Reforming Catalyst for Energy Saving: Features & Case Studies

Sanjeev Mehta
• Table of Contents

Primary Reforming Catalyst

- Performance Parameters and Unique Features of the Catalyst
- Operating References
- New Development in Primary Reforming Catalyst
- Case Studies- Primary Reforming Catalyst

Secondary Reforming Catalyst

- Secondary Reforming Catalyst- Unique Features of the Catalyst, Operating References and Case Studies
Increase Plant Efficiency – Innovative Reformer Shape: ReforMax 330 LDP (Low Differential Pressure)

- Catalyst Performance Parameters, advantages of the 10 hole LDP Shape
ReforMax®330 Primary Reforming Catalyst

Catalyst Performance Parameters

- **Intrinsic Activity**
  - Ni/Support Interaction
  - Ni Dispersion
  - Ni Content
  - Support Formulation

- **Apparent Activity**
  - Diffusion: Bulk, Film, Pore, Knudsen
  - Pore Volume
  - Pore Size Distribution
  - Geometric Surface Area

- **Pressure Drop**
  - Shape
  - Physical Integrity

- **Stability**
  - Ni/Support Interaction
  - Physical Integrity

- **Heat Transfer**
  - Shape
  - Density
  - Pressure Drop

- **Carbon Formation Potential**
  - Support Formulation
  - Promoters
ReforMax®330 - Performance Leading Reforming Catalyst

Influencing factors in the shape development

• Size

• Aspect ratio

• Void spaces (holes and external channels / ribs etc.)

• Packing property (void fraction between particles)

  ➢ small size results in high GSA

  ➢ every parameter influencing DP will impact GSA

  ➢ crush strength as limiting boundary
Steam Methane Reforming Catalyst Portfolio

Primary Reformer Catalyst Portfolio

**ReforMax 250 FH** (Naphtha)
- Ni: 20 wt%
- K₂O: 6 wt%
- Carrier: Balance
- Shape: 5 holes, 16 x 16 mm
- Density: ~1000 Kg/m³

**ReforMax® 210 LDP** (LPG, Butane)
- Ni: 15 wt%
- K₂O: 2 wt%
- Carrier: Balance
- Shape: 10 holes, 19 x 12 mm
- Density: ~850 Kg/m³

**ReforMax 330® LDP** (NG)
- Ni: 11 wt%
- Carrier: Balance
- Shape: 10 holes, 19 x 16 mm
- Density: ~850 Kg/m³
ReforMax®330 - Performance Leading Reforming Catalyst

Innovative Shape

**Süd-Chemie Shapes:**

Impossible to align holes or bridges:

- Uniform Stress Pattern
- Strong Structure
ReforMax®330 - Performance Leading Reforming Catalyst

Low Pressure Drop of LDP Shape

**Relative Pressure Drop**

<table>
<thead>
<tr>
<th>Shape</th>
<th>Relative Pressure Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring 16x16x6</td>
<td>100</td>
</tr>
<tr>
<td>Ring 16x10x8</td>
<td>120</td>
</tr>
<tr>
<td>EW 16x8</td>
<td>97</td>
</tr>
<tr>
<td>LDP 19x16*</td>
<td>65</td>
</tr>
</tbody>
</table>

*Note: LDP 19x16 is marked with an asterisk.*
ReforMax®330 - Performance Leading Reforming Catalyst

Excellent Side Crush Strength of LDP Shape

<table>
<thead>
<tr>
<th>Side crush strength [kg]</th>
<th>Ring 16x16x6</th>
<th>Ring 16x10x8</th>
<th>EW 16x8</th>
<th>LDP 19x16</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>800</td>
<td>350</td>
<td>400</td>
<td>700</td>
</tr>
</tbody>
</table>
ReforMax®330 - Performance Leading Reforming Catalyst

High Geometric Surface Area of LDP Shape

High GSA results in:
- Higher Activity
- Lower Tube wall temperature
ReforMax®330 - Performance Leading Reforming Catalyst

Carrier Material (Calcium Aluminate)

Hibonite as basis for the extreme stability

(1) CaO + Al₂O₃ ↔ CaAl₂O₄
(2) CaAl₂O₄ + Al₂O₃ ↔ CaAl₄O₇
(3) CaAl₄O₇ + 4 Al₂O₃ → CaAl₁₂O₁₉ (Hibonite)

