ADVANCED TECHNOLOGIES FOR EFFICIENT AMMONIA PLANTS

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AmmoniaCasale

Advanced Technologies

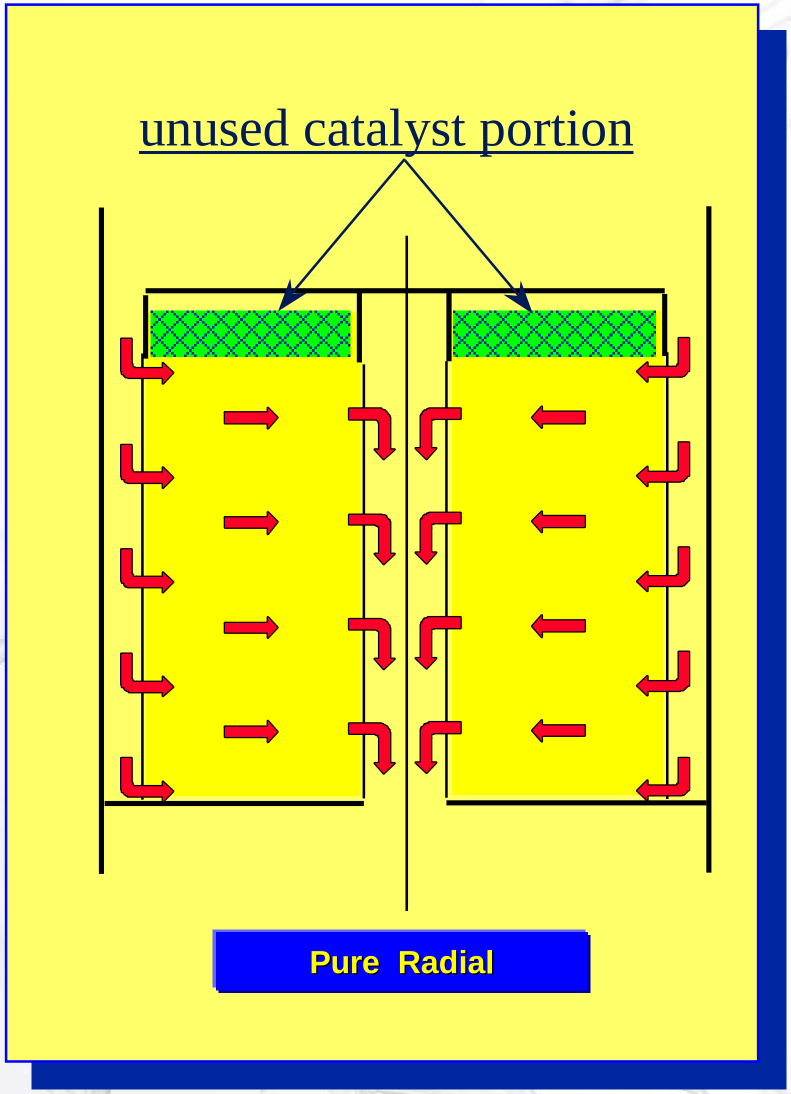
- **Casale axial-radial design for catalytic beds**
  Application in: Pre-reformer design
  CO shift converter
  Ammonia converter

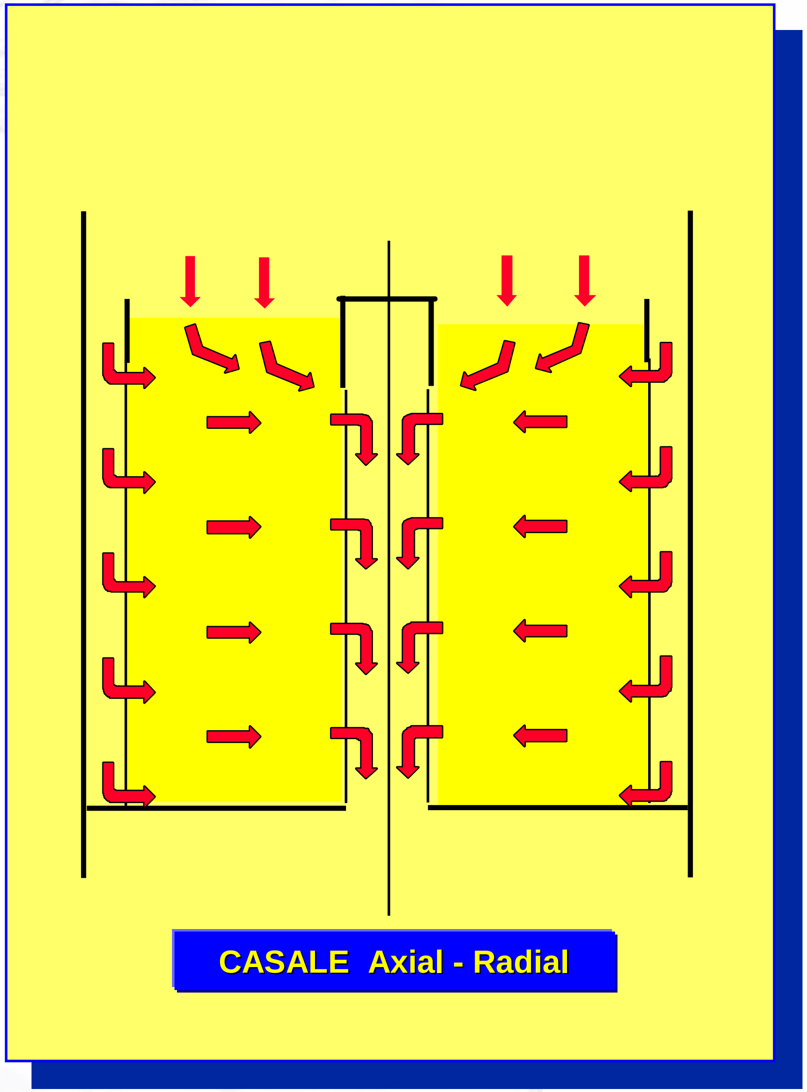
- **Casale Pseudo isothermal ammonia converter design**

- **Third part technologies for CO_2 removal (in Case History)**

Axial-Radial Catalyst bed

Axial-Radial concept: Full Catalyst Utilization





Axial-Radial benefits

Low Pressure Drop

Full Catalyst Utilization

Proven design (more than 400 beds in operation)

Simple mechanical construction

Easier catalyst loading / unloading

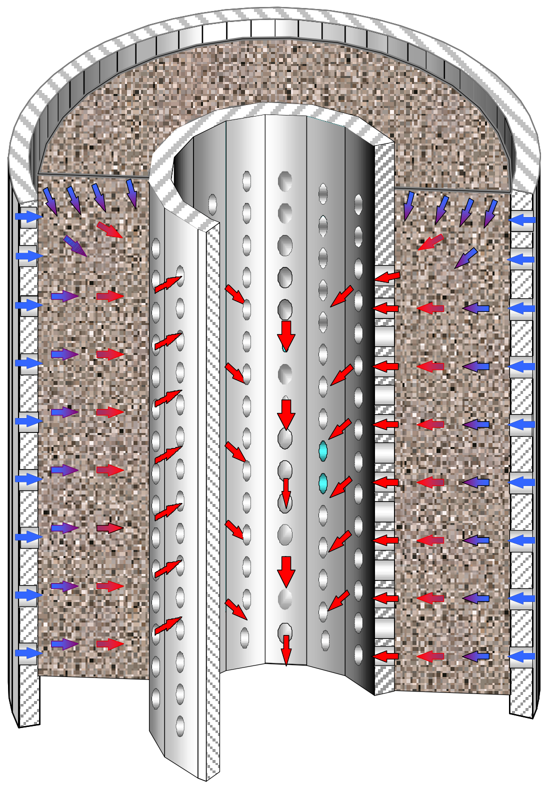


Fig. 2 - Axial-radial flow pattern - Full catalyst

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

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2$

Exothermic reactions

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$

$CO + H_2O \leftrightarrow CO_2 + H_2$

Pre-reformer

Light feed (like natural gas) give a temperature fall, heavier feedstock (like nafta) give a temperature rise across the catalystic 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

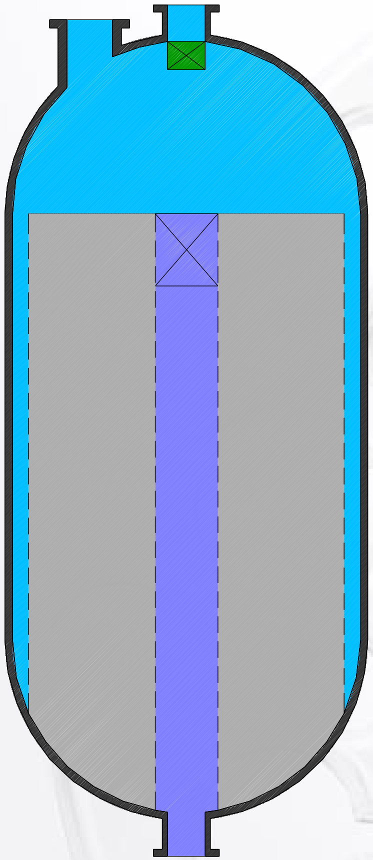
Pre-reformer

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.

