High-Temperature Sulfur Removal in Gasification Applications

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What is Gasification?

Gasifier Section:
- Controlled chemical reaction
- Typically > 2300 deg F
- Up to 1200 psig
- Organics Destroyed
- Short residence time (seconds)
- Reduced O₂ Environment

Quench Section:
- Gas and molten ash quenched in circulating water bath
- Ash/slag discharged as inert, glassy frit (saleable product)

Products (syngas):
- CO
- H₂

By-products:
- H₂S
- Ash (slag)
- CO₂
- Steam

CO/H₂ ratio can be adjusted

ASU Products (syngas):
- CO
- H₂

Gas Clean-Up Before Product Use!

Slag (Inert Minerals/Ash from Coal)
Gasification Chemistry

- **Gasification with Oxygen**
  
  \[ C + \frac{1}{2}O_2 \rightarrow CO \]

- **Combustion with Oxygen**
  
  \[ C + O_2 \rightarrow CO_2 \]

- **Gasification with Carbon Dioxide**
  
  \[ C + CO_2 \rightarrow 2CO \]

- **Gasification with Steam**
  
  \[ C + H_2O \rightarrow CO + H_2 \]

- **Gasification with Hydrogen**
  
  \[ C + 2H_2 \rightarrow CH_4 \]

- **Water-Gas Shift**
  
  \[ CO + H_2O \rightarrow H_2 + CO_2 \]

- **Methanation**
  
  \[ CO + 3H_2 \rightarrow CH_4 + H_2O \]

**Gasifier Gas Composition (Vol %)**

<table>
<thead>
<tr>
<th>Component</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>25 - 30</td>
</tr>
<tr>
<td>CO</td>
<td>30 - 60</td>
</tr>
<tr>
<td>CO₂</td>
<td>5 - 15</td>
</tr>
<tr>
<td>H₂O</td>
<td>2 - 30</td>
</tr>
<tr>
<td>CH₄</td>
<td>0 - 5</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.2 - 1</td>
</tr>
<tr>
<td>COS</td>
<td>0 - 0.1</td>
</tr>
<tr>
<td>N₂</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>Ar</td>
<td>0.2 - 1</td>
</tr>
<tr>
<td>NH₃ + HCN</td>
<td>0 - 0.3</td>
</tr>
</tbody>
</table>

**Ash/Slag/PM**

Coal → Oxygen → Steam
What is IGCC?

PRE-COMBUSTION Treatment of Pollutants
• High pressure
• Low Volume
• Concentrated stream (easier to treat)

Gasifier (quench)
Coal + H₂O → CO₂ + H₂ + Water-Gas Shift Reaction

Particulate Scrubber
Low Temp Gas Cooling
Shift Rxn (optional)
Mercury Removal > 90-95% Removal

Sulfur Removal & Recovery
98-99.9+% Removal

CO/H₂ (Syngas)

CO₂ Capture/Sequestration (concentrated stream)

Electricity > 90-95% Removal

Non-Leachable Heavy Metal Removal

Slag/Frit

Compressed Air to ASU

Air Separation Unit (ASU)
O₂

Sulfur

Coal

H₂O

Electricity

Steam Turbine

HRSG

Combustion Turbine

Electricity

Compressed Air to ASU

What is IGCC?

Flexibility for CO₂ Capture/Sequestration (concentrated stream)
Contaminants in Coal-Derived Syngas

<table>
<thead>
<tr>
<th>Element</th>
<th>Species</th>
<th>Range of Concentrations in Coal</th>
<th>Range of Concentrations in Syngas</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>H₂S, COS, CS₂</td>
<td>0.3 – 3.6 wt%¹</td>
<td>750-7000 ppmv as H₂S and 25-200 ppmv as COS²</td>
</tr>
<tr>
<td>N</td>
<td>NH₃, HCN</td>
<td>1.1 – 1.6 wt%¹</td>
<td>50-800 ppmv as NH₃²</td>
</tr>
<tr>
<td>Cl</td>
<td>HCl, metal chlorides</td>
<td>0.0032-0.37 wt%³</td>
<td>170-830 ppmv as HCl²</td>
</tr>
<tr>
<td>Hg</td>
<td>Hg (g)¹, Hg(CH₃)₂¹</td>
<td>0.02-1 μg/g³</td>
<td>1.3-63 ppbv⁴</td>
</tr>
<tr>
<td>As</td>
<td>As₂ (g)¹, As₄ (g)², AsH₃ (g)¹, AsS (g)², and other FeAs species¹</td>
<td>0.5-80 μg/g³</td>
<td>84-1300 ppbv⁴</td>
</tr>
<tr>
<td>Se</td>
<td>H₂Se (g)¹²</td>
<td>0.2-1.6 μg/g³</td>
<td>32-2600 ppbv⁴</td>
</tr>
<tr>
<td>Cd</td>
<td>Cd (g)¹, CdS (condensed)¹, CdCl₂ (g)¹</td>
<td>0.1-3 μg/g³</td>
<td>11-340 ppbv⁴</td>
</tr>
</tbody>
</table>

¹ Equilibrium calculations by Diaz-Somoano (2003) at 572 to 932°F.
² Data survey of four types of gasifiers conducted by Bakker (1998).
³ Typical concentrations in the world's coal as examine by Swaine (1990).
⁴ Calculated concentrations based on elemental concentration in coal and assuming complete vaporization.

