Low Temperature Operation of Methanation Catalyst At RCF-Thal

Presentation By,

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Welcomes

Delegates present for Ammonia Catalyst Seminar 2016
Overview of RCF

Govt. of India Undertaking, Incorporated in 1978 with the re-organisation of erstwhile FCI. It is a Miniratna company.

80 % GOI holding

Two units  – Trombay
   – Thal

Trombay and Thal units certified under IMS (QMS, EMS & OHSAS)

MoU signing with GOI since 1988.
Rated excellent since 2002-03
RCF Trombay Unit  
(Products & Yearly Capacity)

- Urea (3.3 LMT)
- Suphala (15:15:15) (4.2 LMT)
- Suphala (20:20:0) (2.7 LMT)
- Sujala (0.06 LMT)
- Biola (150 KL)
- Microla (450 KL)

- Ammonia (4.13 LMT)
- Nitric Acid (3.63 LMT)
- Methanol (0.70 LMT)
- Methyl Amine (0.052 LMT)
- Ammonium Bicarbonate (0.25 LMT)
- Sodium Nitrite/Nitrate (0.052 LMT)

- Sulphuric Acid (0.99 LMT)
- Phosphoric Acid (0.33 LMT)
RCF Thal Unit
(Products & Yearly Capacity)

Urea
(20 LMT)

Ammonia
(11.55 LMT)

Formic Acid
(0.1 LMT)

DMAc
(0.05 LMT)

Methyl Amine
(0.11 LMT)

DMF
(0.025 LMT)

Argon
(0.14 LMT)
RCF Thal: Background

- First Mega Fertilizer unit set up using Natural gas from Bombay high.

- Commissioned in 1984-85.

- First Fertilizer Unit in India with Distributed Control System (DCS)
Ammonia Process at RCF-Thal

• The Process is based on Steam Reforming of Natural gas.

• Technology is supplied by M/s HTAS Denmark.
Catalysts Used in Ammonia Plants

- Hydrogenation of NG: NiMox
- Desulphurization: ZnO
- Reforming: NiO on Alumina
- HT CO Conversion: Fe$_2$O$_3$, Cr$_2$O$_3$
- MT & LT CO Conversion: CuO, ZnO
- Methanator: NiO on Alumina
- Ammonia Synthesis: Fe$_3$O$_4$
Ammonia Plant, RCF Thal

Technology : Haldor Topsoe
Design Capacity : 2 x 1750 = 3500 MTPD
Improvement Schemes at RCF-Thal Unit

1. **1984-85**: Initial set up.
   - Ammonia Plants: 2x1350 MTPD
   - Initial Ammonia energy: 9.5 Gcal/MT

2. **1996-98**: Ammonia Revamp scheme
   - Capacity increased to 2x1500 MTPD.
   - Energy of Ammonia reduced from 9.5 Gcal/MT to 8.9 Gcal/MT.

   - Due to shortage of NG, Ammonia feed converted 50% on Naphtha & 50% on NG.
4. **2011-12**: Ammonia Revamp scheme

- Increased Ammonia production capacity to $2 \times 1750 = 3500$ MTPD

- Ammonia Energy reduction by 0.75 Gcal/MT.
## RCF Thal Plant Performance
*(Current vis-à-vis Initial)*

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Initial (1984-85)</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia Production</td>
<td>MTPD</td>
<td>2700</td>
<td>3800</td>
</tr>
<tr>
<td>Ammonia Energy</td>
<td>Gcal/MT</td>
<td>9.5</td>
<td>8.15</td>
</tr>
<tr>
<td>Urea Production</td>
<td>MTPD</td>
<td>4500</td>
<td>6200</td>
</tr>
<tr>
<td>Urea Energy</td>
<td>Gcal/MT</td>
<td>7.5</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Ongoing Energy Reduction Plan at RCF Thal

- Replacing existing Steam Turbo Generators by Gas Turbo Generators with HRSG for power & steam production.

- Total estimated Gas saving - 0.25 MMSCMD

- Ammonia Energy reduction from 8.12 Gcal/MT to 7.7 Gcal/MT.

- Urea Energy reduction from 5.8 to 5.45 Gcal/MT.
Methanation Process

• The carbon oxides (CO and CO2) are severe poisons to the ammonia synthesis catalyst.

• Methanation is the final part of the gas purification, where residual carbon oxides are converted into methane, which acts as an inert gas in the ammonia synthesis loop.

