furnace will be absorbed quickly into the DGM solvent. The product liquid sulfur would be separated from the solvent/gas mixture in the bottom three-phase separator section. The separated liquid sulfur will be processed in a DURCO type filter to remove trace solid compounds, if any. A part of the product sulfur will be fed to the sulfur/oxygen furnace and the rest (stream 18) would be handled in a pit identically to the scheme employed in a conventional Claus plant.

The cost of the UCSRP-HP absorber/reactor was estimated based on feedback from Sulzer Inc.²⁰

A high-pressure Separator is used primarily to recover DGM solvent (and the water vapor present in the syngas feed to the Sulfur reactor and that formed from the H₂S/SO₂ reaction) from the syngas product from the UCSRP plant. A DGM slipstream is treated by hydrocyclones to remove any precipitated heavy metal salts that may not have been removed by the water filter. The separator bottoms product is sent to a low-pressure separator which is used to recover (1) DGM solvent and water in a DGM distillation unit and (2) dissolved gases.

As in the DOE Case 2, we have designed for no loss of hydrogen or carbon monoxide in the H₂S removal process. We would expect that both physical solvent systems would have some affinity for these components. Selexol, operating at a much lower temperature, should have much higher losses than UCSRP, affecting the power block of the plant.

Scavenging (Sulfur Guard Bed) Unit

A Sulfur Guard Bed (based on the use of ZnO-type adsorbents) would be required for the Chemical cases: syngas applications involving the production of clean liquid/gaseous fuels and for chemicals. The unit will be designed to reduce the H₂S level to below 50 ppbv level. A COS hydrolysis unit is introduced in the UCSRP-HP reactor system to produce a syngas containing about 7.6 ppm H₂S and 0.4 ppm COS. If COS is shown not to form, the COS hydrolysis unit can be eliminated and the zinc oxide guard bed can be made smaller. For IGCC applications, these steps would be bypassed. The mass/energy balance and cost data for this unit were provided to GTI by CrystaTech, Inc. (Austin, Texas).²¹

Single-stage Selexol Process for the Removal of CO₂

For the DOE Case 2 design (with CO₂ capture), a two-stage Selexol process is used to remove both H₂S and CO₂; in contrast, in the DOE Case 1 design, a single stage Selexol process is used to remove H₂S only. We have used the data from these two DOE cases along with design and cost data from Carnegie Mellon's Integrated Environmental Control Model²³ ("IECM") to estimate the mass/energy balances as well as the capital cost data of the single-stage Selexol unit for CO₂ removal in the UCSRP-HP Base Case design. No credit is taken for H₂S removal in this Selexol unit. The treated syngas (stream 14) is sent to the syngas reheat and then to the Power Train.

DURCO Pressure Leaf Filter

As a conservative design feature, the liquid sulfur product from the Sulfur Reactor is processed in a DURCO filter to:

- Remove any trace amounts of solid contaminants (from the trace metals in the syngas feed to the Sulfur reactor) that might be present in the liquid sulfur stream. According to Prof. Lynn, any such solids would remain primarily with the liquid DGM effluent from the Sulfur reactor.
- Enhance smooth operation of the Sulfur/Oxygen submerged combustor unit.

Sulfur/Oxygen Submerged Combustion to Generate Liquid SO₂

A portion of the liquid sulfur phase from the Sulfur Reactor Vessel and the captured ammonia stream from the DGM Distillation Unit are fed to the Sulfur Furnace. A schematic of this process, commercialized by Brown and Root Braun Inc., is shown in Figure 39 of Appendix B.³ As shown, oxygen from the ASU is released below the surface of a pool of boiling sulfur. The sulfur is hotter than its auto ignition temperature (about 500°F); therefore, the oxygen and liquid sulfur react immediately to form SO₂. However, because the “flame” is submerged in the liquid sulfur, vaporization of the liquid sulfur limits the temperature of surrounding liquid to its boiling point. In such a process, SO₂ production is easily controlled by regulating the flow of oxygen. Sulfur is always in excess and, without oxygen flow, everything stops. Ammonia from the DGM distillation unit is converted to N₂ and H₂O as it passes through the furnace. The presence of S₂ vapor prevents any NO_x formation. The combustion gas raises steam in the boiler and then passes through the condenser, where liquid sulfur is collected.

The reactor (furnace) effluent, laden with sulfur vapor, is cooled in a condenser. The minimum temperature of sulfur in this condenser, however, is limited to about 800°F, so that the maximum viscosity of the liquid sulfur effluent is less than about 150 cP (see Figure 40 in Appendix B). The hot, low-viscosity sulfur is returned to the reactor as continuous recycle (Figure 39). After the hot sulfur recycle, very little pure sulfur remains in the SO₂ vapor. A second condenser, operated under conditions similar to the final condensers of a Claus sulfur recovery plant, effectively cools the SO₂ where liquid water, saturated with dissolved SO₂, is condensed. The SO₂ stream leaving the cooler is converted to liquid in another condenser, and then pressurized to the pressure of the reactor column by a pump.

The oxygen (95 mol% purity) requirement for Claus plant in the DOE Case 2 design is about 6,904 lb/h (~ 214 lbmole/h) vs. 6,593 lb/h (~204 lbmole/h) for the UCSRP-HP Base case. The cost of the sulfur furnace was reviewed R. L. Schendel, Brown & Root Braun.

Special Hydrocyclone and Filter Units to Process a Slipstream of DGM Solvent Effluent from the Sulfur Reactor

A small slip-stream of the DGM solvent effluent from the Sulfur reactor would be periodically withdrawn and processed in a hydrocyclone unit to remove any DGM-insoluble metal compounds that could be present in the syngas feed. The liquid effluent from the hydrocyclone unit would then be cooled to potentially precipitate additional metal complexes for removal in a filter unit. The metals-free DGM solvent would be mixed with fresh make-up DGM solvent plus the specific UCSRP catalyst for recycle to the Sulfur reactor.

Issues Related to Corrosion and Solvent Stability

GTI has conducted corrosion tests on metals typically used for process equipment or vessels construction. These metals include carbon steel 140 and stainless steel 304. These tests were

all conducted at the maximum DGM solvent temperature of 285°F conditions for 1000 hs.

The corrosion tests for carbon steel metal show less than 0.5/1000 inch per year loss while stainless steel metal shows less than 0.23/1000 inches per year. . According to the 2005 American Society for Testing and Materials (ASTM) “Corrosion Testing Standards”, the acceptable corrosion rate for process equipment in service for 10 to 20 years is between 5 and 25/1000 inches per year. This ASTM standard is specifically determined for industrial applications where the 5 and 25/1000 inches per year standard corrosion is included as a criterion for the equipment and vessel design. Based on these tests, carbon steel was selected as the appropriate materials of construction for the DGM exposed equipment.

Task 4.0 – Economic Evaluation

Subtask 4.1 – Preliminary Economic Evaluation

GTI performed a preliminary economic evaluation under Subtask 4.1 to qualitatively compare UCSRP-HP with the DOE base line studies for coal to power.

The DOE report entitled, “Cost and Performance Baseline for Fossil Energy Plants,” DOE/NETL-2007/1281, Volume 1⁸ was used as the base line for our preliminary economic evaluation. The Conoco-Phillips’ (CoP) E-Gas gasifier for an IGCC application using Illinois #6 coal without CO₂ capture (Case 3) was used to complement the review that CoP plans to perform for the project. The process flow diagram (PFD) is shown in Figure 34. The cost documentation appears sufficient to allow a differential analysis, where we can use the costs of systems unchanged by our technology and only need costs for the affected systems. This will provide a clearer difference between UCSRP-HP and conventional technologies.

The UCSRP-HP will replace, eliminate, or decrease the size/cost of the process blocks as shown in green on Table 30. The base case equipment sizes for the Syngas Cleanup area are shown in Table 31. This analysis does not yet include the impact on the water and compression systems.

Table 30 Differential Analysis of UCSRP-HP into E-Gas Case

Unit Operation	Effect of UCSRP-HP	Impact
Elevated Pressure ASU	No significant impact	☹️
E-Gas Gasifier	Eliminate recycle of tail gas	😊
Syngas Cooling, Cyclones & Filters	No significant impact	☹️
Syngas Scrubber	No significant impact	☹️
COS Hydrolysis	No significant impact	☹️
Gas Cooling, BFW Heating & Knockout	Reduce cooling requirement, base has cooling from 401 F to 103°F, UCSRP-HP will cool to about <300°F	😊
Sour Water Stripper	Reduced stripping water related to higher temperature	😊
Mercury Removal	Eliminated, included in UCSRP-HP	😊
MDEA	Eliminated, included in UCSRP-HP	😊
Claus Plant	Eliminated, included in UCSRP-HP	😊
Hydrogenation Reactor and Gas Cooling	Eliminated, included in UCSRP-HP	😊
Tail Gas Recycle to Gasifier	Eliminated	😊
Syngas Humidification	No significant impact	☹️
Syngas Reheat	No significant impact	☹️
Gas Turbine Combustor	No significant impact	☹️
Turbines and HRSG	No significant impact	☹️

Table 31 Syngas Cleanup Equipment for Base Case

Description	Type	Design Condition	Operating Qty.	Spares
Mercury Adsorber	Sulfated carbon bed	234.054 kg/h (516,000 lb/h) 39 °C (103 °F) 3.4 Mpa (495 psia)	2	0
Sulfur Plant	Claus type	139 tonne/day (153 tpd)	1	0
Acid Gas Removal Plant	MDEA	213.642 kg/h (471,000 lb/h) 39 °C (103 °F) 3.3 Mpa (485 psia)	2	0
Hydrogenation Reactor	Fixed bed, catalytic	25.401 kg/h (56,000 lb/h)	1	0
Tail Gas Recycle Compressor	Centrifugal	21.772 kg/h @ 6.6 Mpa (48,000 lb/h @ 950 psia)	1	0

Exhibit 3-48 Case 3 Process Flow Diagram, E-Gas™ IGCC without CO₂ Capture

Figure 34 Process Flow Diagram for E-Gas IGCC

Subtask 4.2 – Economic Evaluation

Under Subtask 4.2, a more complete economic evaluation was performed. The design bases for the plant are given above in Subtask 3.2 – Aspen Model, including the process description and material balances. The following section includes scoping economics (total investment costs, CAPEX and OPEX savings and the cost of power generation, energy requirements and overall thermal efficiency for power generation and a comparison of the UCSRP-HP with other developmental sulfur technologies. All the cases presented use the DOE Case 2, GEE Gasifier with carbon capture, as the base case.

Overall Material Balances

The overall material balance for the GTI UCSRP-HP Base Case is presented in Table 29 (with the stream data shown in Figure 33). The material balance was based on maintaining the syngas of DOE Case 2 through Stream 11.

Equipment List

The equipment lists for the GTI UCSRP-HP Base Case is summarized in Table 32. This includes the equipment within Plant Area 5A, Gas Cleanup.

Total Installed Plant Cost Details

The total installed plant costs for various special equipments for the UCSRP-HP Base Case are presented in Table 32. We have followed the cost methodology provided in the DOE Case 2 design. The Total Plant Cost (TPC) and Operation and Maintenance (O&M) costs for the study were estimated by GTI. The estimates carry an accuracy of ± 30 percent, consistent with the screening study level of information available for the various study power technologies.

GTI used vendor quotes and an in-house database and conceptual estimating models for the capital cost and O&M cost estimates. All capital and O&M costs are presented as “overnight costs” expressed in December 2006 dollars. In this study, the first year of plant construction is assumed 2007, and the resulting LCOE is expressed in year 2007 dollars. The capital and operating costs in December 2006 dollars were treated as a January 2007 year cost throughout the report without escalation. In this report, December 2006 dollars and January 2007 dollars are considered to be equal.

Capital costs are presented at the TPC level. TPC includes:

- Equipment (complete with initial chemical and catalyst loadings),
- Materials,
- Labor (direct and indirect),
- Engineering and construction management, and
- Contingencies (process and project).

GTI used the same scaling factors and contingencies as noted in the DOE Case 2.

Table 32 Major Equipment List and Total Plant Costs (2009 \$) for Plant Area 5A

Item	Description	Equipment Cost	Labor + Material	Bare Erected Cost	Engineering + Home Office	Process Contingency	Project Contingency	Total Plant Cost
E-130	Water Cooler	72,000	21,600 (30%)	93,600	9,360	0	9,360 (10%)	\$112,320
C-100+C-103+C-253+C-254	Gas Compressors	511,000	306,000 (60%)	817,600	81,760	0	179,870 (22%)	\$1,079,230
E101-C	Syngas Reheater	2,860,000	858,000	3,718,000	378,000	0	378,000	4,461,600
E-102A	SO ₂ Cooler	447,900	134,370 (30%)	582,270	58,227	0	58,227 (10%)	\$698,724
E-103	2 nd SO ₂ Cooler	96,800	29,040 (30%)	125,840	12,584	0	12,584	\$151,008
E-160 + E-162	Misc. Heat Exchangers	1,007,000	302,100 (30%)	1,309,100	130,910	0	130,910	\$1,570,920
E-250	Syngas Cooler before V-201	3,350,000	1,005,000 (30%)	4,355,000	435,500	0	435,500 (10%)	\$5,226,000
E-252	Stripper Reboiler for DGM/Water Dist.	91,000	27,300 (30%)	118,300	11,830	0	11,850 (10%)	\$141,980
E-253	DGM Dist. Condenser	197,000	59,100 (30%)	256,100	25,610	0	25,610 (10%)	\$307,320
E-254	DGM Dist. Recuperating Heat Exchanger	79,000	23,700 (30%)	102,700	10,270	0	10,270 (10%)	\$123,240
F-100	Molten Sulfur Filter	169,000	50,700	219,700	21,970	0	22,000	\$263,670
F-160	DGM Slip Filter (+2 Spares)	30,000	9,000	39,000	3,900	0	8,580 (22%)	\$51,480
HC-160	Hydroclone (+2 Spares)	45,000	13,500	58,500	5,850	0	12,900 (22%)	\$77,250
High Temperature Insulation			485,000 (Material)	485,000	48,500	0	48,500	\$582,000
P-100	Liquid SO ₂ Pump	14,000	1,120 (8%)	15,120	1,510	0	2,280 (15%)	\$18,910

Pumps: P110, P161, P162, P163, P210, P250	Various Pumps	865,600	69,250 (8%)	934850	93,490	0	140,230 (15%)	1,168,570
SP-100	Sulfur Pit + Transfer Pump	241,000	144,600 (60%)	385,600	38,560	0	38,560	\$462,720
Sulfur Furnace	High-pressure S/O ₂ Furnace	484,000	411,400 (85%)	895,400	89,540	89,540 (10%)	197,000 (22%)	\$1,271,480
Sulfur Reactor	Sulfur Reactor/Absorber	312,000	265,200 (85%)	577,200	57,720	86,600 (15%)	144,300 (25%)	\$865,820
Sulfur Reactor 3-phase Sep.	Sulfur Reactor 3-phase Sep.	228,000	68,400 (30%)	296,400	29,640	0	29,640 (10%)	\$355,680
V-100	HP Sep/Water Contactor	82,000	24,600 (30%)	106,600	10,660	0	10,660	\$127,920
V-103	Sulfur Condenser	20,000	6,000 (30%)	26,000	2,600	0	2600	\$31,200
V-130	LP Sep. in HP water Quench	12,000	3,600 (30%)	15,600	1,560	0	1560	\$18,720
V-201	HP Separator	210,000	63,000 (30%)	273,000	27,300	0	27,300 (10%)	\$327600
V-202	LP Sep. for DGM/water Dist	77,000	23,100 (30%)	100,100	10,010	0	10,000 (10%)	\$120,110
V-251	DGM Distillation Column	98,000	29,400 (30%)	127,400	12,740	0	28,030 (22%)	\$168,170
V-252	DGM Dist. Water Vessel	16,000	4800 (30%)	20800	2,080	0	2080 (10%)	\$24,960
V-253	DGM Dist Cond. Vessel	61,000	18,300 (30%)	79,300	7,930	0	7900	\$95,130
V-254	Water/NH ₃ Stripper	120,000	36,000 (30%)	156,000	15,600	0	34,320 (22%)	\$205,920
X-100	Filter	317,000	95,100 (30%)	412,100	41,210	0	61,815 (15%)	\$515,125
E-DOE-HE	DOE Heat Ex. (Credit)	3,604,000	1,081,200	4,685,200	468,520	0	468,520	(\$5,622,240)
TOTAL (2009 \$)								\$15,002,537

Energy/Utility Requirements, Plant Performance & Overall Sulfur Balances

Power requirements for various pumps and compressors: Base Case Design

For the UCSRP-HP Base Case, the power requirements for various (1) pumps are about 1,130 HP and (2) compressors are about 632 HP; the total need for these pumps and compressors is 1,762 HP or 1,314 kW

Table 33 provides a comparison of the overall plant performance for the DOE Case 2 and the UCSRP-HP Base Case. The power production was the same for both plants. The difference in saleable power is the difference in the auxiliary load. As seen here, the Claus Plant Tail Gas Recycle Compressor, first stage Selexol Unit Auxiliaries, and the Claus Plant/Tail Gas Unit Auxiliaries consumed 4,751kWe more than the UCSRP Units and Sulfur Furnace. This resulted in a slight efficiency increase for the UCSRP-HP from about 32.5% for the DOE Case 2 to about 32.8% for the UCSRP-HP Base Case design.

Table 33 Plant Performance Summary

	DOE Case 2	UCSRP Design Case 1
Dry Coal Feed Rate, lb/h	444,737	444,737
Total Thermal Input, kWt	1,710,780	1,710,780
Power Summary, kWe		
Gas Turbine Power	464,010	464,010
Sweet Gas Expander Power	6,260	6,260
Primary Steam Turbine Power	<u>274,690</u>	<u>287,500</u>
Total Power Generation, kWe	744,960	757,770
Auxiliary Load Summary, kWe		
Claus Plant Tail Gas Recycle Compressor	990	0
Selexol Unit Aux.	17,320	12,445
Claus Plant/TGTU Aux.	200	0
UCSRP Units + Sulfur/O₂ Furnace	--	1,314
Balance of Plant	<u>170,775</u>	<u>170,775</u>
Total Auxiliaries, kWe	189,285	184,534
NET POWER, kWe	555,675	573,236
Net Extra Power Production, kWe	--	17,561
Total Thermal Input in Coal Feed, kWt	1,710,780	1,710,780
Net Plant Efficiency, % (HHV)	32.5	33.5

Sulfur Balance

Table 34 shows the sulfur balance in the three cases. The sulfur balance given in the DOE Case 2 does not account for all of the sulfur in the initial coal feed; there is a difference of about 94 lb/h between the sulfur in the coal and the shifted gas. We performed the balance starting with the shifted gas (Stream 11). The DOE Sulfur Out values were as given in Exhibit 3-37. The stack gas

levels correspond to 56, 34, and essentially zero lb/h SO₂ being emitted in the DOE Case 2, UCSRP Base Case and UCSRP Case 2 (chemical applications), respectively.

Table 34 Sulfur Balances for DOE Case 2, UCSRP Base Case, and UCSRP Case 2

	Sulfur In, kg/h (lb/h)				Sulfur Out, kg/h (lb/h)		
	DOE Case 2	UCSRP Base Case	UCSRP Case 2		DOE Case 2	UCSRP Base Case	UCSRP Case 2
Shifted Syngas	5,654.5 (12,466)	5,654.5 (12,466)	5,654.5 (12,466)	Elemental Sulfur	5,676.3 (12,514) ^a	5,643.2 (12,441)	5,643.2 (12,441)
				Stack/Product Gas	12.7 (28)	7.7 (17)	~0
				Waste-water	8.2 (18)	3.6 (8)	3.6 (8)
				ZnO Bed			7.7 (17)
Total	5,654.5 (12,466)	5,654.5 (12,466)	5,654.5 (12,466)	Total	5,697.2 (12,560)	5,654.5 (12,466)	5,654.5 (12,466)

a. For DOE Case 2, the dry coal feed rate is 444,737 lb/h & the elemental sulfur level is 2.82%. Thus, the total sulfur in feed coal is 12,542 lb/h (vs. 12,560 lb/h reported in the DOE Sulfur Balance data). Based on the Stream 11 data, the Shifted Syngas contains 12,466 lb/h of sulfur (as H₂S); this figure is higher than the 12,514 lb/h reported as “Elemental Sulfur” production (Stream 18 from the Claus Plant) in Exhibit 3-37 of the DOE report.

Solvent Make-up Rate: UCSRP-HP Base Case

For this Base case, the DGM solvent make-up rate is estimated at ~ 1,800 lb/day and the 3-Pyridyl methanol catalyst usage would be about 10 lb/day (at ~0.5 lb catalyst per 100 lb solvent), based on the vapor pressure losses of DGM at the High-Pressure Separator conditions.

DOE Case 2 vs. GTI UCSRP-HP Base Case

The methodology given in the referenced DOE report was followed to evaluate the UCSRP-HP process. Relative to the results for the DOE Case 2 that uses conventional cold gas cleanup scheme with Selexol/Claus/Tail Gas type H₂S removal processes, our study shows significant economic and environmental advantages (see Table 39) for the UCSRP-HP Base Case design:

- A net CAPEX savings of about \$123 MM (December 2006 dollars) based on the conservative design and ± 30% cost estimate basis;
- The overall thermal efficiency (HHV basis) would increase from about 32.5% for the DOE Case 2 to about 33.5% for the UCSRP-HP design;
- An increase of about 17.6 MW (~3.2 %) in net power sale;
- A reduction of about \$9.60/MWh (~9.3%) in the cost of power production with carbon capture, CO₂ compression plus transport/storage/monitoring; and

- A reduction in total SO₂ emission of about 22 lb/h.
- In addition, preparing the syngas for a chemical application that requires <50 ppb sulfur in the syngas would increase the required CAPEX by about \$10.1MM and the COE would increase by about \$1.80/MWh if the syngas was used for power generation in a near zero SO₂ discharge IGCC plant.

Table 35 Comparative Data on CAPEX: DOE Case 2 vs. UCSRP-HP Base Case

Case	DOE IGCC Case 2	GTI UCSRP-HP
Dry Coal feed rate, lb/h	444,737	444,737
Total SO ₂ emission, lb/h	56	34
Total Plant Cost, \$MM (Dec. 2006 \$)		
Plant Area 5A Gas Cleanup		
5A.1 Selexol System*	172.0	70.0
5A.2 Elemental Sulfur plant	32.8	--
5A.3 Mercury Removal	3.2	--
5A.5 UCSRP**	--	14.6
Affected subtotal	208.0	84.6
Remaining Area 5 Items	21.9	21.9
Area 5A Total	229.9	106.5
Remainder of Plant	1,098.3	1,098.3
Total Plant Cost	1,328.2	1,204.8
Capital Savings		123.4

* Selexol System:

DOE IGCC Case 1 – Single-Stage H₂S removal (43,585 lbmoles/h, \$80.8MM

DOE IGCC Case 2 – Dual-Stage H₂S and CO₂ removal (62,118 lbmoles/h, \$172MM);

UCSRP-HP – Single-Stage CO₂ removal only.