Reactions 1 and 2 are reversible

- Alumina is available to form nickel aluminate (spinel)

Reaction 3 is not reversible

- Alumina is not available to form spinel

Better Coke resistance. Can be started up directly with Natural Gas/steam

Benefits:

- Efficient Heat Transfer
- No need to load pre reduced catalyst in the top portion of the reformer
- Easy start ups
- Catalyst can be steamed for longer time
ReforMax®330 - Performance Leading Reforming Catalyst

Benefits

• Lower tube wall temperatures (⇒ longer lifetime of tubes)

• Lower CH₄ concentration at tubes outlet
  ➢ Higher H₂ yield
  ➢ Lower inert level and less purge in ammonia synthesis loop
    ➢ Increased ammonia production or energy saving

• Lower pressure drop (ReforMax® 330 / 210 LDP)
  ➢ Reduction of syngas compression energy
## Performance in Ammonia Plants

- Operations at wide range of S/C from as low as 2.6
- Experience in both Top Fired as well as Side Fired reformers
- Lower TWT’s
- High throughput

<table>
<thead>
<tr>
<th>Ammonia Plant</th>
<th>K1</th>
<th>IF1</th>
<th>NN</th>
<th>Z</th>
<th>B2</th>
<th>B3</th>
<th>D</th>
<th>B,A</th>
<th>P2, I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformer Licensor</td>
<td>KBR</td>
<td>KBR</td>
<td>KBR</td>
<td>KBR</td>
<td>HTAS</td>
<td>HTAS</td>
<td>HTAS</td>
<td>KBR</td>
<td>KBR</td>
</tr>
<tr>
<td>Capacity, MTPD</td>
<td>1890</td>
<td>1250</td>
<td>950</td>
<td>800</td>
<td>450</td>
<td>450</td>
<td>380</td>
<td>2506</td>
<td>2000</td>
</tr>
<tr>
<td>MOS</td>
<td>55</td>
<td>15</td>
<td>40</td>
<td>27</td>
<td>55</td>
<td>21</td>
<td>20</td>
<td>46</td>
<td>16</td>
</tr>
<tr>
<td>S/C</td>
<td>2.6</td>
<td>3.3</td>
<td>2.7</td>
<td>3.3</td>
<td>4</td>
<td>4</td>
<td>3.5</td>
<td>2.73</td>
<td>3.1</td>
</tr>
<tr>
<td>CH4 Slip % mol</td>
<td>29.37</td>
<td>13.3</td>
<td>26.5</td>
<td>11.3</td>
<td>10.61</td>
<td>9.3</td>
<td>12.89</td>
<td>24.74</td>
<td>12.62</td>
</tr>
<tr>
<td>T Exit (Deg C)</td>
<td>710</td>
<td>790</td>
<td>725</td>
<td>760</td>
<td>745</td>
<td>750</td>
<td>735</td>
<td>733</td>
<td>793</td>
</tr>
</tbody>
</table>
Performance in Hydrogen/Methanol Plants

