Molecular Sieve
Applications

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Outlines

- Introduction - Molecular Sieve Adsorbents
- Adsorption Principles
- “Dynamic” Adsorption
- Regeneration Methods
- Applications in Titan
- Molecular Sieve Life and Contaminants
- Thermal Effects (Safety Aspects)
- Services Provided
- Conclusion
Introduction - Molecular Sieve Adsorbents

- Crystalline alumino silicate or synthetic zeolites
- Unique structure with regular pore size
Introduction - Molecular Sieve Adsorbents

• Strong adsorptive force to remove many gas or liquid impurities to very low levels (ppm or less)

• Differ from other adsorbents in the form of their isotherms which have a high adsorption capacity for relatively low concentrations of the adsorbate
Synthesis and Preparation of Molecular Sieves

Sodium Silicate → Caustic Soda → Sodium Aluminate → Synthesis → Ion Exchange → Binder → Mixing → Extrusion → Activation → 1.6 - 3.2 mm
Granulation → Activation → 0.7 - 1 - 1.5 - 2 - 5 mm

Activated Powder

1.6 - 3.2 mm
0.7 - 1 - 1.5 - 2 - 5 mm
Adsorption Principles

- A phenomenon of a surface on which a molecule contained in a fluid is fixed on a surface of a solid
- Adsorption of the impurities having lower and/or same size as the pores of the molecular sieve.
Adsorption Principles

- When several impurities having the same size have to be removed, the more polar of them is first adsorbed.
- Physisorption of the impurities (Van der Waals interaction) on the molecular sieve following a extended Langmuir equation.
“Dynamic” Adsorption

- The most common mode of adsorptive separation process employs a fixed bed, cyclic operation.
- Mass Transfer Zone (MTZ) is defined as the bed length (h) through which the concentration of the adsorbate is reduced from initial $C_O$ to desired $C_S$. 
“Dynamic” Adsorption

- Water vapor is adsorbed in a finite length of bed (MTZ) as wet process stream enters fresh molecular sieve bed.
- As wet gas continues to flow, the bed may be divided into 3 zones, saturated (equilibrium) zone, MTZ and active (fresh or regenerated) zone.
“Dynamic” Adsorption

- When the MTZ reaches the outlet end of the bed, the bed is exhausted and regeneration is required.
- The water content is shown to increase in the breakthrough curve as the MTZ moves towards the outlet.
“Dynamic” Adsorption

Saturated mol sieve (no adsorption)

Fresh or regenerated mol sieve
Regeneration Methods

• The saturated mol sieve recovers its adsorption capacity after desorption - this is regeneration

• Four methods available commercially:
  * Thermal swing - heating the bed to a temperature at which the adsorptive capacity is reduced to a low level
  * Pressure swing - reducing adsorptive capacity by lowering pressure at constant temperature
Regeneration Methods

* Inert purge stripping - passing a fluid containing no adsorbable molecules and in which the adsorbate is soluble without changing temperature or pressure

* Displacement desorption - passing a fluid containing a high concentration of an adsorbable molecule without changing temperature or pressure
Applications in Titan

- The necessity of water removal is to prevent any hydrates in subsequent low temperature equipment.

Discussion of molecular sieves application in Titan will be limited to the following:

- Cracked Gas Dryers
- Liquid Dryers
- Hydrogen Dryers
Cracked Gas Dryers

Process Flow Diagram

- From CG Subcooler Knock Out Drum
- Drying
- Process
- Regeneration
- To HP Depropanizer
- CW
- Steam
- Reactivation Gas Supply
- To Fuel System
- To HP System
Cracker 1

- One vessel on drying mode and one vessel on regeneration or standby mode
- Presently, the dryer vessels are loaded with mol sieves from two different vendors
- Fixed adsorption cycles of 60 to 70 hours
Cracked Gas Dryers