1 Determined in Canadian feed-coals (Goodarzi, 2002).
2 Data survey of four types of gasifiers conducted by Bakker (1998).
3 Typical concentrations in the world's coal as examine by Swaine (1990).
4 Calculated concentrations based on elemental concentration in coal and assuming complete vaporization.
AGR Technologies Can Provide Near 100% Sulfur Removal If Required

(AGR = Acid Gas Removal)

Major Technology Options:

- **MDEA** (methyl diethanolamine) – Chemical absorption, 98% to 99+% S removal, large CO$_2$ slip (unless use a second stage for CO$_2$ recovery), moderate operating temperature, lowest AGR capital cost

- **Selexol™** (primarily dimethyl ethers of polyethylene glycol, DEPE) – Physical absorption, 99+% S removal, variable CO$_2$ slip (based on design), higher AGR cost than MDEA but overall AGR/SRU system costs similar

- **Rectisol™** (methanol) - Physical absorption, 99.5% to 99.9+% S removal, complete CO$_2$ removal possible, highest AGR cost, coldest operating temperatures

- **Warm Syngas Cleanup** - New technologies (e.g., RTI/Eastman) being developed that operate at high temperatures (300-600°C) and at sub to low ppm (<10) sulfur levels. Lowest capital and operating cost option with significant improvement in overall efficiency.
Integrated Gasification Combined Cycle (IGCC)

R&D objective: Platform of warm syngas cleaning technologies providing improved efficiency, environmental performance, and cost
Contaminants removed by high-temperature syngas cleaning technology platform include:

- Sulfur (H₂S, COS)
- Contaminant heavy metals
- Acid gases (CO₂)

Key Feature
Thermal efficiency is maintained by avoiding condensation of steam.
Warm Gas Sulfur Removal

- Sorbent Development
- Process Development
- Compatibility with other contaminant removal processes
- Process Integration
  - IGCC (power generation)
  - Chemical/fuels applications
Sulfur Sorbents

- Metal oxides react with H$_2$S and COS to form metal sulfides
  \[\text{MeO} + \text{H}_2\text{S} = \text{MeS} + \text{H}_2\text{O}\]

- Most of these metal sulfides are regenerable with air
  \[\text{MeS} + \frac{3}{2} \text{O}_2 \rightarrow \text{MeO} + \text{SO}_2\]

- Thermodynamic and kinetic limitations provide a list of suitable candidates (ZnO, Fe$_2$O$_3$, CuO, MnO$_2$, CeO$_2$, SnO$_2$, etc.)

- Zinc oxide and iron oxide-based sorbents are most developed.

- ZnO-based materials provide the best overall performance.
**Desulfurization Chemistry for ZnO Sorbents**

- **Desulfurization** (*Absorber*)
  \[ \text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \quad [\Delta G = -73 \text{ kJ}] \]

- **Regeneration** (*Regenerator*)
  \[ \text{ZnS} + \frac{3}{2} \text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2 \quad [\Delta G = -423 \text{ kJ}] \]

- **Sulfur Recovery Options**
  - Claus Process
  - Direct Sulfur Recovery Process (DSRP)
    \[ \text{SO}_2 + \text{H}_2 \ (\text{or CO}) \rightarrow \frac{1}{n} \text{S}_n + \text{H}_2\text{O} \ (\text{or CO}_2) \]
  - Sulfuric acid
Equilibrium H$_2$S Concentration in Syngas as a Function of Temperature and H$_2$O Content
Challenges with ZnO Sorbents

- ZnO based materials are extensively used in chemical industry as guard beds. They work very well, but cannot be regenerated.
- Regeneration of the ZnS to ZnO is highly exothermic ($\Delta H \sim 445$ kJ). Heat removal and reactor design become very important.
- Reduction of ZnO into metallic Zn with highly reducing syngas (e.g., Shell) at high temperatures (>500°C) presents serious problems.
- Sorbent needs to maintain long-term (1-2 year) lifetime without significant deactivation and attrition.
Potential Solutions

- Support ZnO on an inert matrix to provide strength and surface area. Potential supports include: silica, titania, alumina, etc.

- Use a fluidized-bed reactor design to deal with exothermicity of the regeneration reaction.

