Ammonia Casale Technologies

for

Ammonia Plant Revamping

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ABSTRACT

Ammonia Casale has been very active in the field of ammonia plant revamping for many years and has extensive experience in the design and implementation of complete plant revamping projects, including major modifications to reformers, machines, ammonia converters and other equipment.

Casale's ammonia plant revamp strategy has always been to develop and apply new, advanced technologies to obtain the best possible improvement in plant performance at the minimum cost. The performance improvement normally comprises a reduction in energy consumption, an increase in capacity, or a combination of the two.

Projects undertaken range from revamping of ammonia synthesis converters and their supply or revamping of other special equipment such as pre-reformers and shift converters, to the revamping of complete ammonia plants for capacity increase and energy conservation.

This paper presents these technologies and some case histories of the applications.

1. FOREWORD

Ammonia Casale is a company well-known for its know-how, design and in-depth technologies in the field of ammonia plant revamping and complete plant revamping projects. Among others, these include key modifications to ammonia converters, reformers, and other machinery and equipment.

Casale's unique policy has long been based upon the development and application of state-of the-art advanced technologies for ammonia plant revamping, to get the best improvements in plant performance at the minimum cost. The performance enhancements encompass energy consumption reduction, capacity increase, or a combination of the both.

To attain this objective it is essential to identify the most critical items to improve for the best return. Ammonia Casale has done exactly that in very many projects and has developed and applied a number of proprietary improvements, which are presented below. Projects undertaken range from revamping of ammonia synthesis converters and the supply or revamping of other special equipment such as pre-reformers and shift converters, to the revamping of complete ammonia plants for capacity increase and energy conservation.

2. 1. Ammonia Casale Profile

Ammonia Casale S.A. is one of the oldest companies active in the field of synthetic ammonia production, having been established in Lugano (Switzerland) in 1921 for the industrial development and commercialization of Dr Luigi Casale's inventions for the catalytic synthesis of ammonia.

Since the very beginning, and for many years now, Ammonia Casale has been active in the construction of new plants, with over 200 such plants built worldwide.

In the more recent past, activities were devoted to the revamping of existing plants, with more than 200 plants revamped in the last 23 years, and to the design of new plants.
The company is still involved in new plant construction through its licensees.

At the present time, Ammonia Casale is a leader in the design of ammonia synthesis reactors and related process loops.

The company is also a leader in ammonia plant revamping, having its own technologies to upgrade synthesis loop and syngas front-end units.

Plant modernisations represent a very important aspect of Ammonia Casale's support to clients aiming at increasing plant capacity or reducing energy consumption to within limits where the installation of much additional new equipment would entail substantial investment costs. This is achieved by boosting efficiency of key equipment (e.g. reactors), by partial or total replacement of the old internals with new ones, or by "in situ" modifications. Based on prevailing raw material and energy costs, the return on investment is usually high.

The company can also claim the most experience in the comparison of uses of various different commercially available catalysts, and is in a position to guarantee optimal reactor performance with all these catalysts.

The main strength of Ammonia Casale lies in the licensing of its technologies. Most of the technologies are developed in house by a team of very specialized and experienced people. Thanks to the innovative trend set by founder Dr Luigi Casale, plus the heritage and background of subsequent management teams, Ammonia Casale invested significantly in technology development.

During the last decades this discipline evolved from an empirical art with an intuitive sense for good design into a more rationalized activity.

Process design is now supported by sound insight into the chemistry of the processes, catalyst behaviors, kinetic data, heat and mass transfer phenomena, fluid mechanics, science of construction materials, and cost analysis.

Ammonia Casale Technical Services avail themselves of specialists in all the above fields, as well as of sophisticated tools for investigating, analyzing and picturing complex phenomena in a way unachievable with ordinary skilled manual calculations. The process design is based on advanced computer-aided techniques with applications ranging from process flow-sheeting to kinetics, to fluid dynamics simulations and mechanical stress analysis.

In addition to the technology, Ammonia Casale can also provide all services required for the completion of a project, from engineering right down to construction, start-up and operation of the plant.

2. PROPRIETARY TECHNOLOGIES

2.1. Axial-Radial Catalyst Beds

Casale makes maximum use of the axial-radial bed concept, in all catalytic reactors.

