CO₂ Hydrate Process for Gas Separation

Technical Progress Report

Quarterly

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Abstract

This document reports on the activities of the second quarter, April through June, of 2003 for phase 2 of the project on syngas upgrading, a low temperature approach. Modifications were implemented to the hydrogen flow test rig per safety review comments. Delivery of ETM hardware continued and buildup of the ETM system continued. SIMTECHE analyzed the data from flow tests, provided input to the test plan and project review presentation and provided input to the facility requirements specification produced for Tennessee Eastman's consideration. Nexant also helped to analyze the flow test data, prepared the facility requirements specification for consideration by Eastman, and prepared presentation materials for the CO₂ project review. A presentation was made of the program status to the Carbon Sequestration review team in Pittsburgh, Pa on June 3, 2003.

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EXECUTIVE SUMMARY

This document reports on the activities of the second quarter, April thru June, of 2003 for phase 2 of the project on syngas upgrading, a low temperature approach.

Relocation of Test Apparatus

The phase 1 test apparatus has been relocated into an area that can safely contain the hydrogen/H₂S. Prior to the H₂/H₂S/CO₂ runs, the system was operated using Helium/CO₂ mixtures to test the performance.

Inconsistencies in the flow test data was analyzed and it was observed that changes in the conditions in the cylinders were possibly the source. It was difficult to get stable hydrate formation, and the measured gas compositions were far from the 40%CO₂ as specified. The mixed gas cylinders were supplied at 2200psig, and kept outside in very cold conditions. This likely caused CO₂ condensation and unreliable compositions in the feed gas. Subsequent tests were conducted, in which the cylinders were warmed inside the building and rolled to facilitate mixing. The result was a repeatable hydrate formation and concentrations of CO₂ close to 40%.

In general, the He/CO₂ runs without depleted CO₂ concentrations were consistent with earlier Ar/CO₂ runs, except that the temperature rise measure was not consistent. This is yet to be resolved.

A proposed series of H₂/H₂S/CO₂ tests was developed and proposed by SIMTECHE.

Engineering Test Model

Delivery of ETM hardware continued and buildup of the ETM system continued. One of the high-pressure vessels was delivered uncrated with superficial damage. This resulted in schedule slippage because it was necessary to validate the integrity of the vessel.

The Wilson Line tests done on the Johnson finned tailtubes yielded inconsistent data. A meeting was held at LANL to discuss the results and suggest possible causes/solutions. The heat transfer results were much lower than those obtained from the original hardware. It was suggested that airgaps between the tailtube and the finned sleeve was causing the very low heat transfer results. The unit was assembled underwater to ensure that water filled the gaps instead of air, and the tests were repeated. These tests resulted in heat transfer very similar to the original hardware.

A series of proposed tests was developed for the ETM. The proposed test matrix includes 3 test series; (1) Sequentially eliminate one of the six 9-inch tailtube sections, (2) Have alternating cooled and uncooled sections, and (3) add longer Weiland finned sections to enhance cooling and reaction to completion.

MILESTONE PROGRESS

The following table illustrates progress made toward reaching project milestones.

Date	Milestone Title
June 2003	Milestones are in progress
May 2003	Milestones are in progress
April 2003	Milestones are in progress
March 2003	Milestones are in progress
February 2003	Milestones are in progress
January 2003	Milestones are in progress
December 2002	Milestones are in progress
November 2002	Milestones are in progress
October 2002	Validation Tests Complete, Task 2.2B
September 2002	Milestones are in progress
August 2002	Literature Review Complete and Viscometer Operational, Task 2.1B
July 2002	Milestones are in progress
June 2002	Milestones in progress
May 2002	Milestones in progress
April 2002	Engineering Test Model System Design Complete Task 2.3A
March 2002	Task 2.1A Optical Cell Fabricated
February 2002	All milestones are in progress
January 2002	All milestones are in progress

TECHNICAL ACTIVITIES PERFORMED DURING THE REPORTING QUARTER

The major activities for the quarter include:

- Testing of the Relocated phase 1 flow test apparatus
- Buildup of the Engineering Test Model flow test apparatus
- Presentation of the STU Facility Requirements Specification to Eastman
- Presentation of the program status to a review team on June 3, 2003.

Relocation of Phase 1 Test Apparatus

The phase 1 test apparatus has been relocated into an area that can safely contain the hydrogen/H₂S. Prior to the H₂/H₂S/CO₂ runs, the system was operated using Helium/CO₂ mixtures to test the performance.

Inconsistencies in the flow test data was analyzed and it was observed that changes in the conditions in the cylinders were possibly the source. It was difficult to get stable hydrate formation, and the measured gas compositions were far from the 40%CO₂ as specified. The mixed gas cylinders were supplied at 2200psig, and kept outside in very cold conditions. This likely caused CO₂ condensation and unreliable compositions in the feed gas. Subsequent tests were conducted, in which the cylinders were warmed inside the building and rolled to facilitate mixing. The result was a repeatable hydrate formation and concentrations of CO₂ close to 40%.

In general, the He/CO₂ runs without depleted CO₂ concentrations were consistent with earlier Ar/CO₂ runs, except that the temperature rise measure was not consistent. This is yet to be resolved.

A proposed series of H₂/H₂S/CO₂ tests was developed and proposed by SIMTECHE. The proposed test options include proprietary information, but are available upon request.