• Nickel based catalyst is used for methanation.
Methanation Reactions

- Reactions:
  \[ \text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H = -206 \text{ KJ/mol} \]
  \[ \text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H = -165 \text{ KJ/mol} \]

Methanation Reactions are highly exothermic
- +75°C for every 1% CO converted
- +60°C for every 1% CO2 converted
Mechanism of Methanation Reactions

- The reactions are governed by kinetics
- CO inhibits methanation of CO2
- Two stage reaction:
  - CO2 reverse-shifts to CO
    \[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \]
  - CO converted to methane
    \[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]
## Design Parameters of Low Temperature Methanation Process

<table>
<thead>
<tr>
<th>Process Parameters</th>
<th>Unit</th>
<th>Design Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Temp</td>
<td>°C</td>
<td>265</td>
</tr>
<tr>
<td>Outlet Temp</td>
<td>°C</td>
<td>289</td>
</tr>
<tr>
<td>Inlet Pressure</td>
<td>Kg/cm²g</td>
<td>26</td>
</tr>
<tr>
<td>Outlet Pressure</td>
<td>Kg/cm²g</td>
<td>25.8</td>
</tr>
<tr>
<td>CO-CO₂ inlet</td>
<td>Mole %</td>
<td>CO - 0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂ - 0.11</td>
</tr>
<tr>
<td>CO-CO₂ outlet</td>
<td>ppm</td>
<td>CO : 0-0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂ : 0.05-0.2</td>
</tr>
</tbody>
</table>
RCF: Process Requirements

CO+ CO2 at the exit is required to be < 1 ppm

Reasons for low exit CO/CO2:

- Synthesis gas is sent to Thal Ammonia Extension Plant (TAE). CO and CO2 slip if more than 1 ppm leads to choking in process and causes plant load limitation.

- CO and CO2 slip if more than 10 ppm results into poisoning of catalyst in Ammonia Synthesis Converter.
Advantages of Low Temperature Methanation

- Low temperature and high pressure tends to favour the equilibrium conversion.
- Low inlet temperature increases steam production in Converted Gas Boiler thus reducing energy consumption.
- Low outlet temperature reduces loss of heat to cooling tower and reduces load on cooling tower.
- After ageing, inlet temperature has to be increased to increase catalyst activity. Hence low inlet temperature operation initially gives flexibility for increasing temperature as the catalyst ages.
Catalyst Type Used: Meth 135 /C-13-03 by M/s Sudchemie India limited

Chemical Composition

- Nickel: 34.0 ± 2.0 (%wt)
- Alumina: Balance (%wt)

Physical Properties Specifications

- Form/Shape: 3.0-6.0 mm Spheres
- Average Crush Strength: ≥ 6.8 Kg
- Shipping Density: 0.95 ± 0.1 Kg/l
**Methanation Catalyst Reactor**

Gas from CO2 removal section

**Inlet composition** (Dry mole %)
- Ar : 0.31
- CH4 : 0.49
- CO : 0.21
- CO2 : 0.11
- H2 : 73.44
- N2 : 25.44

**Outlet composition** (Dry mole %)
- Ar : 0.31
- CH4 : 1.18
- CO : 0 to 0.08 ppm
- CO2 : 0.05 to 0.2 ppm
- H2 : 94.14
- N2 : 5.71

Height of both catalyst beds is 2650 mm each and diameter is 3800 mm

100 mm layer of ½” alumina balls

265 °C

289 °C

Process gas to ammonia synthesis loop
Catalyst Life

Catalyst in operation since:

- Amm-I: April 2007
- Amm-II: November 2011
# Catalyst Performance
## (Design vs. Actual)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Design</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformer Gas Load</td>
<td>TNCH</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Inlet CO</td>
<td>Mole %</td>
<td>0.21</td>
<td>0.225</td>
</tr>
<tr>
<td>Inlet CO2</td>
<td>Mole %</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>Inlet Temp</td>
<td>°C</td>
<td>298</td>
<td>265</td>
</tr>
<tr>
<td>Outlet Temp</td>
<td>°C</td>
<td>315</td>
<td>289</td>
</tr>
<tr>
<td>Exit CO/CO2</td>
<td>ppm</td>
<td>&lt; 1 (CO+CO2)</td>
<td>CO : 0-0.08 CO2: 0.05-0.2</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>Kg/cm²</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Conclusion

Overall satisfactory performance of Sudchemie make low temperature methanation catalyst w.r.t

• High Activity at inlet temperature of 260-270°C.

• CO/CO2 slip less than 1 ppm.

• High crush strength.

• Faster start up.