This technology was developed for ammonia converters and later applied to shift converters and pre-reformer reactors, since it was demonstrated as being flexible, economical and efficient. Outside the ammonia field, it has also been applied in methanol and formaldehyde synthesis reactors. To date Casale has put more than 500 axial-radial beds into successful service.

In an axial-radial catalyst bed most (about 90%) of the gas passes through the catalyst bed in a radial direction, resulting in much lower pressure drop than in an axial-flow catalyst bed. The balance passes down through a top layer of catalyst in an axial direction, thus eliminating the need for a top cover on the catalyst bed (Fig. 1).

Mechanically the bed is very simple, being made only of two vertical perforated walls and of one bottom closure plate. The absence of a top cover greatly simplifies and facilitates the construction of the converter internals, allowing at the same time the full utilization of the catalyst volume.

The materials used for its construction varies according to the application. It can be carbon steel, stainless steel or Inconel, the latter being used for wire meshes only.

The essential advantages of the axial-radial catalyst bed concept are the same wherever in the ammonia plant it is applied, namely:

- low pressure drop;
- use of small-size catalyst.

The low pressure drop is, self-evidently, an important energy-saving feature, since it reduces the load on the compressors used to drive the gas through the plant. Often compressor capacity is a limiting factor on overall plant capacity, but these machines are always very expensive and it is therefore desirable to avoid the need to replace or modify them unless absolutely necessary.

The smaller the size of the individual catalyst particles is, the greater its resistance to gas flow will be. On the other hand, its activity is greater because of the greater efficiency factor. So, when installed in a catalyst bed with an inherently low pressure drop, such as the axial-radial bed configuration, a small-sized catalyst will attain either a better conversion efficiency or the same conversion efficiency from a smaller amount of catalyst, at a lower pressure drop.

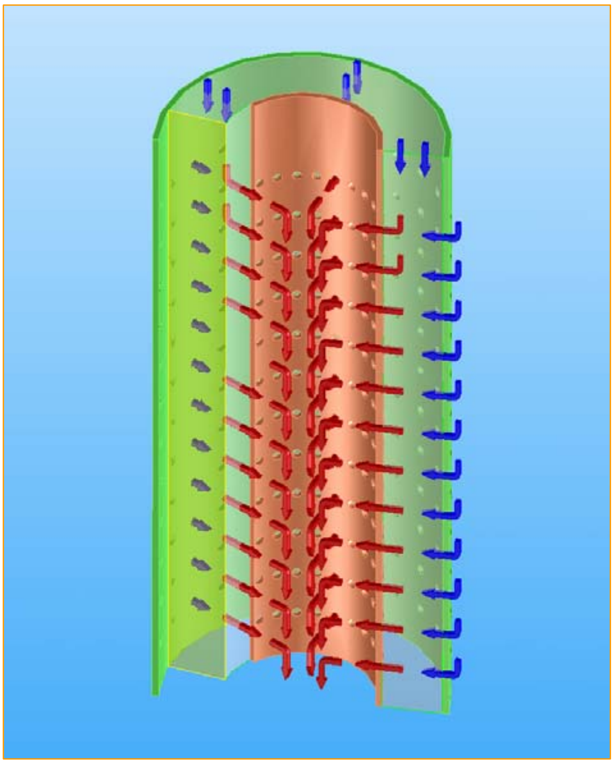

Fig. 1: Gas Distribution in an Axial-Radial Catalyst Bed

Similarly, where the catalyst is susceptible to poisoning, as in a pre-reformer or low-temperature shift converter, it is possible to attain the same catalyst service life using a smaller catalyst volume – or, if the same volume of catalyst is used, a longer service life – in comparison with the larger-particle catalyst.

Catalyst loading and unloading is very easy: the axial-radial bed is completely open on the top, allowing easy access to the bed for loading, even in small-diameter vessels, while the bed can be simply unloaded through drop-out pipes provided at the bottom of the bed.

Among the operational advantages of the axial-radial configuration, the temperature profile across the catalyst bed can be measured and followed easily by installing thermocouples in different positions in a radial direction in the bed.