<table>
<thead>
<tr>
<th>Hydrogen Plant</th>
<th>I-B</th>
<th>E1</th>
<th>M 1</th>
<th>M 2</th>
<th>HPV 2</th>
<th>IG 1</th>
<th>IB 2</th>
<th>IP 3</th>
<th>IB 1</th>
<th>G</th>
<th>GII</th>
<th>ZI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Licensor</td>
<td>Technip</td>
<td>Technip</td>
<td>Technip</td>
<td>Technip</td>
<td>Technip</td>
<td>Linde</td>
<td>Linde</td>
<td>HTAS</td>
<td>HTAS</td>
<td>ICI</td>
<td>ICI</td>
<td>Lurgi</td>
</tr>
<tr>
<td>Capacity, TPA</td>
<td>25,000</td>
<td>7,000</td>
<td>34,400</td>
<td>34,400</td>
<td>36,000</td>
<td>38,000</td>
<td>20,000</td>
<td>70,000</td>
<td>34,000</td>
<td>370*</td>
<td>570*</td>
<td>5000*</td>
</tr>
<tr>
<td>MOS</td>
<td>65</td>
<td>78</td>
<td>75</td>
<td>52</td>
<td>24</td>
<td>12</td>
<td>11</td>
<td>28</td>
<td>21</td>
<td>32</td>
<td>46</td>
<td>42</td>
</tr>
<tr>
<td>Feed</td>
<td>CH4 Rich Gas</td>
<td>Naphtha</td>
<td>Naphtha + Mix Pentanes</td>
<td>Naphtha + Mix Pentanes</td>
<td>CH4 Rich Gas</td>
<td>CH4 Rich Gas</td>
<td>CH4 Rich Gas</td>
<td>Naphtha +NG</td>
<td>CH4 Rich Gas</td>
<td>NG</td>
<td>NG</td>
<td>NG</td>
</tr>
<tr>
<td>S/C</td>
<td>2.6</td>
<td>NA</td>
<td>3.3</td>
<td>3.4</td>
<td>3.1</td>
<td>2.95</td>
<td>3.2</td>
<td>2.95</td>
<td>3.1</td>
<td>3.2</td>
<td>3.2</td>
<td>2.6</td>
</tr>
<tr>
<td>T Exit</td>
<td>895</td>
<td>860</td>
<td>849</td>
<td>849</td>
<td>900</td>
<td>860</td>
<td>850</td>
<td>925</td>
<td>925</td>
<td>840</td>
<td>825</td>
<td>710</td>
</tr>
<tr>
<td>CH4 Slip % mol</td>
<td>4.6</td>
<td>NA</td>
<td>3.7</td>
<td>3.4</td>
<td>2.4</td>
<td>3.7</td>
<td>4.7</td>
<td>2.9</td>
<td>2.5</td>
<td>2.9</td>
<td>3.1</td>
<td>26.1</td>
</tr>
</tbody>
</table>

* Methanol Plant (MTPD)

- Successful Performance at high heat flux, high exit temperatures, low S/C, high throughputs and in all Licensors
Primary Reforming Catalyst : Case Studies

- A 2300 MTPD KBR Ammonia plant in Australia-severe conditions
- 1950 MTPD KBR Plant in Western India
- A CO plant (HTAS) in Iran operations under severe conditions
- A 1250 MTPD KBR plant in North India
- A 800 MTPD KBR plant in Western India
- High Heat Flux Operation in a HTAS Licensed H2 Plant in India, operating on NG
- High Heat Flux operation in a HTAS Licensed H2 Plant in India, operating on Naphtha
Case Study 1: Successful performance under severe operating conditions

Ammonia plant in Australia (KBR / Production Rate 2300 mtpd)

<table>
<thead>
<tr>
<th>Loaded catalyst:</th>
<th>ReforMax 210 (15.4 m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ReforMax 330 (23.1 m³)</td>
</tr>
<tr>
<td>Steam/Carbon ratio:</td>
<td>2.9</td>
</tr>
<tr>
<td>Tube outlet temperature:</td>
<td>730 °C</td>
</tr>
<tr>
<td>Heat Flux:</td>
<td>95,000 Watts/m²</td>
</tr>
</tbody>
</table>

- Lifetime: > 6 years
- Methane conversion close to equilibrium all over the lifetime
Case Study 2 - Excellent performance at severe conditions in India

Revamp of a KBR plant from 1675 MTPD to 1890 MTPD

- Plant decided to continue with the old reformer tubes

<table>
<thead>
<tr>
<th>Loaded catalyst:</th>
<th>ReforMax 210 (40%) ReforMax 330 (60%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>1943</td>
</tr>
<tr>
<td>Steam/Carbon ratio:</td>
<td>2.6 – 2.7</td>
</tr>
<tr>
<td></td>
<td>(3.6 – 3.7 before revamp)</td>
</tr>
<tr>
<td>Pressure drop:</td>
<td>2.16 kg/cm²</td>
</tr>
<tr>
<td></td>
<td>(More than 3 kg/cm² before revamp)</td>
</tr>
</tbody>
</table>

- More than 55 months of operating time so far with no change in SOR performance
- Estimated life at these severe conditions is at least (5) years
Case Study 3 – High Temperature Operation in HTAS Licensed Reformer

SITUATION

• Location: Iran Plant : F, HTAS Licensed CO plant
• Catalyst Volume: 8.7 M3

SPECIFIC CUSTOMER NEED

• Reliable and proven catalyst which can operate at High Temperature

BENEFIT OF INSTALLING REFORMAX®

• In operation for the last 30 months, with reformer exit temperature of 940 deg C and heat flux > 100,000 W/m2. Tube wall Temperatures lower!

