Warm Gas Multi-contaminant Removal System
(Contract No. DE-SC0008243)

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Project Objectives

- The project objective is to demonstrate techno-economic viability of a synthesis gas purification system to eliminate potential catalyst poisons and environmental pollutants from coal-derived synthesis gas
  - A high temperature sorbent is used for operation above the dew point of the synthesis gas
  - The sorbent is operated in a regenerable manner for NH$_3$ and Hg
  - All other contaminants (trace metals, HCN etc.) is removed irreversibly

- Project Tasks
  - Scale-up the production of the sorbent
  - Carry out multiple cycle to demonstrate long-term durability of the sorbent
  - Design a slipstream test unit for proof-of concept evaluations
    - 1 to 10 SCFM raw synthesis gas treatment capacity
  - Complete a high fidelity process design and economic analysis

- Project Duration
  - 3 years
  - Completion Date – 08/01/2019
Background

- Coal-derived synthesis gas contains a myriad of trace metal contaminants

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>Hg (ppm)</th>
<th>As (ppm)</th>
<th>Se (ppm)</th>
<th>Cd (ppm)</th>
</tr>
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<tbody>
<tr>
<td>Pittsburg</td>
<td>0.11</td>
<td>4.1</td>
<td>0.6</td>
<td>0.06</td>
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<td>Elkhorn/Hazard</td>
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<td>4.0</td>
<td>3.1</td>
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<td>Illinois No.6</td>
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<td>2.2</td>
<td>0.15</td>
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<tr>
<td>Wyodak</td>
<td>0.19</td>
<td>1.3</td>
<td>1.6</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Bool et al., 1997

- Removal of trace metals is critical to control emissions from advanced power cycles that use coal-derived synthesis gas feed
  - Mercury is singled-out for particular scrutiny because of its effects on humans and wildlife

- The nitrogen in the coal is converted to the NH$_3$ and HCN which will be converted into NOx in an IGCC plant

- Removal of metal contaminants and NH$_3$/HCN is also important for chemical manufacturing processes
  - Arsenic, HCN, NH$_3$ are a potent poisons for the catalysts used in the WGS and Fischer Tropsch synthesis
Warm Gas Contaminant Removal

- NH₃ removal is commonly accomplished by using a water scrubber, where NH₃ is reacted with a mildly acidic solution to be converted into a stable salt solution.
- These scrubbers typically run at low temperature to increase the NH₃ solubility (the critical first step is the dissolution of NH₃ in the scrubbing solution).
- These scrubbers do not reduce the NH₃ concentration to very low levels and do not remove contaminants such as hydrogen cyanide (HCN).
- For trace metals, the existing clean-up technologies based on physical adsorbents are also limited to low temperatures.
- The objective is to develop a sorbent-based for warm gas clean-up technology.
  - For a GE gasifier with water quench, the dew point is ~245°C (480°F).
- Warm temperature gas cleaning has major benefits:
  - Improves the efficiency of the power cycle.
  - Eliminate the need for any heat exchange equipment.
  - Eliminate the difficulties processing the condensate.
- Hg (also Se) has a very high vapor pressure over any surface at 200°C or higher temperatures (i.e., difficult to achieve high removal efficiency)
  - The resulting low capacity increases the cost of using expendable sorbents
- NH₃ removal using one-time use sorbents is also impractical as it is present in relatively high concentrations (200 to 1500 ppmv range)
TDA’s Multi-contaminant Removal Process

- Hg and NH₃ are removed at high temperature
- The sorbent is regenerated using a combination of temperature and pressure swing
- The off-gas from the sorbent bed is cooled enabling the use of low temperature sorbents or scrubbers
Early Testing at UNDEERC

- Operation of the regenerable Hg sorbent has been demonstrated in two test campaigns at UNDEERC
  - SUFCo bituminous (May 2008)
  - Oak Hills Lignite (June 2008)

- Specifications of EERC Transport reactor demonstration unit (TRDU)
  - Operating P=125 psig
  - 10,000 SCFH syngas treatment
Test Results at UNDEERC

Halogenated Carbon, $T=215^\circ C$ (420$^\circ F$)

- TDA sorbent achieved over 95% Hg removal efficiency and outperformed commercial halogenated carbon
- EERC Report November 2007 “Gasification of Lignites to Produce Liquid Fuels, Hydrogen and Power”
- Stable operation over 10 cycles at UNDEERC and over 30 at TDA
Key R&D Needs

- Demonstrating the combined NH$_3$ and Hg removal capability using a regenerable sorbent
  - Optimize and scale-up the sorbent
  - Laboratory experiments
  - Demonstrate long-term durability of the sorbent over many cycles
  - Slipstream evaluations using actual coal-derived synthesis gas for proof-of-concept evaluations
  - Complete a high fidelity process design and economic analysis
Sorbent production was scaled up using high throughput manufacturing equipment.