The cost of the single-stage H₂S removal process would be \$80.8 x (62,118/43,585)^{0.65}
= \$102MM The cost of the single-stage CO₂ removal process would be \$172-102 = \$70

** UCSRP

Prorate costs from Table 32 by the CEPCI to reflect costs in 2006\$. CEPCI (Chemical Engineering Plant Cost Index) Y-2006- 499.6 and Y-2009-521.9

Table 36 UCSRP Base Case Initial and Annual Operating and Maintenance Costs

				Cost Base (Dec)		2006	
UCSRP-Base Case GEE Radiant Only IGCC w/CO ₂				Capacity Factor, %		80	
	UCSRP-HP Base Case					DOE Case 2	Notes
	Initial	Per Day	Unit Cost	Initial	Annual Cost	Annual Cost	
TOTAL FIXED OPERATING COSTS					\$ 22,043,485	\$ 24,306,610	a
VARIABLE OPERATING COSTS							
Maintenance Materials Costs					\$ 22,284,397	\$ 24,602,924	b
Consumables							
Water (/1,000 gallons)	-	6,594	1.03	\$ -	\$ 1,983,139	\$ 1,983,139	
Chemicals							
MU & WT Chem (lb)	137,493	19,642	0.16	\$ 22,659	\$ 945,198	\$ 945,198	
Carbon (Mercury Removal) (lb)	-	-	-	\$ -	\$ -	\$ 33,872	
COS Catalyst (lb)	-	-	-	\$ -	\$ -	\$ -	
WGS Catalyst (ft ³)	6,288	4.3	475	\$ 2,986,800	\$ 596,410	\$ 596,410	
Selexol Solvent (gal)	250	36	12.9	\$ 1,650	\$ 135,616	\$ 271,232	
Claus Catalyst (lb)	-	-	-	\$ -	\$ -	\$ 82,125	
DGM Solvent (lb)	4,000	1,800	1.4	\$ 3,300	\$ 735,840	\$ -	
DGM Catalyst (lb)	-	10	6.65	\$ -	\$ 19,418	\$ -	c
Subtotal Chemicals					\$ 2,432,482	\$ 1,928,837	
Waste Disposal							
Heavy Metals (lb)					\$ 27,206	\$ 13,603	d
Bottom Ash (ton)		659	15.45		\$ 2,973,464	\$ 2,973,464	
Subtotal Waste Disposal					\$ 3,000,670	\$ 2,987,067	
TOTAL VARIABLE OPERATING COSTS					\$ 29,700,688	\$ 31,501,967	
FUEL (ton)					\$ 73,835,368	\$ 73,835,368	
Notes:							
	a Prorated by ratio of total CAPEX						
	b Prorated by ratio of total CAPEX						
	c 0.5 lb/100 lb DGM						
	Based on disposal cost twice that of DOE Base Case. Heavy metals will be in 50% water slurry,						
	d much more concentrated than loaded on carbon bed.						

Table 37 Comparative Data on Power Production, Total CAPEX and Cost of Power

	DOE Case 2	GTI UCSRP-HP
Coal Feed Rate, dry, lb/h	444,737	444,737
Gas Turbine, MWe	464.0	464.0
Sweet Gas Expander, MWe	6.3	6.3
Steam Turbine, MWe	274.7	287.5
Total Auxiliaries, MWe	-189.3	-184.5
Net Power for Sale, MWe	555.7	573.3
Thermal Efficiency, % (HHV)	32.5	33.5
Total CAPEX, \$MM	1,328	1,205
Levelized Cost of Electricity, LCOE, \$/MWh *	103.0	93.4

* DOE Economic Model (based on High-risk economic parameters : (i) Capital Charge factor of 0.175, (ii) Coal Levelization Factor of 1.2022, (iii) O&M Levelization at 1.1568. The details on the estimated LCOE cost data for the DOE Case 2 and the UCSRP-HP Base Case are given in Table 38.

Table 38 Components of Levelized Cost of Electricity

Cost Item, mills/kWh	DOE Case 2	UCSRP-HP Base Case	UCSRP-HP Case 2
Capital	59.68	52.47	52.97
Fixed	7.22	6.35	6.41
Variable	9.36	8.55	9.80
Coal	22.79	22.09	22.11
CO₂ TS&M	3.91	3.91	3.91
Total	102.96	93.37	95.20

GTI UCSRP-HP Design Case 2: Achieve a H₂S Level in Product Syngas <50 ppbv

GTI UCSRP-HP Design Case 1 removed sufficient sulfur from the raw syngas so that the SO₂ releases from the power plant were in accord with the environmental target of 0.0128 lb/MMBtu from the DOE study.⁸ The DOE Case 2 SO₂ emissions were 56 lb/h (0.096 lb/MMBtu) and GTI UCSRP-HP emissions were 34 lb/h. This resulted from the combustion of 4 ppm H₂S and 4.1 ppm COS in the feed to the power block in the GTI case (assuming no H₂S removal in the Selexol CO₂ removal process).

GTI UCSRP-HP Case 2 removed additional H₂S and COS in order to achieve <50 ppbv in the feed to the Selexol unit. In this design, the GTI UCSRP Base Case would be modified to include a

COS hydrolysis unit as well as a sulfur scavenger unit to process the syngas effluent from the UCSRP reactor. All upstream equipment and material and energy balances would remain the same, including the coal feed to the plant. The downstream Syngas Expander will produce less power as described below. The design includes two scavenging towers in lead lag configuration filled with zinc oxide scavenger and a third vessel in standby. The design is based on 95 – 100% of the zinc oxide is utilized in removing COS and H₂S, as per vendor literature for lead lag systems. The 3 vessel system is designed at 110%, i.e., 10% overdesign factor. Each zinc oxide scavenger vessels is sized to contain enough material (plus 10% excess) so that it will last 90 days before being taken out of the “lead” position; before being taken off line, emptied and having the zinc oxide scavenger replaced. The CAPEX data for this scavenger unit (to reduce H₂S level from ~4 ppmv to about 50 ppbv) was provided by CrystaTech Inc.

For the COS hydrolysis unit, we have used the capital cost data from the DOE Case 1 design² with a scaling factor of 0.5 based on the total amount of COS reacted. The estimated total installed cost for the COS reactor is \$1.1 MM (2006\$).

Scavenger Unit (H₂S level reduced to 50 ppbv from 4 ppmv)

- Equipment cost of the scavenger unit: \$2.9 MM (Year 2006\$)
- Labor/Material @ 85%: \$2.47
- Bare Erected cost: \$5.37 MM
- Engineering @ 10%: \$0.54 MM
- Project contingency: (@15%): 0.81 MM
- Total Installed Cost: \$6.7 MM (Year 2006 \$)
- For the revised case with the inlet H₂S level of ~8 ppm, the capital cost for the scavenger unit would be about \$9.0 MM (Y-2006\$).
- According to CrystaTech, the annual cost for the scavenger (ZnO adsorbent) is estimated at about \$2.2 MM/year (to reduce H₂S level from ~4.4 ppmv to <50 ppbv). Therefore, for the revised case (with inlet H₂S level of ~8 ppmv), the annual cost of scavenger is about \$4.4 MM.
- The pressure drop for COS Hydrolysis and Scavenger Units are assumed to be 30 psi, reducing the power produced by the Syngas Expander by ~0.5MWe.

The downstream equipment and material and energy balances would reflect the decreased levels of H₂S and the decreased power from the Syngas Expander. Utilizing DOE’s economic model, the LCOE would increase by \$1.83/MWh to \$95.20/MWh to achieve a near zero SO₂ emission for the plant, as shown in Table 38.

Economic Potential for the Integration of Key Membrane Technologies for the Removal of CO₂ and H₂ with the UCSRP-HP Sulfur Removal Process in IGCC Applications

The economic potential of integrating UCSRP-HP with (1) the LANL/SRI’s PBI (polybenzimidazole), high-temperature (~250-450°C), polymeric CO₂-removal membrane, (2) the GTI/ProGen’s CarboLock Membrane for CO₂ removal, and (3) an advanced H₂-separation membrane that would meet specific year-2015 performance targets¹⁰ assumed by DOE/Noblis LLC were also examined. For these economic evaluations, it is assumed that the CO₂ product would need to meet the Kinder-Morgan specifications for existing commercial CO₂ pipelines¹¹. These cases were compared to the published data on RTI’s warm gas cleanup (WGC) process.

The COE data for these integration options are compared in Table 40 with those derived from literature information, namely:

Case 1	DOE Case 1: This case represents a nominal net 550 MW IGCC plant with no CO ₂ capture ⁵ using sulfur impregnated carbon beds for mercury removal, single-stage Selexol for H ₂ S removal, and Claus/Tail Gas for sulfur recovery.
Case 2	DOE Case 2: This case represents a nominal net 550 MW IGCC plant with CO ₂ capture ⁵ using the conventional cold gas cleanup (CGCU) of scheme sulfur impregnated carbon beds for mercury removal, dual-stage Selexol process for the removal of H ₂ S and CO ₂ , and Claus/Tail Gas for sulfur recovery.
Case A	This case uses Case 2 and incorporates UCSRP-HP for multicontaminant removal with conventional Selexol process for CO ₂ removal as explained in the previous section of this report.
Case B	This case uses Case A (UCSRP-HP) with GTI/PoroGen's CarboLock membrane contactor ¹² with Selexol for CO ₂ removal rather than conventional columns.
Case C	This case is the published SRI study ¹³ that uses LANL/SRI's PBI membrane for hydrogen/acid gas separation and purification of the CO ₂ stream by a single-stage Selexol/Claus/Tail Gas process for sulfur recovery from the CO ₂ -rich stream.
Case D	This case uses Case C and incorporates UCSRP-HP for multicontaminant removal (from the CO ₂ -rich stream) downstream of LANL/SRI's PBI membrane rather than the Selexol/Claus/Tail Gas trains.
Case E	This case is the published DOE/Noblis report ^{14,15} that uses RTI's warm gas cleanup (WGC) process for multicontaminant removal and a single-stage Selexol process for CO ₂ capture.
Case F	This case is the published DOE/Noblis report ^{14,15} that uses RTI's WGC process for multicontaminant removal and an Advanced H ₂ Membrane (performance projections by DOE/Noblis ¹⁰) for CO ₂ removal.
Case G	This case uses Case A and incorporates an Advanced H ₂ Membrane for H ₂ /CO ₂ separation.

Figure 35 shows how various developmental technologies affect the cost of electricity. The horizontal line marked "1" is the COE without carbon capture (Case 1). Point "2" is the base case for carbon capture using "conventional" capture technology (Case 2). The line 2-A-B-G represents incorporating UCSRP-HP for multicontaminant removal with Selexol for CO₂ removal (Case A), GTI/PoroGen's CarboLock membrane contactor with Selexol rather than conventional columns for CO₂ removal (Case B), and an Advanced H₂ membrane for CO₂ removal (Case G). Line 2-C-D represents incorporating the PBI membrane for H₂/acid gas separation with purification of the CO₂ stream by a single-stage Selexol/Claus/Tail Gas process for sulfur recovery (Case C) and UCSRP-HP for multicontaminant removal (Case D). Line 2-E-F represents incorporating WGC for multicontaminant removal with a single-stage Selexol for CO₂ removal (Case E) and an Advanced H₂ membrane for CO₂ removal (Case F).

These cases show that UCSRP-HP can make a positive impact with new developmental technologies and become a viable alternative to competing multicomponent cleanup technologies.

Table 39 Comparative COE Data: DOE Case 2 vs. UCSRP-HP

	DOE Case 2	GTI UCSRP-HP Base Case	GTI UCSRP-HP Chemical Case
Coal Feed Rate, dry, lb/h	444,737	444,737	444,737
SO ₂ Emissions (lb/h)	56	34	~0
Gas Turbine, MWe	464.0	464.0	464.0
Sweet Gas Expander, MWe	6.3	6.3	5.8
Steam Turbine, MWe	274.7	287.5	287.5
Total Auxiliaries, MWe	<u>-189.3</u>	<u>-184.5</u>	<u>-184.5</u>
Net Power for Sale, MWe	555.7	573.3	572.8
Thermal Efficiency, % (HHV)	32.5	33.5	33.4
Total CAPEX, \$MM (Y- 2006 \$)	1,328	1,205	1,215
Cost of Power, \$/MWh (or mills/kWh)**	103.0	93.4	95.2

** DOE Economic Model to determine LCOE: Levelized Cost of Electricity

Table 40 Comparative Data for COE (including CO₂ capture, compression, transport, plus storage/monitoring)

Design Case	H ₂ S Removal Option	CO ₂ Removal Option	COE, \$/MWh	COE Differential, %
DOE-1	Selexol	None	77.8	Base
DOE-2	Selexol	Selexol	103.0	32.4
A	UCSRP-HP	Selexol	93.4	20.1
B	UCSRP-HP	GTI/ PoroGen CarboLock Membrane Contactor w/Selexol	91.7	17.9
C	Selexol	LANL/ SRI PBI Membrane	98.2*	26.2
D	UCSRP-HP	LANL/ SRI PBI Membrane	94.7	21.7
E	RTI	Selexol	101.6	30.6
F	RTI	Advanced H ₂ Membrane	89.6	15.2
G	UCSRP-HP	Advanced H ₂ Membrane	88.8	14.2

* SRI reported \$94.3/MWh COE without CO₂ TS&M (of ~ \$3.9/MWh)

Figure 35 Comparative Data for COE Using Multiple Technology Pathways and Integrations

** See Table 4 for related design cases

Task 5.0 –Bench-Scale Experiments

Figure 36 Pressure Drop Measurements in the Bench-Scale Unit

Mass transfer data collected prior to installing Chiller-3 and 60ft tube and shell heat exchanger was analyzed. The data shows a mass transfer (moisture removed) dependence on inlet liquid temperature due to increased liquid flow rate.

Figure 37 Mass Transfer Dependence on Liquid Temperature

Figure 38 H₂S Solubility in DGM Solvent at 250 °F

The amount of H₂S absorbed increased with increase in liquid flow rate and higher H₂S concentration in the feed gas.

Determination of heat transfer coefficients was completed as shown in Table 41

Table 41 Heat Transfer Coefficient Testing Results

Liquid flow (gpm)	Gas flow (acfh)	L/G	H _{gas} Btu/(lb _{gas} *ft packing)	H _{liquid} Btu/(lb _{liquid} *ft packing)
10.1	273.7	0.10	0.2	0.85
30.1	323.2	0.25	0.2	0.85
50	273.7	0.46	0.2	0.84
50	175.2	0.75	0.2	0.85
49.9	125.1	1.04	0.2	0.84

GTI was not able to complete the proposed test plan for reaction kinetics due to numerous test interruptions from GCV-100 failure causing pressure build up, sulfur condensation in feed line. It can be seen that more H₂S is absorbed into the solvent with SO₂ present due to the overall reaction

As the reaction proceeds in the liquid phase, more H₂S dissolves into the liquid hence the decreased concentration in the product gas.

Table 42 Kinetics and Reactivity Data

Pressure	Gas flow	H ₂ S flow	SO ₂ flow	Temp	Liquid flow	Inlet concentration (ppmV)		Outlet concentration (ppmv)	
psig	acfh	slpm	slpm	° F	gph	H ₂ S	SO ₂	H ₂ S	SO ₂
209.0	114.9	5.10	7.54	258	16.8	5471.7	2426.9	272.3	

Identified Issues for Future Modifications

- During the SO₂/H₂S absorption/reaction, the pressure control valve, GCV-100, for V-100 wouldn't control pressure leading to pressure build up in V-100 and frequent shut downs (30min after start of test). It was later discovered that GCV-100 has a maximum operating temperature of 150°F above which the minimum torque required to open the valve could not be achieved.
The valve manufacturer suggested that (i) a longer stem to help dissipate most of the heat before it got into the body and control of the valve (ii) a better valve that could handle temperatures in excess of 300°F could be purchased. GTI could not proceed due to a lack of funds for the project.
- The gas feed line to V-100 has a check valve that would plug due to condensed sulfur. This line should be heat traced and insulated to prevent heat losses that would result in sulfur condensation.
- The recycle pump, P-101, stop solvent recirculation once the pressure differential between V-102 on the suction side and V-100 on the delivery side exceeds 50psi. The pressure in V-102 has to be lowered significantly (lower than 50psi) to allow all/most of dissolved H₂S and SO₂ to desorb thus returning a lean solvent to V-100. A new pump that can allow up to 350 psid across would be better for this application.
- Suction and delivery lines to Pump 101 have to be re-fabricated to include a bypass for priming of the pump.

Conclusions and Recommendations

The following conclusions and recommendations were reached in this project:

- UCSRP-HP continues to be a promising technology to decrease the cost of producing power from coal while enhancing the environmental benefits of IGCC over alternative coal-based power generation options.
- Aspen Plus simulations indicate complete removal of ammonia (NH_3), hydrogen chloride (HCl) and hydrogen selenide (H_2Se) in the aqueous scrub step of the UCSRP-HP process.
- Thermodynamic considerations point to minimal formation of COS in the UCSRP-HP reactor for a CO_2 rich feed as compared to a CO-rich-feed gas stream.
- Removal of heavy metals, including mercury, arsenic and selenium have been demonstrated in the laboratory. Selenium removal was greater in water than DEG.
- For economic evaluations of various novel technologies for sulfur removal and carbon capture in IGCC applications, estimates for COE would depend on overall thermal efficiency for power generation as well as the capital cost requirements.
- As an example, the RTI WGC technology for sulfur removal has demonstrated relatively high thermal efficiency; however, based on the DOE/NETL estimates, the COE with carbon capture for Case E (RTI WGC with single-stage Selexol for carbon capture) has been estimated at only ~1.4% lower relative to the DOE Case 2 (CGCU with two-stage Selexol).
- In contrast, for Case A (using the UCSRP-HP technology for sulfur removal and the single-stage Selexol for carbon capture), a COE reduction of ~9.1% relative to the DOE Case 2 is estimated. This is primarily due to a significant savings in capital cost for the UCSRP-HP process.
- As indicated in the Design Case G, integration of the UCSRP-HP process for sulfur removal with an Advanced H_2 Membrane for H_2/CO_2 separation could lead to a COE value that would be only about 15% higher than DOE's baseline cost projections (in DOE Case 1) for a no carbon capture IGCC plant.
- The COE for Case G is similar (at about 15% increase relative to the no carbon capture case) to that estimated by DOE/Noblis for the Case F using the RTI process for sulfur removal and the Advanced H_2 Membrane process for CO_2 removal.
- Further laboratory- and bench-scale testing and process simulation studies are required in preparation to a slip-stream test of UCSRP-HP on actual coal-derived syngas.
 - Experimentally determine:
 - Detailed reaction kinetics and mass transfer data for SO_2 and H_2S reaction in a suitable co-current down-flow absorber/reactor containing Sulzer SMVTM-type contactors. Such studies should include reactor operations with both excess H_2S as well as excess SO_2 at the reactor outlet.
 - Such studies should also include determination of the extent and kinetics of COS formation in such reactions using typical levels of H_2 , CO, CO_2 , H_2O and H_2S found in coal-derived syngas with or without WGS processing to determine if COS hydrolysis is required.
 - Solubility data for major syngas components in DGM solvent.
 - The efficacy of the high-pressure water contactor system for the removal of various metal compounds from coal-derived syngas at pressures of about 400-800 psig and gas temperatures of about 300-450°F.
 - To minimize DGM vapor losses with non-DGM type solvents used in the CO_2 removal step, experimental data should be collected to evaluate the efficacy

of DGM solvent as a physical solvent for CO₂ removal from coal- or biomass-derived syngas streams.

- Process simulation and cost studies should proceed in parallel with the R&D program. It is anticipated that further development will result in reducing the need for a number of conservative overdesign decisions made in the base case. For example, the sulfur absorber/reactor was oversized by 30% with respect to vendor guidelines; the COS hydrolysis unit was included for the GTI Case 2 design (to achieve H₂S levels of below 50 ppbv) although COS formation appears to be controllable by the presence of water vapor and SO₂ in the product gas with H₂S and CO₂; and two backup processes were included to removal and collect heavy metals removed from the gas stream. Further research should also justify decreasing the process contingencies applied to the base equipment costs.
- Sulfur purification
 - Determine if sulfur purity equivalent to the Claus process can be obtained or whether any additional purification steps (e.g., the need for a DURCO type liquid sulfur filter to remove specific metal compounds) should remain in the plant design.
- Obtain bench-scale data with feed gas from an operating coal gasifier to identify the effect of any trace components.
- Process simulation studies should also examine the integration with additional gasifier technologies, including a dry-feed gasifier that will have less water vapor in the syngas. Development of a technology that can efficiently remove water vapor from the syngas stream, such as GTI's Transport Membrane Contactor²², could have a significant impact on the thermal efficiency of the process. A preliminary evaluation estimated that replacing the four heat exchangers in the base design with a TMC would result in
 1. A 29 psia higher pressure inlet gas to the gas turbine resulting in an increase power production in the syngas expander of 0.56MW.
 2. A reduced heat loss due to condensation forming in the heat exchanges of 18.9 MWh.
 3. A reduced energy usage in the Water/Ammonia stripper related to reduced water load of 12.9 MW.
 4. Assuming 33% efficiency in the steam turbine plus the additional power from the turbine, the TMC plant would produce about 11 MW more power, resulting in an efficiency of 33.4% compared to 32.5% for the DOE Case 2.

LIST OF ACRONYMS AND ABBREVIATIONS

3-HP	3-pyridyl carbinol (also known as 3-pyridinemethanol)
Acfm	Actual cubic feet per minute
AGR	Acid gas removal
ASTM	American Society for Testing and Materials
ANSI	American National Standards Institute
As	Arsenic
AsH ₃	Arsine
ASU	Air separation unit
Atm	Atmospheres of pressure
BFD	Block flow diagram
BFW	Boiler feed water
Btu	British thermal unit
Btu/h	British thermal unit per hour
Btu/kWh	British thermal unit per kilowatt hour
Btu/lb	British thermal unit per pound
Btu/scf	British thermal unit per standard cubic foot
CAPEX	Capital expenditures
CCF	Capital Charge Factor
Cd	Cadmium
CDR	Carbon Dioxide Recovery
CF	Capacity factor
CFM	Cubic feet per minute
Cm	Centimeter
CO	Carbon monoxide
CO ₂	Carbon dioxide
COE	Cost of electricity
CoP	ConocoPhillips
COR	Contracting Officer's Representative
COS	Carbonyl sulfide
cP	CentiPoise
CS	Carbon steel
CT	Combustion turbine
CTG	Combustion Turbine-Generator
DCS	Distributed control system
DEG	Diethylene glycol
DGM	Diethylene glycol methyl ether
DI	De-ionized
Dia.	Diameter
DO	Direct Oxidation (of H ₂ S to sulfur)
DOE	Department of Energy
DP	Differential pressure
DSRP	Direct Sulfur Recovery Process
E-Gas™	ConocoPhillips gasifier technology
EPA	Environmental Protection Agency
ft	Foot, Feet
ft, w.g.	Feet of water gauge
GADS	Generating Availability Data System