- Develop a fluidizable sorbent material (50-200 micron particle size) with high reactivity and attrition resistance.
- Development of RTI-3 Sorbent
- Development of a fast fluidized-bed reactor or transport reactor system for desulfurization
- Integration of the process with a commercial gasifier
- Development of ancillary technologies to deal with other contaminants and CO$_2$ at high-temperature, high-pressure conditions.
- Maximize thermal efficiency, and reduce overall capital and operating costs over the conventional systems.
- Demonstrate the operability and reliability of the process with real syngas over extended period of time.
Transport Reactor Desulfurization System

- Reactor design identical to a conventional FCC design
- Smaller inventory needed
- Gas residence time of 1-2 seconds for absorption and regeneration
- Handles fines in feed gas
- Easier temperature control
- Need for high sulfur capacity eliminated
- Smaller foot-print, less capital costs
- Need a sorbent with high reactivity and attrition resistance
Sorbent Development Criteria

COST

REACTIVITY
- CIRCULATION RATE
- RISER DENSITY
- MAKE-UP RATE

ATTRITION

ABSORPTION
- 1-2 s contact time
- ≤ 10 ppmv H₂S leakage
- Consistent performance

REGENERATION
- Light-off at 1000 °F
- No O₂ breakthrough
- Oxidation with neat air

PARTICLE SIZE
- 80 μm APS (FCC type)
- Can be produced by spray drying

BULK DENSITY
- ≥ 50 lb/ft³

DISPOSAL OF FINES
RTI-3 Sorbent

- ZnO supported on zinc aluminate
- Unique nanostructure with grain size <50 nm and high dispersion of ZnO in the matrix
- Produced by spray drying in commercial size equipment
- US patent granted to RTI (US Patent: 6,951,635)
RTI’s high-temperature, high-pressure bench-scale sorbent test facility
Effluent Sulfur Concentrations

Temperature: 600°F
Pressure: 280 psig
Composition (vol%)
- CO: 21.1
- H₂: 14.5
- CO₂: 4.4
- H₂S: 0.5
- H₂O: 59.5
RTI-3 Regeneration Profiles

Temperature: 1000 °F
Pressure: 280 psig
Composition (vol%):
- \( \text{N}_2 \) 91.0
- \( \text{O}_2 \) 9.0
Sorbent Attrition Data

Figure 3. Attrition indices results from attrition resistance testing of RTI-3 and ECAT
RTI-3 Sorbent Scale-Up

- 1 lb - NIRO spray dryer (RTI)
- 100 lb (pilot plant)
- 600 lb (manufacturing plant and 24 ft spray dryer)
- 2000 lb (manufacturing plant and 24 ft spray dryer)
  - Material field tested at ChevronTexaco
- 8,000 lb (manufacturing plant and 24 ft spray dryer)
  - Material being field tested at Eastman
- Sorbent production scale up complete with demonstrated production
  - Using commercial scale equipment
  - By reputable catalyst manufacturer
  - In large batches
- Received R&D 100 Award (2004)
RTI Sorbent Testing at KBR TRTU
Proof of Concept / Design Basis

**Sorbent**: RTI-3; spray dried 80 microns

**Operating Conditions:**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Adsorption</th>
<th>Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°F)</td>
<td>600-900</td>
<td>1100-1300</td>
</tr>
<tr>
<td>Pressure (psig)</td>
<td>135</td>
<td>135</td>
</tr>
<tr>
<td>Composition (vol%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S + COS</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>Steam</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td>6</td>
</tr>
</tbody>
</table>

**Performance:**

<table>
<thead>
<tr>
<th>Sulfur Leak (ppmv)</th>
<th>&lt;1 (600°F)</th>
<th>&lt;10 (900°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur Loading (wt%)</td>
<td>~8</td>
<td></td>
</tr>
<tr>
<td>Attrition*</td>
<td>9 (Fresh)</td>
<td>9 (used)</td>
</tr>
</tbody>
</table>

* Davison attrition index Fresh FCC Catalyst =10
Process Development Challenges

- No high-pressure, high-temperature fluidization data available in literature to design a prototype.
- Extensive cold flow testing was conducted.
- Hydrodynamics at high-pressures did not fit any available models.
- Stable sorbent circulation in controlled manner between absorber and regenerator became a major challenge.
- Mixing of syngas (in absorber) and oxygen (in the regenerator) had to be minimized.
- Control philosophy was developed to devise robust process control.
ZnO + H₂S → ZnS + H₂O
ZnO + COS → ZnS + CO₂

\[ \text{ZnS+3/2O}_2 \rightarrow \text{ZnO+SO}_2 \]
Schematic of Eastman Field Test
Various Installations of HTDS

Eastman Gasification Plant

RTI Desulfurization Unit / DSRP
Typical Sulfur Concentrations in Effluent Syngas (Eastman 2005)

Dirty Syngas Composition: $\text{H}_2\text{S}$ 9,400 ppmv  
COS 22 ppmv
Typical Sulfur Concentrations in Effluent Syngas (Eastman 2006-2007)

Dirty syngas composition: 7,771 ppmv H$_2$S
440 ppmv COS

- H$_2$S removal > 99.97%
- COS removal > 99.96%
Desulfurization Process Stability

H$_2$S removal > 99.97%

Sulfur rate (kg/h)

Regeneration rate

Desulfurization rate

Effluent sulfur concentration (ppbv)

22 hours
### HTDS Field-Testing at Eastman

All data are averages over multiple hours of operation.