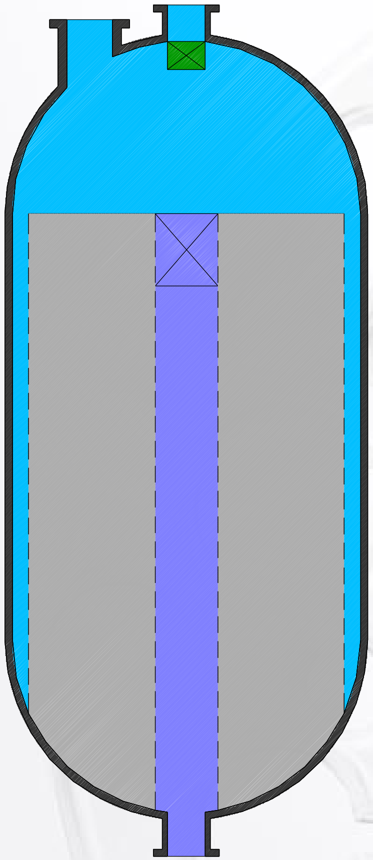
Pre-reformer



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

Axial Radial 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

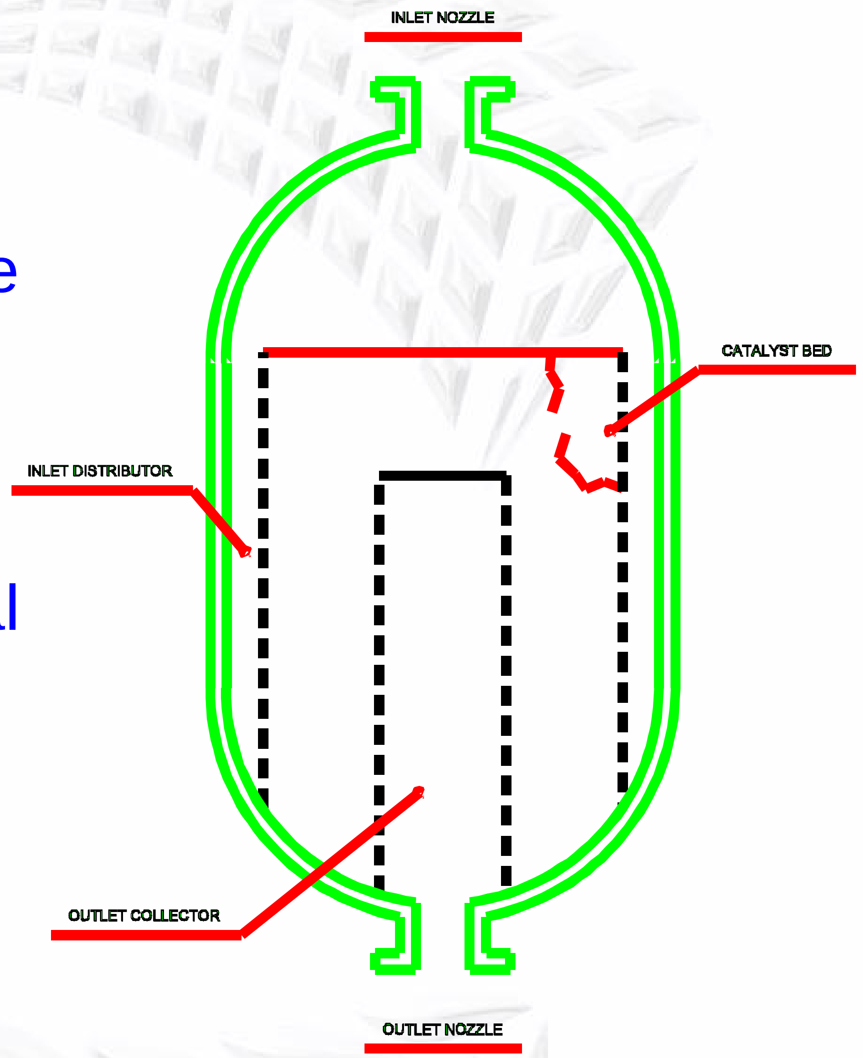
Benefits for Revamping cases

- 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

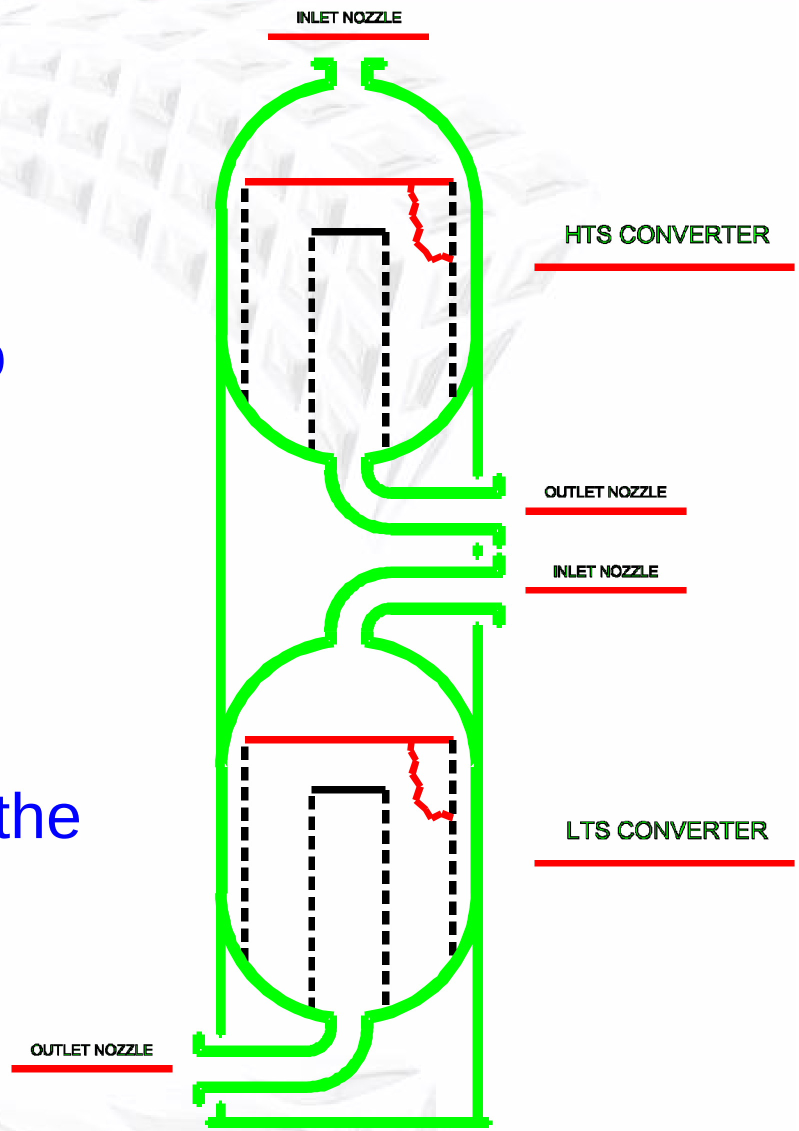
- Slimmer and cheaper pressure vessel
- Lower catalyst volume
- Simple and proven mechanical design



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

		Revamped	Original
Production rate	MTD	1’200	1’000
Pressure drop HTS	bar	0.25	0.55
Pressure drop LTS	bar	0.22	0.55
CO out LTS	% mol	0.11	0.25

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

Ammonia Casale experience

IN SITU MODIFICATIONS

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

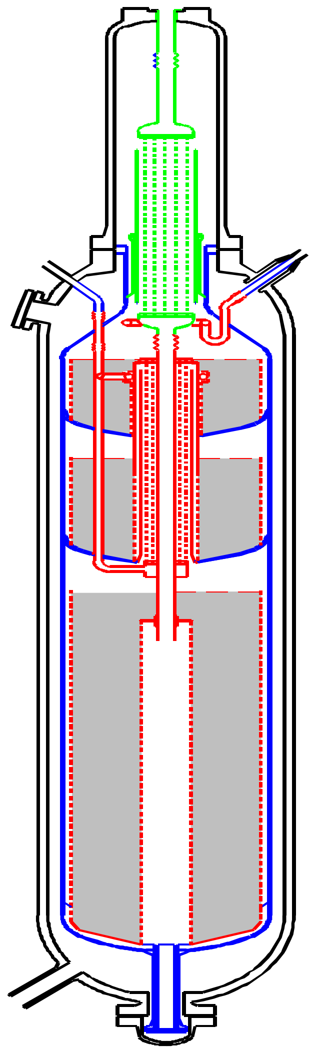
COMPLETE NEW CARTRIDGES

• more than 70 converters of 12 different types successfully in service since 1985

Ammonia Converter

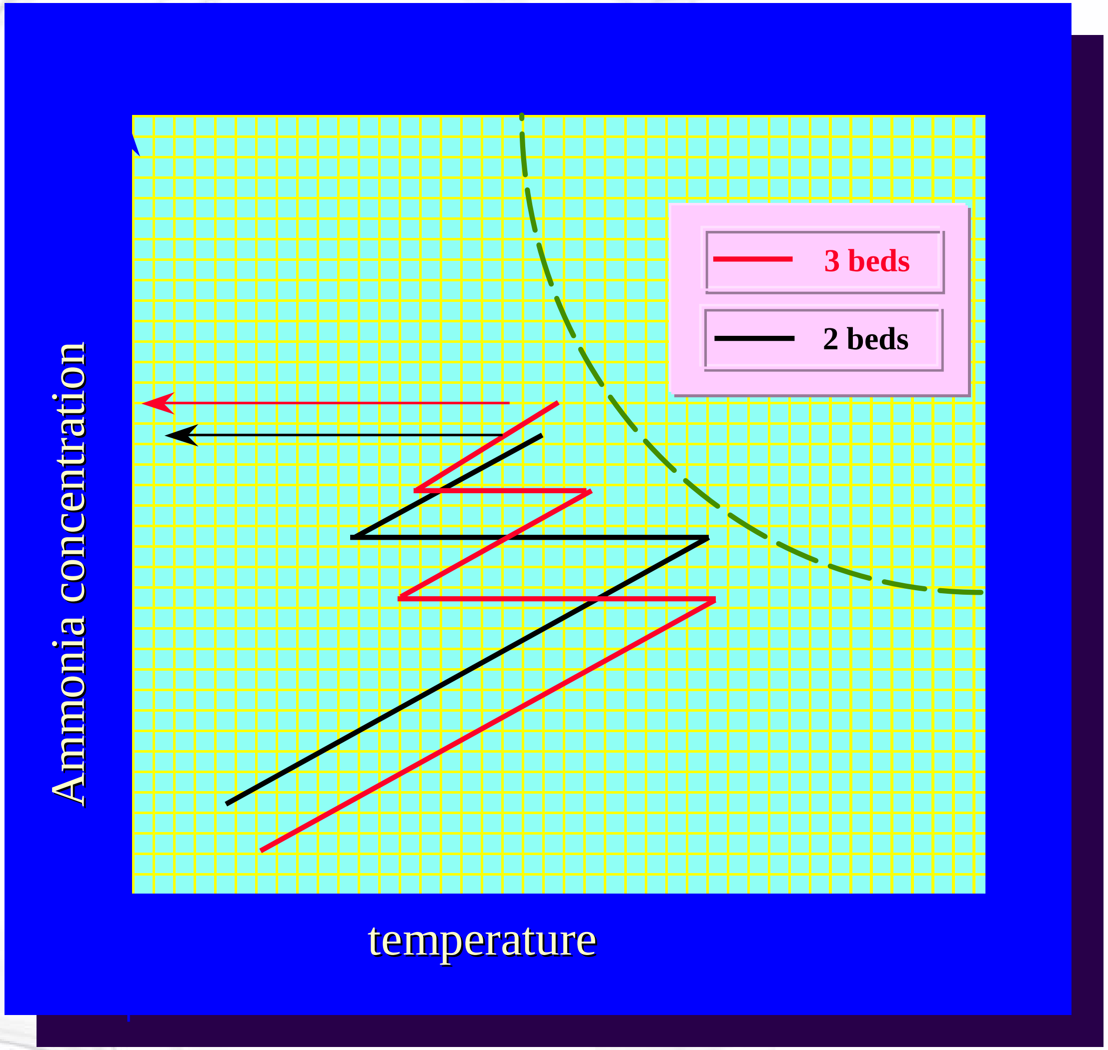
- AXIAL - RADIAL gas flow for full catalyst utilization