- **Operating Conditions (Adsorption Step)**

  - Design operating conditions are:
    - Temperature \( \sim 10.5^\circ C \)
    - Pressure \( \sim 15 \text{ kg/cm}^2 \text{g} \)
    - Flow rate \( \sim 76 \text{ ton/h} \)
    - Water content \( \sim 886 \text{ ppmv} \)
# Cracked Gas Dryers

- **Comparison of Breakthrough Test**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Vessel A Mol Sieve X</th>
<th>Vessel S Mol Sieve Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol sieve type</td>
<td>1/8” and 1/16”</td>
<td>1/8” and 1/16”</td>
</tr>
<tr>
<td>Date of b’thru test</td>
<td>Mol sieve life of 4 months</td>
<td>Mol sieve life of 7 months</td>
</tr>
<tr>
<td>Feed rate</td>
<td>59.6 ton/h</td>
<td>58 ton/h</td>
</tr>
<tr>
<td>Water content</td>
<td>787 ppmv</td>
<td>900 ppmv</td>
</tr>
<tr>
<td>Adsorption time</td>
<td>83.5 hours</td>
<td>76 hours</td>
</tr>
<tr>
<td>Adsorption capacity</td>
<td>13.78 gH₂O/100g mol sieve</td>
<td>13.92 gH₂O/100g mol sieve</td>
</tr>
<tr>
<td>Mol sieve life</td>
<td>42 months to date</td>
<td>18 months to date</td>
</tr>
</tbody>
</table>
Cracked Gas Dryers

- **Operating Conditions (Regeneration Step)**

  - Regeneration period of 48 hours
  - Design regeneration conditions are:
    - Depressurised to 4 kg/cm²g
    - Heat to bed temperature of 200°C
    - Regen gas flow rate is 6 tons/h
Cracked Gas Dryers

- Typical Regeneration Curve (Mol Sieve Y)

- Mol Sieve X has similar regeneration curve
**Liquid Dryers**

- **Process Flow Diagram**

- Liquid drain
- To fuel gas system
- Depressurizing to CGC suction drum
- Liquid drain
- Liquid drain
- Process liquid to HP Depropanizer
- Regen gas from Demethanizer System
- Heater
- Steam
- Coalescer
- Water
- Process liquid from CG knock out drum
- Dryers
- Purge gas from CG Dryers
- Process liquid to HP Depropanizer
Cracker 1

- One vessel on drying mode and one vessel on regeneration mode
- Fully automatic operations by PLC
- Fixed adsorption cycles of 24 hour
- Have used mol sieves from two different vendors
Liquid Dryers

* Operating Conditions (Adsorption Step)*

- Design operating conditions are:
  - Temperature ~ 10.5°C
  - Pressure ~ 18.6 kg/cm²g
  - Flow rate ~ 7736 kg/h
  - Water content ~ 420 ppmw
## Liquid Dryers

### Comparison of Breakthrough Test

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mol Sieve X</th>
<th>Mol Sieve Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol sieve type</td>
<td>1/16” 3 Å</td>
<td>1/16” 3 Å</td>
</tr>
<tr>
<td>Date of b’thru test</td>
<td>Mol sieve life of 7 months</td>
<td>Mol sieve life of 15 months</td>
</tr>
<tr>
<td>Flow rate</td>
<td>9300 kg/h</td>
<td>12500 kg/h</td>
</tr>
<tr>
<td>Water content</td>
<td>420 ppmw</td>
<td>420 ppmw</td>
</tr>
<tr>
<td>Adsorption time</td>
<td>36 hours</td>
<td>25 hours</td>
</tr>
<tr>
<td>Adsorption capacity</td>
<td>15.62 gH₂O/100g mol sieve</td>
<td>14.58 gH₂O/100g mol sieve</td>
</tr>
<tr>
<td>Mol sieve life</td>
<td>35 months</td>
<td>24 months *</td>
</tr>
</tbody>
</table>