Gal	Gallon
gal/MWh	Gallon per megawatt hour
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectroscopy
GEE	GE Energy
GRI	Gas Research Institute
GTI	Gas Technology Institute
Gpm	Gallons per minute
gr/100 scf	grains per one hundred standard cubic feet
GT	Gas turbine
H	Hour
H ₂	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen sulfide
H ₂ Se	Hydrogen selenide
H ₂ SO ₄	Sulfuric acid
HAZOP	Hazard and Operational review
HCl	Hydrochloric acid
Hg	Mercury
HETP	Height equivalent to a theoretical plate
HHV	Higher heating value
Hp	Horsepower
HP	High pressure
HRSG	Heat recovery steam generator
HSS	Heat stable salts
HTDP	High temperature desulfurization process
HX	Heat exchanger
ICAP	Inductively coupled argon plasma emission spectroscopy
ICCI	Illinois Clean Coal Institute
In.	Inch
IEEE	Institute of Electrical and Electronics Engineers
IECM	Carnegie Mellon's Integrated Environmental Control Model
IGCC	Integrated gasification combined cycle
IP	Intermediate pressure
kg/GJ	Kilogram per gigajoule
kg/h	Kilogram per hour
kJ	Kilojoules
kJ/h	Kilojoules per hour
kJ/kg	Kilojoules per kilogram
KO	Knockout
Kp	Equilibrium constant in terms of gaseous partial pressures
kPa	Kilopascal absolute
kW	Kilowatt
kWe	Kilowatts electric
kWh	Kilowatt-hour
L	Liter
LANL	Los Alamos National Laboratory
Lb	Pound
lb/h	Pounds per hour
lb/ft ²	Pounds per square foot

lb/MMBtu	Pounds per million British thermal units
lb/MWh	Pounds per megawatt hour
LCOE	Levelized cost of electricity
LHV	Lower heating value
LP	Low pressure
Lpm or L/min	Liters per minute
M	Meters
m/min	Meters per minute
m ³ /min	Cubic meter per minute
MAF	Moisture and Ash Free
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MFC	Mass flow controllers
Mils	1000 th of an inch
MJ/Nm ³	Megajoule per normal cubic meter
MMBtu	Million British thermal units (also shown as 10 ⁶ Btu)
MMBtu/h	Million British thermal units (also shown as 10 ⁶ Btu) per hour
MMkJ	Million kilojoules (also shown as 10 ⁶ kJ)
MMkJ/h	Million kilojoules (also shown as 10 ⁶ kJ) per hour
MNQC	Multi Nozzle Quiet Combustor
NOTICE	No Tie In Claus Expansion
MPa	Megapascals
MWe	Megawatts, electric
MWh	Megawatt-hour
MWt	Megawatts, thermal
N/A	Not applicable
NaOH	Sodium hydroxide
NETL	National Energy Technology Laboratory
Ng/m ³	Nanogram per cubic meter
NH ₃	Ammonia
NH ₄ Cl	Ammonia chloride
NH ₄ HS	Ammonia sulfide
(NH ₄) ₂ Se	Ammonia selenide
Nm ³	Normal cubic meter
NO _x	Oxides of nitrogen
NRTL	Nonrandom, two liquid equation of state model
NTU	Number of transfer units
O&M	Operation and maintenance
OD	Outside diameter
OPEX	Operating and maintenance costs
OSHA	Occupational Safety and Health Administration
PBI	Polybenzimidazole
PC	Pulverized coal
PEL-TWA	Permissible exposure limit – Time Weighted Average
PID	Proportional–Integral–Derivative controller
PLC	Programmable Logic Controller
ppb	Parts per billion
ppbv	Parts per billion by volume
ppbw	Parts per billion by weight
PPE	Personal protection equipment

ppm	Parts per million
ppmv	Parts per million by volume
ppmw	Parts per million by weight
PSA	Pressure Swing Adsorption
psia	Pounds per square inch absolute
psid	Pounds per square inch differential
psig	Pounds per square inch gage
P-V-T	Pressure – Volume – Temperature
Qty	Quantity
RH	Reheater
RTI	Research Triangle Institute
S	Sulfur
SCFD	Standard cubic feet per day
scfh	Standard cubic feet per hour
scfm	Standard cubic feet per minute
Sch.	Schedule
scmh	Standard cubic meter per hour
SCOT	Shell Claus Off-gas Treating
Se	Selenium
SGS	Sour gas shift
SMV	Static mixer vessel
Slpm	Standard liters per minute
SO ₂	Sulfur dioxide
SO _x	Oxides of sulfur
SRI	SRI International
SRU	Sulfur recovery unit
SS	Stainless steel
STG	Steam turbine generator
STP	Standard temperature and pressure
STR	Stripper column
SWGS	Sour Water Gas Shift
TBD	To be determined
TCR	Total capital requirement
TCD	Thermal Conductivity Detector
TGTU	Tail gas treating unit
TMC	Transport Membrane Contactor
Tonne	Metric Ton (1000 kg)
TPC	Total plant cost
TPD	Tons per day
TPH	Tons per hour
TPI	Total plant investment
TS&M	Transport, storage and monitoring
UCB	University of California, Berkeley campus
UCSRP	University of California Sulfur Recovery Process
UCSRP-HP	University of California Sulfur Recovery Process – High Pressure
V-L	Vapor Liquid portion of stream (excluding solids)
VLE	Vapor liquid equilibrium
vol%	Volume percent
WGC	Warm gas cleanup
WGS	Water gas shift

wt%	Weight percent
Y	Year
ZnO	Zinc oxide
\$/MMBtu	Dollars per million British thermal units
\$/MMkJ	Dollars per million kilojoule
$\mu\text{g}/\text{m}^3$	Micrograms per cubic meter

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Appendix A – Bench-scale Unit Construction and Commissioning Activities

Construction Activities

1. The discharge ports of seven relief valves on liquid filled vessels were plumbed to the vent header. In the event of a relief discharge, the vent header would have filled up with liquid and dump contents on the roof. To mitigate this effort a blow-down drum was installed. Then the relief valve discharge ports on liquid filled vessels were plumbed to the blow-down drum and the blow-down drum was vented to the vent header
2. The relief valves protecting vessels from rupture were sized to discharge at 1440 psig while the maximum operating pressure of the vessels in the plant were designed for 1315 psig. The relief valve is required to be set at a lower pressure than the maximum allowable operating pressure of the device it is protecting. To mitigate this, the relief valves were resized to discharge at 1300 psig.
3. The two Chromalox heat exchangers were sized for 1000 psig at 300°F. The plant is to operate at 1000 psig so the maximum operating pressure of the vessel needs to be greater than 1000 psig, specifically at least 1315 psig. To mitigate the effort, two new Chromalox heat exchangers were specified with a maximum operating pressure of 1315 psig at 300°F.
4. Two plastic 55 gallon feed drums and two plastic 165 gallon waste product drums were installed on the Bench Scale Unit. The Bench Scale Unit is on the second floor of the building at GTI with no secondary containment vessels. To mitigate any potential spill, secondary containment vessels were purchased and installed.
5. The two plastic 55 gallon feed drums blocked the normal egress of a walkway resulting in a building code violation. To mitigate the issue, the two 55 gallon feed drums were moved and re-plumbed to provide adequate egress.
6. Six Sharpe electric operated control valves do not meet the temperature and pressure requirements of the plant. The most cost effective way to mitigate this issue was to remove the valve seat and stem and replace them with ones that meet the temperature and pressure requirements of the plant.
7. Twenty-five PGI bleeder valves did not meet the low temperature requirements of the plant and also they require valve stem extensions so they can be operated while insulated. Since the valve bodies did not meet the low temperature requirements of -40°F, new valves and valve stems are required to replace the old ones.
8. Fifty Parker valve stems are not accessible to turn with insulation on them. To mitigate the issue, fifty 2" valve stem extensions will be ordered and replaced with the shorter ones.
9. Five Apollo valves did not meet the high temperature and high pressure requirements of the plant. Since the valve body did not meet the high temperature and high pressure requirements of the plant, they were replaced with Parker valves.
10. Sixteen Parker check valves did not meet the acid gas requirements for the plant because they contained Viton seats. Viton is unsatisfactory for use in an acid gas environment. Since Parker does not provide Kalrez valve seats for its check valves, the valves were replaced with Swagelok check valves with Kalrez seats.
11. A Nowata filter with brass internals did not meet the acid gas requirements for the plant. Brass is unsatisfactory for use in an acid gas environment. A new stainless steel Nowata filter was purchased with stainless steel internals and replaced the inferior model.
12. The main feed pump P-101 was not relieved properly. A relief valve was installed so in

the case of a high pressure event or a blockage downstream of the pump, the pump will recirculate the feed back into the feed tanks.

13. Nineteen Omega Engineering pressure transducers and differential pressure transducers do not meet the high temperature requirements of the plant. This is a real problem for the UCSRP-HP high temperature process. The plant will operate at 275°F and the transducers are good up to only 220°F. The most cost effective way to mitigate this issue is to not have any insulation around the transducers while operating the plant, allowing the additional heat to dissipate. Therefore temperature monitoring of the transducers will be required. "Caution Hot" signs will be required to alert any operator working on the plant of the temperature hazard.
14. Removing molten sulfur at 275°F and 1000 psig from vessel V-102 with a spigot was considered inadequate and very unsafe. To mitigate this issue, a sulfur removal system was designed and installed. A 300cc high pressure Hoke vessel was installed below vessel V-102. The Hoke vessel has block valves upstream and downstream that feeds into a vented 5 gallon steel vessel. The Hoke vessel can be filled with liquid sulfur at high pressure, safely isolated from vessel V-102, and then discharged into a vented 5 gallon steel vessel.

Commissioning Activities

1. The unit was pressure tested and all leaks were fixed.
2. Calibrated all level transmitters and pressure differential indicators
3. Developed a display screens for the all vessels, pumps, and all major equipment including electrically controlled valves.
4. Installed a PLC to run and control the unit
5. Set up control schemes for all: valves; pumps; level, flow, temperature, and pressure controllers
6. Set up Start-up Permissives to prevent unsafe start up of the unit. Each permissive would have be complete before major equipment like the gas and liquid heaters can start.
7. Added a bypass line to better control gas flow rates from the compressor to the bench scale unit.
8. Changed suction line for liquid feed pump, P-100, from a ½" to 1". This ensured that the higher flows could be attained without exceeding allowable power requirements for the pump.
9. Added contact debounce timers for P-102 and P-103 water pumps to prevent contact chatter when the water level high limits are reached.
10. Tested the operation of the automatic water level controls for V-200 and V-300.
11. Revised the control schemes for V-101 Flash Separator (Once-through Mode via SCV-101A) and V-102 Sulfur Separator (Recycle Mode via SCV-101B).
12. Modified the liquid level control for V-102 by controlling the speed of the liquid recycle pump, P-100.
13. Programmed level alarms for V-102 utilizing the level transmitter signal and the point level FCI Model FLT-93S flow / level switch LS-102.
14. Calibrated the liquid level transmitters for V-101 and V-102.
15. Installed a Precision Digital Vigilante Model PD-158 8-Point alarm panel and moved the Allen-Bradley PanelView Plus terminal from the Skid-1 panel board to the alarm station panel board that is mounted next to the entrance to the gas research laboratory.
16. Developed and programmed a 35-Point Alarm Screen for the two A-B PanelView displays to augment the unit alarms & safeguards capabilities.

17. In addition, to enhance the operator's information displays, two "Startup Permissives" screens were programmed for the PanelView displays.
18. Wired the Ametek Moisture Analyzer signal to the PLC and programmed the signal to display on the PanelView terminals.
19. Incorporated a number of alarms and safeguards to alert the operators of potential danger. Reviewed and revised the alarm & safeguards table for Excel. The PLC control program was revised to incorporate the changes.
20. H₂S and LEL monitors were connected to the PLC to enable emergency shut down if any dangerous concentrations of H₂S and CH₄ were detected in the enclosure.
21. Corrected the PanelView display screens to reflect the alarms & safeguards changes.
22. Specified and installed ten isolation relays from Allen-Bradley to isolate the eight gas inlet valves from the PLC to prevent further loss of the PLC output relay contacts. One isolation relay is a spare.
23. Installed the 10th isolation relay as part of a "Loss of PLC Control" watchdog alarm circuit utilizing a Brentek Model P8-WDT24/PLC timer.
24. Changed the logic of the unit temperature, pressure and flow out-of-limit alarm outputs from a latch/unlatch output that requires the panel board green reset pushbutton to be pressed for every nuisance alarm to a 10-second alarm delay timer output. An out-of-limit condition must last longer than 10 seconds to result in an alarm and only those that result in a unit shutdown per the safeguards table require pressing the alarm reset push button.
25. Calculated the sulfur collection volume to the vessel weir (11.5 gal.) and the volume of the level transmitter end to the weir (1.9 gal.) in the sulfur separator vessel, V-102 (vessel total volume to the top of the weir = 13.4 gal.)
26. Checked operation of the FCI level point level switch, LSH-102.
27. Calibrated V-102 level transmitter, LT-102 (0-15 in. H₂O).
28. Set V-102 level control output direction to reverse acting (SP-PV).
29. An additional Type "T" thermocouple was installed through the bottom of V-102. It is installed utilizing a 6-inch thermo well and is screwed into the ½" FPT bottom opening no. 6 and protrudes 2-inches into the sulfur collection area. The thermocouple is located 10.5-inches from the sulfur collection weir and is labeled as TE-102-3 on the unit PID drawing.
30. Fixed various errors and discrepancies on the computer screens. The permissives screens were modified to reflect the position of the unit run mode switches (Dehydration, Absorption or Sulfur recovery).
31. Continued refining the unit control and display screens including the addition of process heaters H-200 and H-300, V-104 pressure control and level control, and V-102 pressure and level control.
32. Added a controlled emergency shutdown of the unit via three pushbutton switches: two mounted just inside of hallway doors on either side of the unit and a third switch located by the makeup nitrogen cylinder. This will allow for thermal expansion of the process and cooling fluids if power is turned off to the unit. These switches parallel existing controlled shutdown logic. We will review this logic next month.
33. Added miscellaneous limits screen for unit gas moisture, V-105 PH, and the hydrocarbon gas LEL and Sulfur gas detectors.
34. PT-104 calibrated to 0-1200 psig from 0-3000 psig for greater resolution.
35. DPT-5 (V-100 Top to V-103 Differential pressure) pulled and sent back to Omega Engineering for repair. LT-105 pulled and recalibrated 0-100 in. H₂O to replace DPT-5.
36. Installed an APC Model SC-1000 Uninterruptible Power Supply to provide power to the Allen-Bradley Programmable Logic Controller (PLC) for alarm purposes in the event the

unit loses AC power.

37. Installed a redundant 24 vdc power supply to the PLC controller I/O in Skid-1. Also added a second 24 vdc power supply to each of the Allen-Bradley Flex I/O cabinets, Skid-2, Heater Chiller and the Switch Rack panels. This splits the 24 vdc power between analog I/O and digital I/O per the manufacturer recommendation.
38. Installed ph probe and transmitter for the V-105 scrubber.
39. Wired signal leads from Ametek Moisture analyzer to PLC input.
40. Called Chromalox to determine the correct over temperature setpoints for the Watlow Model 94 temperature switches that protect H-200 and H-300 heaters.
41. Replaced LT-105 level transmitter when it returned from Omega repair (calibrated 0-17 in. H₂O).
42. Updated all unit electrical drawings (PLC I/O and the MCC motor control cabinet drawing).
43. Placed the unit electrical drawings and the printed copy of the PLC program into the orange unit binder.
44. Prepared safety and operating instructions.

Appendix B – Brown and Root Braun’s SO₂ Generation Process

Brown and Root Braun’s **SO₂ generation process**, that uses submerged combustion of liquid sulfur with oxygen (Figures 39 and 40), was commercialized for their NOTICE (No Tie In Claus Expansion) TECHNOLOGY for sulfur production.⁹ The first generator to use this technology has been in commercial operation since 1989 at the Calabrian Corp. chemical plant in Port Neches, Texas.⁹

Figure 39 Schematic for Submerged Sulfur/Oxygen Combustion Process

Figure 40 Submerged Sulfur Combustion and Viscosity of Liquid Sulfur

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SECTION 2: CRYSTASULF-DO SULFUR RECOVERY

FINAL REPORT

GTI PROJECT NUMBER 20251

DOE PROJECT NUMBER DE-FC26-05NT42458

Development of an Integrated Multi-Contaminant Removal Process Applied to Warm Syngas Cleanup for Coal-Based Advanced Gasification Systems

Section 2: Bench-scale Development of CrystaSulf-DO for the Removal of Hydrogen Sulfide in Coal Gasification Syngas Streams

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Abstract

This project met the objective to further the development of an integrated multi-contaminant removal process in which H_2S , NH_3 , HCl and heavy metals including Hg , As , Se and Cd present in the coal-derived syngas can be removed to specified levels in a single/integrated process step. The process supports the mission and goals of the Department of Energy's Gasification Technologies Program, namely to enhance the performance of gasification systems, thus enabling U.S. industry to improve the competitiveness of gasification-based processes. The gasification program will reduce equipment costs, improve process environmental performance, and increase process reliability and flexibility.

Two sulfur conversion concepts were tested in the laboratory under this project, i.e., the solvent-based, high-pressure University of California Sulfur Recovery Process – High Pressure (UCSRP-HP) and the catalytic-based, direct oxidation (DO) section of the CrystaSulf-DO process. Each process required a polishing unit to meet the ultra-clean sulfur content goals of <50 ppbv (parts per billion by volume) as may be necessary for fuel cells or chemical production applications. UCSRP-HP was also tested for the removal of trace, non-sulfur contaminants, including ammonia, hydrogen chloride, and heavy metals. For each process, a bench-scale unit was commissioned and limited testing was performed with simulated syngas. Aspen-Plus®-based computer simulation models were prepared and the economics of the UCSRP-HP and CrystaSulf-DO processes were evaluated for a nominal 500 MWe, coal-based, IGCC power plant with carbon capture. This report covers the progress on the CrystaSulf-DO technology development. The UCSRP-HP technology is covered in Volume 1.

This project was undertaken to expand on work previously performed by CrystaTech and the Gas Technology Institute (GTI) with funding from various industrial clients in the area of hydrogen sulfide (H_2S) removal from coal gasification syngas streams. In that previous work, commercially available catalysts were tested for Direct Oxidation (DO) of H_2S to sulfur at pressure ranging from atmospheric to 800 psig and temperature from 250 °F to 600 °F. The equipment used for the project, the Catalyst Test Unit (CTU), is located in GTI's facilities in Des Plaines, IL and has been described in a previous publication.¹ Other operating parameters were also evaluated during the previous work. While much information was gathered and advancements were made, there was no clear catalyst or set of operating conditions that could be identified as acceptable for removal of large amounts (at least 70%) of H_2S in the syngas stream by converting it to sulfur. This current project sought to use the results of the previous work and identify a catalyst and operating conditions that would be more successful for converting H_2S to sulfur in coal gasification syngas streams.

CrystaTech and GTI discovered previously that many different catalysts could be used to convert H_2S into sulfur in gasification syngas streams, all with varying degrees of success. However, there were consistently two things generally common to all of the tests: first, was that when sulfur and carbon monoxide were present at high temperature (+ 250 °F) a significant amount of carbonyl sulfide (COS) was formed, and second, was that, as the temperature was increased, less H_2S was converted to sulfur. These observations and others were incorporated into the test plan for the current work under this project.

This section will provide a brief summary of the project test results; following sections will provide all of the detail by task. Based upon the data that was gathered during this testing program, the following conclusions have been made:

- When operating the DO reactor above the sulfur dewpoint temperature, i.e., above approximately 260 °F, the O₂ added to the process to react and convert H₂S into sulfur also reacts with and consumes CO and H₂, which is a significant drawback for a commercial unit.
- Based upon the above conclusion the majority of this work was conducted at sulfur sub-dewpoint temperature; at sub-dewpoint the sulfur accumulates on the catalyst rather than “dripping off”. Because of the sulfur accumulation on the catalyst, the DO reactor should be operated in a multiple bed configuration, where one catalyst bed is in service at sulfur sub-dewpoint and the other is being regenerated at above sulfur dewpoint temperature
- Catalyst D was tested during September for 100 hours in a multiple bed configuration where H₂S was converted to sulfur and adsorbed for 6 hours followed by a 6 hour regeneration step with nitrogen flowing at approximately 600 °F. However, the final cycle of the regeneration was not successful, indicating that a different regeneration approach is required, or that the catalyst has a very short lifetime. The vendor for Catalyst D was consulted for a different regeneration approach. The vendor successfully regenerated the catalyst at 572 °F in a flowing air stream for 2 hours.
- The long term test of Catalyst C in multiple bed operation was not successful.

Table of Contents

Disclaimer	143
Legal Notice	144
Abstract	145
Table of Contents	147
Table of Figures 149	
Table of Tables 151	
Approach	152
Scope of Work 152	
Tasks to be Performed 152	
Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup	152
Subtask 2.4 – CrystaSulf-DO Sulfur Removal.....	152
Subtask 2.5 – Syngas Component Effects on SO ₂ Formation	153
Task 3.0 – Computer Simulation Model.....	153
Subtask 3.1 – Preliminary Aspen Model	153
Subtask 3.2 – Aspen Model	153
Task 4.0 – Economic Evaluation.....	154
Subtask 4.1 – Preliminary Economic Evaluation.....	154
Subtask 4.2 – Economic Evaluation.....	154
Task 8.0 – Project Management and Reporting	154
Task Descriptions and Results.....	155
Task 2.4 CrystaSulf-DO Bench-scale Feasibility Tests for Multi-Contaminant Cleanup	
155	
Subtask 2.4.1 Catalyst Evaluation	155
Subtask 2.4.2 Operating Condition Optimization	177
Subtask 2.4.3 Long Term Testing.....	186
Subtask 2.4.4 Vapor-Liquid Equilibria Experiments.....	218
Subtask 2.5 Syngas Component Effects on SO ₂ Formation.	231
Task 3.0. Computer Simulation	240
CrystaSulf-DO Process Model	240
CrystaSulf-DO Process Description.....	240
Task 4.0. Economic Evaluation	247
Recommendations for Future Testing	257
References.....	258

List of Acronyms and Abbreviations.....	259
Biography.....	260

Table of Figures

Figure 41 Inlet and outlet gas composition of the CTU during a blank run, i.e., no catalyst.....	160
Figure 42 Inlet and outlet gas composition of the CTU during the test of Catalyst G ..	163
Figure 43 Inlet and outlet gas composition of the CTU during the repeat test of Catalyst G	165
Figure 44 Inlet and outlet gas composition of the CTU during the test of Catalyst D...	167
Figure 45 Inlet and outlet gas composition of the CTU during the test of Catalyst	169
Figure 46 Inlet and outlet gas composition of the CTU during the test of Catalyst H...	170
Figure 47 Inlet and outlet gas composition of the CTU during the test of Catalyst I	172
Figure 48 Inlet and outlet gas composition of the CTU during the test of Catalyst F ...	174
Figure 49 Inlet and outlet gas composition of the CTU during the test of Catalyst C...	176
Figure 50 Inlet and outlet gas composition of the CTU during the test of Catalyst G ..	179
Figure 51 Inlet and outlet gas composition of the CTU during the test of Catalyst D...	182
Figure 52 Inlet and outlet gas composition of the CTU during the above sulfur dewpoint test of regenerating the Catalyst D.....	184
Figure 53 Inlet and outlet gas composition of the CTU during the 30 hour test of Catalyst G	187
Figure 54 Inlet and outlet gas composition of the CTU during the 46 hour test of Catalyst D.....	191
Figure 55 Inlet and outlet gas composition of the CTU during the sulfur sub-dewpoint operation test of Catalyst D	192
Figure 56 Inlet and outlet gas composition of the CTU during the above sulfur dewpoint test of regenerating the Catalyst D.....	193
Figure 57 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst C long term test.....	199
Figure 58 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst C long term test.....	200
Figure 59 Inlet and outlet gas composition of the CTU during the third cycle of the Catalyst C long term test.....	201
Figure 60 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst D long term test.....	205
Figure 61 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst D long term test.....	206
Figure 62 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst D long term test.....	208
Figure 63 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst D long term test.....	209

Figure 64 Inlet and outlet gas composition of the CTU during the third cycle of the Catalyst D long term test.....	210
Figure 65 Inlet and outlet gas composition of the CTU during the fourth cycle of the Catalyst D long term test.....	211
Figure 66 Inlet and outlet gas composition of the CTU during the fifth cycle of the Catalyst D long term test.....	212
Figure 67 Inlet and outlet gas composition of the CTU during the sixth cycle of the Catalyst D long term test.....	213
Figure 68 Inlet and outlet gas composition of the CTU during the seventh cycle of the Catalyst D long term test.....	214
Figure 69 Inlet and outlet gas composition of the CTU during the eighth cycle of the Catalyst D long term test.....	215
Figure 70 Inlet and outlet gas composition of the CTU during the ninth cycle of the Catalyst D long term test.....	216
Figure 71 Solubility of hydrogen in RSC-103 solvent.....	221
Figure 72 Solubility of hydrogen in RSC-202 solvent.....	222
Figure 73 Solubility of hydrogen in RSC-312 solvent.....	223
Figure 74 Solubility of hydrogen in CrystaSulf solution.....	224
Figure 75 Solubility of carbon monoxide in RSC-103 solvent.....	226
Figure 76 Solubility of carbon monoxide in RSC-202 solvent.....	227
Figure 77 Solubility of carbon monoxide in RSC-312 solvent.....	228
Figure 78 Solubility of carbon monoxide in CrystaSulf solution	229
Figure 79 Comparison of Henry's Law Constants (m3kPa/mol) for Hydrogen and Carbon Monoxide for CrystaSulf Solution Components and CrystaSulf Solution with some Organic Solvents and Water. ²	230
Figure 80 Inlet and outlet gas composition of the CTU during the test of Catalyst A..	232
Figure 81 Inlet and outlet gas composition of the CTU during the test of Catalyst A at 500 °F	233
Figure 82 Inlet and outlet gas composition of the CTU during the test of Catalyst A at 600 °F without H ₂ and CO addition	234
Figure 83 P&ID - DO Units.....	244
Figure 84 PFD CrystaSulf and Guard Bed Units.....	245
Figure 85 PFD - CrystaSulf Units Continued	246

Table of Tables

Table 43 Catalyst Evaluated in this Project.....	156
Table 44 Catalyst Evaluation Test Conditions	156
Table 45 Blank Test run with H ₂ S Check	158
Table 46 Verification of the concentrations and flow rates in the CTU	159
Table 47 Simulation of Multiple Bed Operation – Test Conditions for Long Term Testing	197
Table 48 Beginning, Final and Average H ₂ S Conversions for Each Cycle	217
Table 49 Solubility of Hydrogen in CrystaSulf Solution Components and in CrystaSulf Solution, Henry's law constants	220
Table 50 Solubility of Carbon Monoxide in CrystaSulf Solution Components and in CrystaSulf Solution, Henry's law constants.....	225
Table 51 Complete Results from Blank, Catalyst Screening and Long term Catalyst Tests	236
Table 52 Heat and Material Balance.....	243
Table 53 Cost Estimate Summary for CrystaSulf-DO by Unit.....	248

Approach

Scope of Work

The objective of this project is to develop an integrated multi-contaminant removal process in which H_2S , NH_3 , HCl and heavy metals including Hg , As , Se and Cd present in the coal-derived syngas can be removed to specified levels in a single/integrated process step.