<table>
<thead>
<tr>
<th></th>
<th>300</th>
<th>450</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (psig)</td>
<td>300</td>
<td>450</td>
<td>600</td>
</tr>
<tr>
<td>Inlet S concentration (ppmv)</td>
<td>8,661</td>
<td>6,935</td>
<td>8,381</td>
</tr>
<tr>
<td>Effluent S concentration (ppmv)</td>
<td>5.9</td>
<td>7.8</td>
<td>5.7</td>
</tr>
<tr>
<td>S absorbed (lb/h)</td>
<td>4.1</td>
<td>4.2</td>
<td>4.8</td>
</tr>
<tr>
<td>S removal (%)</td>
<td>99.93</td>
<td>99.89</td>
<td>99.93</td>
</tr>
</tbody>
</table>

HTDS operation time > 2,750 h of actual syngas desulfurization

*(cumulative to date)*
Particle Size Distributions

Fresh

Used
## Sorbent Characterization Results

<table>
<thead>
<tr>
<th></th>
<th>Fresh Sorbent</th>
<th>Spent Sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Attrition Index* (KBR Test)</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>(EMN Test)</td>
<td>1.0</td>
</tr>
<tr>
<td>Bulk Density (lb/ft³)</td>
<td>119</td>
<td>127</td>
</tr>
<tr>
<td>Particle Size Distribution [d₅₀] (µm)</td>
<td>60.4</td>
<td>75.5</td>
</tr>
<tr>
<td>Sulfur Loading (wt%)</td>
<td>8</td>
<td>9</td>
</tr>
</tbody>
</table>

* Relative Attrition Ratio = (Davison Index [target material])/(Davison Index [FCC catalyst])
Successful Process Demonstrations

- Stable operation of pressurized transport desulfurization system
  - 2,783 hours of Syngas Operations
    - 346 hr longest continuous run
    - 61% On-stream availability from 2/18/07
    - Most downtime caused by support/ancillary equipment
- Desulfurization performance
  - H\(_2\)S and COS removal
  - Effluent sulfur < 10 ppmv (Inlet sulfur ~8000 ppmv)
- Solids circulation
  - Attrition loss~ 10-50 kg/MM kg circulated (FCC ~50-100 kg/MM kg circulated)
- Thermally neutral process operation over an acceptable temperature range
- Operating controls provide stable solids circulation and process performance
- Commercial startup/shutdown plans being tested
Direct Sulfur Recovery Process (DSRP)

- Reaction chemistry:
  \[
  \begin{align*}
  \text{SO}_2 + 2\text{H}_2 & \rightarrow \frac{1}{n} \text{S}_n + 2\text{H}_2\text{O} \\
  \text{SO}_2 + 2\text{CO} & \rightarrow \frac{1}{n} \text{S}_n + 2\text{CO}_2
  \end{align*}
  \]

- Temperature: 500-600°C

- Pressure: 300 psig (favors higher pressures)

- Catalyst: Molybdenum sulfide on alumina

- Reactor design: Fixed bed
### DSRP Field-Testing at Eastman

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regeneration Off gas (SCFH)</td>
<td>1256</td>
</tr>
<tr>
<td>Syngas flow (SCFH)</td>
<td>72</td>
</tr>
<tr>
<td>SO$_2$ Inlet Concentration (ppmv)</td>
<td>24,125</td>
</tr>
<tr>
<td>SO$_2$ Outlet Concentration (ppmv)</td>
<td>22</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>99.91</td>
</tr>
</tbody>
</table>

Data are averages over multiple runs.

DSRP Integrated operation time ~50 h of actual syngas desulfurization
55 lbs of sulfur collected (Predicted production 61 lb)
*(cumulative to date)*
## Chemical Nature of Gaseous Trace Element Species in a Coal Gas Stream