2.2. Secondary Reformer Burner

Ammonia Casale has available, through its sister company Casale Chemicals S.A., an advanced design for the secondary reformer burner. The Casale Advanced Secondary Reformer Burner achieves the following goals:

- low pressure losses in both air and primary reformer streams (<1 bar in the air stream);
- low temperature of the burner surfaces exposed to the flames;
- superior mixing in the flame;
- reduced flame length, avoiding catalyst impingement even at high operating loads

soot-free combustion;

- homogeneous gas composition and temperature distribution at catalyst bed entrance;
- protection of the refractory lining from the hot core of the flame (max. wall temperature (1100-1200 °C).

Introducing this design into an existing plant reduces the pressure loss in the process air, thus increasing the air compressor capacity and/or reducing its energy consumption. On account of the very even gas composition at the surface of the catalyst bed and the greater amount of the reaction that has already taken place in the top space of the reactor, it is possible to obtain greater service life from the catalyst and/or to reduce the catalyst volume.

Casale burners are in use in six ammonia plants and seven more are being installed.

3. CASE HISTORIES

3.1. Ultrafertil, Cubatão – Pre-Reformer Installation

Ultrafertil, a fertilizer company in Brazil and an existing client of Ammonia Casale, has an ammonia plant based on steam reforming technology at Cubatão, Brazil, fed by both refinery off-gas and naphtha. Originally designed for a capacity of 450 t/d, the plant was operating at about 520 t/d at the time the revamp project was determined.

The flow rate and composition of the off-gas fluctuated considerably as a result of changes in feedstock, load and product range in the refinery. To safeguard the primary reformer from the ill effects of a possible sudden increase in the carbon content of the feedstock, it had to be operated at a very high steam : carbon ratio.

The client requested Ammonia Casale to find the best revamping options for increasing the plant capacity in two stages, first to 600 t/d and then to 800 t/d, while reducing energy consumption and phasing out the use of naphtha as feedstock on account of its cost.

Fig. 2: The Recently installed Pre-Reformer

The single most beneficial choice seemed to be to install a pre-reformer to stabilise the composition of the gas entering the primary reformer and to reduce the duty on the primary reformer. To attain the first capacity increase target (600 t/d), the reforming furnace burners were replaced, some alterations were made to the reforming furnace heat recovery train and a new, high-efficiency ammonia converter with Casale axial-radial technology was installed. The converter was completely replaced because the pressure shell of the old one was extensively cracked and could no longer be considered safe. This phase of the work was completed in July 2001. The performance of the pre-reformer and the new synthesis converter are shown in Tables 1 and 2.

Table 1: Pre-Reformer Performance		
	Process Guarantees	*Test-Run*
Conversion of C_2H_6, %	>85	98.7
Conversion of C_{3+1}, %	>95	100

Table 2: Synthesis Loop Performance		
	Process Guarantees	*Test-Run*
Converter Capacity, t/d	600	> 616
NH_3 at 3rd bed outlet, %	15.8	> 16.08
Converter pressure drop, bar	2.8	2.8

The second phase of the work (expansion to 800 t/d) comprised replacing the reformer tubes, revamping the shift converters, CO_2 removal system and the feed gas, air and synthesis gas compressors, and installing a new purge gas recovery unit. Minor changes to the heat exchangers, pumps and piping were are also planned.

Ammonia Converter Revamps

Ammonia Casale has revamped and started up more than 190 converters of different types with capacities ranging from less then 300 t/d to more than 2,000 t/d. A good example of this activity is provided by the revamp of four 900 t/d Kellogg ammonia converters at CF Industries in Louisiana, USA.

Ammonia Casale revamped these converters in 1986, adopting the first generation of internals (four beds, three quenches). Subsequently, at the end of their catalyst life, they were revamped again adopting new and more efficient internals: (three beds, quench and interchanger).

Table 3 shows the performance achieved.

Table 3: Operating Data for Revamped Kellogg Converters at CF Industries		
Case	*Original Revamp ACSA-Kellogg*	*Second Revamp ACSA*
Ammonia Production, t/d	1.287	1.475
Catalyst age, years	10	10
Inerts at converter inlet, mol %	9.8	7.7
NH_3 at converter inlet, mol %	2.6	1.4
Inlet temperature, °C	139	148
NH_3 at converter outlet, mol %	14.4	16.9
Pressure at converter outlet, bar a	137	138
Outlet Temperature, °C	299	371

Ammonia Casale has revamped converters of practically all types, including two-bed traditional radial designs in 12 plants. The largest so far is the Yara plant at Brunsbüttel, Germany, which had run at 2,050 t/d since 1989 and was recently further upgraded to 2,200 t/d. This plant includes a booster converter, consisting of a single catalyst bed, added downstream the existing main reactor.

