Advanced Technologies

- Casale axial-radial design for catalytic beds
  Application in: Pre-reformer design
  CO shift converter
  Ammonia converter

- Casale Pseudo isothermal ammonia converter design

- Third part technologies for CO₂ removal (in Case History)
Axial-Radial Catalyst bed
Axial-Radial concept: Full Catalyst Utilization

unused catalyst portion

Pure Radial

CASALE Axial - Radial
Axial-Radial benefits

- Low Pressure Drop
- Full Catalyst Utilization
- Proven design (more than 400 beds in operation)
- Simple mechanical construction
- Easier catalyst loading / unloading

Fig. 2 - Axial-radial flow pattern - Full catalyst
Ax-rad technology for Pre-Reforming Reactor
Pre-reformer

Adiabatic reactor where all heavier HC are methanated and shift and methane steam reforming reactions move to equilibrium, over suitable Ni based catalyst, stabilizing and reducing the load on the existing primary reformer.

**Endothermic reactions**

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \]
\[ \text{C}_n\text{H}_m + n\text{H}_2\text{O} \rightarrow n\text{CO} + (n+m/2)\text{H}_2 \]

**Exothermic reactions**

\[ \text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \]
\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]
Light feed (like natural gas) give a temperature fall, heavier feedstock (like nafta) give a temperature rise across the catalytic bed.

Typical operating parameters, for Natural gas feedstock (depending from catalyst mfr recommendation):
Steam to carbon ratio: 1.6 – 3.5
T operating range: 450°C-600°C
Pre-reformer

Large application in plant revamping for steam reformer debottlenecking (plant capacity increase), thanks to the use of

**Axial Radial Flow Pattern**

that allows lower pressure drop and therefore can be easily adjusted in series to the existing steam reformer.
Axial-radial flow: Low Pressure Drop

- energy saving
- higher capacity
- smaller size catalyst
Pre-reformer

Small Size Catalyst

- higher Sulphur pick up
- higher activity
- longer life
- smaller catalyst volume
Ax-rad technology for Shift Converters
Main advantages typical of Axial-Radial technology

- Low pressure drop
- Pressure drop stable with time
- Use of more active small size catalyst
- Lower CO slip, higher NH3 production
Axial Radial Shift Converters

Benefits for Revamping cases

• Allows for large plant capacity increase

• Small size catalyst is more resistant to poisoning therefore has a longer life

• Protection against water carry over
Axial Radial Shift Converters

For new plants

- Slimmer and cheaper pressure vessel
- Lower catalyst volume
- Simple and proven mechanical design
Axial Radial Shift Converters

For revamping

• Easy fitting of the new internals into existing vessel

• No modification or welding to the existing pressure vessel

• Achievements of all advantages of the axial radial design
Axial Radial Shift Converters

Example of application:
HTS and LTS Revamping in two Kellogg plants in China

<table>
<thead>
<tr>
<th></th>
<th>Revamped</th>
<th>Original</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production rate</td>
<td>MTD</td>
<td>1’200</td>
</tr>
<tr>
<td>Pressure drop HTS</td>
<td>bar</td>
<td>0.25</td>
</tr>
<tr>
<td>Pressure drop LTS</td>
<td>bar</td>
<td>0.22</td>
</tr>
<tr>
<td>CO out LTS</td>
<td>% mol</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Ax-radial technology for Ammonia Converter
Ammonia Casale experience

- PIONEER OF SYNTHETIC AMMONIA INDUSTRY
- 86 YEARS OF EXPERIENCE IN AMMONIA PLANT DESIGN
- MORE THAN 160 CONVERTERS IN OPERATION WITH AXIAL-RADIAL TECHNOLOGY
IN SITU MODIFICATIONS

• more than 70 axial M. W. Kellogg converters successfully revamped by Casale since 1986

COMPLETE NEW CARTRIDGES

• more than 70 converters of 12 different types successfully in service since 1985
• AXIAL - RADIAL gas flow for full catalyst utilization

• THREE BED LAY-OUT for maximum conversion efficiency
The THREE bed configuration leads to higher ammonia concentration at converter outlet.
THREE BEDS LAY-OUT

Catalyst volume [m³]

Ammonia net value [%]

- 3 beds
- 2 beds

Highest Ammonia Concentration at converter outlet
Reactor type
3 beds, quench and interchanger

3 BEDS
QUENCH
INTERCHANGER
BOTTOM EXCHANGER
Reactor type
3 beds with two interchangers

3 BEDS

FIRST INTERCHANGER

SECOND INTERCHANGER
The Pseudo Isothermal Design

Next generation is

Pseudo Isothermal Design

![Diagram showing Ammonia conversion vs Temperature with I.A.C. catalyst temperature profile, Equilibrium line, and Max reaction rate curve]
The Pseudo Isothermal Design

- It is based on an isothermal design, with direct heat removal by cooling plates immersed in the catalyst bed.