<table>
<thead>
<tr>
<th>Element</th>
<th>&gt;1000°C</th>
<th>400° to 800°C</th>
<th>100° to 400°C</th>
<th>&lt;100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>AsO, AsS, As</td>
<td>AsO, As, As₂S₃</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Be</td>
<td>Be(OH)₂</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Hg</td>
<td>Hg, HgS, HgO</td>
<td>Hg</td>
<td>Hg, HgCl₂</td>
<td>Hg, HgCl₂</td>
</tr>
<tr>
<td>B</td>
<td>HBO</td>
<td>HBO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>VO₂</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Se</td>
<td>H₂Se, Se, SeO</td>
<td>H₂Se</td>
<td>H₂Se</td>
<td>H₂Se</td>
</tr>
<tr>
<td>Ni</td>
<td>NiCl</td>
<td>Condensed Species</td>
<td>Ni(CO)₄</td>
<td>Ni(CO)₄</td>
</tr>
<tr>
<td>Co</td>
<td>CoCl₂, CoCl</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Sb</td>
<td>SbO</td>
<td>SbO</td>
<td>Sb₂S₃</td>
<td>Sb₂S₃</td>
</tr>
<tr>
<td>Cd</td>
<td>Cd</td>
<td>Cd</td>
<td>CdCl₂</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Pb</td>
<td>PbS, Pb, PbCl₂</td>
<td>PbS, Pb, PbCl₂</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn</td>
<td>Zn, ZnCl₂</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
</tbody>
</table>
Multicontaminant Control

Removal of other pollutants from syngas is necessary to reduce the overall cost of IGCC-based systems.

In addition to sulfur, RTI and Eastman are pursuing removal of a host of other contaminants from syngas at high-temperature, high-pressure conditions:

- $\text{NH}_3$, HCl, HCN
- Heavy metals (Hg, As, Cd, Se)
Ammonia Effluent Profiles
(1-inch Fixed-Bed Reactor Testing)

<table>
<thead>
<tr>
<th>Process cycle</th>
<th>Temperature (°F)</th>
<th>Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>392</td>
<td>200</td>
</tr>
<tr>
<td>Regeneration</td>
<td>752</td>
<td>14.7</td>
</tr>
</tbody>
</table>

- Demonstrated highly acidic molecular sieves for regenerative NH₃ adsorption/desorption process
HCl Removal Performance

- Demonstrated HCl removal to <50 ppb (time h) NaHCO$_3$ supported on sepiolite

- Space velocity = 2,000 h$^{-1}$
- Inlet HCl level = 50 ppm
- $T = 350 °C$

<table>
<thead>
<tr>
<th>Residual HCl vapor concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>Diatomaceous earth sorbent</td>
</tr>
<tr>
<td>Sepiolite/NaHCO$_3$ sorbent</td>
</tr>
</tbody>
</table>
Schematic of Mercury Exposure Apparatus

Test Gas:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>30 ppbV</td>
</tr>
<tr>
<td>H₂</td>
<td>19 vol. %</td>
</tr>
<tr>
<td>CO</td>
<td>27 vol. %</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.5 vol. %</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.5 vol. %</td>
</tr>
<tr>
<td>CO₂</td>
<td>Balance</td>
</tr>
</tbody>
</table>
Capacity values were determined when effluent Hg concentration was between 10% and 20% of feed concentration.
Schematic of Arsine Exposure Apparatus

Components within dashed line configured in chemical fume hood.

AsH₃ = 10 ppm
CO₂ = 51.5%
CO = 27%
H₂ = 20%
H₂O vapor = 1.5%
H₂S = 0.5%
### Summary of Arsine Capacity Tests

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Exposure temp. (°C)</th>
<th>GHSV (h⁻¹)</th>
<th>Matrix</th>
<th>Capacity (wt%)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTI-8</td>
<td>250</td>
<td>15,000</td>
<td>Dirty syngas A</td>
<td>0.22</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>15,000</td>
<td>Clean syngas</td>
<td>&gt;1.35</td>
<td>-</td>
</tr>
<tr>
<td>Impregnated carbon</td>
<td>250</td>
<td>15,000</td>
<td>Dirty syngas A</td>
<td>&gt;1.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>15,000</td>
<td>Dirty syngas A</td>
<td>&gt;8.0</td>
<td>-</td>
</tr>
<tr>
<td>Commercial Sorbent A</td>
<td>200</td>
<td>15,000</td>
<td>Dirty syngas A</td>
<td>3.0</td>
<td>90</td>
</tr>
<tr>
<td>Süd-Chemie Sample A</td>
<td>200</td>
<td>15,000</td>
<td>Dirty syngas B</td>
<td>&gt; 6.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>15,000</td>
<td>Dirty syngas A</td>
<td>&gt;1.9</td>
<td>-</td>
</tr>
</tbody>
</table>
IGCC: Low-Risk Option for Carbon Capture (~1/3 the cost for PC)

DOE Report "Major Environmental Aspects of Gasification-Based Power Generation Technologies", December 2002
**Goal:** Regenerable high-temperature CO$_2$ sorbent with potential of producing high-pressure CO$_2$ byproduct

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightleftharpoons \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3
\]

\[\Delta H^\circ_{298K} = -142.0 \text{ kJ/mol}\]

