Selection of Wash Systems for Sour Gas Removal

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Outline

— Overview of Absorptive Sour Gas Removal Processes

— Criteria for Choice of Absorptive Sour Gas Removal Processes

— Comparison of Amine Wash Processes and the Rectisol® Process
  - Qualitative comparison
  - Case Studies: Sour gas removal for
    1. Fuel gas production for IGCC from coal
    2. Coal to Liquid (CtL) process
    3. Biomass to Liquid (BtL) process

— Summary and Conclusion
Overview of Absorptive Sour Gas Removal Processes

— **Chemical sour gas removal processes:**

  Acid gases are chemically bound to the solvent.
  
  - Amines: e.g. MEA, DEA, DIPA, MDEA, MDEA+additive (e.g. aMDEA® process)
  - Liquid oxidation process on iron basis for removal of $H_2S$: e.g. SulFerox®, LO-CAT®

— **Physical sour gas removal processes:**

  Acid gases are dissolved in the solvent.
  
  - Methanol (Rectisol® process)
  - Polyethylenglycol Ether (e.g. Selexol®, Genosorb®, Sepasolv® processes)
  - n-Methyl-2-Pyrrolidone (NMP; e.g. Purisol® process)

— **Physical-chemical sour gas removal processes:**

  - Methanol + Amine (e.g. Amisol® process)
  - Sulfolane + Amine (e.g. Sulfinol® process)
Criteria for Choice of Absorptive Sour Gas Removal Processes

Technical requirements

— Quality of feed gas to sour gas removal unit
— Quality of purified synthesis gas
— Quality of other product gases
— Operability
— Availability of solvent and of required utilities
— Environmental regulations

Commercial decision criteria

— Investment costs, operational costs
— Net present value, internal rate of return
— Risk (Proven technology? Reference plants?)
Comparison of Amine Wash Processes and Rectisol®

Linde applies mainly two types of absorptive sour gas removal processes:

Amine Wash Processes
- Chemical sour gas removal process
- Additives can be used to increase/decrease the CO₂ reaction rate in the solvent.
- CO₂ and H₂S are washed out simultaneously.
  A selective, i.e. separate, removal of CO₂ and H₂S is not possible.

Rectisol®
- Physical sour gas removal process
- The process was jointly developed by Linde and Lurgi.
- The Rectisol® process uses methanol as wash solvent.
- A selective or nonselective removal of CO₂ and H₂S can be realised.
Simplified PFD of a 1-stage Amine Wash Process

Absorption Section

Purif. Gas

BFW

Feed Gas

Regeneration Section

Flash Gas

Sour Gas ($CO_2$, $H_2S$)

WW

Antifoam Dosing Unit

steam
Simplified PFD of a 2-stage Amine Wash Process

Absorption Section

Purif. Gas

BFW

Feed Gas

Regeneration Section

Flash Gas

Sour Gas (CO₂, H₂S)

WW

Antifoam Dosing Unit

Antifoam Dosing Unit
Linde’s Amine Wash Units in Hungary and China

1-stage Amine Wash Unit
Kazincbarcika, Hungary

2-stage Amine Wash Unit
Daqing, China
Simplified PFD of a selective Rectisol® Process
- Selective removal of H₂S/COS & CO₂, high CO₂ capture

Absorption Section

Cold Regeneration
CO₂ Production

Hot Regen.

H₂S Fraction

Feed Gas

Methanol Injection

Refr.

Waste Water

Purif. Gas

LP-CO₂

MP-CO₂

Containing CO₂
Containing Sulphur
Linde’s Rectisol® Wash Unit in China

Selective Rectisol® Wash Unit, Jilin, China
## Typical Operating Conditions of Amine Wash Processes and Rectisol®

<table>
<thead>
<tr>
<th>Absorber</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+30 °C to +70 °C</td>
<td>10 bar(a) - 80 bar(a)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feed Gas</th>
<th>CO₂ Content</th>
<th>Max. Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt; 2 mol%</td>
<td>depending on feasible column diameter</td>
</tr>
<tr>
<td></td>
<td>&gt; 10 mol%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Purified Gas</th>
<th>CO₂ Content</th>
<th>H₂S + COS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 ppmv - 5 mol%</td>
<td>5 ppmv</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sulphur free CO₂ Product</th>
<th>not feasible</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Sulphur Product</th>
<th>not feasible</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Amine Wash</th>
<th>Rectisol®</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-20 °C to -60 °C</td>
</tr>
</tbody>
</table>

- Process configuration with less CO₂ removal is feasible

### Feed Gas CO₂ Content
- Depending on feasible column diameter
- Max. Flow

### Purified Gas CO₂ Content
- 15 ppmv - 5 mol%
- 5 ppmv

### Sulphur free CO₂ Product
- Not feasible

### Sulphur Product
- Not feasible

\[ \text{Sulphur free CO}_2 \text{ Product} \]

\[ \text{Sulphur Product} \]
Qualitative Comparison of Amine Wash Processes and Rectisol®

**Rectisol®**
- Purified gas virtually free of sulphur components.
- CO₂ streams virtually free of sulphur components.
- Sour gas stream with H₂S content > 25 mol%.
  → stream can be further processed in a Claus plant.
- Handling of trace components is well understood (e.g. NH₃, COS, HCN, metal carbonyls, aromatic hydrocarbons).
- Refrigeration unit is required.

