Purge gas recovery
An attractive scheme for methanol-ammonia co-production

John Pach, John Brightling
& Terry Fitzpatrick

Agenda

- Introduction
- Methanol plant design
- Hydrogen recovery
- Ammonia loop design
- Advantages
- Conclusion

John Pach – Johnson Matthey Process Technologies

Katalco

Heysham, UK before 1960

Billingham 1970s – 2000s
Co-production with ammonia loop

Ammonia Loop

Carbon Dioxide

PSA

Hydrogen

Loop Purge

Methanol Plants

Fuel

Nitrogen

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Steam reforming

SMR + ATR
## Typical syngas compositions

<table>
<thead>
<tr>
<th>Syngas technology</th>
<th>R ratio</th>
<th>CO/CO₂</th>
<th>% CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR</td>
<td>2.9</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>SMR+CO₂</td>
<td>2.1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>SMR+ATR</td>
<td>2.1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>GHR+ATR</td>
<td>2.1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Gasifier – coal¹</td>
<td>2.05</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Gasifier - biomass</td>
<td>2.05</td>
<td>5</td>
<td>&gt;5</td>
</tr>
</tbody>
</table>

- R ratio – Excess H₂, \( R = \frac{([H₂]-[CO₂])}{([CO]+[CO₂])} \)
- CO/CO₂ – Heat of reaction/ reactivity
- CH₄ – Loop efficiency

¹ Entrained flow gasifier

## Methanol plant hydrogen balance

- Typical SMR with NG feed has 40% excess hydrogen
  - Hydrogen export
  - CO₂ addition
  - ATR flowsheets
  - Fuel
  - Ammonia
Methanol plant hydrogen balance

- Typical SMR with NG feed has 40% excess hydrogen
  - Ammonia
    - Optimized methanol plant
    - High efficiency ammonia loop
    - Minimal cross connections/interactions

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Methanol purge gas treatment

- Need to remove
  - H₂O
  - CO
  - CO₂
- Need to recover hydrogen
  - PSA
  - Nitrogen wash
- Need to add nitrogen

PSA

`Katalco`
Advantages
- No energy requirement
- No feed pre-treatment
- Pure hydrogen
- Stoichiometric nitrogen requirement

Disadvantages
- Hydrogen recovery of order 80-90% so 10-20% is lost to fuel
- Can constrain loop operating pressure, if pressure let down is to be avoided.

Nitrogen wash

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Nitrogen wash

Advantages
- Hydrogen recovery >99% → 10-20% more ammonia than with PSA
- Operating pressure range encompasses that of methanol synthesis loops
- Very pure stream of H₂ and N₂ in the ratio 3:1

Disadvantages
- Additional purification steps
- Much higher nitrogen requirement than the PSA scheme → larger ASU
- Additional utility requirements
- The waste gas stream contains the excess nitrogen
- Higher capital cost

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Ammonia synthesis

- HP steam
- BFW
- Make-up gas
- Syngas compressor
- Refrigeration
- Purge
- C.W.
- NH₃ (liquid)

Ammonia loop design

- High efficiency loop
  - virtually inert free
- High make-up gas pressure
  - Small syn gas compressor
- Steam for ammonia loop generated
  - After the ammonia converters
  - Fired heater
    - Fuel gas from hydrogen recovery system.
    - Natural gas
  - Ammonia steam system is independent of methanol steam system.
    - Enhanced reliability
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Flexibility

- Whilst some co-production schemes lack the flexibility to adjust ammonia and methanol production to meet local market needs, an ammonia loop is very flexible
  - Increase ammonia production and reduce methanol production
    - Send methanol plant syn gas to ammonia loop via HRU
  - Reduce ammonia production for a fixed methanol production rate
    - Use methanol purge gas as fuel.
  - Change both ammonia and methanol rates
    - Adjust flow through the reformer
Operating costs

Efficiency
- **30.2 GJ/te product** (7.2Gcal/te)
  - Hot Middle Eastern climate
  - Includes ASU
  - 1MWh = 10.8GJ

O & M costs
- For many plants
  - No increase in operating and maintenance staff for over that required for stand alone methanol plant.
  - Fewer pieces of equipment to maintain
    - reduced turnaround cost.

<table>
<thead>
<tr>
<th>Comparison with stand alone plants</th>
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<tbody>
<tr>
<td><strong>Stand alone</strong></td>
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<tr>
<td>Methanol plant</td>
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<tr>
<td>Primary reformer</td>
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<tr>
<td>Secondary reformer</td>
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<tr>
<td>Air compressor</td>
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<tr>
<td>HTS &amp; LTS</td>
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<tr>
<td>Wet CO₂ removal</td>
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<td>Methanator</td>
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<td>SGD</td>
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<tr>
<td>SGC</td>
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<tr>
<td>Ammonia loop</td>
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<tr>
<td>Ammonia refrigeration</td>
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<tr>
<td>ASU</td>
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<tr>
<td>HRU</td>
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Conclusion

• Johnson Matthey and ThyssenKrupp Uhde offer state of the art designs for dedicated methanol plants, for dedicated ammonia plants and for an ammonia-methanol co-production scheme which does not compromise operability or reliability and which possesses excellent plant economics.
• We can assist operators to compare the viability of dedicated production assets with that of a co-production facility and provide whichever technology is the best fit for any particular project.