Tasks to be Performed

The specific objectives of this project include:

8. Testing the feasibility of sulfur removal concepts at lab scale. Two sulfur conversion concepts will be tested: (1) The solvent-based high pressure University of California Sulfur Recovery Process - High Pressure (UCSRP-HP), and (2) the catalyst-based direct oxidation (DO) section of the CrystaSulf-DO process. It is anticipated that each process may need a polishing unit to meet the cooperative agreement maximum sulfur goal (50 ppbw), and that the CrystaSulf process will be used in concert with the CrystaSulf-DO process to obtain these ultra-clean levels.
9. Testing the GTI trace-contaminant process feasibility at lab scale.
10. Exposing the UCSRP-HP solvent and CrystaSulf catalysts to syngas with typical contaminants that may be present in the feed to a syngas cleanup reactor.
11. Investigation of long-term solvent and catalyst stability.
12. Testing the UCSRP-HP bench-scale unit with up to 20 lb/day sulfur production capacity to gather data for further verification of the process concept, measuring contaminant removal efficiencies, determining reaction kinetics and optimizing the process parameters for designing a pilot-scale demonstration unit for Phase-II study.
13. Development of Aspen-Plus based computer simulation models.
14. Evaluating the economics of the UCSRP-HP and CrystaSulf processes, each combined with the GTI trace-contaminant cleanup process, applied to syngas cleanup for a nominal 500 MWe coal-based IGCC power plant with carbon capture.

To meet these objectives, the following tasks will be performed for the CrystaTech-DO process. Tasks related to development of UCSRP-HP are included in the Volume 1 report.

Task 2.0 – Lab-Scale Feasibility Tests for Multi-Contaminant Cleanup

Subtask 2.4 – CrystaSulf-DO Sulfur Removal

Demonstrate the potential for the CrystaSulf-DO concept to be able to remove sulfur (SO_2 , H_2S and COS) at conditions as representative as practical of the anticipated commercial unit. Establish the equilibrium solubility of hydrogen

and carbon monoxide in CrystaSulf solution. Determine the effect of temperature and pressure and other process variables on the total sulfur removal, and gather the data needed to determine the optimum amount of sulfur that can be removed using the CrystaSulf-DO process. The goal is 80-90% H₂S conversion at 400 psi without significant loss of fuel value (i.e., minimal conversion of H₂ or CO). If H₂S conversions are sufficiently high and H₂ and CO conversions are sufficiently low, conduct a long-term test to observe any deactivation of the catalyst.

Subtask 2.5 – Syngas Component Effects on SO₂ Formation

Conduct SO₂ formation catalyst tests at pressure and temperature conditions to determine operating conditions for conversion of a portion of the H₂S to SO₂, as needed for the Claus reaction, without significant loss of fuel value.

Task 3.0 – Computer Simulation Model

Subtask 3.1 – Preliminary Aspen Model

Based on the data gathered during Task 2, develop Aspen-Plus based computer simulation models that will be used to design the bench-scale test plan, and for process optimization and economic analysis of the UCSRP-HP and CrystaSulf-DO sulfur removal processes, each in combination with the GTI trace contaminant removal system. Include any needed syngas polishing units in the model. Syngas purity after all cleanup processes must be at the levels shown below:

Contaminant	Maximum After Cleanup
H ₂ S	50 ppbw
NH ₃	0.1 vol%
HCl	1 ppm
Hg	5 ppbw
Se	0.2 ppm
As	5 ppb
Cd	30 ppb

Subtask 3.2 – Aspen Model

Based on the data gathered during Tasks 2 and 5, develop an Aspen-Plus based computer simulation model that will be used for process optimization, economic analysis, and planning and designing a pilot-scale unit for Phase 2. Include any needed syngas polishing units in the model. Syngas purity after the cleanup must be at the levels shown in the Subtask 3.1 chart.

Task 4.0 – Economic Evaluation

All analysis will be consistent with the most recent version of NETL’s “Quality Guidelines for Energy System Studies”. Comparison evaluations will utilize NETL system reports as the basis where possible.

Subtask 4.1 – Preliminary Economic Evaluation

Based on the results of Subtasks 2.1, 2.2, 2.3 and 3.1, compare the economic potential of the following: (1) UCSRP-HP with the GTI trace-contaminant cleanup process, (2) CrystaSulf-DO with the GTI trace-contaminant cleanup process, and (3) conventional processes. For the hydrogen production case, assume the water-gas-shift reaction is performed on dirty syngas, with the cleanup occurring on the shifted syngas. Determine the optimum sulfur removal split between the UCSRP-HP and a polishing bed, and among the DO, CrystaSulf and a polishing processes. Syngas purity, after all cleanup processes, must be at the levels shown in the Subtask 3.1 chart. Perform the analysis including the creation of sequestration-ready CO₂.

Subtask 4.2 – Economic Evaluation

Based on the results of Subtasks 2.1, 2.2, 2.3, 2.5, 4.1, and Tasks 3.0 and 5.0, compare the economic potential of the following: (1) UCSRP-HP with the GTI trace-contaminant cleanup process and (2) conventional processes. For item (1), determine the optimum sulfur removal split (if any) between the developing processes and a polishing bed. Determine if it is more cost effective to reuse the trace contaminant solvent or not. Syngas purity, after all cleanup processes, must be at the levels shown in the Subtask 3.1 chart. Perform the analysis on a nominal 500 MWe, coal-based IGCC power plant with carbon capture.

Task 8.0 – Project Management and Reporting

GTI shall provide overall project management to include, as a minimum, technical status and administrative reports as required under terms and conditions of the Agreement with DOE. Project management activities shall also include supplying periodic information to the COR for the DOE-NETL metrics, planning and progress reporting programs.

Task Descriptions and Results

Task 2.4 CrystaSulf-DO Bench-scale Feasibility Tests for Multi-Contaminant Cleanup

Subtask 2.4.1 Catalyst Evaluation

The objective of this Task was to confirm the results of previous work performed in identification of a direct oxidation catalyst that will convert 80% of the H₂S in the syngas into elemental sulfur. CrystaTech and GTI have previously tested two direct oxidation catalysts, Catalyst C and Catalyst G, with good results for H₂S conversion. Initial testing will seek to replicate prior direct oxidation test results.

The catalyst reactor has been altered by the addition of a special coating on the walls of the DO reactor that has been shown to reduce “wall effects” and help prevent the formation of COS and the loss of CO and/or H₂, while allowing H₂S conversion to sulfur in the catalyst bed. This has been discussed in a previous publication.¹ the performance of all of the catalysts will be compared by evaluating them at baseline operating conditions. The catalysts used in this project are included in Table 43 below, and the catalyst baseline operating conditions used for evaluating the catalysts are shown in Table 44.

Table 43 Catalyst Evaluated in this Project

	Catalyst	Status at GTI
1	Catalyst G	Received
2	Catalyst B	Received
3	Catalyst F	Received
4	Catalyst E	Due to supply problems, removed from test plan
5	Catalyst A	Received (For H ₂ S conversion to SO ₂ only)
6	Catalyst I	Received
7	Catalyst H	Received
8	Catalyst C	Signed NDA, Used catalyst leftover from testing in 2005
9	Catalyst D	Received

Table 44 Catalyst Evaluation Test Conditions

Pressure	400 psig	H₂	20%
Temperature	255-280 °F	CO	40%
O₂/H₂S ratio	0.6 – 0.8	CO₂	15%
SV (actual)	(target) 1000 hr ⁻¹	H₂O	5%
		H₂S	2000 ppmv

The general test procedures for catalyst evaluation are as follows:

- Achieve pressure of 400 psig and gas flow rates for required space velocity (SV) in units of hour⁻¹ (actual)
- Heat the CTU with N₂ flowing
- Add H₂, CO, CO₂ and H₂O (reduce the N₂ to the setpoint)
- Add H₂S and O₂ to the required composition (this is the start of the test)
- Adjust the temperature as necessary
- Measure the H₂S conversion
- Measure any COS and/or SO₂ formation
- Measure any loss of CO and/or H₂
- Continue until stable conditions and H₂S conversion are achieved

Each test typically required a full day for a given set of operating conditions. Data was evaluated the following day. Once previous results were reproduced and additional blank tests were performed to verify the performance of the CTU and associated analytical equipment, then the catalysts were tested to ensure that the previously chosen catalyst achieved optimum H₂S conversion with minimum loss of CO and/or H₂.

Unit Startup test results

The CTU was operated without catalyst to confirm proper metering, pressure and temperature settings. Three tests were run and are described below.

In the first experiment the inlet and outlet gas concentrations were measured to verify that without catalyst in the bed the inlet and outlet gas component concentrations were approximately equal. The results were somewhat unexpected and are shown in Table 45 and summarized below.

- Lower than expected inlet H₂S concentration was detected by the GC. The cylinder used had a concentration lower than specified resulting in the inability to reach the expected 0.2% concentration.
- Period 3 included water introduced into the pre-heater. It can be seen that H₂S and COS concentrations in the outlet gas changed drastically from their previous values.
- In period 4 no H₂S was detected by the GC. The inlet gas was also analyzed and the inlet H₂S concentration was also reported as zero.
- The GC was not calibrated for oxygen determination.

Table 45 Blank Test run with H₂S Check

		Period 1		Period 2		Period 3		Period 4	
GAS	inlet flow (slpm)	inlet mol%	outlet mol%	inlet mol%	outlet mol%	inlet mol%	outlet mol%	inlet mol%	outlet mol%
H ₂	3.84	24.0758	22.9748	23.7488	22.9711	23.4504	23.1885	23.8548	23.1043
N ₂	6.34	37.1153	35.800	37.3039	35.7732	37.4789	35.6135	37.2938	35.4647
CO	5.00	31.2239	33.3416	31.1907	33.2517	31.4759	33.4734	31.3922	33.4736
CO ₂	2.88	8.8332	8.6541	9.0273	8.8926	9.3709	8.5788	8.7817	8.5868
H ₂ S	0.152	0.0311	0.0415	0.0532	0.0436	0.0619	0.0031	0.0	0.0
COS	0.0	0.0	.00135	0.0	0.0137	0.0	0.0019	0.0	0.0
O ₂ /air	0.986								
SO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
						H ₂ O introduced during period 3			

Conditions: T_{ave} = 266 °F, P_{ave} = 384 psig, Outlet Gas Flow = 16.3 lpm, and Water flow = 1.39 gpm (Water was added in periods 3 and 4 only)

A second test with higher inlet H₂S was conducted however, it was stopped in the middle before GC outlet concentrations were recorded because the fume hoods in the lab malfunctioned. When the test was resumed, the total pressure of the CTU had dropped to 70 psig every time a sample of the inlet gas concentration was taken. Two leaking valves were discovered and replaced before testing resumed.

A third test run was performed before the end of February and the results are included in Table 46. The concentrations measured by the GC continued to disagree with expected amounts based upon the blended gas from the various gas supply cylinders. Highly accurate mass flow controllers are used to blend the gas, and the accuracy of the controllers has been verified. At this point the calibration of the GC was determined to be inaccurate. The GC was recalibrated.

A standard for oxygen to calibrate the GC for oxygen content was ordered and received. The GC was calibrated for oxygen, recalibrated for the other gases and was expected to be ready to be operated with the CTU in March 2008. Towards the end of February, 2008, the GC was needed for another experiment that put this project on hold for about 4 weeks. The CTU was determined to be fully operational and catalyst evaluation tests were expected to begin by mid March 2008.

Table 46 Verification of the concentrations and flow rates in the CTU

		Period 1		Period 2		Period 3	
GAS	inlet flow (slpm)	inlet mol%	outlet mol%	inlet mol%	outlet mol%	inlet mol%	outlet mol%
H ₂	5.00	25.6169	25.5089	25.7909	25.5005	25.8084	25.5208
N ₂	6.63	48.7624	48.7264	49.4553	48.6284	49.832	48.5087
CO	3.85	24.9396	24.9369	23.9709	24.8684	23.5612	25.0787
CO ₂	0.65	0.0055	0.0121	0.0055	0.023	0.0054	0.0176
H ₂ S	1.99	2.5027	2.4677	2.6399	2.4504	2.6572	2.4289
COS	0.0	0.0080	0.0189	0.0083	.0141	.0084	.0148
O ₂ /air	1.04						
SO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				H ₂ O was introduced at the beginning of period 2			

Conditions: T_{ave} = 267.7 °F, P_{ave} = 390.7 psig, Outlet Gas Flow = 16.28 lpm, Water flow = 1.37 gpm.

Second Startup Test

Blank Test – Additional blank runs were performed near the end of March 2008 to compare the inlet and outlet gas component concentrations. After lining-out the unit, the blank run inlet and outlet gas concentration data was gathered and is shown in the graph in Figure 41. In this blank run, i.e., without any catalyst in the reactor bed, the outlet gas concentrations should be the same as the inlet.

March 26, 2008 Blank CTU Test

Figure 41 Inlet and outlet gas composition of the CTU during a blank run, i.e., no catalyst

Blank Test Results - In the operation of the CTU, either the inlet or the outlet gas composition is measured, but not both simultaneously. Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 4.5	Achieved stable gas conditions	wet inlet gas
4.5 – 5.7		wet outlet gas
5.7 – 7.1	Stopped O ₂ addition to observe impact of O ₂ on COS formation	wet outlet gas
7.1 – 8.0		wet inlet gas
8.1	Stopped test	

The data shows that in general there is a slightly lower H₂S amount measured in the outlet versus the inlet gas without catalyst present in the reactor bed. The empty reactor bed is operated at temperature so the generally accepted conclusion is that some H₂S reacts with the walls of the reactor and tubing, i.e., a slightly reduced amount of H₂S is expected in the outlet gas during the blank run. Approximately 5% of the inlet H₂S is removed or converted to sulfur by this mechanism of wall effects. At about 5.7 hours Elapsed Time (ET) into the test, the O₂ addition was stopped to observe the affect of O₂ on the formation of COS as measured in the outlet gas. The data indicates that we should expect a baseline amount of about 130 - 140 ppmv H₂S and CO that are converted to COS in the outlet gas in blank tests without catalyst and in the presence of O₂. Without O₂ addition to the inlet gas, only 55 ppmv COS is measured in the outlet gas; 0 ppmv COS is measured in the inlet gas. This conversion of CO and sulfur to COS is most likely due to the wall effects of the small reactors that are used in bench-scale testing and should be significantly reduced in percent conversion of the reactants in commercial scale operation. As this project proceeds we may consider subtracting this blank amount (approximately 130 ppmv) of COS from the outlet gas composition data gathered during catalyst testing. The results are included in full table of results, Table 51, after the section discussing Subtask 2.5 below.

The extreme dips of CO concentration, e.g., the dip at 4 hours ET, are due to the CO gas supply cylinder running low in flow and required swapping of one cylinder to the next, so for one measurement, the CO is very low, near zero.

Catalyst G Catalyst Screening Test – Catalyst G was loaded into the 1" diameter reactor and tested for conversion of H₂S to sulfur. The reactor bed volume was 59 cc. The space velocity at average actual reactor operating conditions was 1000 Hr⁻¹. The temperature ranged from 240 – 276 °F during the tests with an average of 245 °F. At 245 °F sulfur may solidify on the catalyst, so in future tests the reactor will be operated at

temperatures in the range of 250 – 260 °F. The operating pressure was nominally 400 psig.

Catalyst G Screening Test Results - Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 2.4	Achieved stable gas conditions	
2.4 – 3.5		inlet gas
3.5 – 5.2		outlet gas
5.2 – 6.2	Started water at 5.2 ET	wet inlet gas
6.2 – 7.6		wet outlet gas
7.7	Stopped test	

The test was divided into 2 time periods: period A extending from 2.4 to 5.2 hours ET and period B extending from 5.2 to 7.6 hours ET. During the Catalyst G screening test run, approximately 30 – 45% of the inlet H₂S was converted to sulfur. The results are included in Table 47. COS formation during the blank test, i.e., no catalyst in the reactor bed, while O₂ was added to the inlet gas, was about 135 ppmv; during the Catalyst G test the COS concentration was about 145 ppmv. This indicates that CO and sulfur react to form roughly the same amount of COS in the presence of O₂ with or without this catalyst present. So we can conclude that there will most likely always be a baseline amount of conversion of CO and sulfur to COS in the presence of O₂. In future catalyst evaluation tests if a significant increase (+250 ppmv) in formation of COS is observed, then that catalyst was eliminated from consideration as a CrystaSulf-DO catalyst candidate.

March 28, 2008 Catalyst G Test

Figure 42 Inlet and outlet gas composition of the CTU during the test of Catalyst G

When O₂ is added to the gas stream it may react with CO to form CO₂ and/or H₂ to form H₂O. Both of these reactions consume the value of the gas stream and are unwanted side reactions of O₂. The results shown in Table 51 demonstrate that under the correct operating conditions, excess O₂ can be measured in the outlet gas rather than reacting according to the unwanted side reactions. This indicates that excess O₂ can be added to the gas stream to enhance the conversion of H₂S to sulfur without causing a negative impact upon the value of the gas stream, i.e., without reacting with CO and H₂ in the unwanted side reactions.

Catalyst G Test - In April, 2008, the Catalyst G test that was conducted in March was repeated. The results from both tests were very similar and are included in Table 51 at the end of the section describing Subtask 2.5. The data are shown below in Figure 43.

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 4.5	Achieved stable gas conditions	dry inlet gas
4.5 – 5.5		dry outlet gas
5.5 – 6.6		wet inlet gas
6.6 – 9.0		wet outlet gas

The reactor bed volume was 55 cc. The space velocity at average actual reactor operating conditions was 924 Hr⁻¹. The average reactor temperature was 253 °F during the test. The operating pressure was approximately 400 psig.

During the Catalyst G repeat test run, approximately 58% of the inlet H₂S was converted to sulfur without water vapor in the inlet gas and 46% was converted with water in the inlet gas. The results are included in Table 51. COS formation during the test was in the range of 100 ppmv, which is similar to the amount of COS formed in a blank run, i.e., no catalyst in the reactor bed.

The results from this test and the previous test performed in March indicate that 40 – 60% of the H₂S is converted to sulfur during the screening tests, and that water effects the conversion of H₂S to sulfur by lowering the conversion rate by about 15%, e.g., 58% H₂S was converted without water in the inlet gas and 46% was converted with water in the inlet gas. The results also indicate that COS does not form when the reactor is operated at sub-sulfur-dew point temperature.

April 1, 2008 Test of Catalyst G

Figure 43 Inlet and outlet gas composition of the CTU during the repeat test of Catalyst G

Catalyst D – An experimental catalyst prepared by an outside laboratory, was tested at sub-sulfur-dew point temperature. Beginning with this test the inlet H₂S concentration was increased to about 3000 ppmv for comparison to previous data and to simulate higher sulfur content in the gasifier feedstock. The data are shown below in Figure 44.

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 3.4	Achieved stable gas conditions	dry inlet gas
3.4 – 5.3		dry outlet gas
5.3 – 6.5		wet inlet gas
6.5 – 7.9		wet outlet gas
7.9 – 8.4		wet inlet gas
8.4 – 9.5		wet outlet gas

The reactor bed volume was 63 cc. The space velocity at average actual reactor operating conditions was 945 Hr⁻¹. The average reactor temperature was 277 °F during the test. The operating pressure was nominally 400 psig.

From ET of 3.4 – 5.3 hours, the outlet H₂S measurement slowly increased with only slight indication that a plateau outlet H₂S concentration was being reached. At 5.3 hours ET, the water was added to the inlet gas composition and the inlet gas composition was measured by the GC from 5.3 hours to 6.5 hours ET as shown in Figure 44. However, at ET 6.5 hours when the gas stream was switch to measure the outlet gas composition, the H₂S concentration was significantly lower at approximately 950 ppmv with essentially no production of COS. This improvement in H₂S conversion could have been caused by surface reactions / adsorption on the catalyst over the initial period, or by the addition of water. The results indicate that the Catalyst D performs slightly better than Catalyst G in H₂S conversion without COS formation, at these operating conditions. Catalyst G converted a net amount of 46% of the inlet H₂S to sulfur whereas Catalyst D converted 56%. Full results are in Table 51.

April 23, 2008, Catalyst D Test

Figure 44 Inlet and outlet gas composition of the CTU during the test of Catalyst D

Catalyst B – Catalyst B was tested at approximately the same operating conditions for comparison of H₂S conversion. The data are shown below in Figure 45.

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 4.0	Achieved stable gas conditions	dry inlet gas
4.0 – 4.7		dry outlet gas
4.7 – 6.0		wet inlet gas
6.0 – 7.0		wet outlet gas
7.0 – 7.5		wet inlet gas

The reactor bed volume was 62 cc. The space velocity at average actual reactor operating conditions was 886 Hr⁻¹. The average reactor temperature was 275 °F during the test. The operating pressure was nominally 400 psig.

The results from testing Catalyst B indicate that when water is included in the inlet gas approximately 100 ppmv COS is produced which is similar to the blank run, so effectively, no COS is produced by interaction with the catalyst when water is included in the inlet gas. However, the results also show that only about 17% of the inlet H₂S is converted to sulfur at these operating conditions. Catalyst B is not a good candidate for CrystaSulf-DO and no further testing of this catalyst will be conducted.

Catalyst H – Another experimental catalyst prepared by an outside laboratory, was tested at approximately the same operating conditions for comparison of H₂S conversion. The data are shown below in Figure 46.

Below is a description of the timing of gas composition measurements:

April 25, 2008, Catalyst B Test

Figure 45 Inlet and outlet gas composition of the CTU during the test of Catalyst

Figure 46 Inlet and outlet gas composition of the CTU during the test of Catalyst H

Elapsed Time of Test, hr	Event	Stream Measured
0 – 6.5	Achieved stable gas conditions	dry inlet gas
6.5 – 7.4		dry outlet gas
7.4 – 8.1		wet inlet gas
8.1 – 9.7		wet outlet gas
9.7 – 10.2		wet inlet gas
10.2 – 11.0		wet outlet gas

The reactor bed volume was 61 cc. The space velocity at average actual reactor operating conditions was 842 Hr⁻¹. The average reactor temperature was 288 °F during the test. The operating pressure was nominally 400 psig.

In the dry gas, essentially 100% of the inlet H₂S was converted to COS by Catalyst H. After water was included in the inlet gas, the COS production slowly decreased across the 4 hours after the start of water injection with no signs of reaching steady state before the test had to be stopped. This result could be explained by the addition of water, or by the conditioning of the catalyst overtime. The results indicate that most likely, the effect is due to water injection because there were steady state operating results from 6.5 to 7.5 hours ET and because the results continually and gradually changed from the time water injection was started. At the end of the test, the results showed approximately 45% conversion of H₂S to sulfur and 45% conversion to COS, with gradually improving results, i.e., lower COS production and higher H₂S conversion overtime. While the results of this test indicate that this catalyst should be eliminated from further testing during this project, it may be a candidate for longer term testing due to the gradually improving results. Catalyst H was intended to be considered for a long term test but there was insufficient time and resources to consider it and sufficient performance from other catalyst so as not to require any further testing of this catalyst.

Catalyst I – A third experimental catalyst prepared by an outside laboratory, was tested at approximately the same operating conditions for comparison of H₂S conversion. The inlet H₂S gas composition was set at about 2000 ppmv to compare with results gathered in previous testing. The data are shown below in Figure 47.

Figure 47 Inlet and outlet gas composition of the CTU during the test of Catalyst I

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 6.4	Achieved stable gas conditions	dry inlet gas
6.4 – 7.4		dry outlet gas
7.4 – 8.3		wet inlet gas
8.3 – 9.3		wet outlet gas

The reactor bed volume was 67 cc. The space velocity at average actual reactor operating conditions was 810 Hr⁻¹. The average reactor temperature was 270 °F during the test. The operating pressure was approximately 400 psig.