- The catalyst beds are axial-radial, for low pressure drop, and use of small-size catalyst.

- It grants performances superior to any other design, that allows the synthesis loop equipment to cope with the increased capacity, + 40 %, even with the higher inerts concentration.
The IMC design is based on the use of plates as cooling elements immersed in the catalyst bed.
The plates are hollow, obtained from two metal sheet, welded along the perimeter and spot welded on the surface, and pressurized.

The final shape is similar to a pillow.
The plates are arranged radially and along concentric circular sectors.

The plates are, internally fed by the cooling medium.

The elements are supported at the bottom.

A central pipe is acting as access for the lower converter part.
The gas cooled design has the ability to follow the highest reaction rate curve, allowing higher performances for the same catalyst volume.
CASE HISTORIES
Examples of applications
1 – Axial radial technology application
2 – Full plant revamping, MW Kellogg design
3 - Full plant revamping, Brown design
AXIAL RADIAL TECHNOLOGY APPLICATION:

HYDRO AGRI
Brunsbüttel
Germany
The retrofit of the plant was performed in order to:

- reduce the plant energy consumption;
- increase the production from 2050 MTD up to 2200 MTD;
- optimize the plant;
- Main area of intervention: HTS and ammonia synthesis loop.
The original HTS Axial internals have been replaced with the Axial-radial ones.

Smaller catalyst volume has been loaded after the revamping.

The retrofit of the HTS was performed in order to achieve the following targets:
- reduce the converter pressure drop;
- reduce the CO slip outlet the converter.
ADDITIONAL 4\textsuperscript{TH} AMMONIA BED

- Full catalyst utilization;
- Simple and robust construction;
- Easiest Catalyst loading and unloading;
- The achieved targets have been:
  - to reduce the synloop pressure;
  - to increase the ammonia conversion per pass;
# Achieved Performance

<table>
<thead>
<tr>
<th></th>
<th>Before revamping</th>
<th>After revamping</th>
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</thead>
<tbody>
<tr>
<td>HTS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure drop (bar)</td>
<td>1.84</td>
<td>0.85</td>
</tr>
<tr>
<td>CO slip (%mol dry)</td>
<td>8.40</td>
<td>5.31</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Before revamping</th>
<th>After revamping</th>
</tr>
</thead>
<tbody>
<tr>
<td>4th additional ammonia bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3^{\text{out conv.}}$ (%mol dry)</td>
<td>16.43</td>
<td>23.03</td>
</tr>
<tr>
<td>Pressure inlet converter (bar)</td>
<td>215.7</td>
<td>177.5</td>
</tr>
</tbody>
</table>
Complete ammonia plant revamping
Al-Bayroni, Al-Jubail, Saudi Arabia
Al Bayroni Ammonia plant revamping

- Original design by Kellogg for a capacity of 1000 MTD with natural gas as raw material.
- Revamped by Topsoe in 1989 (converter + H.R.U.) to increase the production to 1200 MTD.
- Capacity of the plant before CASALE revamping: 1170 MTD.
- Plant start-up after CASALE retrofit was in February 2002, test-run in August 2002.
• Production increase to 1300 MTD.
• Energy saving: reduction of energy consumption from 9.8 to 9.5 Gcal/MT.
• Reduction of cooling water consumption:
  • 10% reduction on the specific consumption.
• Reliability improvement.
• Tight schedule: 12 months between effective date and start-up.
• The revamping project is conceived in two steps:

Before CASALE revamping:
1170 MTD

1st STEP:
1300 MTD
(on stream, present capacity 1320 MTD)

2nd STEP:
1800 MTD

• 1\textsuperscript{st} STEP (already on stream): \textbf{Low Capital Costs}
  - avoid main modifications to compressors and primary reformer;
  - all new equipment sized for the final step;
  - possible changes in NG composition to be considered in design;
  - plant shall be operated with additional sections isolated;
  - trip of new sections shall not involve the trip of the plant.
• Primary reformer: duty on radiant section & ID fan.
• Steam system: temperature of superheated steam.
• Process air supply.
• Energy consumption in CO$_2$ removal system.
• Syngas compressor (suction pressure).
• Synthesis loop & refrigeration system.
Reforming section