3.2 Al-Bayroni Fertilizer Co., former Samad

In 2002 Ammonia Casale completed the revamp of a 1,000-t/d (original capacity) ammonia plant based on Kellogg technology at the Al-Bayroni Fertilizer Company, located in Al-Jubail, Kingdom of Saudi Arabia. This plant originally started up in March 1983. It uses natural gas for both feed and fuel.

The plant had been revamped once before in 1989 by replacement of the converter internals with a traditional two-bed one-interchanger design, (not a Casale design) and installation of a membrane-type hydrogen recovery unit, which allowed it to operate at a capacity of about 1,170 t/d.

The main goal of the project was to increase production capacity to 1,300 t/d. Further targets were energy saving, reducing cooling water consumption and improving reliability.

A second step of capacity increase was also considered, meanwhile the natural gas quality of the Al-Bayroni plant has considerably changed with a higher content of nitrogen. Casale adapted their studies on plant production and efficiency improvement to the new design basis. All the new equipment had therefore to be designed for the highest capacity.

An important requirement was the very tight project schedule. The project started in October 2000. All the engineering and procurement services for the de-bottlenecking project were completed in September 2001. A turnaround took place in January 2002, and all modifications were made during the period of a standard shut-down. Start-up followed immediately after.

Since every modification to machinery is very expensive, and because it would have been quite uneconomic to reharp reformer because the existing tubes were almost new, Casale prepared a minimum-investment revamping option according to the following guidelines:

- Main rotating equipment would not be revamped or replaced;
- No modifications would be made to the primary reformer section;
- Modifications to the equipment had to be suitable for the further capacity expansion;
- Possible variations in natural gas quality had to be considered;
- The plant should be able to operate at original capacity when new sections were isolated;
- Possible trips in new sections should not trip the existing plant.

The capacity expansion was limited to1,300 t/d by the suction capacity of the existing synthesis gas compressors.

The feed gas desulphurization, feed gas compression, secondary reformer and methanation sections were suitable for the new operating conditions and needed no modifications.

The following modifications were implemented:

Pre-reforming and Primary Reforming

The primary reformer of the Samad ammonia plant is a typical Kellogg top-fired unit with 416 catalytic tubes arranged in eight rows. The reformer tubes were replaced in 1997 with new HK40 tubes identical in every respect with the original tubes.

Without upgrading the reformer tubes the heat flux to the primary reformer could be increased only marginally. Therefore, to increase the capacity of the reformer up to the level needed for the capacity expansion, the steam : carbon ratio had to be decreased. On account of the high concentration of higher hydrocarbons in the natural gas, this could only safely be done by installing a pre-reformer. (Fig. 3).

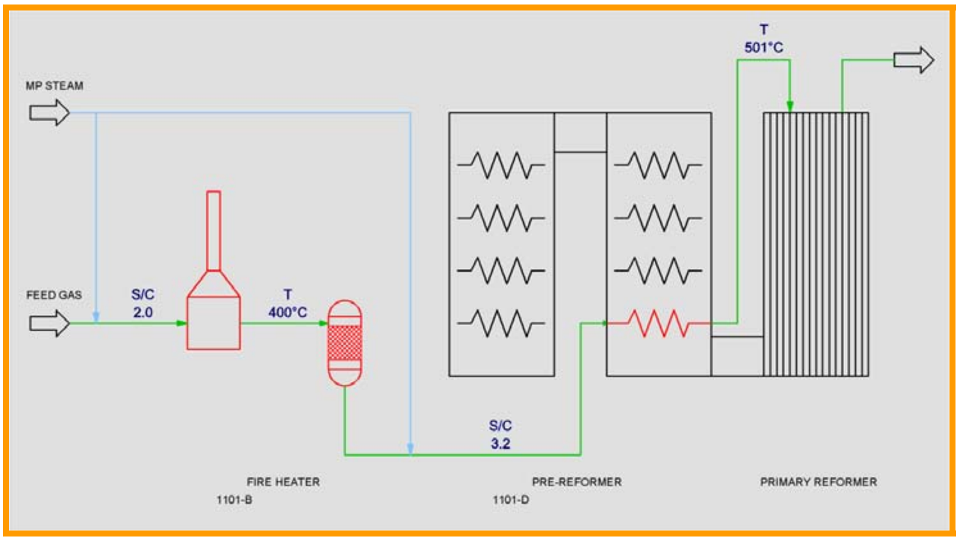

Fig. 3: New Fired Heater and Pre-Reformer

The advantages of the use of the pre-reformer and of the fired heater can be summarized as follows:

- the S/C ratio could safely be reduced;

- every possible change in natural gas composition could be accommodated.

Process Air

This section was designed to provide sufficient process air for a production of 1,000 t/d of ammonia under normal conditions.. Any increase in plant capacity therefore required debottlenecking of this compressor. This was accomplished by the following main modifications:

- addition of an air booster driven by a back-pressure steam turbine;
- addition of an after-cooler downstream the new air booster;

The booster was sized to be able to accommodate the prospective future major expansion up to 1800 MTD.

Shift Conversion

The high pressure drop in the shift converters (0.5 bar in the HTS and 0.6 bar in the LTS for new catalysts; and >1.0 bar each for the aged catalysts for both reactors) was due to the axial-flow design of these converters. Retrofitting with Casale axial-radial internals reduced the pressure drop to about 0.3 bar, correspondingly increasing the suction pressure of the synthesis gas compressor. This pressure increase was very important to allow this machine to achieving the higher capacity without any modification to the make-up stages.

The advantages that resulted from this revamping can be summarized as follows:

- lower pressure drop;
- lower CO slip and thus lower inerts concentration in the make-up gas for the whole Campaign;
- longer catalyst life;
- catalyst protection against water droplets.

CO_2 Removal

The carbon dioxide removal system was an inhibited MEA system. The CO_2 content of the purified gas was satisfactorily low (around 120 ppm) but corrosion problems were observed. For the revamp the BASF aMDEA process was adopted by means of a simple solvent swap. None of the equipment needed modification. This change reduced the specific energy consumption, making it possible to reduce the S/C ratio.

Synthesis Loop

The reduction of the steam / carbon ratio and the revamping of the shift converter internals allowed an increase in plant throughput without appreciably increasing the system pressure drop. To allow the synthesis loop to handle the increased flow new **synthesis converter internals** were provided. The existing cartridge was a two-bed inter-cooled design installed in the 1989 revamp. This was replaced by a new three-bed axial-radial cartridge with one quench inlet between the first and second beds and one interchanger between the second and third beds. The greater conversion efficiency and lower pressure drop of the new converter internals meant that both the required gas recycle rate and the energy needed to drive it round the system were reduced, so the **recirculator wheel** of the main compressor was replaced by a new one designed for the revised flow conditions. The spare energy, resulting from the reduced recirculation power requirement, provided the additional power needed to maximise the discharge pressure of the make-up gas compression stages at the increased suction flow rate without any other modification to the compressor or its turbine drive.

On account of the better converter performance and higher loop operating pressure, not only the ammonia concentration but also the temperature at the converter outlet were higher. The latter was above the design value for the metallurgy of the existing converter outlet pipe and for the boiler feed water preheater, so both were replaced.

The improved performance of the synthesis loop significantly reduced the specific chiller duty, allowing the plant capacity increase to be borne by the refrigeration compressor and its steam driver without any modification.

Table 4 compares the performance of the plant before and after the revamp.

Table 4: Al-Bayroni Plant Performance Before and After Revamp		
	Before revamp	*After revamp*
Production, t/d	1170	1312
Specific energy consumption, Gcal/tNH_3		about 6 % reduction
Sea water consumption, m^3/tNH_3		about 7 % reduction

3.3 PCS Nitrogen Trinidad, O3 Plant

The 03 ammonia plant is an original C.F. Braun design that was constructed in 1965 in Brea California. The plant was relocated to Trinidad in 1994. The design capacity at that time was 680 MTD. Some minor modifications increased the plant's production rate to 753 MTD.