During the test of Catalyst I, roughly 10% of the inlet H₂S was converted to sulfur with or without water vapor in the inlet gas. The results are included in Table 51, which follows section 1.4 below. The vendor, was informed of these results and we are awaiting their reply. Based upon the positive results observed when testing of other similar-type metal doped catalysts, we suggest that the production of this particular batch of catalyst was faulty. Because we have two other similar metal based, commercially available catalysts to use in this project, we will stop testing the Catalyst I.

Catalyst F – Catalyst F was tested at sulfur sub-dewpoint conditions. For this test the inlet H₂S concentration was kept at about 2000 ppmv for comparison to previous data. The data are shown below in Figure 48.

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 3.8	Achieved stable gas conditions	dry inlet gas
3.8 – 5.2		dry outlet gas
5.2 – 6.0		wet inlet gas
6.0 – 7.0		wet outlet gas

May 5 2008, Catalyst F Test

Figure 48 Inlet and outlet gas composition of the CTU during the test of Catalyst F

The reactor bed volume was 64 cc. The space velocity at average actual reactor operating conditions was approximately 845 Hr⁻¹. The reactor temperature was in the range of 270 - 274 °F during the test. The operating pressure was nominally 400 psig.

The results from the test of Catalyst F indicate that the catalyst is not very good for H₂S conversion under the tested conditions. However, the results during water addition indicate that any COS formation may be reversed by reaction with water in the gas phase across this catalyst. Therefore, we may consider using this catalyst in the outlet or bottom of the reactor bed in combination with a second catalyst that may be more reactive to H₂S conversion. The results are included in Table 51, which follows the section discussing Subtask 2.5 below.

Catalyst C – Catalyst C was tested at sulfur sub-dewpoint temperature. For this test the inlet H₂S concentration was kept at about 3000 ppmv for comparison to previous data. The data are shown below in Figure 49.

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 1.5	Achieved stable gas conditions	dry inlet gas
1.5 – 2.5		dry outlet gas
2.5 – 4.0		wet outlet gas
4.0 – 4.9		wet inlet gas
4.9 – 8.0		wet outlet gas

The reactor bed volume was 60 cc. The space velocity at average actual reactor operating conditions was 853 Hr⁻¹. The average reactor temperature was 306 °F during the test. The operating pressure was approximately 400 psig.

During the test of Catalyst C, roughly 70% of the inlet H₂S was converted to sulfur without water vapor in the inlet gas and 55% with water vapor in the inlet gas. The results are included in Table 51, which follows the section discussing Subtask 2.5 below. This result is as expected based upon previous testing and agrees well with previous data for this catalyst.

June 2 2008, Catalyst C Test

Figure 49 Inlet and outlet gas composition of the CTU during the test of Catalyst C

Screening Test Conclusion

The screening tests indicate that the two catalysts that converted the most H₂S into sulfur were Catalyst D and Catalyst C. Those 2 catalysts will be subjected to long term testing. In addition, Catalyst G which is fabricated slightly different than Catalyst C but is of the same or very similar composition was also tested in a long term test.

Subtask 2.4.2 Operating Condition Optimization

This task includes results that are also discussed in Tasks 1.1 and 1.3. Previous work performed by CrystaTech and GTI with the support of various clients from industry showed that the operating conditions above the sulfur dewpoint (400 - 600 °F) caused significant production of COS in gasification syngas streams that contain percent level CO content (over 1-2 % CO). The production of COS essentially such that the H₂S that was converted into sulfur was reacted with CO to form COS in a 1-to-1 ratio, i.e., no net sulfur was removed from the gas stream, rather the H₂S and an equivalent molecular amount of CO was converted to COS. While the results of that previous testing are confidential, the experience was drawn upon for this project and future work. In addition, during the previous work performed at elevated temperature, carbon deposition on the catalyst surface and on the reactor tubing walls was also observed. In general those results indicate that for syngas streams, the O₂ in the gas will react with H₂S and CO unless the reactor is operated at sulfur sub-dewpoint temperature. During previous testing, when operating at 260 – 280 °F instead of over 400 °F we have observed:

- Higher percent H₂S conversion to sulfur;
- Much lower COS formation, usually no more COS is formed than is observed in the blank test; and
- No visible carbon deposition on the catalyst or the inside walls of the reactor.

However when operating at sulfur sub-dewpoint temperature (260 -280 °F), the catalyst appears to accumulate sulfur rather than allowing the formed sulfur to leave the catalyst surface or “drip off”. Therefore the sulfur will need to be removed from the catalyst, i.e., the catalyst must be regenerated. This condition causes the need for operating the DO process in a multiple bed configuration where one reactor is in service operating at sulfur sub-dewpoint conditions and a second reactor is operating at elevated temperature with clean gas at atmospheric pressure to regenerate the catalyst and vaporize the sulfur from the catalyst.

Even though previous work indicated that elevated temperature was not a good approach for operating in coal gasification syngas, we decided that we should verify that result and that we should try an intermediate temperature such as 300 °F. During the long term tests, H₂S conversion to sulfur decreases overtime presumably as the catalyst surface and pores become filled and plugged with condensed, molten sulfur. The operating temperature is above the freezing point but below the dewpoint of sulfur. Therefore in one test with Catalyst D performed on May 20, 2008 in a long term test, we raised the temperature to 460 °F in an attempt to heat the catalyst and evolve the formed sulfur, hopefully without forming COS. That test of high temperature operating condition was not successful, COS was formed; this result is part of the long term testing section of Task 1.3 but is repeated below as part of this operating condition optimization task.

As part of this task of optimizing operating conditions, we tested higher temperature and higher O₂ / H₂S ratio using Catalysts G, D and C. The detailed results are presented

below and are included in Table 51 following the Subtask 2.5 section. A brief summary of the results include:

- The best operating temperature range was 255 – 280 °F.
- O₂ / H₂S ratio of 0.6 to 0.8 seems to be sufficient although we did not optimize this sufficiently by testing lower ratios such as 0.4 – 0.5.
- The catalyst operating at sulfur sub-dewpoint temperature will accumulate sulfur and will require regeneration, i.e., DO reactors cannot be operated continuously at sulfur sub-dewpoint temperature.

Catalyst G, at increased O₂ and temperature – Catalyst G was tested under slightly different operating conditions that included higher O₂ / H₂S ratio and higher temperature. In previous tests of Catalyst G, the O₂ / H₂S ratio ranged from 0.6 to 0.8, while in this test the ratio was 0.9. In previous tests the temperature was held in the range of 260-270 °F while for this test the temperature ranged from 280 – 300 °F. The data are shown below in Figure 50.

May 7 2008, Catalyst G Test

Figure 50 Inlet and outlet gas composition of the CTU during the test of Catalyst G

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 2.5	Achieved stable gas conditions	
2.5 – 3.9		dry inlet gas
3.9 – 5.1		dry outlet gas
5.1 – 6.2		wet outlet gas
6.2 – 7.3		wet inlet gas
7.3	Reactor temp raised to 300 °F	
7.3 – 9.3		wet outlet gas
9.3 10.1		wet inlet gas

The reactor bed volume was 51 cc. The space velocity at was 1070 Hr⁻¹ at the 270 °F operating temperature and 1106 Hr⁻¹ at the 300 °F operating temperature. The operating pressure was nominally 400 psig. The results are included in Table 51, which follows the section discussing Subtask 2.5 below.

In dry gas (from 0 – 5.1 hours ET) an average of 49% of the H₂S was converted into sulfur. However, the H₂S in the outlet gas seemed to be steadily increasing over the time period, indicating that the conversion rate was slowly decreasing, thus slowly losing catalytic activity. After water addition was started, a step change in H₂S conversion was observed with an average conversion rate of 43%, for the period with water addition. At 7.3 hours ET, the reactor temperature was raised from approximately 270 °F to 300 °F. The increase in temperature was done to observe the effect on net H₂S conversion to sulfur. The temperature increase caused an increase in the H₂S conversion to sulfur, raising it to 46%. H₂S overall conversion increased to near 50%, however some of the H₂S was converted to COS instead of sulfur, thus reducing the conversion rate of H₂S to sulfur down to 46%. In the results from this test and in previous tests, a correlation was noted between H₂S conversion and temperature changes during the experiment. As the temperature is increased, the H₂S conversion increases, unfortunately, as the temperature is increased more of the H₂S is converted into COS. Overall, when operating at sub-dewpoint conditions, the catalyst activity seems to degrade overtime, and perturbations such as raising the temperature (while remaining sub-dewpoint), seem to temporarily increase H₂S conversion, but only temporarily, as the conversion rate continues to decrease over time. Increased oxygen in the inlet gas did not result in increased H₂S conversion to sulfur, nor did it result in increased COS production. Both of these results of increased oxygen in the inlet gas are important in optimizing the O₂ / H₂S ratio; currently that optimized ratio appears to be in the range of 0.6 to 0.7.

Catalyst D, at increased O₂ and temperature – An experimental catalyst prepared by an outside laboratory, was tested for a second time at higher reactor temperature and O₂ addition rate. The data are shown below in Figure 51.

In previous test of this catalyst, the temperature was in the range of 270-280 °F while for this test the temperature ranged from 300 - 315 °F. In the previous test the O₂ / H₂S ratio was in the range of 0.62 – 0.65 and for this test the ratio was 0.75 – 0.79.

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 2.5	Achieved stable gas conditions	
2.5 – 3.7		dry inlet gas
3.7 – 5.0		dry outlet gas
5.0 – 5.9		wet inlet gas
5.9 – 6.8		wet outlet gas

The reactor bed volume was 59 cc. The space velocity at was approximately 970 Hr⁻¹. The operating pressure was nominally 400 psig. During the test, the temperature fluctuated between 270 and 320 °F with the average being about 300 °F; there is no explanation for this problem at this time. The results are included in Table 51, which follows the section discussing Subtask 2.5 below.

May 8 2008, Catalyst D Test

Figure 51 Inlet and outlet gas composition of the CTU during the test of Catalyst D

The results from this test are somewhat suspect because they agree neither with a previous test nor a subsequent test that will be described later in this report. However, the results for this test will be summarized in the event that in the future a reason for this discrepancy can be found. During this test, without water in the inlet gas, the H₂S conversion to sulfur was 5% due largely to the formation of 500 ppmv COS which is equivalent to converting 24% of the inlet H₂S into COS rather than into sulfur. After water was added to the inlet gas only 4% of the inlet H₂S was converted into COS resulting in about 20% of the inlet H₂S being converted into sulfur. The operating temperature for this test was 30 – 40 °F higher than the operating temperature of the previous test of this catalyst and the O₂ / H₂S ratio was also about 0.2 higher for this test. These operating condition changes were expected to improve the conversion of H₂S into sulfur and instead they had no effect or perhaps a negative effect. Again, these results were contradicted by a previous test and a test that will be described later in this report. Reviewing the results from other tests for Catalyst D that are found in Table 51, H₂S conversions average about 40 – 50% which all contradict the results of this test. In addition, the graphs of data for Catalyst D show H₂S conversion results that range from 90% conversion down to 40% before the catalyst is regenerated during long term testing. Again, that data contradicts the results from this test, therefore the results from this test should be considered suspect.

Catalyst D, 460 °F – An experimental catalyst prepared by an outside laboratory, was tested for a third time at higher reactor temperature after 20 hours of long term testing in an attempt to regenerate the catalyst. The data are shown below in Figure 52.

May 19-21, 2008, Long Term Test of Catalyst D, Above Sulfur Dewpoint

Figure 52 Inlet and outlet gas composition of the CTU during the above sulfur dewpoint test of regenerating the Catalyst D

Below is a description of the timing of gas composition measurements or other events for only the high temperature portion of the test:

Elapsed Time of Test, hr	Event	Stream Measured
31.7	Raised reactor temp to 460 °F	
31.7 – 34.0	Achieved stable conditions	wet outlet gas
34.0 – 34.9		wet outlet gas
34.9 – 35.5		wet inlet gas
35.5 – 37.2		wet outlet gas
37.2 – 37.8		wet inlet gas
37.8 – 39.4		wet outlet gas
39.4 – 40.0		wet inlet gas
40.0 – 41.4		wet outlet gas
41.4	Stopped water addition due to leak	
41.4 – 42.4		dry inlet gas
42.4 – 43.2		dry outlet gas
43.2 – 43.5		dry inlet gas
43.5 – 45.2		dry outlet gas
45.2	Start water addition	
45.2 – 46.4		wet outlet gas

The reactor bed volume was 59 cc. The space velocity ranged from 940 to 950 Hr⁻¹, at the sulfur sub-dewpoint operating conditions and approximately 1150 Hr⁻¹ at the above sulfur dewpoint conditions. The operating pressure was nominally 400 psig. The results are included in Table 51, which follows the section discussing Subtask 2.5 below.

The results from phase 1 of the test, i.e., the sulfur sub-dewpoint operations, indicate that the catalyst converts 90% of the H₂S into sulfur without water added to the gas, and 80% with water added to the gas for the first 10 hours of the test. However, overtime the catalyst activity seems to decrease, e.g., the average H₂S converted into sulfur in the 15 – 22 hours ET time period is 30%. This steady decrease in catalyst activity towards H₂S conversion into sulfur at sulfur sub-dewpoint conditions confirms the need to investigate

a multiple bed operation under which one catalyst reactor is in service and the other is being regenerated.

The results from phase 2 of the test, i.e., the above sulfur dewpoint operations, indicate that the catalyst converts an average of 25% of the H_2S into sulfur. This is calculated using the data from 39 – 42 hours ET as shown in Figure 52. This time period was chosen because the COS content measured in the outlet gas was continually decreasing. Unfortunately the COS concentration in the outlet gas did not reach a steady state before the end of the test. Further complicating the data gathered at this time period was the leak in the water system causing the need to stop water addition. This catalyst test demonstrated that the catalyst could be regenerated, that a multiple bed configuration was probably required for sulfur sub-dewpoint DO reactor operation in coal gasification syngas streams and set the conditions for the long term testing that will be described in the Task 1.3 section.

Two minor modifications were made to the CTU during July 2008. The first was the addition of longer tubing for the gas pre-heater section. The added tubing length should increase the efficiency of the pre-heater to better pre-heat the gas and more efficiently vaporize the added water. The second modification was a larger sulfur knockout vessel. This vessel was no longer heated so that the sulfur solidified and remained in the vessel, thus preventing the problem of solid sulfur accumulation in the downstream tubing. During regeneration of the catalyst, the sulfur knockout will be opened and the molten sulfur will be drained from the system. The operating conditions and procedure for the long term tests of multiple bed configuration will be described in the Task 1.3 section below.

Subtask 2.4.3 Long Term Testing

Catalyst G, 30 hour test – Catalyst G was tested for an extended operating period of 30 hours; for 24.5 hours H_2S and air were passed across the catalyst. The O_2 / H_2S ratio ranged from 0.75 to 0.8 during the test and the temperature typically ranged from 300 – 312 °F. The data are shown below in Figure 53.

May 12-13, 2008, Long Term Test of Catalyst G

Figure 53 Inlet and outlet gas composition of the CTU during the 30 hour test of Catalyst G

Below is a description of the timing of gas composition measurements or other events:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 4.1	Achieved stable gas conditions	
4.1 – 5.4		dry inlet gas
5.4 – 5.9		dry outlet gas
5.9 – 7.6		dry inlet gas
7.6 – 8.8		dry outlet gas
8.8 – 9.5		dry inlet gas
9.5 – 10.0		dry outlet gas
10.0	Water addition started	
10.0 – 11.1		wet outlet gas
11.1 – 11.9		wet inlet gas
11.9 – 13.5		wet outlet gas
13.5 – 14.7		wet inlet gas
14.7 – 16.9		wet outlet gas
16.9 – 18.0		wet inlet gas
17.8	Change out of empty H ₂ S and CO ₂ supply cylinders causing upset flow conditions	
18.0 – 18.5		wet outlet gas
18.5 – 20.4		wet inlet gas
20.4 – 22.2		wet outlet gas
22.2 – 23.0		wet inlet gas
23.0 - 23.7		wet outlet gas
23.7	Shutdown, water buildup in trap, possible sulfur plugging	

Elapsed Time of Test, hr	Event	Stream Measured
25.0	Restart gas flow, no H ₂ S or air	
25.5 – 26.6		dry inlet gas
26.6 – 27.8		dry outlet gas
27.8 – 28.5		wet inlet gas
28.5 – 29.8		wet outlet gas
29.8 – 30.1		wet inlet gas
30.1	Shutdown due to gas flow problems	

- 30.1 hours of elapsed time, shutdown due to gas flow problems, pressure drop across the unit is rising, had to continually raise the supply gas pressure to the Mass Flow Controllers (MFC) to get gas to flow through those controllers – indicated increasing pressure drop across system and further indicated plugging somewhere in the system
- After shutdown of air and H₂S, performed some tests to identify where the plug was – the plug was in the reactor. Indicated catalyst bed plugging.

The reactor bed volume was 54 cc. The space velocity ranged from 1080 to 1120 Hr⁻¹. The operating pressure was nominally 400 psig. The results are included in Table 51, which follows section Subtask 2.5 below.

During the run there were 3 operating upset conditions, one at 17.8 - 20 hours ET a second at 23.7 to 25.0 hours ET and a third that caused the test to be shutdown. The first process upset at 17.8 hours ET was due to changing out gas cylinders, replacing used cylinders with full ones. The second process upset at 23.7 hours ET was due to limited gas flow through the Mass Flow Controllers (MFC) that are used to meter each gas into a manifold. At the time of the shutdown the problem was thought to be limited to a full water knock out container, once that container was drained, gas flow resumed easily. At the end of the test, limited gas flow through the MFC was again a problem, so we stopped the test to investigate the location of the plug. The plugged area was discovered to be in the reactor. The most likely source of the plug is buildup of sulfur on the catalyst during the sub-dewpoint operation. As further support for that theory, very little < 5 grams of sulfur has ever been removed from the sulfur knockout container following the reactor, and very little sulfur, <10 grams, has been found in the tubing and valves downstream of the sulfur knockout container. This one test should have produced about 30 grams. So while this one test should have produced about 30 grams of sulfur, only about 15 grams of sulfur can be accounted for since the start of testing. While this catalyst was weighed at the start of the test, it was not weighed at the end of the test. However, the catalyst that was used on May 7, 2008 was weighed before and after the run. During the course of that test, the catalyst gain about 24 grams in mass, no sulfur was found in the sulfur knockout container, and about 16 grams of sulfur should have

been produced during that run. The mass gain of the catalyst more than accounts for the mass of sulfur that may have been formed during that test on May 7, 2008.

The results and observations from this test, the test from May 7, 2008 and the results of the next test of Catalyst D on May 19, 2008 indicate that the sulfur remains on the catalyst during sub-dewpoint operation. Hence, perhaps the process will require a catalyst regeneration step during which the catalyst will be heated to drive off the accumulated sulfur.

Catalyst D, 46 hour test – An experimental catalyst prepared by an outside laboratory, was tested for an extended operating period of 46 hours; for 41 hours H₂S and air were passed across the catalyst. The O₂ / H₂S ratio ranged from 0.7 to 0.8 during the test. The test was conducted in 2 phases. The first phase was reactor operation at sulfur sub-dewpoint temperature (< 320 °F) that lasted from startup until 22 hours ET and the second phase was above dewpoint (approx. 460 °F) operation lasting from about 31 to 46 hours ET. From 22 to 27 hours ET there was a process upset condition and data from that period has been excluded from the results discussions and results table. From 27 to 31 hours ET sulfur sub-dewpoint operating conditions were re-established. The temperature data was established from manual recordings in the notebook because the data file containing the temperature and pressure data for this test could not be found on the computer hard drive at the end of the test. A graph of all of the test results is shown below in Figure 54. Since this test was divided into 2 phases, 2 additional figures were created showing each phase. Phase 1, operation at sulfur sub-dewpoint conditions is shown in Figure 55, and phase 2, operation at above sulfur dewpoint conditions in shown in Figure 56.

This test was separated into 2 phases because after about 22 hours of operation it was obvious that the catalyst could not be commercially operated under the sulfur sub-dewpoint conditions for a continuous or “near-infinite” time period. The H₂S conversion into sulfur had started at near 90% but decreased to 30% over the course of the first 22 hours of the test. After 22 hours ET and after the water addition problem was solved at 27 hours ET, a decision was made to elevate the operating temperature to above sulfur dewpoint to observe if the catalyst activity could be regenerated. Phase 2 is that test of catalyst regeneration.

May 19-21, 2008, Long Term Test of Catalyst D

Figure 54 Inlet and outlet gas composition of the CTU during the 46 hour test of Catalyst D

May 19-21, 2008, Long Term Test of Catalyst D, Sulfur Sub-dewpoint

Figure 55 Inlet and outlet gas composition of the CTU during the sulfur sub-dewpoint operation test of Catalyst D

May 19-21, 2008, Long Term Test of Catalyst D, Above Sulfur Dewpoint

Figure 56 Inlet and outlet gas composition of the CTU during the above sulfur dewpoint test of regenerating the Catalyst D

Below is a description of the timing of gas composition measurements or other events:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 5.1	Achieved stable gas conditions	
5.1 – 5.7		dry inlet gas
5.7 – 6.7		dry outlet gas
6.7	Water addition started	
6.7 – 7.9		wet outlet gas
7.9 – 8.7		wet inlet gas
8.7 – 9.9		wet outlet gas
8.8 – 10.6		wet inlet gas
10.6 – 12.3		wet outlet gas
12.3 – 13.0		wet inlet gas
13.0 – 14.8		wet outlet gas
14.8 – 15.5		wet inlet gas
15.5 – 16.7		wet outlet gas
16.7 – 17.7		wet inlet gas
17.7 – 18.9		wet outlet gas
18.9 – 19.9		wet inlet gas
19.9 – 21.0		wet outlet gas
21.0 – 22.1		wet inlet gas
22.1 – 26.2		wet outlet gas
23.2	Water addition problems discovered	
26.2	Stopped water addition, emptied water knockout container	

Elapsed Time of Test, hr	Event	Stream Measured
26.2 – 28.8		dry outlet gas
28.8 – 29.5		dry inlet gas
29.5 – 30.7		dry outlet gas
30.7	Water addition started	
30.7 – 31.7		wet outlet gas
31.7	Raised temp to 460 °F	
31.7 – 34.0	Achieved stabile conditions	
34.0 – 34.9		wet outlet gas
34.9 – 35.5		wet inlet gas
35.5 – 37.2		wet outlet gas
37.2 – 37.8		wet inlet gas
37.8 – 39.4		wet outlet gas
39.4 – 40.0		wet inlet gas
40.0 – 41.4		wet outlet gas
41.4	Stopped water addition due to leak	
41.4 – 42.4		dry inlet gas
42.4 – 43.2		dry outlet gas
43.2 – 43.5		dry inlet gas
43.5 – 45.2		dry outlet gas
45.2	Restart water addition	
45.2 – 46.4		wet outlet gas
46.4	Shutdown	

The reactor bed volume was 59 cc. The space velocity ranged from 940 to 950 Hr^{-1} , at the sulfur sub-dewpoint operating conditions and approximately 1150 Hr^{-1} at the above sulfur dewpoint conditions. The operating pressure was nominally 400 psig. The results are included in Table 51, which follows section describing Subtask 2.5 below.

The results from phase 1 of the test, i.e., the sulfur sub-dewpoint operations, indicate that the catalyst converts 90% of the H_2S into sulfur without water added to the gas, and 80% with water added to the gas for the first 10 hours of the test. However, overtime the catalyst activity seems to decrease, e.g., the average H_2S converted into sulfur in the 15 – 22 hours ET time period is 30%. This steady decrease in catalyst activity towards H_2S conversion into sulfur at sulfur sub-dewpoint conditions confirms the need to investigate a multiple bed configuration operation under which one catalyst reactor is in service and the other is being regenerated.

The results from phase 2 of the test, i.e., the above sulfur dewpoint operations, indicate that the catalyst converts an average of 25% of the H_2S into sulfur. This is calculated using the data from 39 – 42 hours ET. This time period was chosen because the COS content measured in the outlet gas was continually decreasing. Unfortunately the COS concentration in the outlet gas did not reach a steady state before the end of the test. Further complicating the data gathered at this time period was the leak in the water system causing the need to stop water addition. The COS concentration appears to be steadily decreasing near the end of this test which indicates that perhaps this catalyst should be retested at above sulfur dewpoint conditions throughout the test period.