- Sorbent development
  - 1 kg of fixed-bed material
  - Several promising fluidized-bed formulations being tested
- Bench-scale testing
  - Multicycle adsorption/regeneration
  - Real syngas exposure
Regenerable CO$_2$ Sorbent Candidate

CO$_2$ / N$_2$

Clean Syngas

Raw Syngas
# CO$_2$ Capacity

## TGA

<table>
<thead>
<tr>
<th>Condition</th>
<th>CO$_2$ Capacity in 20% CO$_2$/N$_2$ (wt%)</th>
<th>CO$_2$ Capacity in Clean Syngas (wt%)</th>
<th>CO$_2$ Capacity in Raw Syngas (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without promoter</td>
<td>9</td>
<td>17</td>
<td>19</td>
</tr>
<tr>
<td>With Promoter A</td>
<td>16</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>With Promoter B</td>
<td>23</td>
<td>29</td>
<td>30</td>
</tr>
</tbody>
</table>

## Fixed-bed

![CO$_2$ Capacity vs Temperature](image)

- **From Syngas**
- **From CO Shift**
Demonstration of High-Purity H₂ Production

Effluent Gas from Treatment
with Regenerable CO₂ Sorbent and WGS Catalyst

![Graph showing gas composition over time](image)
Acid Gas Removal Using Polymer Membranes

- Low temperature reverse selective membranes
- Can permeate $\text{CO}_2$, $\text{H}_2\text{S}$ and COS from syngas
- Can be potentially combined with amine systems
Permeability in Rubbery and Glassy Polymers: Effect of Penetrant Size

\[ P = S \times D \]

Solubility selectivity \( \alpha_{A/B} = \frac{P_A}{P_B} = \left( \frac{S_A}{S_B} \right) \left( \frac{D_A}{D_B} \right) \)

Mobility selectivity

1 barrer = \(10^{-10} \text{cm}^3\text{(STP)}\cdot\text{cm}/(\text{cm}^2\cdot\text{s}\cdot\text{cmHg})\)
Novel Reverse-Selective Membranes for Bulk H₂S and CO₂ Removal

**H₂S/H₂ Tradeoff**

- **H₂S permeability (barrer)** vs. **H₂S/H₂ selectivity**
  - Color points – New ether-containing polymers studied as dense films in this project; Mixture results
  - Black points – Conventional polymers reported in literature; Mostly pure-gas data

**CO₂/H₂ Tradeoff**

- **CO₂ permeability (barrer)** vs. **CO₂/H₂ selectivity**

**1 barrer = 10⁻¹⁰ cm³(STP)·cm/(cm²·s·cmHg)**
Membrane Development Accomplishments

- Created a reference source for mixed-gas permeabilities for various syngas species, including H$_2$S, COS, SO$_2$, and CO
- Synthesized polymer films with H$_2$S/H$_2$ selectivities >30
- Found strong dependence of selectivity on temperature
- Discovered unusual permeation properties of fluorinated polymers for H$_2$S separation
- Published results in three peer-reviewed articles, with one in the journal *Science*
- Produced three bulk-desulfurization spiral-wound membrane modules (0.75-m$^2$ membrane area each)
- Designed and constructed skid-mounted field-test membrane system
  - Shipped to test site at Eastman Chemical

*A spiral-wound membrane module to be used in field test*
Membrane Skid System
Technical and Economic Evaluation

- Process integration in an IGCC plant
- Process integration for chemicals/fuels
- Capital and operating cost estimation
- Thermal efficiency advantages
- Scale up issues/sizes for full commercial unit
- Technology risk analysis and mitigation
Potential Integration Schemes for Multicontaminant Cleanup
## Comparison of Desulfurization Processes

<table>
<thead>
<tr>
<th></th>
<th>Selexol</th>
<th>RTI/Eastman</th>
<th>Rectisol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>&lt;20</td>
<td>Syngas dew point to radiant cooler</td>
<td>-40</td>
</tr>
<tr>
<td>Sulfur removal (ppmv)</td>
<td>&lt;20</td>
<td>&lt;10</td>
<td>0.1</td>
</tr>
<tr>
<td>COS hydrolysis required</td>
<td>Yes (?)</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Capital cost ($/kW)</td>
<td>160</td>
<td>70-100</td>
<td>~190</td>
</tr>
<tr>
<td>Operating costs (¢/kWh)</td>
<td>~0.1</td>
<td>&lt;0.1</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>Thermal efficiency</td>
<td>Base</td>
<td>1.7–2.7%</td>
<td>&lt;Base</td>
</tr>
<tr>
<td>Commercially available</td>
<td>Now</td>
<td>2008</td>
<td>Now</td>
</tr>
</tbody>
</table>