- THREE BED LAY-OUT for maximum conversion efficiency



Three Beds Configuration

The THREE bed configuration leads to higher ammonia concentration at converter outlet



THREE BEDS LAY-OUT

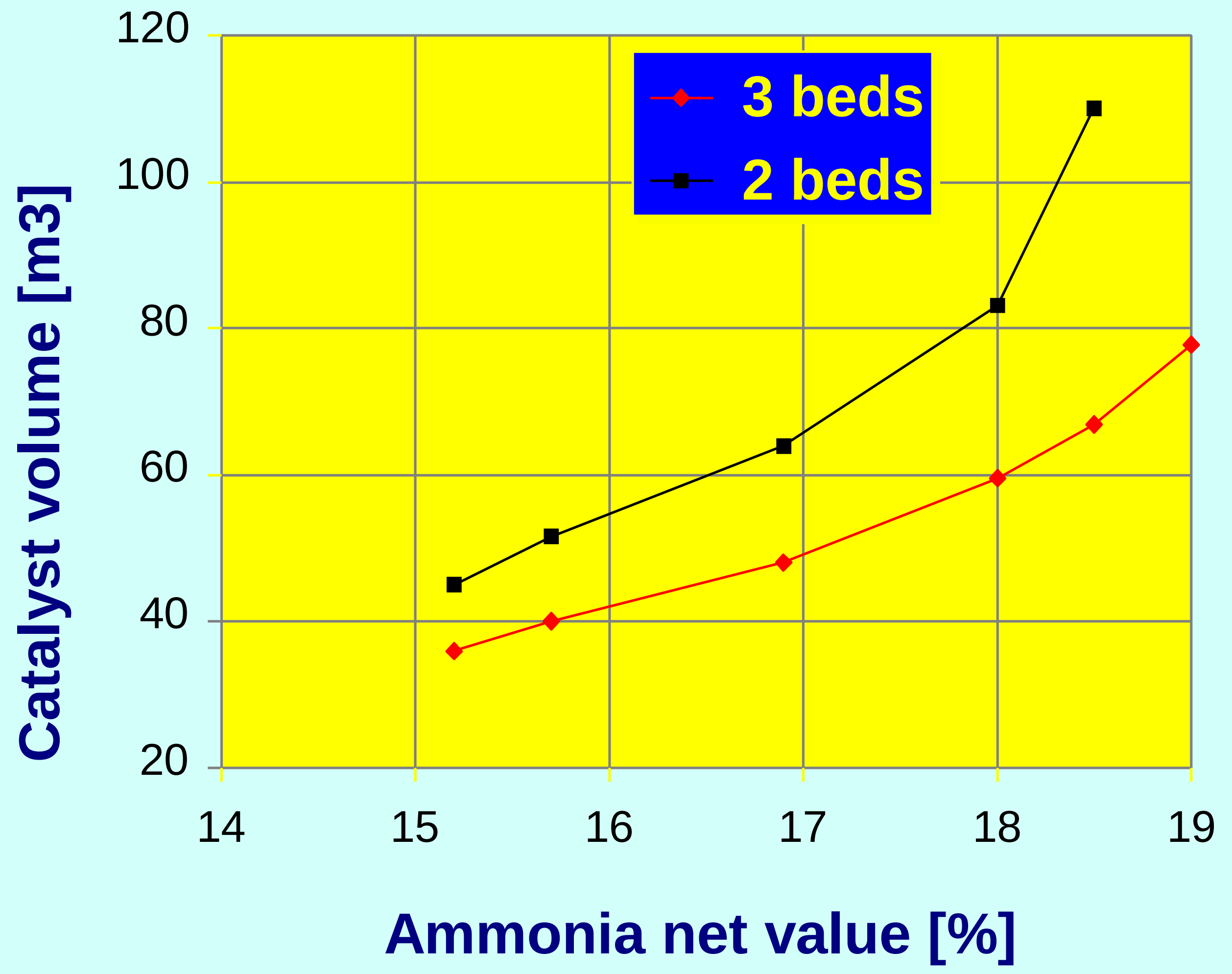
Highest

Ammonia

Concentration

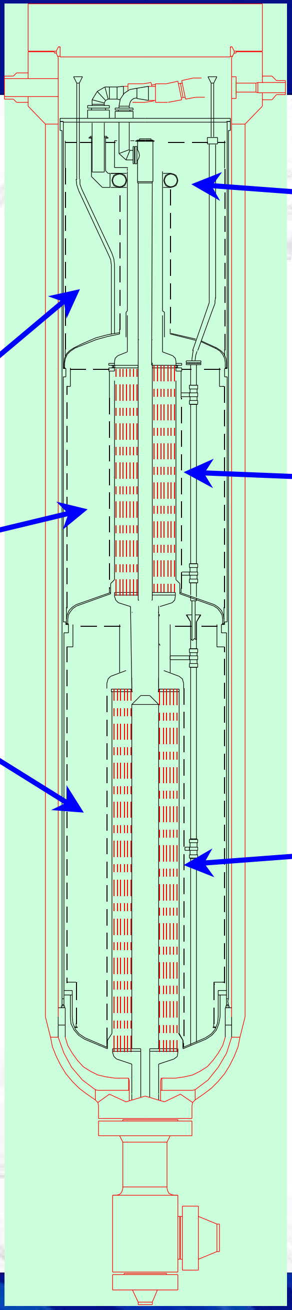
at converter

outlet



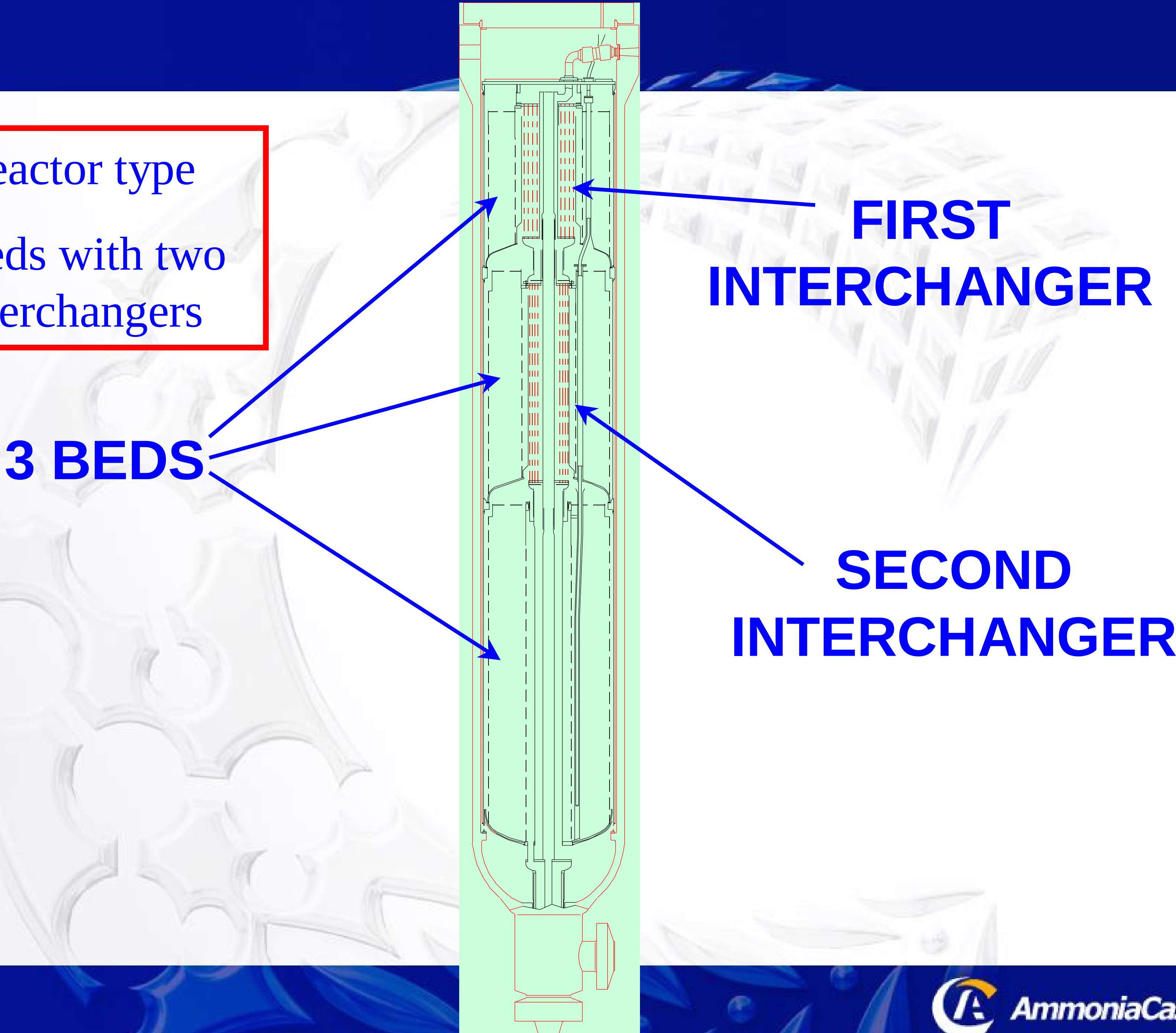
Reactor type

3 beds, quench and interchanger



Reactor type

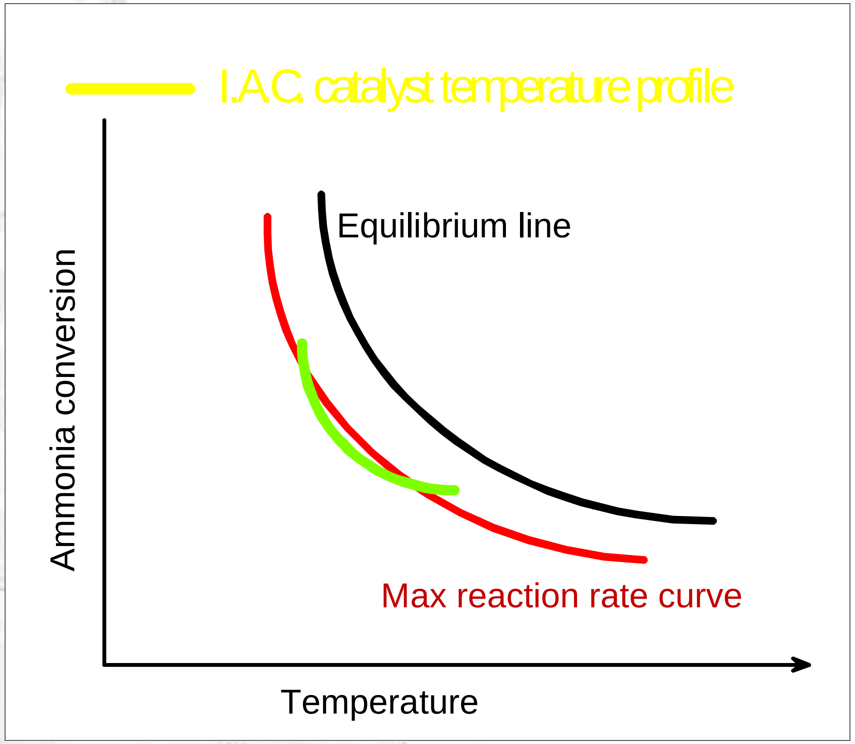
3 beds with two interchangers



The Pseudo Isothermal Design

Next generation is

Pseudo Isothermal Design