- Batch size 80 kg
- Final product 1/16” cylindrical extrudates with very high mechanical integrity
- Crush strength >2 lbf/mm
- (1/8” or ¼” size is also possible)
Setup Used in Contaminant Removal Tests

- High T/High P test rig capable of simulating synthesis gas compositions
- Nova Analyzer for H₂, CO, CO₂, CH₄ measurements
- SPM/Honeywell analyzer was used for AsH₃ and HCN detection
- Tekran 330 CEM for Hg analysis
Typical Test Profile – NH$_3$ Removal

- Sorbent Volume: 600 ml
- Total Flow: 5 slpm (N$_2$ Bal)
- NH$_3$ Feed Concentration: 2000 ppm
- H$_2$O Concentration: 10%
- Adsorption Temp: 180°C/250°C
- Regeneration Temp: 250°C/285°C
- Adsorption Pressure: 1.38 MPa (200 psig)
- Regeneration Pressure: 0.03 MPa (5 psig)
- GHSV: 500 hr$^{-1}$
- L/D: 2.4
Regenerable NH$_3$ Removal

Adsorption: T=200-250°C, P= 100 psig, NH$_3$ Inlet = 2,000 ppmv, GHSV = 2,000 h$^{-1}$, simulated synthesis gas
Regeneration: T= 250-300°C, P=10 psig under N$_2$ flow, GHSV = 200 h$^{-1}$

- TDA sorbent maintained a stable capacity ~700 cycles (achieving over 5% wt. NH$_3$ capacity)
Hg Removal

Absorption: $T = 240°C$, $P = 2.5$ psig, $Hg = 70$ ug/m$^3$, GHSV = 3,000 h$^{-1}$
Regeneration: $T = 280°C$, $P = 1$ psig under N$_2$ flow, GHSV = 200 h$^{-1}$

- TDA sorbent also maintains a stable capacity for Hg over multiple cycles (3 cycles were completed to demonstrate the concept)
HCN and AsH₃ Removal

**T = 240°C, HCN = 10 ppmv, P= 300 psig, GHSV = 7,500 h⁻¹**

- Sorbent also achieved over 3% wt. HCN capacity with very high removal efficiency

**T= 245°C, P= 350 psig, AsH₃ Inlet= 1.22 ppmv, H₂S Inlet= 20-4,800 ppmv, GHSV= 180,000 h⁻¹**

- In presence of 20 ppmv H₂S, 7.1% wt. capacity was achieved (at breakthrough)
  - Sorbent also achieved 8.5% wt. sulfur capacity
Testing at NCCC/PSDF In a 4-Bed PSA

4-bed PSA Skid

Gas Conditioning Skid

• A 4-bed PSA field unit designed to evaluate a pre-combustion CO$_2$ removal sorbent qualified for use at NCCC/PSDF is used for proof-of-concept evaluations
Field Test Units Installed at NCCC
NCCC Test Results

Adsorption: T=200-250°C, P= 100 psig, NH₃ Inlet = 2,000 ppmv, GHSV = 2,000 h⁻¹, simulated synthesis gas
Regeneration: T= 250-300°C, P=10 psig under N₂ flow, GHSV = 200 h⁻¹

- Three cycles were performed by “only” applying pressure swing
- First cycle had a very high capacity as in the consecutive ones sorbent is not fully regenerated
Prototype Control System

TPO Period 2:51
Gas Molecular Weight 28.060

Controller Status
- Actonate AC Power
- Start Cycling
- Startup System
- Idle System

Controller Setpoints
- N2 MFM
  - ON
  - (11.45 LPM), (139.4 SLPM)
- Setpoint
  - 0 CCM
  - 4 CCM
  - 51 SCCM
- Pause

Flow Check
- TC-101
  - 54.6 C
  - 200.1 psi
- TC-202
  - 115.4 C

NH3 Monitor
- 0 ppm

NH3 Concentration
- 20.84 PPM
- Auto Bed Switch
  - ON
- Breakthrough Limit
  - 50 PPM

START/STOP SAMPLE LOGS
- SPM Analyzer
  - Off Time: 0.0 min
  - On Time: 0.0 min
  - 0.0 min
- Thermo NH3 Analyzer
  - Record NH3 Log
- Pressures, Temps, Flows
  - 0.1 scfm
  - 0.0 scfm
- Record Data Log

Sorbet Bed A
- TC-103A
  - 155.8 C
- TC-102A
  - 115.9 C
- TC-104A
  - 110.7 C

Sorbet Bed B
- TC-103B
  - 156.0 C
- TC-102B
  - 135.9 C

Disposable Bed
- TC-201
  - 199.8 psi
- TC-207
  - 29.4 C

Regen N2
- TC-206A
  - 87.9 C
  - 36.3 C
  - 12.2 psia
- TC-208A
  - 20.0 psi
- TC-206B
  - 33.3 C
  - 81.5 C
  - 12.2 psia

HPLC Pump
- OFF

11.9 psia
188.0 psi
A slipstream test unit is being fabricated to demonstrate continuous removal of NH₃ and Hg using coal derived synthesis gas.

Originally, we have designed a unit that is capable of treating 10 SCFM of synthesis gas for testing at the NCCC.

A smaller unit is now being built to treat up to 1 SCFM synthesis gas.
The cost of removing NH$_3$, Hg, AsH$_3$ and HCN contaminants are estimated as ~$3.7$ MM per year ($10.1$ MM with annualized capital cost).
Acknowledgement

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