Table 47 Simulation of Multiple Bed Operation – Test Conditions for Long Term Testing

H₂S Conversion Portion of the Cycle (converting H ₂ S to sulfur and absorbing sulfur onto the catalyst at sulfur sub-dewpoint temperature, 260 °F)				
Pressure	400 psig		H₂	20%
Temperature	255-280 °F		CO	40%
O₂/H₂S ratio	0.6 – 0.8		CO₂	15%
SV (actual)	(target) 1000 Hr ⁻¹		H₂O	5%
			H₂S	2000 ppmv
Catalyst Regeneration Portion of the Cycle (vaporizing the sulfur and desorbing it from the catalyst at 600 °F)				
Pressure	Approx. 0 psig		H₂	0%
Temperature	580 -620 °F		CO	0%
O₂/H₂S ratio	na		CO₂	0%
SV (actual)	na		H₂O	0%
			H₂S	0 ppmv
			N₂	100%

The general procedure for simulation of multiple bed operation for long term testing is as follows:

- Achieve pressure of 400 psig and gas flow rates for required SV in units of hour⁻¹ (actual)
- Heat the CTU with N₂ flowing
- Add H₂, CO and CO₂
- Add water to the inlet gas
- Add H₂S and O₂ to the required composition
- Adjust the temperature for operating at sulfur sub-dewpoint temperature (260 – 300 °F)
- Measure the H₂S conversion
- Measure any COS and/or SO₂ formation
- Measure any loss of CO and/or H₂
- Measure the inlet and outlet gas composition for 6 hours
- Stop H₂S and O₂ addition

- Stop H₂, CO, CO₂ and water addition
- Continue flowing N₂ (only N₂ gas is flowing)
- Depressurize the CTU to atmospheric pressure
- Raise the temperature to regeneration conditions (approximately 600 °F)
- Open the sulfur KO vessel drain valve
- Turn on the sulfur KO vessel heat trace and control vessel surface temp at 270 - 300 °F
- Allow the N₂ gas and molten sulfur to flow out of the sulfur KO vessel drain valve
- Operate this regeneration condition for 4 hours (approximately 1 hour will have already elapsed in getting to this point in the regeneration cycle – for 5 hours total)
- After 5 hours after the start of the regeneration, lower the temperatures and re-establish the sulfur sub-dewpoint operating conditions (usual takes about 1 hour), repeat from the first step above

Catalyst C – Catalyst C was tested in a long term test where H₂S was converted to sulfur and adsorbed onto the catalyst at sulfur sub-dewpoint temperature for 6 hours, followed by high temperature regeneration (for approximately 6 hours) at 500 °F for the first cycle and 600 °F in the subsequent 2 additional cycles.

The data for the first cycle is shown below in Figure 57, the second cycle in Figure 58 and the third cycle in Figure 59.

August 18-21, 2008, Catalyst C Test

Figure 57 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst C long term test

August 18-21, 2008, Catalyst C Test

Figure 58 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst C long term test

August 18-21, 2008, Catalyst C Test

Figure 59 Inlet and outlet gas composition of the CTU during the third cycle of the Catalyst C long term test

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 9.3	Tested blank levels (without catalyst). Achieved stable gas conditions	
9.3 – 10.3		wet inlet gas
10.3 – 11.4		wet outlet gas
11.4 – 11.8	Process upset, leakage	
11.8 – 12.1		wet inlet gas
12.1 – 12.8	Process upset, outlet gas scrubber plugged	
12.8 – 13.0		wet inlet gas
13.00 – 13.8		wet outlet gas
13.8 – 14.1	Process upset, leakage	
14.1 – 14.5		wet inlet gas
14.5 – 15.3		wet outlet gas
15.3 – 21.4	Regeneration cycle #1 at 500 °F	
21.4 – 22.1		wet inlet gas
22.1 – 24.9		wet outlet gas
24.9 – 25.5	Process upset, outlet gas scrubber plugged	
25.5 – 27.1		wet outlet gas
27.1 – 27.8		wet inlet gas
27.8 – 33.5	Regeneration cycle #2 at 600 °F	
33.5 – 52.7	Process upset, sulfur plugging in the gas tubes and pressure control valve	
52.7 – 53.9		wet inlet gas
53.9 – 56.6		wet outlet gas

Elapsed Time of Test, hr	Event	Stream Measured
56.6 – 57.7	Process upset, changing gas supply cylinders	
57.7 – 58.1		wet inlet gas
58.1 – 58.8		wet outlet gas
58.8 – 64.6	Regeneration cycle #3 at 600 °F	
64.6 – 66.5	Tried to improve H ₂ S conversion at higher temperature, approximately 400 °F	wet inlet gas
66.5 – 68.2		wet outlet gas
68.2	Stop test, insufficient H ₂ S conversion to sulfur to warrant continuing	

The reactor bed volume was 60 cc. The space velocity at average actual reactor operating conditions was 740 Hr⁻¹ during the first two cycles and 775 Hr⁻¹ during the third. The average reactor temperature was 280 °F for the first two cycles and 315 °F for the third. The operating pressure was approximately 400 psig. The regeneration temperature was 500 °F for the first cycle and 600 °F for the second and third cycles.

During the long-term test of Catalyst C approximately 18 – 30% of the inlet H₂S was converted to sulfur during each of the three cycles that were performed. The results are included in Table 51, which follows section 1.4 below. The data from these results do not agree with the results gathered during the evaluation catalyst testing of Catalyst C. The evaluation test results showed approximately 50% conversion of H₂S into sulfur, whereas the long term test results show 18 – 30% conversion of H₂S into sulfur. Currently we can find no explanation for this discrepancy. We stopped the long term test of Catalyst C due to the low conversion rate just mentioned and due to the lack of agreement with previous evaluation test results. We decided to test Catalyst D, which showed the highest H₂S to sulfur conversion during the evaluation tests.

Catalyst D – Catalyst D was tested in a long term test where during each cycle H₂S was converted to sulfur and adsorbed onto the catalyst at sulfur sub-dewpoint temperature for 6 hours, followed by high temperature regeneration at 600 °F; two cycles were performed. Catalyst D will be retested in a long term test scheduled for September.

The data for the first cycle is shown below in Figure 60 and the second cycle in Figure 61.

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
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Elapsed Time of Test, hr	Event	Stream Measured
0 – 0.77	Achieved stable gas conditions	
0.77 – 1.6		wet inlet gas
1.6 – 3.5		wet outlet gas
3.5 – 4.3		wet inlet gas
4.3 – 6.9		wet outlet gas
6.9 – 12.1	Regeneration cycle #1 at 600 °F	
12.1 - 12.7		wet inlet gas
12.7 – 14.1		wet outlet gas
14.1 – 14.6		wet inlet gas
14.6 – 16.2		wet outlet gas
16.2 – 16.7		wet inlet gas
16.7 – 18.3		wet outlet gas
18.3 – 26.2	Regeneration cycle #2 at 600 °F Repaired a leak	
26.2 – 27.4		wet inlet gas
27.4 – 30.7		wet outlet gas
30.8	Stopped Test

Figure 60 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst D long term test

Figure 61 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst D long term test

The reactor bed volume was 60 cc. The space velocity at average actual reactor operating conditions was 745 Hr^{-1} . The average reactor temperature was 284 °F for the first cycle and 275 °F for the second. The operating pressure was approximately 400 psig. The regeneration temperature was approximately 600 °F.

The average H_2S conversion into sulfur during the first cycle was 56% and during the second cycle was 44%. During the regeneration portion of the first cycle, the temperature of the catalyst bed was maintained over 500 °F for 3.2 hours and 2.6 hours of that time was over 600 °F. During the regeneration portion of the second cycle, the temperature of the catalyst bed was maintained over 500 °F for 5 hours and 1 hour of that time was over 600 °F. After the second regeneration, the unit was restarted for a third cycle to measure the level of H_2S conversion after the second regeneration. At the start of the third cycle, 90% of the inlet H_2S was converted to sulfur; after 3 hours into the third cycle, the H_2S conversion rate declined to about 60%. This information indicates that a longer high temperature regeneration cycle (over 500 °F) may improve the H_2S conversion for the cycle immediately following.

H_2S conversion into sulfur is highest when using Catalyst D in the reactor, however, the conversion rate also decreases the fastest. During cycle 1, H_2S conversion started at 79% and decreased down to 46% after 6 hours. During cycle 2, H_2S conversion started at 69% and decreased down to 30% after 6 hours. During cycle 3, H_2S conversion started at 93% and decreased down to 63% after 3 hours. The manufacturer will be contacted to determine if the active component of the catalyst composition can be increased to help effect a longer high H_2S conversion rate. In addition, the amount of catalyst packed into the bed could be increased, effectively reducing the space velocity, which in turn has the negative impact of increasing the bed pressure drop and increasing the overall catalyst expense. Alternately, perhaps the cycle time could be shortened to 3 hours and the number of catalyst beds increased to compensate for the shorter the conversion/adsorption cycle compared to the 6 hour regeneration cycle. This could require up to 4 catalyst beds for the process, which also is a negative impact on expense. This concern of how to increase the high H_2S conversion time of Catalyst D will continue to be explored after this project is complete.

Catalyst D – Catalyst D was tested in a long term test where H_2S was converted to sulfur and adsorbed onto the catalyst at sulfur sub-dewpoint temperature for 6 hours, followed by high temperature regeneration (for approximately 6 hours) at 600 °F.

The data for the first cycle is shown below in Figure 62, the second cycle in Figure 63 and so on through the ninth cycle in Figure 70.

Figure 62 Inlet and outlet gas composition of the CTU during the first cycle of the Catalyst D long term test

September 22 - 26, 20088, Catalyst D Long Term Test

Figure 63 Inlet and outlet gas composition of the CTU during the second cycle of the Catalyst D long term test

Figure 64 Inlet and outlet gas composition of the CTU during the third cycle of the Catalyst D long term test

Figure 65 Inlet and outlet gas composition of the CTU during the fourth cycle of the Catalyst D long term test

Figure 66 Inlet and outlet gas composition of the CTU during the fifth cycle of the Catalyst D long term test

Figure 67 Inlet and outlet gas composition of the CTU during the sixth cycle of the Catalyst D long term test

Figure 68 Inlet and outlet gas composition of the CTU during the seventh cycle of the Catalyst D long term test

Figure 69 Inlet and outlet gas composition of the CTU during the eighth cycle of the Catalyst D long term test

Figure 70 Inlet and outlet gas composition of the CTU during the ninth cycle of the Catalyst D long term test

Catalyst D was tested in a long term test where during each cycle H₂S was converted to sulfur and adsorbed onto the catalyst at sulfur sub-dewpoint temperature for 6 hours, followed by high temperature regeneration at 600 °F. At the high temperature, the pressure was also reduced from 400 psig down to atmospheric (as described above in the procedure section), the valve at the bottom of the sulfur knockout pot was left open with nitrogen flowing. As time passed, the sulfur slowly dripped from the open valve during regeneration. After 2 hours or so, the sulfur stopped flowing, however regeneration was continued for about 4 - 5 hours total at 600 °F. This procedure was repeated for each cycle.

The reactor bed volume was 60 cc. The space velocity at average actual reactor operating conditions ranged from 725 to 750 Hr⁻¹, depending upon the temperature. The average reactor temperature ranged from 265 to 280 °F for each cycle, except for the last cycle, the 9th cycle, where some temperature increase and decrease effects were investigated. The operating pressure was approximately 400 psig. The regeneration temperature was approximately 600 °F.

Shown above in Figure 62 through Figure 70, the H₂S conversion at the beginning of each cycle is near 90% but quickly degrades and near the end of each cycle is below 50% or even below 40%. The beginning, final and average conversions for each cycle are shown in Table 48 below.

Table 48 Beginning, Final and Average H₂S Conversions for Each Cycle

Cycle Number	Beginning H ₂ S Conversion (%)	Final H ₂ S Conversion (%)	Average H ₂ S Conversion (%)
1	99	44	79
2	89	42	56
3	88	25	60
4	92	38	52
5	89	39	58
6	90	30	55
7	50	40	40
8	86	12	43

Catalyst D shows significant promise for use in controlling H₂S in syngas streams in a multiple bed configuration. However, as noted in this long term test, the catalyst activity slowly degraded throughout the week as evidenced in the average H₂S conversion and inability to fully regenerate the catalyst after each cycle. The catalyst vendor was consulted and the used catalyst was shipped back to him. The catalyst vendor was able to analyze the spent catalyst with XRD (X-ray Diffraction) and XPS (X-ray Photoelectron Spectroscopy) to determine that the catalyst surface was poisoned with bonded sulfur. However, after heating the catalyst to 572 °F in a flowing air stream for 2 hours, he re-

analyzed the sample and found no difference between air-regenerated catalyst and a sample of fresh catalyst.

In conclusion, it is possible that after regeneration in a flowing nitrogen stream at 600 °F, we could add a step where for 1 to 2 hours we could flow air across the catalyst at 600 °F to complete the regeneration of the catalyst. In past literature searching I have found studies that have used hot air streams across a catalyst of this nature to generate SO₂ from a sulfur saturated catalyst, so we would want to test this thoroughly, i.e., we need to test air regeneration, nitrogen regeneration first, followed by air regeneration, and vary the time that the nitrogen and air are flowed across the catalyst. The tests would be to minimize the amount of SO₂ generated by the catalyst regeneration step. One very important point is that CrystaSulf, which is the polishing unit that follows the direct oxidation unit in CrystaSulf-DO, readily absorbs SO₂ and reacts SO₂ with H₂S in a liquid phase Claus reaction. So the formed SO₂ could be utilized, i.e., any SO₂ formation is not a problem.

Subtask 2.4.4 Vapor-Liquid Equilibria Experiments.

The effort to gather the data for Vapor-Liquid Equilibria (VLE) of CO and H₂ in CrystaSulf solution was performed by GTI. The objective of the VLE testing was to determine the solubility of each gas in the three individual CrystaSulf solution components (RSC-103, RSC-202 and RSC-312) and in the blended CrystaSulf solution at temperatures of 100, 125 and 150 °F and pressures of 300, 600 and 900 psig. The test approach is to use a high-pressure VLE test cell. Each CrystaSulf component or the base CrystaSulf solution, and test gas (H₂ or CO) will be introduced into the cell and mixed while the temperature and pressure are controlled at the desired conditions. The mixer will be turned off to allow the cell contents to settle and then a small sample of each phase (liquid or gas) will be removed from the cell and analyzed for the CO or H₂, RSC-103, RSC-202 and RSC-312 using a GC. The GC results will indicate the solubility of each component in each phase, e.g., the amount of CO gas in the liquid phase and the amount of CrystaSulf solution component in the gas phase.

CrystaSulf solution will be prepared using the same composition of each CrystaSulf reagent as is typical of a new plant and to that mixture we will add 0.5 M sulfur, 0.05 M water, 0.02 M H₂SO₄ and 0.03 M SO₂. This mixture will be called the base CrystaSulf solution composition.

Solubility of Hydrogen and Carbon Monoxide in blended CrystaSulf Solution and in the individual CrystaSulf Solution Components

VLE Summary

This Section includes Henry's law constants for the solubility of H₂ and CO in CrystaSulf solvents, solubility plots and calculation procedure, and comparison of gas solubility in CrystaSulf solvents with some organic solvents and water.

VLE Solubility Calculation

The solubility is calculated from the initial and final gas conditions in the VLE head space volume. The solvent vapor pressure is neglected in the estimation of the gas solubility, i.e., the vapor phase is assumed to consist of a single component only (H₂ or CO). Under these conditions the gas solubility can be easily estimated as

$$S_g = \frac{n_i - n_f}{V_L} = \frac{V_G}{V_L R} \left[\left(\frac{P_i}{z_i T_i} \right)_i - \left(\frac{P_f}{z_f T_f} \right)_f \right]$$

where,

S_g – Gas solubility (M)

n_i – initial number of moles input (mol)

n_f – final number of moles at equilibrium (mol)

V_L – Volume of solvent charged into the VLE cell (L)

V_G – Volume of gas in the VLE head space (L)

P – Pressure in the VLE head space (psi)

T – Gas temperature (K)

Z – Compressibility factor

R – Universal Gas Constant (= 1.20542 L psi /mol K)

Henry's Law Constant

The mole based Henry's law constant (H_n) can be written as

$$H_n = \frac{(P_f / z_f T_f)}{\left((P_i / z_i T_i) - (P_f / z_f T_f) \right)} \frac{V_L}{V_G} R T_f$$

The compressibility factor for the gases (H_2 or CO) is calculated using REFPROP (NIST, Standard Reference Data Program).

Using the expression for solubility in the equation for Henry's law constant H_n ,

$$H_n = \frac{(P_f / z_f)}{S_g}$$

The Henry's law constant is the slope of pressure versus gas solubility.

Solubility of Hydrogen in CrystaSulf Solution Components

The Henry's law constants for the solubility of hydrogen in CrystaSulf solution components are given in Table 49.

Table 49 Solubility of Hydrogen in CrystaSulf Solution Components and in CrystaSulf Solution, Henry's law constants

Solvent	Henry's Law Constant (m ³ kPa/mol)		
	100 °F	125 °F	150 °F
RSC-103	18.1	17.5	17.5
RSC-202	27.7	25.1	24.8
RSC-312	16.4	15.0	15.1
CrystaSulf	23.8	22.3	23.0

* Experimental data: Pressure range (300 – 900 psi)

Solubility Plots of Hydrogen in CrystaSulf Solution Components

Figure 71 Solubility of hydrogen in RSC-103 solvent

Figure 72 Solubility of hydrogen in RSC-202 solvent

Figure 73 Solubility of hydrogen in RSC-312 solvent

Figure 74 Solubility of hydrogen in CrystaSulf solution

Solubility of Carbon Monoxide in CrystaTech Solvents

The Henry's law constants for the solubility of carbon monoxide in CrystaTech solvents are given in Table 50.

Table 50 Solubility of Carbon Monoxide in CrystaSulf Solution Components and in CrystaSulf Solution, Henry's law constants

Solvent	Henry's Law Constant (m ³ kPa/mol)		
	100 °F	125 °F	150 °F
RSC-103	20.3	14.6	13.6
RSC-202	11.4	11.5	11.6
RSC-312	9.8	8.9	8.4
CrystaSulf	13.1	11.8	10.5

* Experimental data: Pressure range (300 – 900 psi)

Solubility Plots of Carbon Monoxide in CrystaSulf Solution Components and in CrystaSulf Solution

Figure 75 Solubility of carbon monoxide in RSC-103 solvent

Figure 76 Solubility of carbon monoxide in RSC-202 solvent

Figure 77 Solubility of carbon monoxide in RSC-312 solvent

Figure 78 Solubility of carbon monoxide in CrystaSulf solution

Figure 79 Comparison of Henry's Law Constants (m3kPa/mol) for Hydrogen and Carbon Monoxide for CrystaSulf Solution Components and CrystaSulf Solution with some Organic Solvents and Water.²

Subtask 2.5 Syngas Component Effects on SO₂ Formation.

Catalyst A – Catalyst A was tested at above sulfur dewpoint conditions of 500 °F with an additional increase in temperature to 600 °F near the end of the test. The objective was to convert a portion of the H₂S into sulfur and a portion into SO₂. The full test data are shown below in Figure 80, the data for the test period at 500 °F is shown in Figure 81 and the data for the SO₂ production period at 600 °F is shown in Figure 82.

Below is a description of the timing of gas composition measurements:

Elapsed Time of Test, hr	Event	Stream Measured
0 – 2.9	Achieved stable gas conditions	
2.9 – 3.7		dry inlet gas
3.7 – 5.2		dry outlet gas
5.2 – 6.2		wet outlet gas
6.2 – 7.0		wet inlet gas
7.0 – 8.4		wet outlet gas
8.4	Increased reactor temp to 600 °F	
8.4 – 9.9		wet outlet gas
9.9	Air / H ₂ S ratio increased to range of 1.9 to 2.0 from range of 0.7 – 0.8	
9.9 – 10.5		wet outlet gas
10.5 – 10.9		wet inlet gas
10.9	Stopped adding CO and H ₂ to the inlet gas	
10.9 – 11.7	no CO and H ₂ added - done to verify that SO ₂ could be formed by reaction across this catalyst as expected, but CO and H ₂ interfere with SO ₂ production	wet outlet gas

May 22, 2008, Catalyst A Test

Figure 80 Inlet and outlet gas composition of the CTU during the test of Catalyst A

May 22, 2008, Catalyst A Test, 500 °F

Figure 81 Inlet and outlet gas composition of the CTU during the test of Catalyst A at 500 °F

May 22, 2008, Catalyst A Test, 600 °F, Effect of CO and H₂ on SO₂ Production

Figure 82 Inlet and outlet gas composition of the CTU during the test of Catalyst A at 600 °F without H₂ and CO addition

The reactor bed volume was 61 cc. The space velocity at was approximately 1175 Hr^{-1} at 500°F and 1315 Hr^{-1} at 612°F . The operating pressure was nominally 400 psig. During the test from 7.0 – 7.9 hours ET, the COS concentration in the outlet gas was very high, in the range of 0.35 – 0.38 % and there is no correlation between this suddenly high level of COS and any particular operating condition. The analytical data was rechecked to ensure there were no errors in the COS measurement and there were no errors. There is currently no explanation for the high level of COS at that ET time during the test. The results are included in Table 50, which follows this section.

For this catalyst test, essentially no net sulfur was produced by conversion of H_2S into sulfur. All the H_2S that was converted appeared to be converted into COS and furthermore, since the O_2 was consumed, it probably reacted with H_2 or CO and converted them into H_2O or CO_2 , respectively. The object of this test was to produce some SO_2 as the CrystaSulf unit that is expected to be in the gas path as the polishing unit following this direct oxidation reactor requires SO_2 to react with H_2S in the gas stream for removal of H_2S via the liquid phase Claus reaction. No SO_2 was formed in the syngas, however, after the CO and H_2 were stopped, the SO_2 did form in the outlet gas. Therefore in the presence of N_2 , CO_2 and water vapor, this catalyst will convert H_2S into SO_2 by reaction with O_2 . From this data it could be expected that this catalyst will also converted H_2S into SO_2 by reaction with O_2 with natural gas as the background gas, and this test of Catalyst A in natural gas for H_2S conversion to SO_2 is suggested. Catalyst A is not recommended for further testing in syngas for H_2S conversion to sulfur and/or SO_2 .

Results from tests performed during this project indicated that SO_2 will most likely not be formed in syngas streams using Catalyst A. Therefore further testing of Catalyst A in syngas streams was cancelled.