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 Pseudo Isothermal Design

The IMC design is based on the use of plates as cooling elements immersed in the catalyst bed

The Pseudo Isothermal Design

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

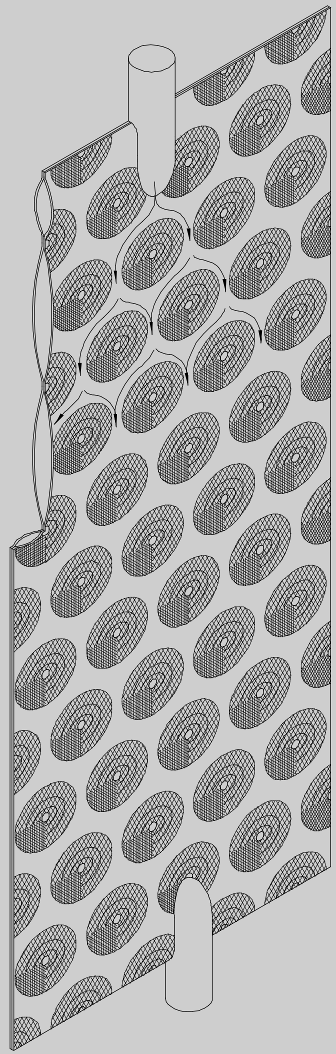


Fig. 3

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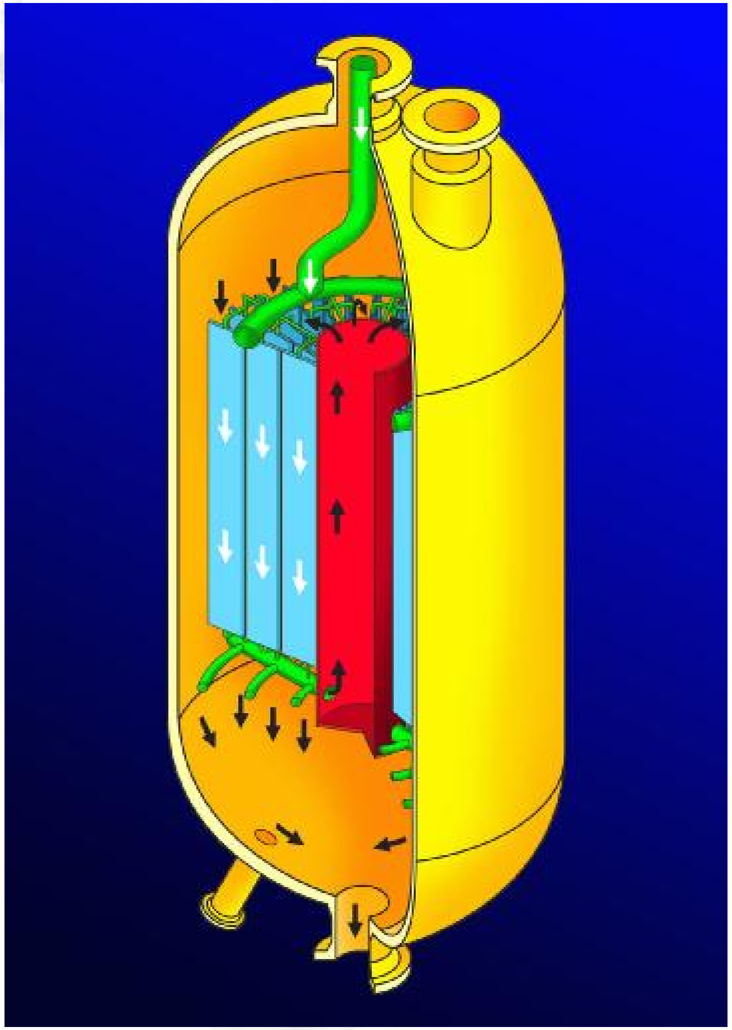
The Pseudo Isothermal Design

- The plates are arranged radially and along concentric circular sectors

- The plates are, internally fed by the cooling medium

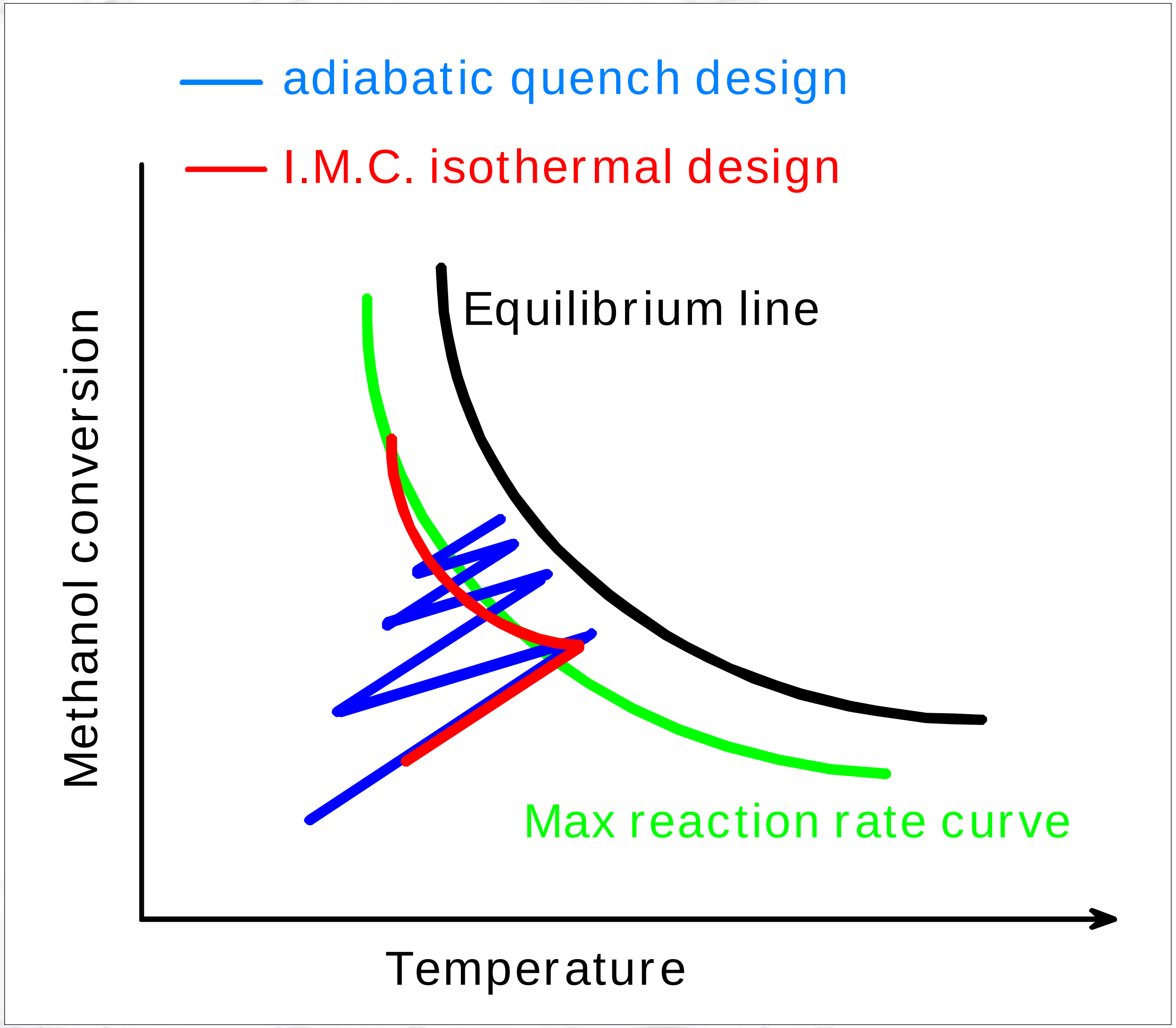
- The elements are supported at the bottom