*Source: Eastman, ChevronTexaco, Nexant (2003)*
### Updated 2007 Cost Estimates

*(Nexant)*

<table>
<thead>
<tr>
<th>Description</th>
<th>2005 IL#6 Base Case</th>
<th>IGCC</th>
<th>2005 IL#6 IGCC with WGCU</th>
<th>2006 IL#6 IGCC</th>
<th>2006 IL#6 WGCU</th>
</tr>
</thead>
<tbody>
<tr>
<td># of Trains</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Installed Cost, $MM (2006)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal Handling &amp; Storage</td>
<td>2</td>
<td>18.4</td>
<td>2</td>
<td>18.4</td>
<td>17.8</td>
</tr>
<tr>
<td>Gasification &amp; Slurry Preparation</td>
<td>2</td>
<td>159.0</td>
<td>2</td>
<td>159.0</td>
<td>151.5</td>
</tr>
<tr>
<td>Spare Gasification Train</td>
<td>1</td>
<td>79.5</td>
<td>1</td>
<td>79.5</td>
<td>75.8</td>
</tr>
<tr>
<td>ASU + O2 Compression</td>
<td>2</td>
<td>79.8</td>
<td>2</td>
<td>84.7</td>
<td>80.9</td>
</tr>
<tr>
<td>LT Gas Cooling/COS Hydro./Hg Removal</td>
<td>2</td>
<td>36.8</td>
<td>2</td>
<td>37.2</td>
<td></td>
</tr>
<tr>
<td>AGR (Seleexol) &amp; SWS</td>
<td>2</td>
<td>139.1</td>
<td>2</td>
<td></td>
<td>133.2</td>
</tr>
<tr>
<td>SWS (Sour Water Stripper) Only</td>
<td></td>
<td>2</td>
<td>0.4</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Sulfur Recovery &amp; TGT</td>
<td>2+1</td>
<td>57.5</td>
<td>2</td>
<td>184.3</td>
<td>37.0</td>
</tr>
<tr>
<td>WGCU/DSRP Systems</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel Gas System</td>
<td>1</td>
<td>4.2</td>
<td>1</td>
<td>5.3</td>
<td>4.3</td>
</tr>
<tr>
<td>PIt. Instru. Air &amp; N2 Systems</td>
<td>1</td>
<td>22.9</td>
<td>1</td>
<td>8.9</td>
<td>23.7</td>
</tr>
<tr>
<td>Gas Turbine Generation</td>
<td>2</td>
<td>141.0</td>
<td>2</td>
<td>141.0</td>
<td>146.5</td>
</tr>
<tr>
<td>HRSG/Boiler Plt./BFW/DM/Cond. Systems</td>
<td>2</td>
<td>47.8</td>
<td>2</td>
<td>56.6</td>
<td>48.8</td>
</tr>
<tr>
<td>Steam Turbine Generation System</td>
<td>2</td>
<td>48.7</td>
<td>2</td>
<td>54.5</td>
<td>49.4</td>
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<tr>
<td>CW Pumps &amp; CT Fans</td>
<td>17.0</td>
<td></td>
<td></td>
<td>18.0</td>
<td>16.4</td>
</tr>
<tr>
<td>BOP</td>
<td>161.3</td>
<td></td>
<td></td>
<td>161.9</td>
<td>175.5</td>
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<tr>
<td>Total Field Cost (TFC)</td>
<td>1013.0</td>
<td></td>
<td></td>
<td>972.5</td>
<td>998.0</td>
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<tr>
<td>Home Office @ 10% of TFC</td>
<td>101.3</td>
<td></td>
<td></td>
<td>97.3</td>
<td>99.8</td>
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<tr>
<td>Contingency</td>
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<td></td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total Installed Cost (TPC)</td>
<td>1114.3</td>
<td></td>
<td></td>
<td>1069.8</td>
<td>1097.8</td>
</tr>
<tr>
<td>Installed Cost, $/Net kW</td>
<td>1997</td>
<td></td>
<td></td>
<td>1742</td>
<td>1967</td>
</tr>
<tr>
<td>Net Reduction</td>
<td></td>
<td></td>
<td></td>
<td>12.7%</td>
<td>20%</td>
</tr>
</tbody>
</table>

**Note:** The data represents the updated 2007 cost estimates for various components of a gasification system, including costs for different configurations and the impact of additional systems and operating costs.
# IGCC Performances
*(Nexant)*

## A. Import or Feeds

<table>
<thead>
<tr>
<th></th>
<th>2005 IL#6 Base Case</th>
<th>2005 IL#6 IGCC with WGCU</th>
<th>2006 IL#6 Base Case</th>
<th>2006 IL#6 IGCC with WGCU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Feed, STPD (AR)</td>
<td>5,763</td>
<td>5,763</td>
<td>5,467</td>
<td>5,467</td>
</tr>
<tr>
<td>95% Oxygen, STPD</td>
<td>4,612</td>
<td>5,038</td>
<td>4,701</td>
<td>4,933</td>
</tr>
<tr>
<td>Make Up Water, GPM</td>
<td>4,165</td>
<td>4,260</td>
<td>5,615</td>
<td>4,154</td>
</tr>
</tbody>
</table>