Table 51 Complete Results from Blank, Catalyst Screening and Long term Catalyst Tests

	Blank Test	Blank Test	Cat. G	Cat. G	Cat. G	Cat. G	Cat. D	Cat. D	Cat. B	Cat. B	Cat. H	Cat. H	Cat. H
Date	3/26/2008	3/26/2008	3/28/2008	3/28/2008	4/1/2008	4/1/2008	4/23/2008	4/23/2008	4/25/2008	4/25/2008	4/30/2008	4/30/2008	4/30/2008
	O2 Addition	O2 Stopped	No water	With water	No water	With water	No water	With water	No water	With water	No water	With water	With water
Pressure, psig			390	392	375	376	392	392	392	393	391	391	391
Temp, F			260	256	251	254	272	277	271	276	292	287	287
Nominal VHSV (hr-1, actual)	na	na	850	841	919	921	935	941	897	901	855	850	850
O2/H2S	0.79	0.00	0.80	0.71	0.64	0.63	0.63	0.64	0.66	0.63	0.90	0.80	0.83
Catalyst	none	none	Catalyst G	Catalyst G	Catalyst G	Catalyst G	Catalyst D	Catalyst D	Catalyst B	Catalyst B	Catalyst H	Catalyst H	Catalyst H
Inlet Gas													
H2S, ppmv	1873	1911	1740	1913	2239	2204	3294	3206	3085	3186	2141	2289	2231
O2, ppmv	1486	0	1389	1350	1438	1397	2086	2067	2039	2018	1919	1835	1847
H2, mole %	17.40	17.79	17.34	17.12	16.51	16.77	14.86	14.83	14.34	14.54	16.09	16.49	16.57
CO, mole %	33.29	35.70	39.02	34.04	39.54	39.60	34.28	34.40	33.07	33.58	36.44	37.70	37.82
CO2 mole %	18.44	18.75	19.06	19.06	17.87	18.11	19.28	19.39	18.40	18.54	16.80	16.98	16.98
H2O, mole % (est. based on H2O feed rate)	5.0	5.0	0.0	7.0	0.0	3.6	0.0	3.1	0.0	5.0	0.0	3.8	3.8
Outlet Gas													
H2S, ppmv	1631	1755	801	1159	867	1069	932	1163	2550	2639	40	48	226
O2, ppmv	1241	0	766	868	655	735	649	741	940	1317	558	445	583
COS, ppmv	137	55	142	144	65	116	182	253	505	108	2218	1543	972
CO2, %	18.4	18.7	19.1	19	18.2	19	19.3	19	18.8	19	17.3	17	17
Sulfur conversion													
H2S converted, ppmv	243	156	938	754	1372	1135	2362	2043	535	548	2102	2241	2005
COS formed by CO+ S, ppmv	137	55	142	144	65	116	182	253	505	108	2218	1543	972
Net sulfur formed (as S), ppmv	106	100	796	610	1307	1019	2180	1790	31	439	none	698	1033
Subdewpoint?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes
H2S conversion, % H2S in feed	13.0%	8.1%	53.9%	39.4%	61.3%	51.5%	71.7%	63.7%	17.3%	17.2%	98.1%	97.9%	89.9%
COS formed by CO+ S, % H2S in feed	7.3%	2.9%	8.2%	7.5%	2.9%	5.3%	5.5%	7.9%	16.4%	3.4%	103.6%	67.4%	43.6%
Net sulfur formed, % of H2S in feed	5.7%	5.2%	45.8%	31.9%	58.4%	46.2%	66.2%	55.8%	1.0%	13.8%	none	30.5%	46.3%
O2 balance (% of inlet gas)													
O2 to H2S + 0.5 O2 -> S + H2O	8.2%	na	33.8%	27.9%	47.7%	40.6%	56.6%	49.4%	13.1%	13.6%	54.7%	61.1%	54.3%
O2 unreacted	83.5%	na	55.2%	64.3%	45.5%	52.6%	31.1%	35.8%	46.1%	65.2%	29.1%	24.2%	31.6%
O2 reacted with CO and H2	8.3%	na	11.1%	7.8%	6.8%	6.8%	12.3%	14.7%	40.8%	21.2%	16.2%	14.7%	14.2%
CO & H2 consumed, % of inlet CO + H2													
CO consumed by CO + S	0.03%	0.01%	0.03%	0.03%	0.01%	0.02%	0.04%	0.05%	0.11%	0.02%	0.42%	0.28%	0.18%
CO and H2 reacted with O2	0.05%	na	0.05%	0.04%	0.03%	0.03%	0.10%	0.12%	0.35%	0.18%	0.12%	0.10%	0.10%
Total CO + H2 Consumed	0.08%	0.01%	0.08%	0.07%	0.05%	0.05%	0.14%	0.18%	0.46%	0.20%	0.54%	0.38%	0.27%

Table 51 Continued

										Catalyst G Extended Run			
										3.3 - 6.4 Hr	6.4 - 13.3 Hr	22 - 24 Hr	
	Cat. I	Cat. I	Cat. F	Cat. F	Cat. G	Cat. G	Inc. Temp	Cat. G	Cat. D	Cat. D	Cat. G	Cat. G	Cat. G
Date	5/1/2008	5/1/2008	5/5/2008	5/5/2008	5/7/2008	5/7/2008	5/7/2008	5/8/2008	5/8/2008	5/8/2008	5/12/2008	5/12/2008	5/12/2008
	No water	With water	No water	With water	No water	With water	With water	No water	With water	No water	With water	With water	With water
Pressure, psig	383	383	387	387	392	392	392	390	390	379	391	394	
Temp, F	275	269	270	274	280	275	303	314	303	303	305	311	
Nominal VHSV (hr-1, actual)	816	809	845	850	1072	1065	1106	974	960	1118	1087	1088	
O2/H2S	0.82	0.85	0.78	0.76	0.91	0.95	1.19	0.78	0.76	0.80	0.78	0.75	
Catalyst	Catalyst I	Catalyst I	Catalyst F	Catalyst F	Catalyst G	Catalyst G	Catalyst G	Catalyst D	Catalyst D	Catalyst G	Catalyst G	Catalyst G	
Inlet Gas													
H2S, ppmv	2214	2192	2120	2160	3375	3357	3040	2120	2160	3251	3157	3157	
O2, ppmv	1822	1859	1660	1651	3087	3192	3604	1660	1651	2604	2461	2377	
H2, mole %	15.64	15.73	15.12	15.18	14.18	15.30	13.88	15.12	15.18	14.73	15.17	15.33	
CO, mole %	37.03	37.72	34.95	35.70	34.66	34.79	33.07	34.95	35.70	16.95	17.08	16.99	
CO2 mole %	20.16	18.82	21.55	20.90	20.19	20.09	19.49	21.55	20.90	19.94	20.38	20.16	
H2O, mole % (est. based on H2O feed rate)	0.0	4.7	0.0	4.0	0.0	1.0	1.0	0.0	4.0	0.0	3.8	4.0	
Outlet Gas													
H2S, ppmv	1882	2000	1523	1642	1617	1878	1549	1523	1642	1582	1895	2177	
O2, ppmv	1517	1622	793	1171	2400	2459	2269	793	1171	1711	1789	1669	
COS, ppmv	37	40	502	87	92	52	86	502	87	95	120	247	
CO2, %	19.7	19	21.5	21	20.4	20	20	21.5	21	20.3	20	20	
Sulfur conversion													
H2S converted, ppmv	332	192	597	518	1759	1479	1491	597	518	1669	1263	980	
COS formed by CO+ S, ppmv	37	40	502	87	92	52	86	502	87	95	120	247	
Net sulfur formed (as S), ppmv	295	152	96	431	1667	1427	1405	96	431	1573	1143	734	
Subdewpoint?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	
H2S conversion, % H2S in feed	15.0%	8.8%	28.2%	24.0%	52.1%	44.1%	49.1%	28.2%	24.0%	51.3%	40.0%	31.0%	
COS formed by CO+ S, % H2S in feed	1.7%	1.8%	23.7%	4.0%	2.7%	1.6%	2.8%	23.7%	4.0%	2.9%	3.8%	7.8%	
Net sulfur formed, % of H2S in feed	13.3%	6.9%	4.5%	19.9%	49.4%	42.5%	46.2%	4.5%	19.9%	48.4%	36.2%	23.2%	
O2 balance (% of inlet gas)													
O2 to H2S + 0.5 O2 -> S + H2O	9.1%	5.2%	18.0%	15.7%	28.5%	23.2%	20.7%	18.0%	15.7%	32.0%	25.7%	20.6%	
O2 unreacted	83.3%	87.3%	47.7%	70.9%	77.7%	77.1%	63.0%	47.7%	70.9%	65.7%	72.7%	70.2%	
O2 reacted with CO and H2	7.6%	7.6%	34.3%	13.4%	-6.2%	-0.2%	16.3%	34.3%	13.4%	2.2%	1.6%	9.2%	
CO & H2 consumed, % of inlet CO + H2													
CO consumed by CO + S	0.01%	0.01%	0.10%	0.02%	0.02%	0.01%	0.02%	0.10%	0.02%	0.03%	0.04%	0.08%	
CO and H2 reacted with O2	0.05%	0.05%	0.23%	0.09%	-0.08%	0.00%	0.25%	0.23%	0.09%	0.04%	0.02%	0.13%	
Total CO + H2 Consumed	0.06%	0.06%	0.33%	0.10%	-0.06%	0.01%	0.27%	0.33%	0.10%	0.07%	0.06%	0.21%	

Table 51 Continued

	Catalyst D Extended Run				High Temp						Catalyst C Extended Run			Catalyst D Extended Run	
	5.3 - 6.6 Hr	6.6 - 10.0 Hr	15 - 22 Hr	39 - 42 Hr					Period One	Period Two	9.4 - 15.3 Hr	21.5 - 27.7 Hr	52 - 68 Hr	9.4 - 15.3 Hr	21.5 - 27.7 Hr
	Cat. D	Cat. D	Cat. D	Cat. D	Cat. A	Cat. A	Cat. C	Cat. C	Cat. C	Cat. C	Cat. C	Cat. C	Cat. C	Cat. D	Cat. D
Date	5/19/2008	5/19/2008	5/19/2008	5/20/2008	5/22/2008	5/22/2008	6/2/2008	6/2/2008	6/2/2008	6/2/2008	8/18/2008	8/19/2008	8/20/2008	8/21/2008	8/22/2008
	No water	With water	With water	With water	No water	With water	No water	With water	With water	With water	With water	With water	With water	With water	With water
Pressure, psig	390	390	390	390	383	383	398	398	398	398	398	398	398	398	398
Temp, F	300	300	300	460	499	499	306	306	306	306	280	280	315	284	275
Nominal VHSV (hr-1, actual)	950	950	950	1150	1176	1176	853	853	853	853	740	740	775	745	745
O2/H2S	0.78	0.76	0.73	0.72	0.72	0.70	0.80	0.80	0.80	0.80	0.68	0.70	0.81	0.81	0.84
Catalyst	Catalyst D	Catalyst D	Catalyst D	Catalyst D	Catalyst A	Catalyst A	Catalyst C	Catalyst C	Catalyst C	Catalyst C	Catalyst C	Catalyst C	Catalyst C	Catalyst D	Catalyst D
											Cycle #1	Cycle #2	Cycle #3	Cycle #1	Cycle #2
Inlet Gas															
H2S, ppmv	3105	3139	3209	3244	3555	3410	3294	3443	3443	3443	3030	3388	3180	3186	3123
O2, ppmv	2412	2398	2340	2349	2558	2371	2650	2770	2770	2770	2071	2378	2560	2588	2613
H2, mole %	14.86	15.12	14.95	15.12	16.09	16.10	15.95	16.32	16.32	16.32	14.56	15.70	15.55	15.45	15.09
CO, mole %	34.66	34.68	34.80	34.44	18.15	18.01	17.90	16.13	16.13	16.13	19.97	20.04	19.87	19.96	19.46
CO2 mole %	20.00	20.63	20.69	20.55	22.19	22.38	22.00	22.62	22.62	22.62	18.31	21.01	21.62	20.83	21.37
H2O, mole % (est. based on H2O feed rate)	0.0	3.0	4.0	2.9	0.0	2.7	0.0	2.5	2.5	2.5	4.6	4.6	4.6	5.3	5.3
Outlet Gas															
H2S, ppmv	7	147	1529	40	1918	2510	819	1524	1460	1460	2473	2295	2662	1265	1664
O2, ppmv	621	355	1013	40	26	34	1533	1861	1753	1753	1775	1592	2119	1237	1597
COS, ppmv	317	424	727	2405	1352	1002	56	37	86	86	26	47	50	144	78
CO2, %	20.5	21	21	21	22.7	23	22.3	22	22	22	21	21	21	21	22
Sulfur conversion															
H2S converted, ppmv	3098	2992	1680	3205	1637	900	2475	1919	1983	557	1092	518	1920	1459	
COS formed by CO+ S, ppmv	317	424	727	2405	1352	1002	56	37	86	26	47	50	144	78	
Net sulfur formed (as S), ppmv	2781	2568	952	799	285	none	2419	1882	1897	530	1045	468	1777	1381	
Subdewpoint?	Yes	Yes	Yes	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
H2S conversion, % H2S in feed	99.8%	95.3%	52.3%	98.8%	46.1%	26.4%	75.1%	55.7%	57.6%	18.4%	32.2%	16.3%	60.3%	46.7%	
COS formed by CO+ S, % H2S in feed	10.2%	13.5%	22.7%	74.1%	38.0%	29.4%	1.7%	1.1%	2.5%	0.9%	1.4%	1.6%	4.5%	2.5%	
Net sulfur formed, % of H2S in feed	89.6%	81.8%	29.7%	24.6%	8.0%	none	73.4%	54.7%	55.1%	17.5%	30.9%	14.7%	55.8%	44.2%	
O2 balance (% of inlet gas)															
O2 to H2S + 0.5 O2 -> S + H2O	64.2%	62.4%	35.9%	68.2%	32.0%	19.0%	46.7%	34.6%	35.8%	13.4%	23.0%	10.1%	37.1%	27.9%	
O2 unreacted	25.7%	14.8%	43.3%	1.7%	1.0%	1.4%	57.8%	67.2%	63.3%	85.7%	66.9%	82.7%	47.8%	61.1%	
O2 reacted with CO and H2	10.0%	22.8%	20.8%	30.1%	67.0%	79.6%	-4.5%	-1.8%	0.9%	0.8%	10.1%	7.1%	15.1%	11.0%	
CO & H2 consumed, % of inlet CO + H2															
CO consumed by CO + S	0.06%	0.09%	0.15%	0.49%	0.39%	0.29%	0.02%	0.01%	0.03%	0.01%	0.01%	0.01%	0.04%	0.02%	
CO and H2 reacted with O2	0.10%	0.22%	0.20%	0.29%	1.00%	1.11%	-0.07%	-0.03%	0.02%	0.01%	0.13%	0.10%	0.22%	0.17%	
Total CO + H2 Consumed	0.16%	0.30%	0.34%	0.77%	1.40%	1.40%	-0.05%	-0.02%	0.04%	0.02%	0.15%	0.12%	0.26%	0.19%	

Table 51 Continued

	Catalyst D Extended Run							
	2.7 - 9.2 Hr	14.3 - 20.4 Hr	25.7 - 31.9 Hr	37.7 - 43.3 Hr	49.6 - 55.6 Hr	62.2 - 67.9 Hr	75.0 - 78.3 Hr	84.4 - 90.4 Hr
	Cat. D	Cat. D	Cat. D	Cat. D	Cat. D	Cat. D	Cat. D	Cat. D
Date	9/22/2008	9/23/2008	9/23/2008	9/24/2008	9/24/2008	9/25/2008	9/25/2008	9/26/2008
	With water	With water	With water	With water	With water	With water	With water	With water
Pressure, psig	398	398	398	398	398	398	398	398
Temp, F	284	275	284	275	284	275	284	275
Nominal VHSV (hr-1, actual)	745	745	745	745	745	745	745	745
O ₂ /H ₂ S	0.83	0.83	0.81	0.82	0.83	0.84	0.80	0.78
Catalyst	Catalyst D	Catalyst D	Catalyst D	Catalyst D	Catalyst D	Catalyst D	Catalyst D	Catalyst D
	Cycle #1	Cycle #2	Cycle #3	Cycle #4	Cycle #5	Cycle #6	Cycle #7	Cycle #8
Inlet Gas								
H ₂ S, ppmv	3259	3204	3209	3122	3201	3264	3279	3214
O ₂ , ppmv	2698	2646	2589	2574	2652	2731	2613	2504
H ₂ , mole %	15.17	15.30	15.36	15.12	15.15	15.34	15.72	15.50
CO, mole %	20.66	20.34	20.65	19.96	20.02	20.22	20.33	17.56
CO ₂ mole %	20.68	21.29	21.52	21.42	20.70	20.08	19.54	20.10
H ₂ O, mole % (est. based on H ₂ O feed rate)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Outlet Gas								
H ₂ S, ppmv	687	1397	1296	1505	1340	1473	1972	1828
O ₂ , ppmv	985	1184	1330	1552	1283	1430	1738	1699
COS, ppmv	111	711	240	177	245	247	105	186
CO ₂ , %	21	21	21	22	20	20	20	20
Sulfur conversion								
H ₂ S converted, ppmv	2572	1807	1913	1617	1861	1791	1306	1386
COS formed by CO+ S, ppmv	111	711	240	177	245	247	105	186
Net sulfur formed (as S), ppmv	2461	1096	1673	1440	1616	1545	1201	1200
Subdewpoint?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
H ₂ S conversion, % H ₂ S in feed	78.9%	56.4%	59.6%	51.8%	58.1%	54.9%	39.8%	43.1%
COS formed by CO+ S, % H ₂ S in feed	3.4%	22.2%	7.5%	5.7%	7.6%	7.6%	3.2%	5.8%
Net sulfur formed, % of H₂S in feed	75.5%	34.2%	52.1%	46.1%	50.5%	47.3%	36.6%	37.4%
O₂ balance (% of inlet gas)								
O ₂ to H ₂ S + 0.5 O ₂ -> S + H ₂ O	47.7%	34.1%	36.9%	31.4%	35.1%	32.8%	25.0%	27.7%
O ₂ unreacted	36.5%	44.7%	51.4%	60.3%	48.4%	52.3%	66.5%	67.9%
O ₂ reacted with CO and H ₂	15.8%	21.1%	11.7%	8.3%	16.5%	14.9%	8.5%	4.4%
CO & H₂ consumed, % of inlet CO + H₂								
CO consumed by CO + S	0.03%	0.20%	0.07%	0.05%	0.07%	0.07%	0.03%	0.06%
CO and H ₂ reacted with O ₂	0.24%	0.31%	0.17%	0.12%	0.25%	0.23%	0.12%	0.07%
Total CO + H₂ Consumed	0.27%	0.51%	0.23%	0.17%	0.32%	0.30%	0.15%	0.12%

Task 3.0. Computer Simulation

The CrystaSulf model has been updated and is now fully functional in the latest version of Aspen Plus software. A complete heat and material balance, process equipment specification sheets and the data required to prepare a Process Design Package is now easily generated from the results from the Aspen calculations. In a similar fashion, a preliminary model for CrystaSulf-DO has been created using Aspen Plus. The VLE data from Task 1.5 has not been fully incorporated into the latest CrystaSulf model. CrystaTech received the final VLE data from GTI in August of 2009 but CrystaTech personnel were and currently are fully committed to other projects as is the Aspen software. Therefore CrystaTech has been unable to integrate the VLE data into the latest version of the Aspen model before the writing of this report. In the near future, as soon as the staff and the Aspen software become available the VLE data will be integrated into the model. For purposes of the economic evaluation section of this report the VLE data are not strictly required. The VLE data provides a refinement to the model, i.e., an improvement, but is not required for an economic evaluation. A portion of the VLE data was integrated into previous, older versions of the Aspen software model as the VLE data became available in the past during the course of the project, but again, not all of the VLE data was available until August of 2009.

CrystaSulf-DO Process Model

In the simulation, a DO reactor (stoichiometric module) was added to the existing CrystaSulf model upstream of H₂S absorber. Based upon the catalyst data from Task 1 results an assumption was made that a DO reactor could be designed with sufficient capacity to provide 80% H₂S conversion to sulfur in a multiple bed configuration and a very low space velocity such as, 250 – 500 Hr⁻¹. The Aspen simulation was created to represent the process as outlined in the Process Flow Diagrams (PFD) shown in Figure 83 through Figure 85. In Figure 83 the Direct Oxidation Reactor module of CrystaSulf-DO is shown, in Figure 84 the CrystaSulf module is shown and in Figure 85 the sulfur burner that supplies SO₂ for the CrystaSulf unit is shown. The heat and material balance in and out of the DO reactor, CrystaSulf unit and the scavenging unit is included in Table 52. COS was not included in the Aspen simulation but is discussed in the economic evaluation and is assumed to be removed by a zinc oxide scavenger following the CrystaSulf unit. The scavenger is discussed in the economic evaluation Task 4 section.

CrystaSulf-DO Process Description

The DO Reactor Unit. The sour syngas enters the heater to the DO unit of CrystaSulf-DO where the temperature of the gas is raised. Typically the DO reactor heater would be used to overheat the sour gas so that the colder air or oxygen stream required to oxidize the H₂S in the DO reactor bed could be added directly to the sour gas immediately before entering the DO catalyst reactor, and the resulting gas stream temperature would be 260 °F. The sour syngas stream then passes through the temperature controlled DO reactors where the direct oxidation of H₂S takes place according to:

Water or steam is used to control the temperature of the DO reactor near 260 °F. In the case that is modeled for this report, a generic syngas stream from a coal IGCC plant, two DO reactors will be in service, so the gas stream is split as is shown in the PFD in Figure 83. The operation of the DO reactors will be described later in this section. The syngas exits the DO reactors and passes through a cooler where the temperature is reduced to 120 °F. Following the

cooler, the gas passes through a knockout to remove water formed from the DO reaction and condensed by the cooler. The gas should have a water dewpoint at 120 °F or lower, as it enters the CrystaSulf unit for proper operation of CrystaSulf.

DO Reactor Operation. As was discussed above, the DO reactors are operated a 260 °F which is sulfur sub-dewpoint temperature; at this condition, the molten sulfur that is formed as a product of the DO reaction will accumulate on the DO catalyst. Based on our previous experience and the results of this project, to definitively prevent the formation of COS and oxidation of H₂ and CO, the DO reactor must be operated at sulfur sub-dewpoint temperature. After 6 hours of online operation during which H₂S is converted into sulfur and water, the two DO reactors (the A set of reactors) are taken out of service and a second set of DO reactors (the B set of reactors) are put into service. While the B set of reactors are in service the A set of reactors will be regenerated. The B set of reactors are de-pressurized to atmospheric pressure. Once atmospheric pressure is reached, the regeneration gas, nitrogen, is started and the regeneration gas heater is also started and set at 600 °F. The regeneration gas cooler is started and automatically controls the temperature of the gas at 265 °F. As the hot nitrogen stream heats the catalyst in the DO reactor, the molten sulfur begins to vaporize from the catalyst. The hot nitrogen gas with sulfur vapor is condensed by the regeneration gas cooler and molten sulfur is formed and collected in the regeneration gas separator. The gas path is shown in the PFD in Figure 83 by the path with the solid black valves. After approximately 4 hours of high temperature regeneration at atmospheric pressure, the catalyst regeneration is complete and the sulfur has been driven off of the catalyst. The regeneration gas heater is stopped and the nitrogen continues to flow until the DO reactor cools to approximately 260 °F which is the normal operating temperature. At this point the reactor is ready to be re-pressurized with syngas and put into standby. A third set of DO reactors (the C set of reactors) is also in standby and ready to be put into service in case the regeneration of the A set takes more than 6 hours to complete or in case the reactors in service (the B set) result in outlet conditions that do not meet H₂S specification and the C set of reactors must be put into service.

The CrystaSulf Unit. The CrystaSulf process has been thoroughly described in other publications and will briefly be discussed here.^{3,4,5} CrystaSulf is a non-aqueous sulfur recovery technology that can be used for direct treatment of gas streams containing H₂S. The CrystaSulf solvent components are high-boiling organics in which sulfur has a high solubility. The solvents catalyze the reaction of H₂S with SO₂ to form elemental sulfur that remains dissolved in the solvent until removed via crystallization.

Sour gas enters the absorber where it contacts the lean CrystaSulf solution and H₂S reacts with dissolved SO₂ to form dissolved sulfur. Lean solution flow rates are typically 20-50 gpm/LTSD (gpm per long ton of sulfur removed per day). Sweet gas exits the absorber at 150-155°F. Gas exiting the absorber passes through a solution recovery cooler and separator to recover vaporized solution components. The product gas will be cooled to approximately 100°F.

Rich solution flows from the absorber bottom to a flash vessel, where it is flashed to near atmospheric pressure. The flash gas stream can be compressed, cooled to remove water and recycled to the absorber inlet providing a zero emissions CrystaSulf plant or the stream could be used as fuel on site. In the case of IGCC plants the flash gas stream will most likely be recompressed. Liquid exiting the flash tank is sent to a crystallizer where the temperature is reduced to 105°F, causing sulfur to crystallize from solution. Depending on sulfur tonnage and other design considerations a cone-bottom, up-flow

spouting bed crystallizer or a scraped surface crystallizer (SSC) design may be used. Typically for IGCC applications an SSC will be used. Either approach produces elemental sulfur particles of approximately 50-400 μm diameter which are removed using a centrifuge or an indexing-belt pressure filter. In the filter the sulfur is rinsed with water and a wash solvent (heptane) to remove solution components from the sulfur product. The wash water and wash solvent are recycled to minimize water and solvent makeup rates. The produced sulfur is over 90 wt% sulfur on a wet basis and over 98 wt% sulfur on a dry basis. The crystallization section is the only place where solid sulfur is present.