* Short run life due to different regeneration conditions
Liquid Dryers

- **Operating Conditions (Regeneration Step)**
  
  - Regeneration period is 24 hours
  - The typical operating conditions are:
    * Depressurised to 4 kg/cm²g
    * Heat to bed temperature of 200°C
    * Regen gas flow rate is 135 kg/h
Hydrogen Dryers

- **Process Flow Diagram**

   - From methanator effluent separator
   - Drying
     - H2 products to plant
   - Regeneration
     - From regeneration gas heater
     - Liquid drain
     - Depressurizing to compressor suction drum
     - To fuel gas system
Cracker 2

- One vessel on drying mode and one vessel on regeneration or standby mode
- Only used mol sieves from one vendor
- Fixed adsorption cycles of 48 hours
Hydrogen Dryers

- **Operating Conditions (Adsorption Step)**

- Design operating conditions are:
  * Temperature ~ 12°C
  * Pressure ~ 30 kg/cm²g
  * Flow rate ~ 1226 kg/h
  * Water content ~ 475 ppmv
## Hydrogen Dryers

### Performance

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Vessel A/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol sieve type</td>
<td>1/8” 3 Å</td>
</tr>
<tr>
<td>Flow rate</td>
<td>1300 kg/h</td>
</tr>
<tr>
<td>Water content</td>
<td>475 ppmv</td>
</tr>
<tr>
<td>Adsorption time</td>
<td>48 hours</td>
</tr>
<tr>
<td>Adsorption capacity</td>
<td>7.59 gH₂O/100g mol sieve</td>
</tr>
<tr>
<td>Mol sieve life</td>
<td>31 months to date</td>
</tr>
</tbody>
</table>
Hydrogen Dryers

• **Operating Conditions (Regeneration Step)**

- Regeneration period of 48 hours
- Design regeneration conditions are:
  * Depressurised to 4 kg/cm²g
  * Heat to bed temperature of 200°C
  * Regen gas flow rate is 600 kg/h
**Services Provided**

Comparison is made on the two vendors for the services rendered to Titan

- Both vendors are technically well versed
- Both vendors are experienced and well known
- Both vendors are willing to conduct breakthrough test but requires planning in advance
Services Provided

• One vendor has regional technical support that can conduct the testing while the other technical support team is based in Europe.

• One vendor is able to predict the mol sieve end of run using a model.
Molecular Sieve Life

Degradation of mol sieve is shown by:-

• shortfall in capacity
• pressure drop increase across the bed

• The aging of mol sieve leads to more frequent regeneration than forecast
• The rate of aging depends on type of service, design and feed characteristics
Contamination of Molecular Sieve

Premature bed aging can be caused by contaminants such as:-

- Oil
- Olefins, diolefins
- Free water or “excess” water
Contamination of Molecular Sieve

• During normal regeneration in the presence of heat, some of the hydrocarbon contaminants decompose and polymerize forming a deposit of coke on the sieve surface

• This blocks the actual adsorption sites and impedes diffusion within the macro pores
Contamination of Molecular Sieve

- Free water attacks the interface between the active zeolite material and clay binders leading to a separation of the two constituents.
- This will lead to formation of powders and eventual caking of mol sieve beds.
Thermal Effects (Safety Aspects)

Temperature rise from heat of adsorption can be caused by:-

- addition of moisture (water) without flooding the bed e.g. during bed loading when vessels are not completely dry
- sudden contact with high concentrations of hydrocarbons having high heats of adsorption such as olefins e.g. during start ups
Conclusion

- Molecular sieves used in each application has been satisfactory
- Mol sieves life for cracked gas dryer and hydrogen dryer are expected to last up to 4 years
- Mol sieves life for liquid dryer was shown to last 2 to 3 years
Conclusion

• Have used molecular sieves from two different vendors
• Vendors are technically competent and services are satisfactory
Thank You

Q & A