- Installation of a pre-reformer reactor $\bar{E}$ safe S/C reduction, less duty on primary reformer.
- New fired heater for the pre-reformer feed $\bar{E}$ less duty required to mixed feed coil, more duty to steam coils.
Reforming section

- Modification of the mixed feed coil (only removal of two rows out of four) to make it suitable for the reduced duty.
Installation of an air booster section including a new filter, a booster driven by a steam turbine, a discharge cooler and a 3-way valve ensures the air supply is completely debottlenecked; booster trip does not cause compressor trip.
High and low Temperature Shift converters

- HTS & LTS retrofit with axial-radial technology, smaller pressure drops (0.8 bar saving), higher pressure at syngas compressor suction, less inerts in synloop.
CO₂ removal section:

- Solution swap from aMEA to aMDEA → lower energy consumption, operation with a low S/C is possible.

No hardware modifications have been done!
Ammonia Synthesis Loop

- Converter retrofit & replacement of the recycle wheel
- Higher conversion, no need to modify the refrigeration system.
# Achieved performances

<table>
<thead>
<tr>
<th></th>
<th>Before revamping</th>
<th>Test-run August '02</th>
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</thead>
<tbody>
<tr>
<td><strong>Production:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MTD</td>
<td>1170</td>
<td>1307</td>
</tr>
<tr>
<td><strong>ENERGY CONSUMPTION</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total specific cons.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gcal/MT$_{NH3}$</td>
<td>9.77</td>
<td>9.46</td>
</tr>
<tr>
<td><strong>SEA COOLING WATER</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific consumption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m$^3$/MT$_{NH3}$</td>
<td>416</td>
<td>388</td>
</tr>
</tbody>
</table>
Complete ammonia plant revamping
03 Ammonia plant, PCS, Trinidad
• The 03 Ammonia Plant is an original Braun 1965 design.
• Relocated to Trinidad in 1994 with capacity of 750 stpd.
• Modified to 830 stpd.
• In 2005 revamped to 1,050 stpd.
Revamp Scheme

• Conversion of the plant from the original Braun purifier design to a conventional ammonia plant operation.

• Shift of reforming load from secondary to primary reformer
  – Extension of primary reformer
  – Installation of pre-reforming section

• The purifier was idled.

• A hydrogen recovery unit was installed to treat the purge gas from the synthesis loop.
• The two converters were retrofitted with the Casale Isothermal Design converter baskets.
  – These are the first of their kind to be installed in ammonia service.
  – They provided reduced pressure drop and improved conversion.

• Most of the new items have been designed considering their suitability for a future capacity increase up to 1200 STD.
Major Changes

- Installation of a Pre-Reformer and Fired Heater.
Pre-Reformer

• Pre-reformer installed to increase the overall reforming capacity of the plant.
  – To compensate for the removal of the excess air at the secondary reformer.
  – To increase plant capacity.

• Pre-reformer – CASALE axial/radial internals.
  – Characteristic low pressure drop (3 psi).
  – Loaded with nickel-based steam reforming catalyst.
Pre-Reformer

- Steam/Carbon ratio of 3.2.

- Inlet temperature of 1,000 deg F.

- Endothermic reaction with temperature drop of 150 deg F.

- Partially reformed exit gas with methane slip of 67%.
Mixed Feed Reheater

- Fired heater with 6 burners operating on a BMS.
- Supplies the heat to increase the gas exiting the pre-reformer to the primary reformer inlet temperature, 1,150 deg F.
- Radiant and Convection Sections.
Mixed Feed Reheater
Primary Reformer

- Original - Foster Wheeler side-fired.
- Onquest Inc. was responsible for the reformer upgrade.
  - Engineering
  - Supply of materials
  - Supervision of construction.
• Tube arrangement changed from staggered to inline.
• Number of tubes increased from 136 to 152.
• Radiant box extended 20’.
• 40 additional burners installed.
• Mixed Feed coil replaced.
• Inlet and outlet headers and pigtails replaced.
Air Blower

• To supplement the Gas Turbine Exhaust being used as combustion air in the primary reformer – air blower was installed.