Reacted SO_2 is replenished by either injecting liquid SO_2 into the lean liquor stream or by burning a portion of the product sulfur to make SO_2 . If the liquid SO_2 approach is selected, the sulfur cake product will be approximately 1.5 times the amount of sulfur removed from the inlet gas stream. If the sulfur burner approach is selected the SO_2 -laden gas stream exiting the package sulfur burner is sent to the SO_2 absorber, where the circulating lean solution contacts the gas stream and removes the SO_2 and converts it into a stable intermediate form. The SO_2 -rich solution then is returned to the main CrystaSulf circulation loop. The SO_2 vent gas stream consists mainly of nitrogen and excess oxygen from the sulfur burner and is typically sent to a low pressure flare for disposal.

A small portion of the inlet H_2S may be converted to salt byproducts during operation of the process. Accumulated salts (if they develop) can be removed from the bulk CrystaSulf solvent using a proprietary on-line removal process, which operates on a small slipstream of CrystaSulf solution. The salts removal process operates intermittently. Salts from the salts tank are captured in a sock filter. The sock filter is periodically cleaned with water, which causes the salts to dissolve into the water, and the resulting salt water (sulfates) is blown down as necessary. The salts and water blowdown stream will flow to the host site wastewater treatment facility for disposal.

The Scavenging Unit. The scavenging unit or final polishing unit is required by this project, to bring the CrystaSulf gas outlet sulfur concentration down to 50 ppbv from 4 ppmv H_2S and 20 ppmv COS. For the generic IGCC coal gasification case specific to this project, the design includes two scavenging towers in lead lag configuration filled with zinc oxide scavenger and a third vessel in standby. The resulting gas stream is 50 ppbv H_2S .

The process operation that has been described above is the basis for the economic evaluation in the next section under Task 4.

Table 52 Heat and Material Balance

Stream No.	DO-1	DO-3	S-3	S-7	
Stream Description	Sour Gas Into DO Reactor	Air In to DO Reactor	Feed to CrystaSulf Preheater	Gas From CrystaSulf, V 1101	Gas From Scavenger, V-1202
Component Mole Fraction *					
H2	0.3140	0.0000	0.3120	0.3133	0.3133
O2	0.0000	0.2100	0.0000	0.0000	0.0000
N2	0.0201	0.7900	0.0337	0.0338	0.0338
CO2	0.1679	0.0000	0.1668	0.1674	0.1674
CO	0.4388	0.0000	0.4359	0.4374	0.4374
C1	0.0455	0.0000	0.0452	0.0454	0.0454
H2S	0.009162	0.000000	0.001826	0.000004	0.000000
SO2	0.0000	0.0000	0.0000	0.0000	0.0000
S-8	0.0000	0.0000	0.0000	0.0000	0.0000
S-8(S)	0.0000	0.0000	0.0000	0.0000	0.0000
RSC-103	0.0000	0.0000	0.0000	0.0000	0.0000
RSC-202	0.0000	0.0000	0.0000	0.0000	0.0000
RSC206	0.0000	0.0000	0.0000	0.0000	0.0000
RSC-312	0.0000	0.0000	0.0000	0.0000	0.0000
RSC-312S	0.0000	0.0000	0.0000	0.0000	0.0000
H2O	0.0045	0.0000	0.0046	0.0027	0.0027
BENZENE	0.0000	0.0000	0.0000	0.0000	0.0000
Component Mass Flow [lb/hr] *					
H2	24,566	0	24,566	24,566	24,566
O2	0	4,547	0	0	0
N2	21,871	14,976	36,846	36,846	36,846
CO2	286,802	0	286,779	286,497	286,497
CO	749,428	0	749,371	748,633	748,633
C1	28,336	0	28,336	28,336	28,336
H2S	12,119	0	2,432	5	5
SO2	0	0	0	0	0
S-8	0	0	0	0	0
S-8(S)	0	0	0	0	0
RSC-103	0	0	0	0	0
RSC-202	0	0	0	26	26
RSC206	0	0	0	0	0
RSC-312	0	0	0	3	3
RSC-312S	0	0	0	0	0
H2O	3,157	0	3,244	1,903	1,903
BENZENE	0	0	0	0	0
Liquid and Vapor Phases					
Total Mole Flow [lbmol/hr]	38,809	677	39,063	38,894	38,894
Total Mass Flow [lb/hr]	1,126,270	19,523	1,131,570	1,126,820	1,126,820
Total Flow [ft ³ /hr]	462,368	7,824	481,511	481,116	481,116
Temperature [deg.F]	120.00	80.00	120.00	100.00	100.00
Pressure [psig]	480.00	480.00	465.00	445.00	445.00
Vapor Frac	1.00	1.00	1.00	1.00	1.00
Liquid Frac	0.00	0.00	0.00	0.00	0.00
Solid Frac	0.00	0.00	0.00	0.00	0.00
Enthalpy [Btu/lbmol]	-104,510	-73	-103,770	-104,070	-104,070
Enthalpy [Btu/lb]	-3,601	-3	-3,582	-3,592	-3,592
Enthalpy [Btu/hr]	-4.06E+09	-4.96E+04	-4.05E+09	-4.05E+09	-4.05E+09
Entropy [Btu/lbmol-R]	-5.14	-6.07	-5.12	-5.38	-5.38
Entropy [Btu/lb-R]	-0.18	-0.21	-0.18	-0.19	-0.19
Density [lbmol/cuft]	0.08	0.09	0.08	0.08	0.08
Density [lb/ft ³]	2.44	2.50	2.35	2.34	2.34
Average MW	29.02	28.85	28.97	28.97	28.97
Liq Vol (60 deg.F) [ft ³ /hr]	33,195	581	33,410	33,308	33,308
Vapor Phase					
Total Flow [MMscfd]	353.46	6.16	355.76	354.23	354.23
Density [lb/ft ³]	2.44	2.50	2.35	2.34	2.34
Viscosity [cP]	0.02	0.02	0.02	0.02	0.02
Heat Capacity [Btu/lb-R]	0.31	0.25	0.31	0.31	0.31
Compressibility Factor	0.28	0.29	0.28	0.28	0.28
Average MW	29.02	28.85	28.97	28.97	28.97

* Composition for liquid and vapor phases.

Figure 83 P&ID - DO Units

Figure 84 PFD CrystaSulf and Guard Bed Units

NOTES
1. Unless otherwise noted, average values are given for streams.

Figure 85 PFD - CrystaSulf Units Continued

Task 4.0. Economic Evaluation

The economic evaluation is based upon a preliminary equipment design and the process model as described under Task 2. CrystaTech has accumulated the data necessary to make an estimate (+/- 30%) of the equipment cost for CrystaSulf-DO, not including installation. CrystaTech routinely provides commercial cost estimates for prospective CrystaSulf clients which are +/- 30 %. The DO reactor and scavenger cost information will be added to CrystaTech's routine CrystaSulf cost estimate and will be included in this section. A list of assumptions for the process model simulation which was also used for the cost estimate this task is listed below.

- DO reactor converts 80% of inlet H₂S to sulfur.
- DO reactor side reaction creates byproduct of 20 ppmv COS.
- DO reactor is controlled temperature at 265 ± 15 °F.
- 2 DO reactors are in service, while 2 DO reactors are in regeneration mode and 2 DO reactors are in standby; there are 6 DO reactor vessels in total in the evaluation.
- Air is injected to provide O₂ for the DO reaction in the DO reactor; provided by an air compressor.
- 100% of the injected O₂ from the air is utilized in the reactor; the compressor is designed for 110% of required duty. The heat and material balance includes only the exact amount of air required to convert 80% of the inlet H₂S to sulfur, i.e., no excess air is included in the simulation, however the cost estimate includes a compressor at 10% overdesign factor.
- CrystaSulf designed to remove H₂S down to 4 ppmv (typical high pressure CrystaSulf commercial application).
- Scavenger: zinc oxide (ZnO), designed in lead-lag configuration with one extra vessel in standby, designed to remove the COS and H₂S down to a total of 50 ppbv. Assumed that 95 – 100% of the ZnO is utilized in removing COS and H₂S, as per vendor literature for lead lag systems. The 3 vessel system is designed at 110%, i.e., 10% overdesign factor. Each ZnO scavenger vessels is sized to contain enough material (plus 10% excess) so that it will last 90 days before being taken out of the “lead” position; before being taken off line, emptied and having the ZnO scavenger replaced.
- The cost estimate is made using the heat and material balance of Table 52 plus a 10% design margin.
- The following tables include the design basis, equipment list, operating information and produced streams for each section or sub-unit of the CrystaSulf-DO process for this generic IGCC coal gasification project. The sections are: the DO reactor unit, CrystaSulf unit, and the scavenging unit.
- The cost estimate is on an uninstalled basis. It also does not include control system; heat tracing; insulation; off skid interconnecting piping and wiring; and initial fill of chemicals, catalysts and scavengers.

The cost estimate is summarized in Table 53.

Table 53 Cost Estimate Summary for CrystaSulf-DO by Unit

Item	DO Unit	CrystaSulf Unit	Scavenging Unit
Capital Cost	\$6,700,000	\$ 17,640,000	\$950,000
Total Annual Operating Cost*	\$ 550,674	\$ 1,511,358	\$ 2,326,168
Chemical	0	1,195,161	0
Catalyst	207,346	0	0
Scavenger	0	0	2,326,168
Compressor Fuel	343,328	316,197	0

*Includes only chemical, catalyst, scavenger and compressor fuel cost. Utility costs are not included.

The preliminary cost estimate for the CrystaSulf-DO generic IGCC application in this project is \$ 25,290,000 +/- 30% capital cost, uninstalled; the total annual operating cost is \$ 4,388,200 +/- 30%, excluding heating, cooling and electric utilities.

DO Reactor Design Basis

Generic IGCC Plant; CrystaSulf portion of CrystaSulf-DO

Specification	Units	Value
Gas pressure	psig	480
Gas temperature	F	260
Gas flow rate	MMscfd	360
Sulfur removed from sour gas	LTPD	97.6
H ₂ S outlet concentration	mole%	0.18

Feed Gas Composition to the DO Reactor		
Component	[Units]	Value
H ₂ S	mole%	0.90
CO ₂	mole%	16.50
CO	mole%	43.13
N ₂	mole%	3.33
O ₂	mole%	0.36
H ₂	mole%	30.86
C1	mole%	4.47
C2	mole%	0.00
C3	mole%	0.00
C4	mole%	0.00
C5	mole%	0.00
C6	mole%	0.00
C7+	mole%	0.00
Mercaptans/RSH	mole%	0.00
SO ₂	mole%	0.00
COS	mole%	0.00
CS ₂	mole%	0.00
Elemental sulfur vapor/S ₈	mole%	0.00
Ammonia/NH ₃	mole%	0.00
Hydrogen cyanide/HCN	mole%	0.00
H ₂ O, saturated at 120 degF	mole%	saturated

Additional Comments:

water vapor saturated at 120 degF
Feed gas after required reaction air added

DO Reactor Budgetary Cost Estimate
Generic IGCC Plant; DO Reactor portion of CrystaSulf-DO

DO Equipment Package
<p><i>Costs are in U.S. dollars.</i></p> <p><i>Equipment modules are ex works (EXW) Houston, TX area fabrication shop.</i></p> <p><i>Control logic document provided; control system not included.</i></p> <p><i>Off-skid instrument and power wiring, insulation and heat tracing not included.</i></p> <p><i>Includes two weeks of startup support; additional assistance is on a time and materials basis</i></p>

Equipment List for Generic IGCC Plant; DO Reactor portion of CrystaSulf-DO

Equipment Included in Equipment Package	Operating	Inline Spare *	Shelf Spare *	Equipment Type
Syngas Heater	1			Shell and tube
Regeneration Gas Heater	1			Shell and tube
Air compressor	1	1		Discharge pressure = 480 psig
DO Reactors, with internal cooling	6			
Regeneration Gas / Molten Sulfur Separator	1			Vertical vessel
Outlet Gas Cooler	1			Air cooler
Outlet Gas Knockout	1			Vertical vessel
Total	12	1	0	

* Inline spares are piped into the process; shelf spares are provided but not installed.

DO Reactor Operating Information

Generic IGCC Plant; DO Reactor portion of CrystaSulf-DO

Chemical costs:		
Catalyst costs (annual)	\$/yr	207,346
(Assume changeout of all catalyst once every 4 years)		
Nitrogen Regeneration Gas (16 hours per day @ 1,257 cfm)	scf / day	1,206,374
Heating requirements:		
Syngas Heater	MMBtu/h	50.80
(Potential recoverable heat from the DO reactor)	MMBtu/h	5.69
(Use recoverable heat from Reactor cooling to preheat air)		
Regeneration Gas Heater	MMBtu/h	0.72
(Operated for 4 hours / 6 hour cycles for 16 hours per day)		
Cooling Requirements:		
DO Outlet Gas Cooler	MMBtu/h	50.30
(A portion of this heat could be used to reheat the gas for the inlet to the CrystaSulf unit, plus cooling will be required)		
Regeneration Gas Cooler	MMBtu/h	0.45
(Not including DO Reactor cooling)		
(Use Reactor cooling to preheat the air)		
Compressor fuel requirements:	\$/yr	343,328

Notes:

1) There is significant uncertainty with the heating and cooling water requirements since a detailed process design has not been completed.

Streams from the DO Reactor Unit

Generic IGCC Plant; DO Reactor Unit of CrystaSulf-DO

	Flow	Potential Contaminants
<i>Gas Phase</i>		
Treated gas, MMscfd	358.3	Approx. 0.182 mol% H ₂ S and 20 ppmv COS
<i>Solid Phase</i>		
Molten Sulfur, LT / day	97.6	Sulfur
Spent Catalyst, lb / year	13,823	Spent catalyst, sulfide and sulfur contaminant (Assume all catalyst changed out once every 4 years)

CrystaSulf Design Basis

Generic IGCC Plant; CrystaSulf portion of CrystaSulf-DO

Specification	Units	Value
Gas pressure	psig	465
Gas temperature	F	120
Gas flow rate	MMscfd	356
Sulfur removed from sour gas	LTPD	24.5
H ₂ S sulfur recovery specification	ppmv	4

Feed Gas Composition		
Component	[Units]	Value
H ₂ S	mole%	0.18
CO ₂	mole%	16.68
CO	mole%	43.59
N ₂	mole%	3.37
O ₂	mole%	0.00
H ₂	mole%	31.20
C1	mole%	4.52
C2	mole%	0.00
C3	mole%	0.00
C4	mole%	0.00
C5	mole%	0.00
C6	mole%	0.00
C7+	mole%	0.00
Mercaptans/RSH	mole%	0.00
SO ₂	mole%	0.00
COS	mole%	0.00
CS ₂	mole%	0.00
Elemental sulfur vapor/S ₈	mole%	0.00
Ammonia/NH ₃	mole%	0.02
Hydrogen cyanide/HCN	mole%	0.00
H ₂ O	mole%	saturated

Additional Comments:

CrystaSulf Budgetary Cost Estimate
Generic IGCC Plant; CrystaSulf portion of CrystaSulf-DO

CrystaSulf Equipment Package	17,640,000
<p><i>Costs are in U.S. dollars.</i></p> <p><i>Equipment modules are ex works (EXW) Houston, TX area fabrication shop.</i></p> <p><i>Control logic document provided; control system not included.</i></p> <p><i>Off-skid instrument and power wiring, insulation and heat tracing not included.</i></p> <p><i>Includes two weeks of startup support; additional assistance is on a time and materials basis</i></p>	

Equipment List for Generic IGCC Plant; CrystaSulf portion of CrystaSulf-DO Application

Equipment Included in Equipment Package	Operating	Inline Spare *	Shelf Spare *	Equipment Type
Solution recovery cooler	1			Air cooler
Solution recovery drum	1			Vertical vessel
Crystallizer	1	1		
Crystallizer recirculation pump	1	1		Centrifugal pump; 1361 gpm; 77 hp per pump
Filter feed pump	1	1		Positive-displacement pump; 107.2 gpm
Crystallizer exchanger	1	1		Q = 9.76 MMBtu/hr
Cooling water pump	1	1		Centrifugal; 2156 gpm; 112 hp per pump
Surge tank	1			Vertical vessel
Solution heater	1			Q = 9.76 MMBtu/hr
Main circulation pump	1	1		Positive displacement; 1220 gpm; 834 hp per pump
Sulfur filter	1	1		Centrifuge System
Wash water pump	1		1	Centrifugal pump; 261 gpm; 17.6 hp per pump
Water separator	1			
Chemical make-up storage tanks	3			
Chemical make-up metering pumps	3			
Salts pump	1		1	68 gpm; 4.9 hp per pump
Salts in-line blender	1			
Salts cartridge filter	1		1	Sock filters
Solvent recovery package	1			7.5 kW required
Clean solvent pump	1		1	Centrifugal; 10.7 gpm; 0.7 hp per pump
Inlet gas preheater	1			Shell and tube (Q = 8.62 MMBtu/hr)
Flash drum	1			
SO2 absorber bottoms pump	1	1		122 gpm; centrifugal; 6.4 hp per pump
Sulfur burner system	1			12.2 LTPD
Flash gas compressor	1			Reciprocating; 1613 hp; discharge pressure = 465 psig
Total	29	8	4	
Unskidded Equipment (Supplied with modules, erected by end user)				
H2S absorber	2			33 bubble cap trays
SO2 absorber	1			Packed tower
Total	3	0	0	
Unskidded Equipment (Supplied by end user)				
Total	0	0	0	

* Inline spares are piped into the process; shelf spares are provided but not installed.

CrystaSulf Operating Information

Generic IGCC Plant; CrystaSulf portion of CrystaSulf-DO

Chemical costs:		
Solution chemical costs	\$/yr	1,118,227
Other chemical costs	\$/yr	76,934
Electricity requirements:	kW	800
Heating requirements:		
Total Usage (could be supplied by cross exchange with DO reactor cooler)	MMBtu/h	18.39
Heating medium		Sat. Steam
Supply temperature	°F	298
Cooling Medium Requirements:		
Total Usage	MMBtu/h	9.76
Cooling medium		Water
Maximum flow rate	gpm	2156
Supply temperature	°F	85
Compressor fuel requirements:	\$/yr	316,197

Notes:

1) There is significant uncertainty with the heating and cooling water requirements since a detailed process design has not been completed.

Streams from the CrystaSulf Unit

Generic IGCC Plant; CrystaSulf portion of CrystaSulf-DO

	Flow	Potential Contaminants
<i>Gas Phase</i>		
Treated gas	355.8 MMscfd	< 4 ppmv H ₂ S
Flash gas to be recompressed	5.742 MMscfd	<20 ppmv H ₂ S, CO ₂ , and hydrocarbons
SO ₂ vent gas	1.8 MMscfd	Trace SO ₂
<i>Liquid Phase</i>		
Salts and water blowdown	469 gal/day	Aqueous sulfate salts (13 wt%)
Cooling water bleed from sulfur burner	3 to 7.6 gpm	1-3 wt% SO ₂ ; < 1.5 wt% SO ₃ as H ₂ SO ₄
<i>Solid Phase</i>		
Produced sulfur	24.5 LTPD	Residual hydrocarbons from solution and wash cycle (<0.7 wt%)

CrystaSulf-DO Scavenger Unit Design Basis

Generic IGCC Plant; Scavenger Unit of CrystaSulf-DO

Specification	Units	Value
Gas pressure	psig	445
Gas temperature	F	100
Gas flow rate	MMscfd	354
Sulfur removed from sour gas	LTPD	0.32
Sulfur outlet concentration	ppbv	50

Feed Gas Composition		
Component	[Units]	Value
H ₂ S	ppmv	4.01
CO ₂	mole%	16.74
CO	mole%	43.74
N ₂	mole%	3.38
O ₂	mole%	0.00
H ₂	mole%	31.33
C1	mole%	4.54
C2	mole%	0.00
C3	mole%	0.00
C4	mole%	0.00
C5	mole%	0.00
C6	mole%	0.00
C7+	mole%	0.00
Mercaptans/RSH	mole%	0.00
SO ₂	mole%	0.00
COS	mole%	0.00
CS ₂	mole%	0.00
Elemental sulfur vapor/S ₈	mole%	0.00
Ammonia/NH ₃	mole%	0.00
Hydrogen cyanide/HCN	mole%	0.00
H ₂ O, saturated at 120 degF	mole%	saturated

Additional Comments:

Scavenger Unit Budgetary Cost Estimate

Generic IGCC Plant; Scavenger portion of CrystaSulf-DO

Scavenger Equipment Package
<p>Costs are in U.S. dollars.</p> <p>Equipment modules are ex works (EXW) Houston, TX area fabrication shop.</p> <p>Control logic document provided; control system not included.</p> <p>Off-skid instrument and power wiring, insulation and heat tracing not included.</p> <p>Includes two weeks of startup support; additional assistance is on a time and materials basis</p>

Equipment List for Generic IGCC Plant; Scavenger portion of CrystaSulf-DO Application

Equipment Included in Equipment Package	Operating	Inline Spare *	Shelf Spare *	Equipment Type
Scavenging Vessel	2	1		Vertical vessel, 12 ft ID. x 25 ft T/T
Total	2	1	0	

* Inline spares are piped into the process; shelf spares are provided but not installed.

Scavenger Operating Information

Generic IGCC Plant; Scavenger portion of CrystaSulf-DO

Chemical costs:		
ZnO Scavenger costs	\$/yr	2,326,168

Streams from the Scavenger Unit

Generic IGCC Plant; Scavenger Unit of CrystaSulf-DO

	Flow	Potential Contaminants
<i>Gas Phase</i>		
Treated gas, MMscfd	354.2	< 50 ppbv total sulfur
<i>Solid Phase</i>		
Produced ZnS, lb/hr	97.5	ZnS; ZnS has a commercial market
Produced ZnS, LT/year	355.3	1 Vessel emptied and refilled every 90 days, the other 2 in service

Recommendations for Future Testing

Based upon the summary conclusions above, the following tests are suggested for any future testing of CrystaSulf-DO.

- Based on a recommendation from the catalyst vendor, Catalyst D should be tested in a multiple bed configuration where H_2S is converted to sulfur and adsorbed for 6 hours followed by a 4 hour regeneration step with nitrogen flowing at approximately 600 °F and then regenerated with air flowing for 2 hours at approximately 600 °F.
- Long term testing of additional catalysts not tested under this project in multiple bed operating mode where the catalyst reactor is cycled between sulfur sub-dewpoint temperature for about 6 hours and then at approximately 600 °F for about 6 hours for multiple cycles, to prove that the catalyst can be regenerated for more than one week.
- Additional testing could be performed that simulates the outlet of a shift reactor where the gas has been shifted from a mixture of CO and H_2 to a gas composed of primarily H_2 . In a H_2 gas stream, the H_2S could be converted to sulfur above the sulfur dewpoint thus eliminating the need to operate the DO reactors at sulfur sub-dewpoint temperature and in a multiple bed configuration. Capital and operating cost savings should be realized when operating at above sulfur dewpoint temperature.

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List of Acronyms and Abbreviations

As	Arsenic
Cd	Cadmium
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
COR	DOE Contracting Officer Representative
COS	Carbonyl Sulfide
CTU	Catalyst Test Unit
DO	Direct Oxidation (of H ₂ S to Sulfur)
DOE	United States Department of Energy
ET	Elapsed Time of Test
GC	Gas Chromatograph
gpm	Gallons per Minute
GTI	Gas Technology Institute
H ₂	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen Sulfide
HCl	Hydrogen Chloride
Hg	Mercury
Hr or hr	Hour
IGCC	Integrated Coal Gasification Combined Cycle
KO	Knock Out
LTSD	Long Ton of Sulfur Removed per Day
M	Molar
MFC	Mass Flow Controller
NETL	National Energy Technology Laboratory
NH ₃	Ammonia
O ₂	Oxygen
PFD	Process Flow Diagram
ppb	Parts per Billion
ppm	Parts per Million
psig	Pound-force per Square Inch, Gauge
S	Sulfur
Se	Selenium
slpm	Standard Liters per Minute
SO ₂	Sulfur Dioxide
SSC	Scraper Surface Crystallizer
SV	Space Velocity
UCSRP-HP	University of California, Sulfur Recovery Process-High Pressure
VLE	Vapor-Liquid Equilibrium
Wt	Weight
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZnO	Zinc Oxide

Biography

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