- A central pipe is acting as access for the lower converter part



The Pseudo Isothermal Design

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

RETROFIT PROJECT GOALS

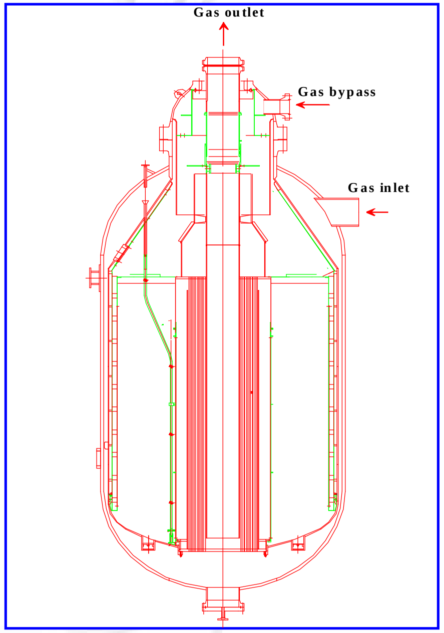
The retrofit of the plant was performed in order to :

- ü reduce the plant energy consumption;
- ü increase the production from 2050 MTD up to 2200 MTD;
- ü optimize the plant;
- ü Main area of intervention: HTS and ammonia syntesis loop

High Temperature Shift Reactor

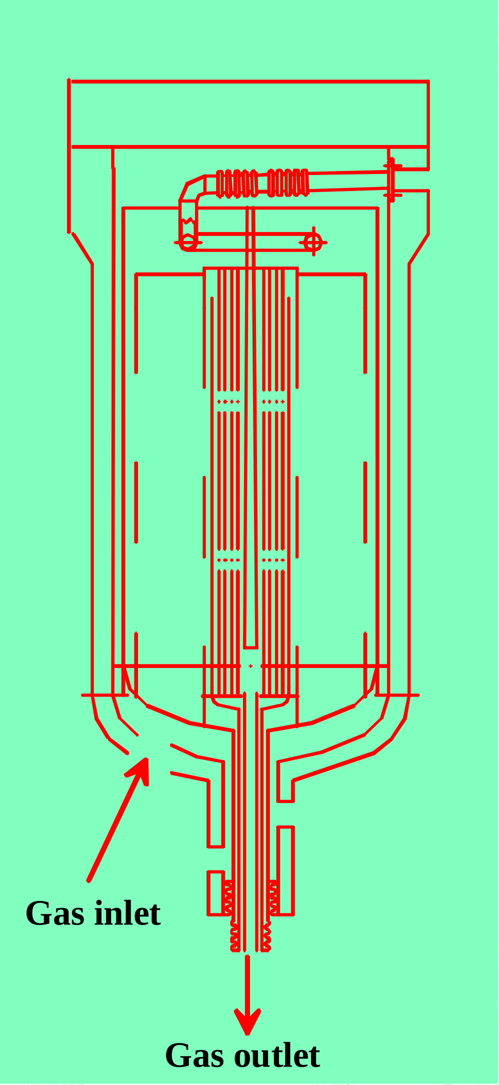
- The original HTS Axial internals have been replaced with the Axial-radial ones

- 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 4TH AMMONIA BED



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

ACHIEVED PERFORMANCE

HTS		
	Before revamping	After revamping
Pressure drop (bar)	1.84	0.85
CO slip (%mol dry)	8.40	5.31

4^{th} additional ammonia bed		
	Before revamping	After revamping
NH_3^{out} conv.(%mol dry)	16.43	23.03
Pressure inlet converter (bar)	215.7	177.5

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.**

RETROFIT PROJECT GOALS

- **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.**

PROJECT CONSTRAINTS

- **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

- **1st STEP (already on stream): <u>Low Capital Costs</u>**

  - 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;

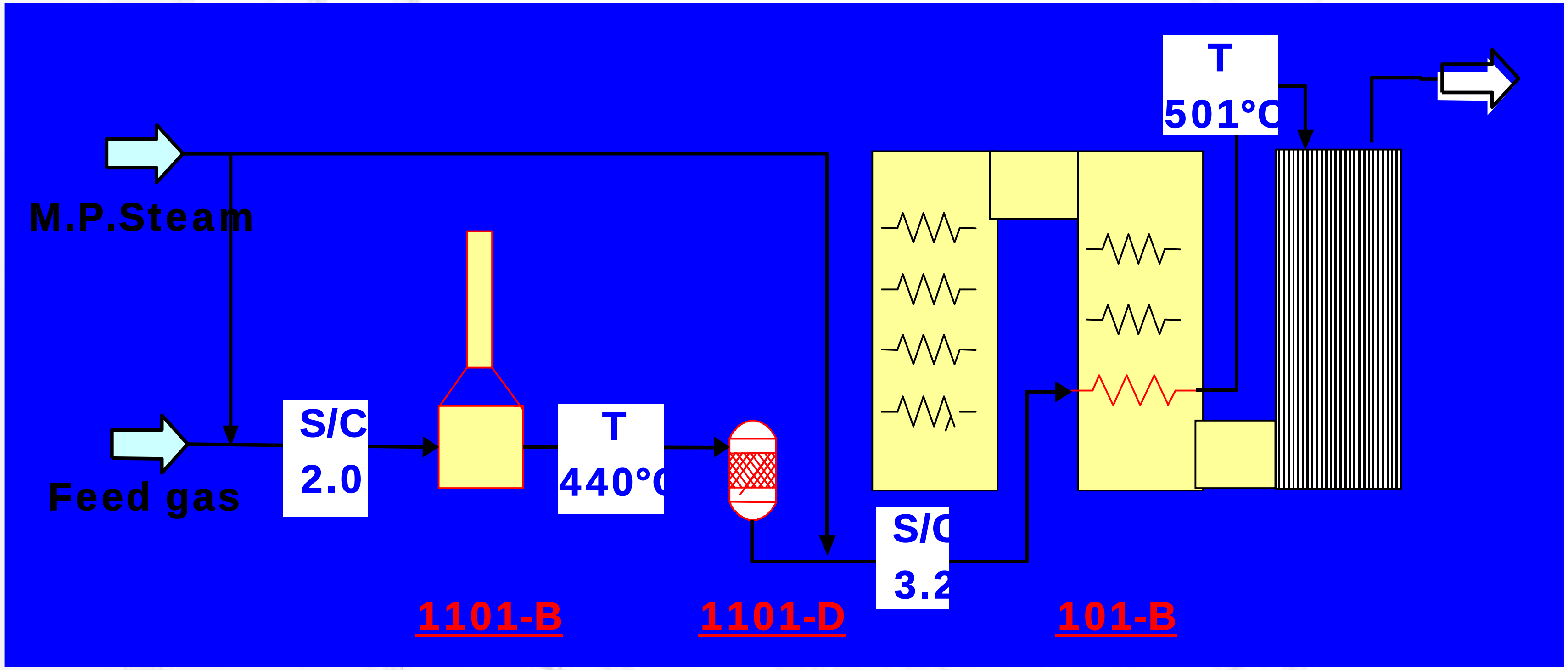
  - trip of new sections shall not involve the trip of the plant.

PLANT BOTTLENECKS

- **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.**

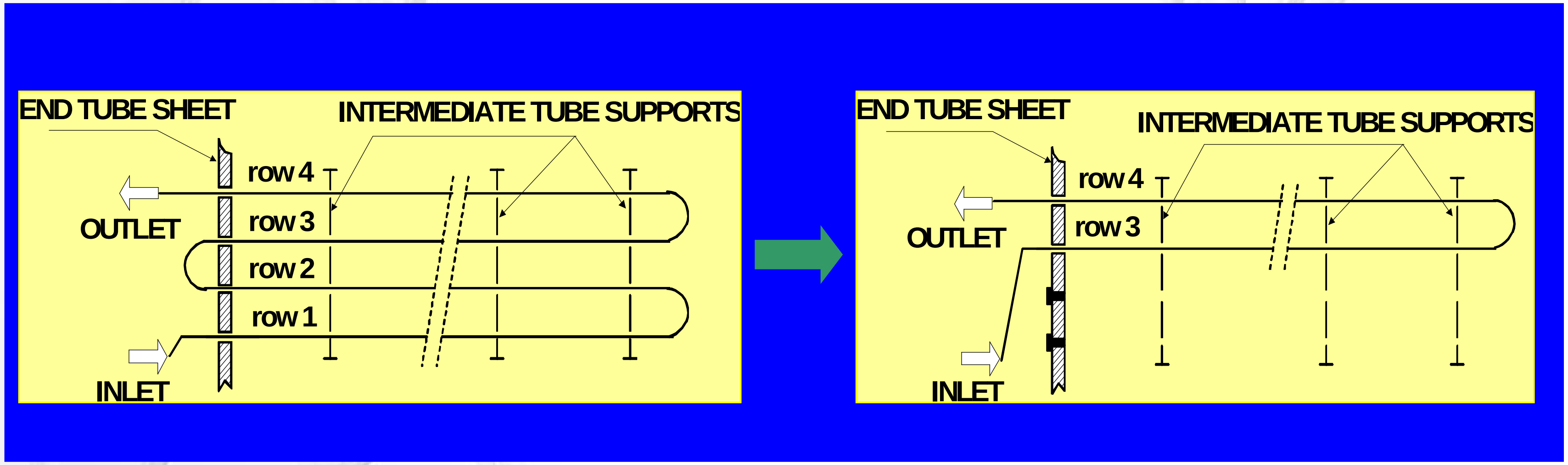
Reforming section

- Installation of a pre-reformer reactor è safe S/C reduction, less duty on primary reformer.
- New fired heater for the pre-reformer feed è 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.**