• A nozzle arrangement was designed to inject this air into the GTE ducting – for adequate mixing.
Secondary Reformer

- Air/Gas ratio: 2.7
- Outlet Temp.: 1,818°F (up from 1,660°F)
- CH₄ Slip: 0.2%
• With the increased Secondary Reformer outlet temperature, a BFW quench was installed at the HTS inlet.
• MDEA strength increased to 45%: according BASF (licensor) indications
• Equipment changes included:
  – Replacement of the Solution Regenerator trays with high efficiency trays.
  – Additional steam reboiler.
  – Two additional regenerator overhead condensers.
  – Additional Overhead Condenser Separator.
CO₂ Removal Modifications

Regenerator trays – trays were assembled prior to the actual revamp and then each tray was packed on a pallet.
Adsorbent bed changed with higher capacity molecular sieve.

Original Dryer

Molecular sieve

Inert material

Revamped Dryer
• LP case rotor suitable –
  − suction pressure increased to 388 psig up from 310 psig result of removal of cryogenic unit.

• The HP case rotor was replaced.

• Change in HP:
  − Pre-revamp 14,600HP
  − Post revamp 17,060HP
## Synthesis Converters

<table>
<thead>
<tr>
<th>Quantity/Type</th>
<th>Pre-Revamp</th>
<th>Post Revamp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Volume, ft³</td>
<td>1,200</td>
<td>1,100</td>
</tr>
<tr>
<td>Outlet Temp, °F</td>
<td>785</td>
<td>825</td>
</tr>
<tr>
<td>Inlet Press, psig</td>
<td>2,150</td>
<td>2,200</td>
</tr>
<tr>
<td>Outlet Press, psig</td>
<td>2,040</td>
<td>2,155</td>
</tr>
<tr>
<td>Diff. Press, psi</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>NH₃ In, %</td>
<td>2.9</td>
<td>2.45</td>
</tr>
<tr>
<td>NH₃ Out, %</td>
<td>13.1</td>
<td>16.8</td>
</tr>
</tbody>
</table>

- **2 - Topsoe TVA**
- **2 – Casale Isothermal**
Order placed for converter baskets – June 2004

Arrived on site – January 2005

Catalyst loading commenced – January 30th 2005

Catalyst loading ended – February 18th 2005.

Actual loading time – 55 hours

Rest of the time - mechanical work/welding associated with assembly of the baskets.
Synthesis Converters

• It is the first of the new generation of ammonia converters designed by AMMONIA CASALE

• It is based on an isothermal design, with direct heat removal by cooling plates immersed in the catalyst bed

• The catalyst beds are axial-radial, for low pressure drop, and use of small-size catalyst

• It grants performances superior to any other design, that allows the synthesis loop equipment to cope with the increased capacity, + 40 %, even with the higher inerts concentration
• All catalyst was screened prior to loading.

• Top beds loaded with pre-reduced catalyst in a conditioned air environment.

• Once loaded the baskets were kept under nitrogen purge.

• Modifications made to the top cover to facilitate the inlet at the top of the vessel.
Synthesis Converters

- New converter basket being lowered into existing shell
- New converter basket in stand loaded with catalyst
An additional BFW heater has been installed in the synthesis loop.

- Location: downstream of the steam generator.
- Duty: 35 mmbtu/hr
• The equipment in the ammonia recovery section was adequate for the revamp.

• Only the Ammonia Absorber was replaced with a high pressure vessel.

• A refurbished Hydrogen Recovery Unit was installed.
Ammonia and Hydrogen Recovery

Ammonia Absorber

Purge Gas

1st Stage Prism Separator

Heater

2nd Stage Prism Separator

Reject Gas

95% H₂

76% H₂

H₂ Product Stream

87% H₂

410#
Ammonia refrigerant compressor

- The room available in syngas dryers, the reduced synloop circulation and a new layout of the refrigerant compressor section avoided the need of the refrigerant compressor steam turbine revamping.
<table>
<thead>
<tr>
<th></th>
<th>Before Revamp</th>
<th>Post revamp Guarantee</th>
<th>Post revamp Test run</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Production</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STPD</td>
<td>830</td>
<td>1,050</td>
<td>1,059</td>
</tr>
<tr>
<td><strong>Energy Saving</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>MBTU/ST</td>
<td>--</td>
<td>3.1</td>
<td>3.22</td>
</tr>
</tbody>
</table>
THANK YOU!