<table>
<thead>
<tr>
<th>Plant</th>
<th>Fanavaran CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOS</td>
<td>30</td>
</tr>
<tr>
<td>S/C</td>
<td>1.44</td>
</tr>
<tr>
<td>Inlet temp (°C)</td>
<td>615</td>
</tr>
<tr>
<td>Exit temp (°C)</td>
<td>940</td>
</tr>
<tr>
<td>CH4 slip,Mol%</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Case Study- 5 : Primary Reforming Catalyst : Outstanding Performance

Location: Top Fired Toyo plant in Western India
Designed capacity: 800 MTPD
Tubes were old (19 years) and were due for change.
High Pressure drop and high tube wall temperature with triple deck loading of competitor’s catalyst, on mix feed (Naphtha+NG)
Client was advised to reduce load with mix feed

Advise on current operation and reliable and proven catalyst which can give lower pressure drop and lower tube wall temperature

Operation near equilibrium. Client is satisfied with the performance.

New Süd-Chemie catalyst of 26 M3 was charged in May-14. Operation near equilibrium

<table>
<thead>
<tr>
<th>Ammonia Plant</th>
<th>Plant Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformer Licensor</td>
<td>Toyo</td>
</tr>
<tr>
<td>Capacity, MTPD</td>
<td>800</td>
</tr>
<tr>
<td>MOS</td>
<td>27</td>
</tr>
<tr>
<td>Feed</td>
<td>NG</td>
</tr>
<tr>
<td>S/C</td>
<td>3.3</td>
</tr>
<tr>
<td>CH4 Slip % mol</td>
<td>13.5</td>
</tr>
<tr>
<td>T Exit (Deg C)</td>
<td>760</td>
</tr>
</tbody>
</table>
Case Study 6 – High Heat Flux with Natural Gas in HTAS Licensed Reformer

**SITUATION**

- **Location**: India (IOCL - P)
- **Licensor**: HTAS
- **Capacity**: 98,000 Nm³/hr
- **Catalyst Volume**: 29.5 m³
- **Feed**: Natural Gas (27900 Nm³/hr)
- **High Heat Flux of > 89000 W/m²**

**SPECIFIC CUSTOMER NEED**

- Reliable and proven catalyst which can operate at High Temperature

**BENEFIT OF INSTALLING REFORMAX®**

- In operation for the last 28 months, with reformer exit temperature of 935 °C and heat flux > 89,000 W/m². Tube wall Temperatures lower!
- Lower pressure drop!
Case Study 7 – Naphtha operation in HTAS Licensed Reformer

SITUATION
- Location: India (IOCL - B)
- Licensor – HTAS
- Capacity: 48,000 Nm3/hr (600 MTPD NH3)
- Catalyst Volume: 14.0 m3
- Feed: Naphtha (12900 kg/hr)
- Heat Flux: > 90000 W/m2

SPECIFIC CUSTOMER NEED
- Reliable and proven catalyst which can operate at High Temperature

BENEFIT OF INSTALLING REFORMAX®
- In operation for the last 21 months, with reformer exit temperature of 935 °C and heat flux > 90,000 W/m2. Tube wall Temperatures lower!
Summary

• Süd-Chemie’s high performance catalysts significantly contribute as follows:

  ➢ The use of Süd-Chemie’s primary reforming catalyst ReforMax® 210/330 LDP has enabled users ease of operations in terms of faster start ups, longer steaming tolerance.

  ➢ The use of Süd-Chemie’s highly active and selective catalysts (e.g. ReforMax® series) ensures that the designed plant performance is closer to the “Start of Run” energy efficiency for a longer time in comparison to standard catalysts with lower methane slip and lower TWT's

  ➢ The LDP shape of the reforming catalyst ReforMax® series has the lowest pressure drop.