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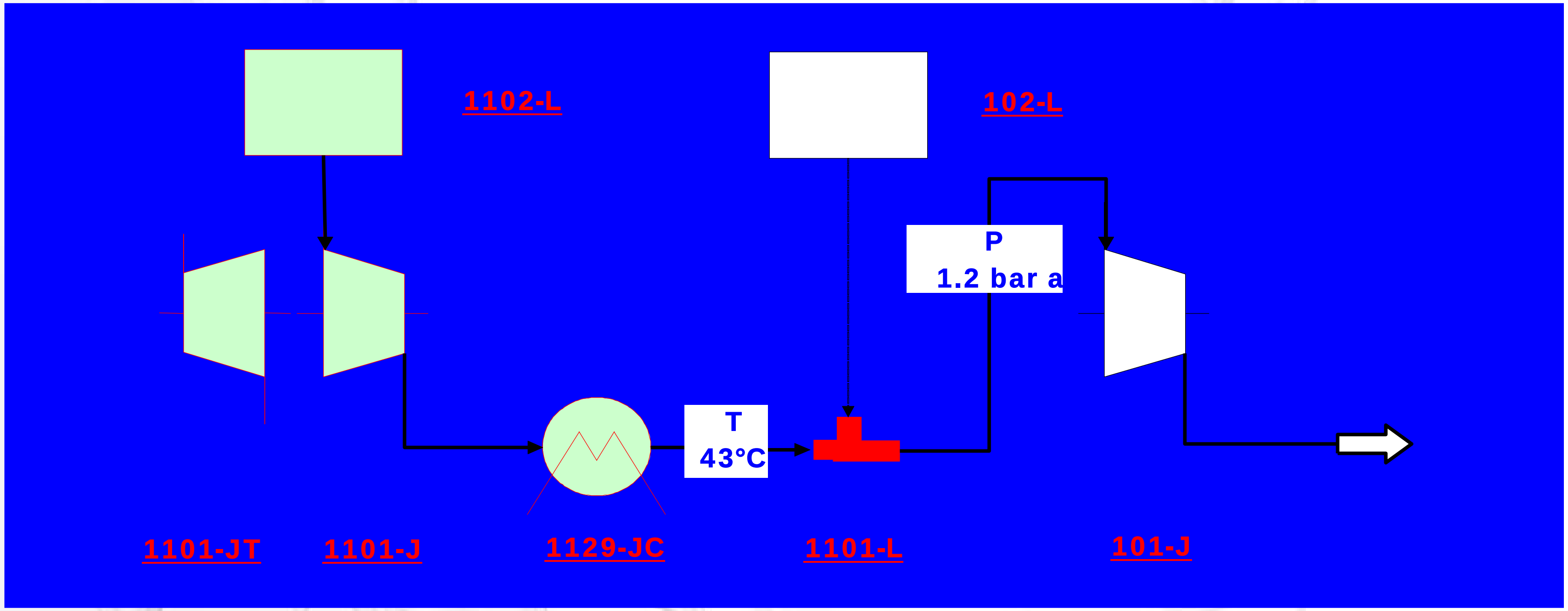
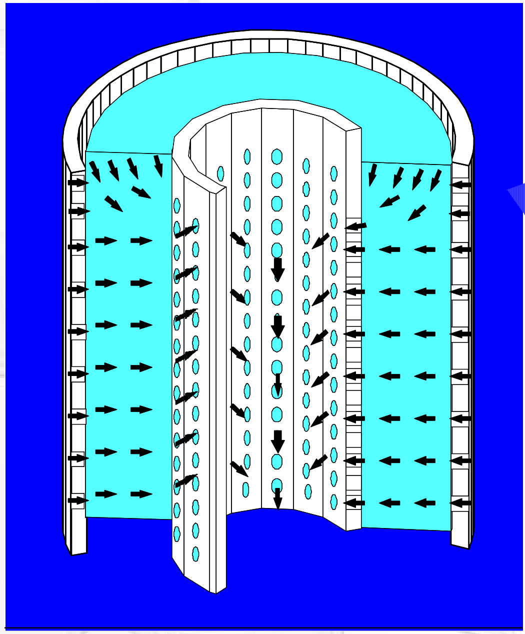
Process air supply

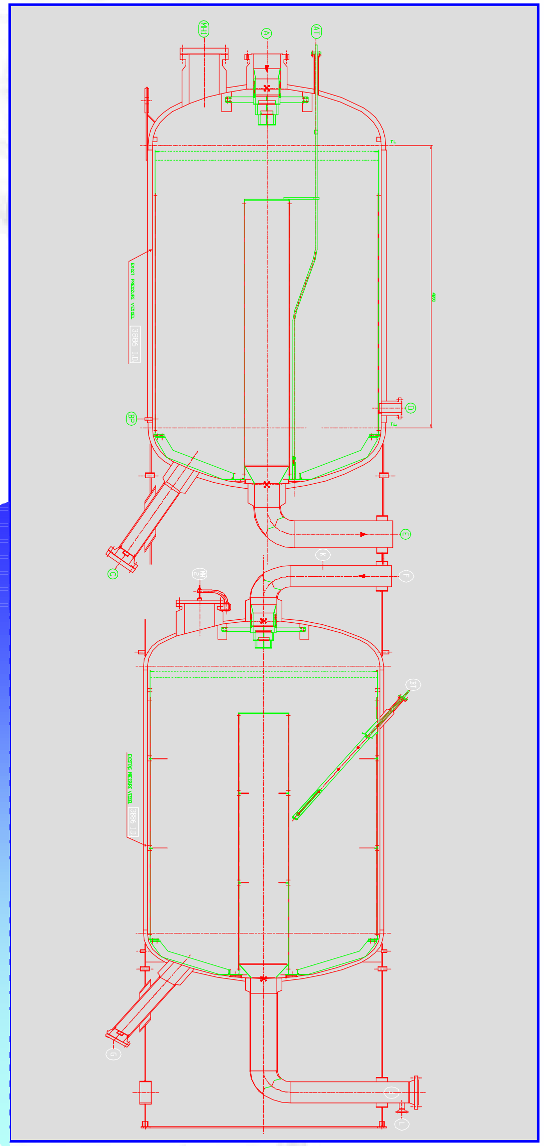
- Installation of an air booster section including a new filter, a booster driven by a steam turbine, a discharge cooler and a 3-way valve è air supply is completely debottlenecked, booster trip does not cause compressor trip.



High and low Temperature Shift converters

- **HTS & LTS retrofit with axial-radial technology è smaller pressure drops (0.8 bar saving), higher pressure st syngas compressor suction, less inerts in synloop.**





CO_2 removal section:

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

No hardware modifications have been done!

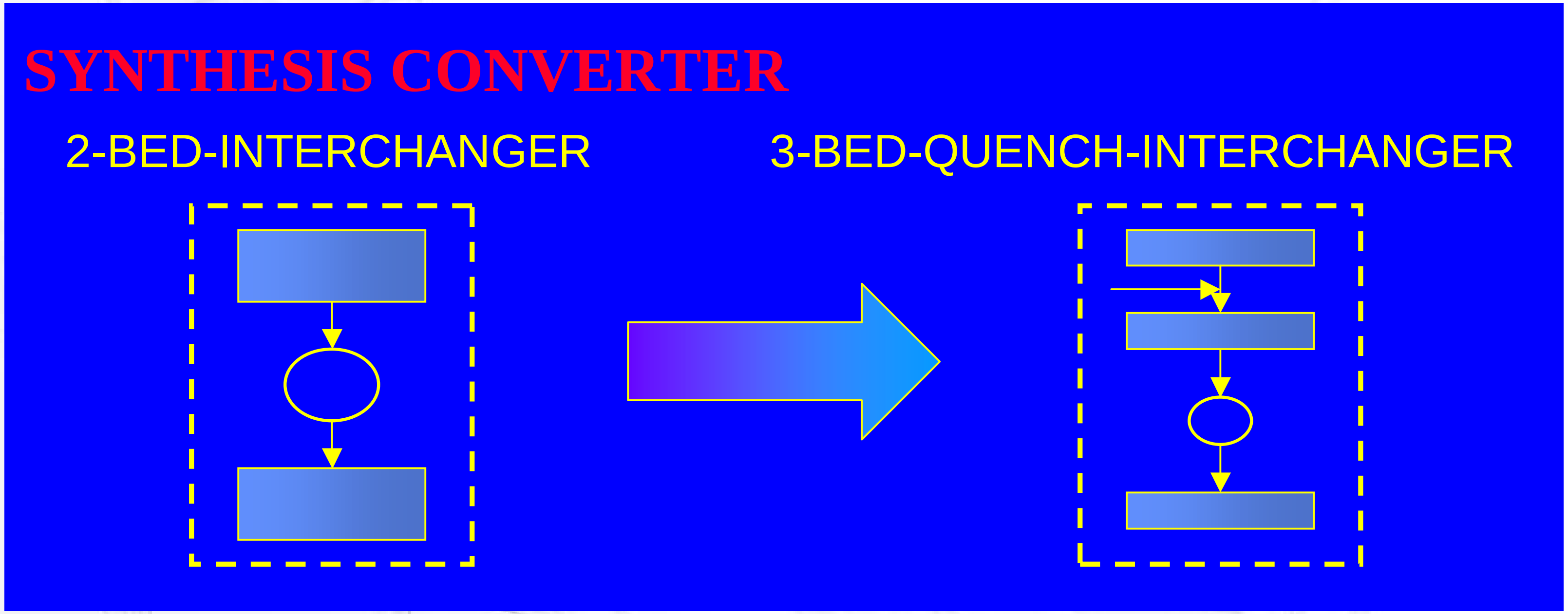
MEA solution

↓

aMDEA solution

Ammonia Synthesis Loop

- Converter retrofit & replacement of the recycle wheel
  è higher conversion, no need to modify the refrigeration system.



Achieved performances

		Before revamping	Test-run August '02
Production:	MTD	1170	1307
ENERGY CONSUMPTION			
Total specific cons.	$Gcal/MT_{NH3}$	9.77	9.46
SEA COOLING WATER			
Specific consumption	m^3/MT_{NH3}	416	388

Complete ammonia plant revamping
03 Ammonia plant, PCS, Trinidad

Background

- 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.