## B. Export or Products

<table>
<thead>
<tr>
<th></th>
<th>2005 IL#6 Base Case</th>
<th>2005 IL#6 IGCC with WGCU</th>
<th>2006 IL#6 Base Case</th>
<th>2006 IL#6 IGCC with WGCU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Power, MW</td>
<td>558</td>
<td>614</td>
<td>588</td>
<td>647</td>
</tr>
<tr>
<td>Sulfur, STPD</td>
<td>256</td>
<td>256</td>
<td>137</td>
<td>137</td>
</tr>
<tr>
<td>Slag &amp; Ash (Incl. Carbon), STPD (dry)</td>
<td>870</td>
<td>870</td>
<td>562</td>
<td>562</td>
</tr>
<tr>
<td>Process Waste Water, GPM</td>
<td>1,248</td>
<td>1,047</td>
<td>2,763</td>
<td>1,039</td>
</tr>
</tbody>
</table>

## C. Thermal Efficiency

<table>
<thead>
<tr>
<th></th>
<th>2005 IL#6 Base Case</th>
<th>2005 IL#6 IGCC with WGCU</th>
<th>2006 IL#6 Base Case</th>
<th>2006 IL#6 IGCC with WGCU</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV, %</td>
<td>36.0</td>
<td>39.6</td>
<td>37.8</td>
<td>41.6</td>
</tr>
<tr>
<td>LHV, %</td>
<td>37.5</td>
<td>41.2</td>
<td>39.6</td>
<td>43.5</td>
</tr>
</tbody>
</table>
Technology Risks for Commercial Deployment

- **Performance in real syngas**
  - Field testing has provided actual performance resulting from exposure to real coal-derived syngas

- **Process reliability**
  - Sorbent performance
    - Extended testing to evaluate long-term chemical deactivation and mechanical attrition
  - Process control and stability
    - Demonstrated and refined ability to control process at stable operating conditions
  - Process integration
    - Demonstrated integrated operation of technology components of syngas cleaning platform

- **Sorbent production scale-up**
  - Commercially manufactured 8,000 lbs of sorbent for pilot-plant testing

- **Process scale-up**
  - Successfully scaled process up to 0.3 MW
  - Actively working on 50-MW demonstration unit
## HTDS Scale-Up Factors

<table>
<thead>
<tr>
<th></th>
<th>EMN Pilot Plant</th>
<th>Prototype</th>
<th>Commercial</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Size (MWe)</strong></td>
<td>0.3</td>
<td>50</td>
<td>600</td>
</tr>
<tr>
<td><strong>Gas Flow (SCFH)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Thousands)</td>
<td>17</td>
<td>2,000</td>
<td>38,000</td>
</tr>
<tr>
<td><strong>Footprint (ft²)</strong></td>
<td>260</td>
<td>1100</td>
<td>3000</td>
</tr>
<tr>
<td><strong>Absorber</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixing Zone</td>
<td>15'H × 2.5&quot;ID</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Riser</td>
<td>40'H × 1.5&quot;ID</td>
<td>80'H × 19&quot;ID</td>
<td>80'H × 5.5&quot;ID</td>
</tr>
<tr>
<td><strong>Regenerator</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixing Zone</td>
<td>10'H × 1.5&quot;ID</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Riser</td>
<td>20'H × 1&quot;ID</td>
<td>80'H × 12&quot;ID</td>
<td>80'H × 3.75&quot;ID</td>
</tr>
<tr>
<td><strong>Sorbent Circulation Rate (lb/h)</strong></td>
<td>500</td>
<td>62,000</td>
<td>1,000,000</td>
</tr>
</tbody>
</table>
Two major gasification technology vendors are evaluating warm syngas cleaning technologies for commercial package.

Two additional gasification technology vendors have shown interest in this technology.

Potential host site for a 50-MWe demonstration plant is being negotiated to demonstrate commercial feasibility of warm syngas cleaning technologies.
Gasification Technologies Program

Clean, Affordable Energy Systems

- Feedstocks Flexibility
- Air Separation
- Oxygen Membrane

Gasification

Products/Byproducts Utilization

Gas Stream Cleanup

Gas Cleaning

H₂/CO₂ Separation

Power

Fuel Cell

High Efficiency Turbine

Process Heat/Steam

Electricity

Fuels

Fuels/Chemicals

Liquid Conversion

H₂

CO₂

Co-Production (co-funded activities)
Project Team

- RTI
- Eastman Chemical Company
- BOC Gases
- ChevronTexaco (CVX)
- Kellogg Brown & Root (KBR)
- Süd-Chemie (SCI)
- SRI International (SRI)
- MEDAL
- The University of Texas at Austin
- DOE/NETL