  ➢ Successful Operation at High Heat Flux . Vast experience in both side fired and Top fired reformers.
Secondary Reforming Catalyst
Typical NH₃ Process
Secondary Reforming Catalyst Reactor Diagram

(LDP : Low Differential Pressure)
Secondary Reforming Catalyst Shapes

- Gattling Gun (GG)
  - Shaped catalyst combination for better gas distribution

- Ribbed Ring
  - Can withstand high temperature without fusion

- LDP
  - Long life – in excess of 15 years with screening and make up once in 5-7 years
Secondary Reforming Catalyst Common Problem and Shape Advantages

- Insufficient Combustion Zone Resulting in Catalyst Fusing, High ATE, High Pressure Drop
- Refractory Wall Bypassing Results in High Wall Temp., High ATE
- Burner Problem Results in poor Combustion, poor flow, Distribution, High ATE

ReforMax 400GG/4ReforMax 410 LDP Advantages

- Higher throughput has reduced the combustion zone, leading to problems of fusing, High ATE and delta P. The use of high GSA – high activity catalyst has helped the user to reduce the volume and obtain lower methane slip, delta P at these higher throughputs.
Heat Shield Catalyst

1. **ReforMax 400 GG (Gattling Gun)**
   - Has successfully replaced Alumina lumps in the top and bottom of the reactor, in several Ammonia plants in India
   
   **Advantages:**
   - Has more voidage than Alumina lumps
   - ReforMax 400 GG has 9% Nickel and hence provides additional reforming
   - Avoid problems of alumina vaporisation and deposition on colder areas in downstream reactors and RGB

2. **ReforMax 420 E**
   - A very high crush strength catalyst used in Oxygen fed Autothermal Reformers.
   - Useful in secondary reformers in excess air/oxygen rich environments, where the combustion zone temperatures are expected to be much higher.
Case Study 1: Outstanding performance

**SITUATION**

- Location: Central India
- Designed capacity: 1850 mtpd

**SPECIFIC CUSTOMER NEED**

- Reliable and proven catalyst for a specific plant design in order to increase production and save energy

**BENEFIT OF INSTALLING REFORMAX®**

> Successfully running even after 19 years of the operation.

<table>
<thead>
<tr>
<th>Ammonia Plant</th>
<th>Plant N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformer Licensor</td>
<td>HTAS</td>
</tr>
<tr>
<td>Capacity, MTPD</td>
<td>1850</td>
</tr>
<tr>
<td>MOS</td>
<td>234</td>
</tr>
<tr>
<td>Feed</td>
<td>NG</td>
</tr>
<tr>
<td>CH4 Inlet</td>
<td>12.4</td>
</tr>
<tr>
<td>CH4 Slip % mol</td>
<td>0.46</td>
</tr>
<tr>
<td>T Exit (Deg C)</td>
<td>949.7</td>
</tr>
</tbody>
</table>
Case Study 2 – High Methane Slip form Secondary Reformer

SITUATION

➢ A 700 MTPD Top fired plant in Western India

➢ Make up Catalyst change out with new catalyst of Secondary Reformer did not give the desired relief in methane slip

JOINT STUDY OUTCOMES

➢ As the methane slips depends upon the proper mixing of the air/Process gas from primary reformer, it was found that the loaded catalyst volume was higher, leading to inadequate combustion zone. It was recommended that the catalyst Volume be reduced by 16%.

CURRENT SITUATION

➢ Methane slip was normalised after successful reduction of catalyst volume and the charge is still in service from 2002 with partial make up in 2011
Summary

• Süd-Chemie’s high performance catalysts significantly contribute as follows:

  ➢ The use of Süd-Chemie’s highly active and selective catalysts (e.g. ReforMax® series) ensures that the designed plant performance is closer to the “Start of Run” energy efficiency for a longer time in comparison to standard catalysts.

  ➢ ReforMax® 400 GG(Gattling Gun)/ ReforMax 410 LDP has benefitted users in terms of better distribution, lower pressure drop and lower methane slip while at the same time allowing lowering the secondary reformer catalyst volumes.

  ➢ Secondary Reforming catalyst from Süd-Chemie have given consistently long life of close to 20 years in several plants.

  ➢ ReforMax 420 is available as an alternative for heat shield catalyst for severe operating conditions in an excess air or oxygen rich environments.
THANK YOU