**Amine Wash**
- No separate production of CO₂ and sulphur fractions possible.
  → Additional process for separation of H₂S and CO₂ needed, if to be further processed in a Claus plant.
- Limited tolerance for trace contaminants.
  → Upstream removal required, e.g. in guard beds.
- No refrigeration unit required.
### Required equipment for Amine Wash units and Rectisol® units

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Amine Wash</th>
<th>Rectisol®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Columns</td>
<td>2 – 4</td>
<td>4 – 10</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>4 – 6</td>
<td>20 – 25</td>
</tr>
<tr>
<td>Vessels</td>
<td>3 – 5</td>
<td>10 – 15</td>
</tr>
<tr>
<td>Pumps</td>
<td>2 – 8</td>
<td>12 – 15</td>
</tr>
<tr>
<td>Filters</td>
<td>2 – 3</td>
<td>2</td>
</tr>
</tbody>
</table>

Choice on the optimum process depends predominantly on:

- CO₂ content of feed gas
- operating pressure
- required quality of products
- feed gas flow rate
- trace components in the synthesis gas produced in the gasification

→ For each application the optimum process has to be chosen individually.
Case Studies: Sour Gas Removal for 1. Fuel Gas Production for IGCC from Coal (1)

Process Specifications:
Syngas to sour gas removal: 500,000 Nm³/h at 35 bar(a)
CO₂ content: 40 mol% → 2 mol%
H₂S content: 0.2 mol% → 5 ppmv
CO₂ recovery rate: > 90%
Sulphur recovery: Claus (Rectisol) / liquid oxidation (Amine W.)
### Case Studies: Sour Gas Removal for 1. Fuel Gas Production for IGCC from Coal (2)

#### Optimum configuration

<table>
<thead>
<tr>
<th>Amine Wash</th>
<th>Rectisol®</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-stage process</td>
<td>selective process</td>
</tr>
</tbody>
</table>

#### Number of trains (transport limitation)

<table>
<thead>
<tr>
<th></th>
<th>Amine Wash</th>
<th>Rectisol®</th>
</tr>
</thead>
<tbody>
<tr>
<td>multiple trains (6)</td>
<td>single train</td>
<td></td>
</tr>
</tbody>
</table>

#### OPEX:

<table>
<thead>
<tr>
<th></th>
<th>Amine Wash</th>
<th>Rectisol®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
<td>300 %</td>
<td>100 %</td>
</tr>
<tr>
<td>Electric Energy</td>
<td>100 %</td>
<td>100 %</td>
</tr>
</tbody>
</table>

#### CAPEX:

<table>
<thead>
<tr>
<th></th>
<th>Amine Wash</th>
<th>Rectisol®</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>95 %</td>
<td>100 %</td>
</tr>
</tbody>
</table>

*) including refrigeration unit

### Conclusion:

**Rectisol® preferred choice:**

- clearly lower OPEX, approx. equal CAPEX
- lower number of trains → easier operability
- virtually sulphur free CO\textsubscript{2} product (suitable for CO\textsubscript{2} sequestration)
- H\textsubscript{2}S enriched sour gas fraction (suitable for Claus Plant)
- better handling of trace components (e.g. COS, HCN, metal carbonyles)
Case Studies: Sour Gas Removal for 2. Coal to Liquid (CtL) Process (1)

<table>
<thead>
<tr>
<th>Syngas to sour gas removal</th>
<th>Purified Syngas</th>
</tr>
</thead>
<tbody>
<tr>
<td>shifted</td>
<td>partially shifted</td>
</tr>
<tr>
<td>3,000,000 Nm³/h</td>
<td>1,500,000 Nm³/h</td>
</tr>
<tr>
<td>32 bar(a)</td>
<td>32 bar(a)</td>
</tr>
<tr>
<td>CO₂ content:</td>
<td></td>
</tr>
<tr>
<td>40 mol%</td>
<td>30 mol%</td>
</tr>
<tr>
<td>H₂S content:</td>
<td></td>
</tr>
<tr>
<td>0.3 mol%</td>
<td>0.3 mol%</td>
</tr>
</tbody>
</table>

- CO₂ content: 40 mol% → 15 ppmv
- H₂S content: 0.3 mol% → 0.1 ppmv (Rectisol®)
- 5 ppmv (Amine W.)