Engineering Test Model Design

Delivery of ETM hardware continued and buildup of the ETM system continued. One of the high-pressure vessels was delivered uncrated with superficial damage. This resulted in schedule slippage because it was necessary to validate the integrity of the vessel.

The Wilson Line tests done on the Johnson finned tailtubes yielded inconsistent data. A meeting was held at LANL to discuss the results and suggest possible causes/solutions. The heat transfer results were much lower than those obtained from the original hardware. It was suggested that airgaps between the tailtube and the finned sleeve was causing the very low heat transfer results. The unit was assembled underwater to ensure that water filled the gaps instead of air, and the tests were repeated. These tests resulted in heat transfer very similar to the original hardware.

A series of proposed tests was developed for the ETM. The proposed test matrix includes 3 test series; (1) Sequentially eliminate one of the six 9-inch tailtube sections, (2) Have alternating cooled and uncooled sections, and (3) add longer Weiland finned sections to enhance cooling and reaction to completion.

Facility Requirements Specification Proposed to Tennessee Eastman

Facility Requirements Specification for the SIMTECHE Slipstream Test Unit

Process Description: The CO₂-Hydrate Slipstream Test Unit (STU) will be used to demonstrate the performance of the hydrate process with a pilot plant processing a slipstream of syngas from an operating gasifier. The test program plans for a nominal 2 years of development testing, although a detailed test plan hasn't been developed yet.

We will design and build the STU as a modularized unit that can be set in place with little disruption to the facility by construction.

The Feed gas is assumed to be at 1000 psig and will be cooled and chilled down to 34 F for the main reaction. It is mixed with CO₂ saturated water to form CO₂-hydrate. The CO₂-hydrate and water will be separated from the hydrogen 'rich' Syngas in the separator. The hydrogen 'rich' syngas, as described below, will be returned to the main process. The CO₂-hydrate and water slurry goes into the hydrate flash reactor where heat is applied, the hydrate decomposes, and CO₂ gas is boiled off from the water as a CO₂-'rich' gas stream. This would be the CO₂ which is sent to sequestration in a commercial use of the process. The remaining water is resaturated with recycled product CO₂ and recycled to the main reactor. An ammonia (or other refrigerant)

refrigeration system will provide the process-cooling requirement. A separate packaged cooling tower can be installed to service the ammonia refrigeration system as well as other process needs.

(1) Feed Gas

‘Desired’ Feed Gas (shifted Syngas) Compositions:

40 vol % CO₂

59 vol % H₂

1 vol % H₂S

MW = 19.1

It is assumed that other gases, such as COS, Argon, methane, etc. are present in smaller quantities. Their compositions aren’t critical, but their presence is desired because this is meant to be a test of the process using a real syngas. We will install secondary shift reactors to get the CO content down to 1-2% in the dry gas, so any stream requiring further shifting will be preferred at shift reactor temperatures.

Desired Feed Gas Flowrate = 351 Lb moles/hr (133,200 SCFD dry basis)

Desired Feed Gas Pressure = 1000 psig

Desired Feed Gas Temp = 34°F

This is not firm, we can work with the operator if this flowrate is excessive. We will do the necessary cooling to produce a feed gas to our reactor at 34°F.

(2) 'Expected' Product gas & Effluents

Note: based on desired feed flow

A. CO₂-depleted Syngas stream flowrate = 230-250 lb moles/hr

To be returned to the main process

Pressure = 950 psig Temp = 34 deg. F (system pressure drop is approximate)

Compositions: H₂ = 80-90 vol %

CO₂ = 10-20 vol %

CO = 1 vol %

Others in small amounts. Most of the H₂S will go into the CO₂ product

B. Product CO₂ flowrate = 100-120 lb moles/hr

This is the stream which would be sent to sequestration

Pressure = 530 psig nominal, ± 300 Temp = 54 deg F (the flash pressure and temperature are important process variables and may vary widely)

Compositions: CO₂ = 96-99 vol %

H₂S = 1-3 vol %

H₂ and others = $\sim 1/2$ vol %

Effluents

(1) Water – sour condensate from cooling the feed gas, and purge water from the process will be produced:

i. Condensate: up to 16 gpm

- ii. Purge water: negligible, but process drains will be required and this must be assumed to be sour water.
- (2) Vent Gas – Connections to a captured vent will be required for relief valves and process vents.
- (3) Refrigerant – Usually a vent stack is used for freon, if using ammonia we will have to connect to the flare
- (4) Cooling Tower Blowdown – minimal, raw water
- (5) Other chemicals: possibly we could be trying 'promoters' to enhance the process, any changes will be done in consultation with the facility owner.

Utilities Requirements

- (6) Power---Average 300 KW & 350 KW maximum. The ammonia refrigeration system compressor may require 2300V power supply.
- (7) Water---Approximately 25 to 30 GPM, mainly as make-up water for the cooling tower. If an air-cooled refrigeration system is used, the usage will be around 2-5 gpm.
- (8) Instrument Air---Average 10-15 SCFM & 35 SCFM maximum.
- (9) Steam (low pressure at 150 psig)---Normally less than 200 lb/hr.
Maximum/Startup = 3,200 lb/hr
- (10) Nitrogen/Air---Normally zero. Require 20-25 SCFM at startup or turnaround.

Control Room

The process control will require roughly 100-200 control inputs/outputs, data logging and control computers, possibly simple PLC devices to shut down and protect the main process.

Personnel

Access to the facility will be required for test personnel to plan and run test campaigns with the STU.