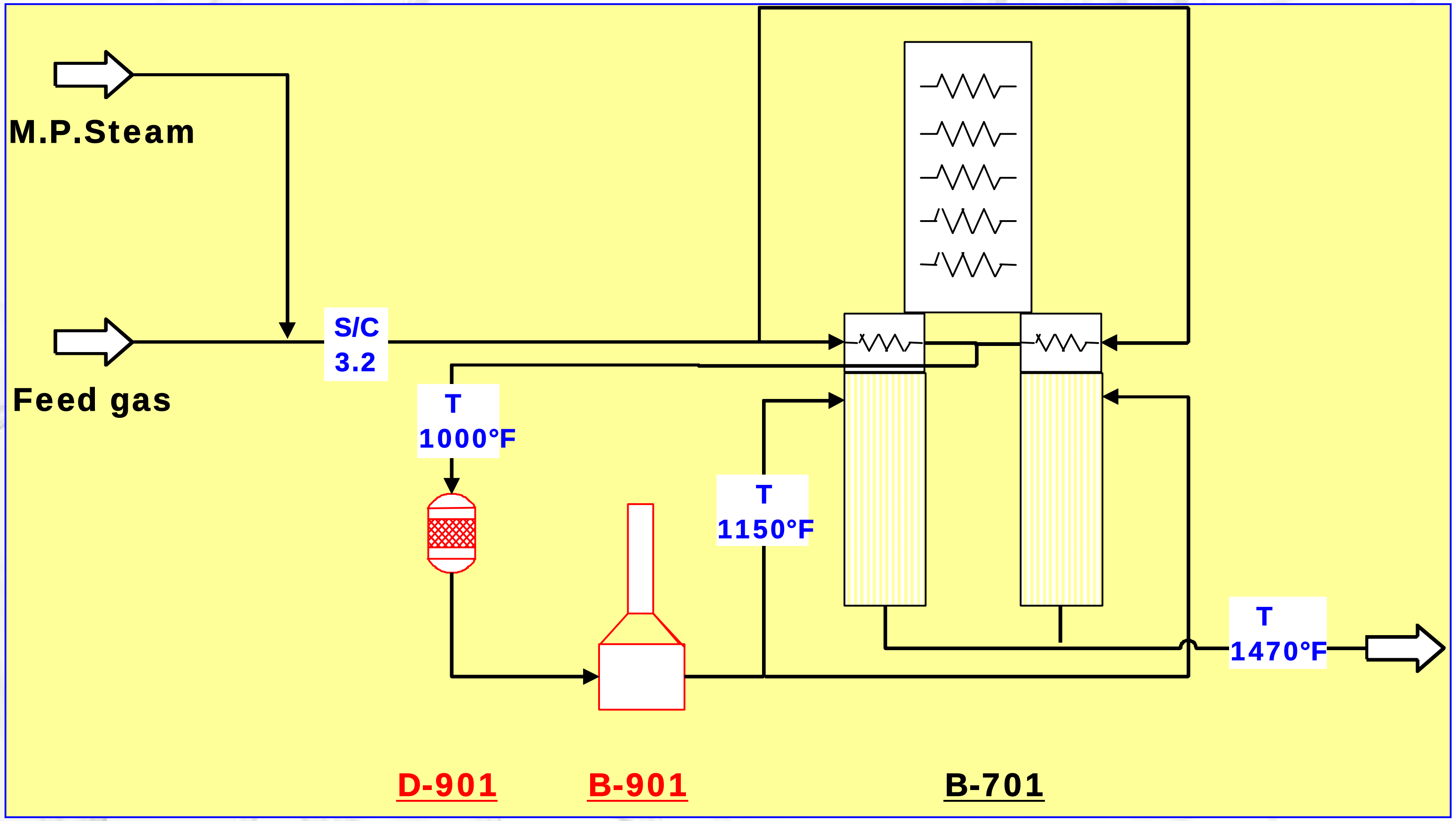
Revamp Scheme

- 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 150degF.
- 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

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.

Primary Reformer

- 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.

Primary Reformer extension

Air Blower

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

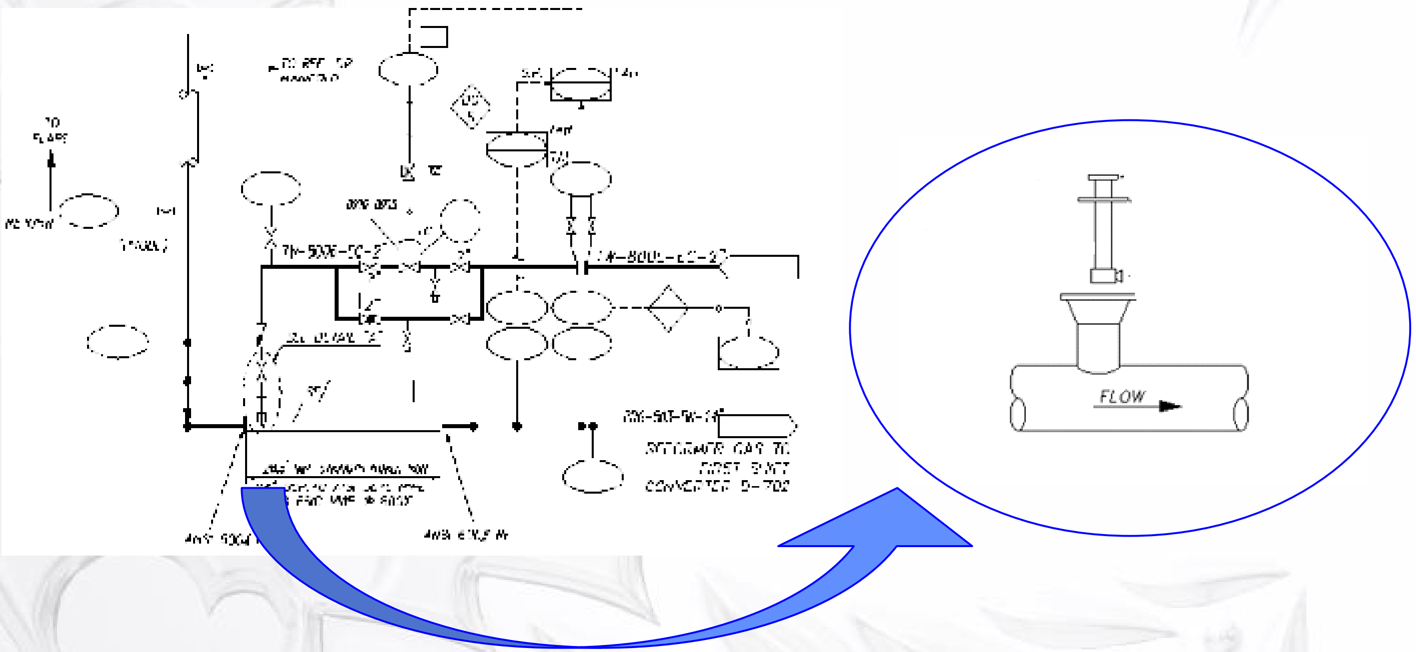
- A nozzle arrangement was designed to inject this air into the GTE ducting – for adequate mixing.

Secondary Reformer

- Air/Gas ratio - 2.7
- Outlet Temp. - 1,818^{o}F (up from 1,660^{o}F)
- CH_4 Slip - 0.2%

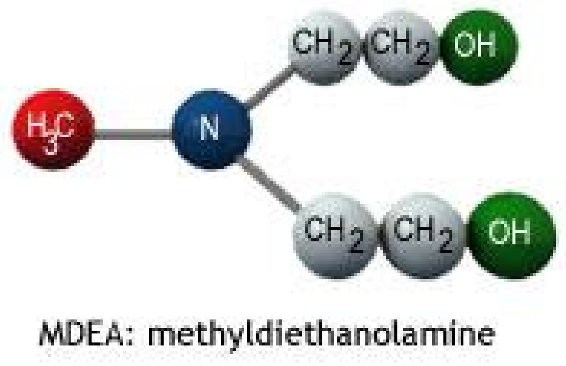
HTS Quench

- With the increased Secondary Reformer outlet temperature, a BFW quench was installed at the HTS inlet.