Syngas from Coal Gasification → Sour CO shift conversion/Heat recovery → Sour gas removal I → Regeneration → Sour gas removal II → Feed gas for FT synthesis

- H₂/CO ≈ 2.0 mol/mol
- MP+LP CO₂ (to sequestration) (CO₂ ≥ 98 mol%)
- H₂S fraction for Claus Plant (Rectisol®)
- for Liquid Ox. (Amine W.)
Simplified PFD of a selective Rectisol® Process
- Selective removal of $\text{H}_2\text{S}/\text{COS}$ & $\text{CO}_2$, high $\text{CO}_2$ capture, shifted/partially shifted configuration

Absorption Section
- Shifted Feed Gas
- LP-$\text{CO}_2$
- MP-$\text{CO}_2$
- Purif. shifted Gas

Cold Regeneration CO$_2$ Production
- Methanol Injection
- Refr.
- Hot Regen.
- C.W.
- Waste Water

Hot Regen.
- H$_2$S Fraction
- Steam
- Waste Water

Part. shifted Feed Gas
- Purif. part. shifted Gas

Methanol Injection
- Refr.
- Steam
- Waste Water
Case Studies: Sour Gas Removal for 2. Coal to Liquid (CtL) Process (2)

Optimum configuration

Number of trains
(hydraulic limitation of column diameters)

- Shifted feed: 12 trains
- Partially shifted: 10 trains

Amine Wash
2-stage process

Rectisol®
shifted/partially shifted config.

4 trains

OPEX:
- Steam: 200%
- Electric Energy: 60%

CAPEX:
- 105%

OPEX:
- Steam: 100%
- Electric Energy: 100% (*)

CAPEX:
- 100% (*)

*) including refrigeration unit

Conclusion:
- Similar OPEX/CAPEX
- Rectisol® preferred choice:
- Unrealistic number of trains for Amine Wash → poor operability
- Virtually sulphur free purified syngas for Fischer Tropsch synthesis
- \( H_2S \) enriched sour gas fraction (suitable for Claus Plant)
**Case Studies: Sour Gas Removal for 3. Biomass to Liquid (BtL) Process (1)**

**Process Specifications:**

- **Synthesis gas to sour gas removal:** 250,000 Nm³/h at 33 bar(a)
- **CO₂ content:** 35 mol% → 2 mol%
- **H₂S content:** 40 ppmv ... 200 ppmv → minimum
- **Sulphur removal:** Liquid oxidation process on basis of iron

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**Syngas from Biomass Gasification**

- **Sulphur removal and recovery**
- **Sweet CO Shift conversion**
- **CO₂ removal**
- **Heat recovery**
- **PSA**

**Feed gas for FT synthesis**

H₂/CO ≈ 2.0 mol/mol
Simplified PFD of a nonselective Rectisol® Process

Absorption Section

Regeneration Section

Feed Gas

Purif. Gas

Methanol Injection

Ref. steam

C.W

Sour Gas (CO₂)

Waste Water

steam
Case Studies
3. Biomass to Liquid (BtL) Process (2)

<table>
<thead>
<tr>
<th>Optimum config.</th>
<th>Amine Wash</th>
<th>Rectisol®</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-stage process</td>
<td></td>
<td>nonselective process</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number of trains</th>
<th>single train</th>
<th>single train</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 parallel absorbers, common regen.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OPEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
</tr>
<tr>
<td>Electric Energy</td>
</tr>
</tbody>
</table>

- higher for Amine Wash compared to Rectisol®
- lower for Amine Wash compared to Rectisol®
- Overall OPEX similar

<table>
<thead>
<tr>
<th>CAPEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>lower for Amine Wash compared to Rectisol®</td>
</tr>
</tbody>
</table>

Conclusion: CAPEX/OPEX ⇒ Amine Wash

In view of the inhomogeneous nature of biomass:
- Amine Wash would require appropriate upstream guard bedding, while Rectisol provides excellent handling of trace components
- Higher stability of methanol compared to amines
⇒ Rectisol® recommended
Arguments for choosing ...

... an Amine Wash Unit

- low partial pressure of CO₂
- low sulphur content
- no trace components
- moderate or low flow rate of feed gas
- moderate or low cost of LP steam

... a Rectisol unit

- high partial pressure of CO₂
- high sulphur content and sulphur free products required
- trace components (e.g. HCN, metal carbonyls, aromatic components)
- high flow rate of feed gas
- high cost of LP steam

For each application the sour gas removal process has to be chosen and optimized individually.
Thank you for your attention.