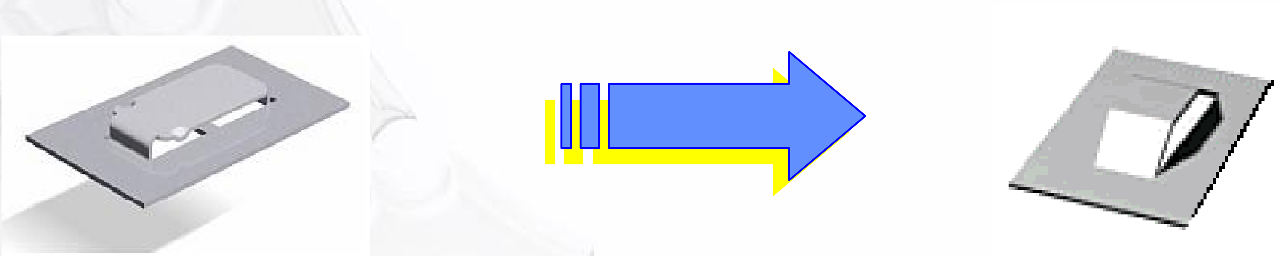
CO_2 Removal

- **MDEA strength increased to 45%: according BASF (licensor) indications**



CO_2 Removal

- **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.**

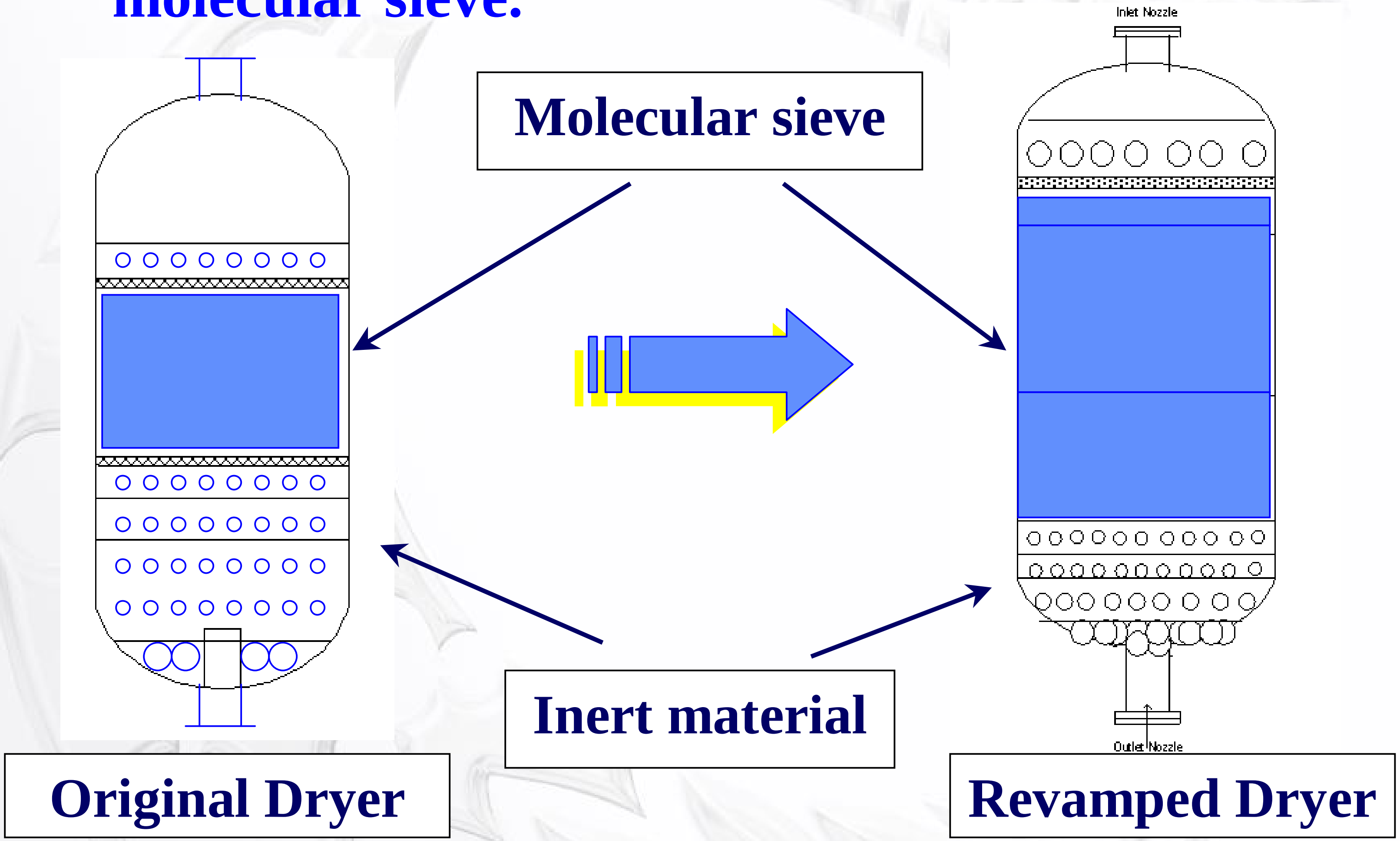


CO_2 Removal Modifications

Regenerator trays – trays were assembled prior to the actual revamp and then each tray was packed on a pallet.

Dryers

Adsorbent bed changed with higher capacity molecular sieve.



Synthesis Loop

- **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

	Pre-Revamp	Post Revamp
Quantity/Type	2 - Topsoe TVA	2 – Casale Isothermal
Catalyst Volume, ft^3	1,200	1,100
Outlet Temp, ^oF	785	825
Inlet Press, psig	2,150	2,200
Outlet Press, psig	2,040	2,155
Diff. Press, psi	100	45
NH_3 In, %	2.9	2.45
NH_3 Out, %	13.1	16.8

Synthesis Converters

- 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

Synthesis Converters

- **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

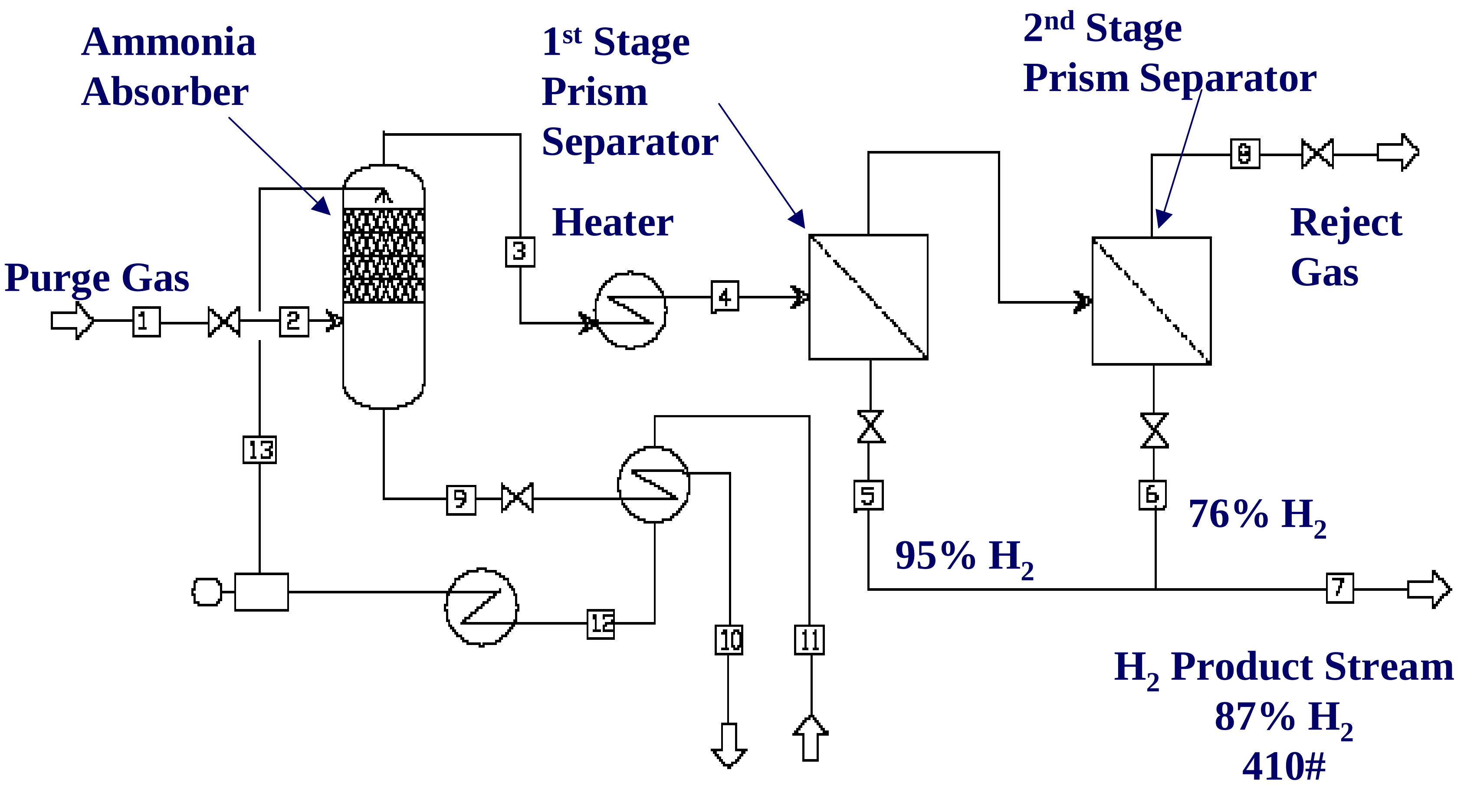
Synthesis Converters: Waste heat boiler

- An additional BFW heater has been installed in the synthesis loop.
- Location - downstream of the steam generator.
- Duty - 35 mmbtu/hr

Ammonia and Hydrogen Recovery

- **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.**

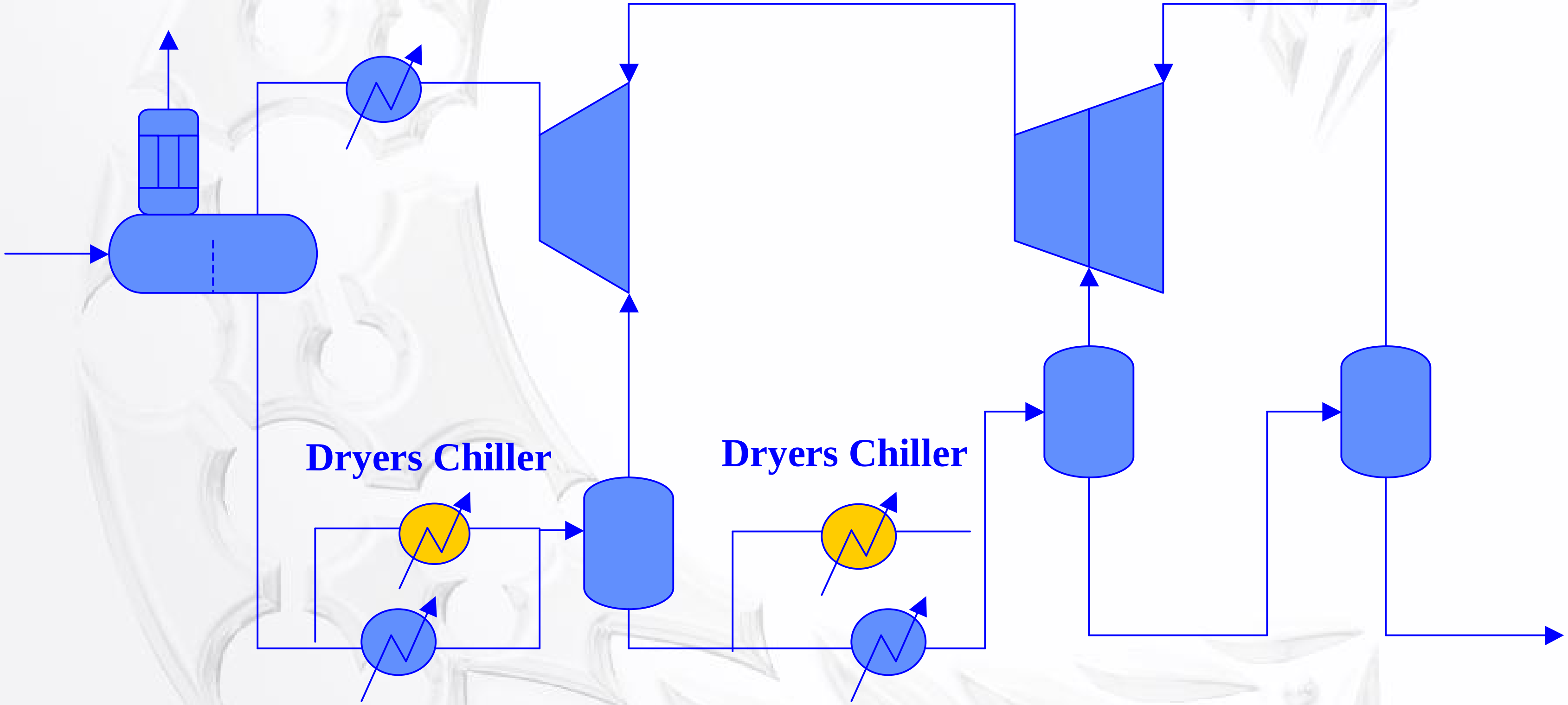
Ammonia and Hydrogen Recovery



Hydrogen Recovery

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.**



Results achieved

		Before Revamp	Post revamp	
			Guarantee	Test run
Production	**STPD**	830	1,050	1,059
Energy Saving	**MBTU/ST**	--	3.1	3.22

THANK YOU !