Following a recent plant revamp engineered by Ammonia Casale, the plant production is now 953 MTD, while the energy consumption is now 9.7 Gcal/MT. The revamp involved converting the plant from the original Braun purifier design operating with 50% excess air in the front end, to a conventional ammonia plant operation. The purifier was idled and a hydrogen recovery unit was installed to treat the purge gas from the synthesis loop.
The two existing converters were retrofitted with 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.

Revamp Scheme

The Braun process is characterized by the introduction of excess air in the secondary reformer. This reduces the load of the primary reformer and requires a cryogenic purifier, downstream of the methanator, to remove the excess nitrogen. This purifier removes almost all of the inerts contained in the gas. There is however, an expander located immediately upstream of the purifier and this creates a large pressure drop.

Therefore, the two main areas that needed to be improved were the reforming section and the synthesis loop.

The following major changes were required for the revamp:

1. Installation of a Pre-reformer.
   This comprised of:
   a. A Pre-Reformer with Casale designed axial-radial internals.
   b. A new fired heater to recover the resulting temperature drop

2. Revamp of the Primary Reformer Involving:
   a. Replacement of the catalyst tubes.
   b. Extension of the radiant section.
   c. Replacement of the mixed feed coil.
   d. Installation of a combustion air blower to supplement the gas turbine exhaust (GTE).

3. Installation of a quench nozzle on the HTS quench.

4. Upgrade of the CO_2 removal system.
   This comprised:
   a. Replacement of the trays in the MDEA Regenerator.
   b. Installation of an additional steam reboiler.
   c. Installation of two additional Regenerator Overhead Condensers.
   d. Installation of an additional Regenerator Overhead Condenser.

5. Idling of the Purifier section.

6. Replacement of the synthesis gas compressor HP rotor.

7. Replacement of the existing two converter internals with the Casale isothermal basket design. This consists of an arrangement of exchanger plates in the axial-radial catalytic beds.

8. Installation of a BFW heater.

9. Installation of a Hydrogen Recovery Unit.
   This is a used unit that was refurbished and was handled as a joint effort between Air Products and PCS Trinidad.

10. Changes in the ammonia recovery section.
    a. Replacement of the MP ammonia absorber with a high pressure absorber.
    b. Installation of a new HP Absorber feed pump.

11. Replacement of the ammonia product pumps.
    This was handled as an internal project at PCS.

12. Replacement/Addition of control valves and PSVs.

Process Details

Pre-Reforming

The pre-reformer section was installed to increase the total reforming capacity of the plant.

The pre-reformer is an Ammonia Casale designed axial-radial adiabatic reactor loaded with a nickel based steam reforming catalyst. Its low pressure drop, of approximately 0,40 bar, is characteristic of the axial-radial design.

The gas leaving the pre-reformer is partially reformed. It then flows to the fired heater, which supplies the heat necessary to increase the temperature to the reformer tube inlet temperature.

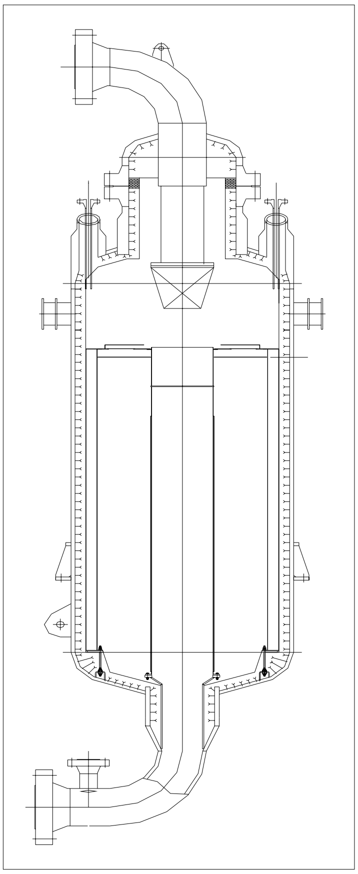

Fig. 4 - PCS Axial-Radial Pre-Reformer

Primary Reformer

The primary reformer was an original Foster Wheeler design side-fired reformer. The tubes were at their end-of-life and the frequent failures were causing severe plant reliability issues. The major changes were:

- Tube arrangement changed from staggered to inline.
- Number of tubes increased
- Extension of the radiant box.
- Installation of additional burners.
- Replacement of the old burner tips.
- Replacement of the mixed feed coil.

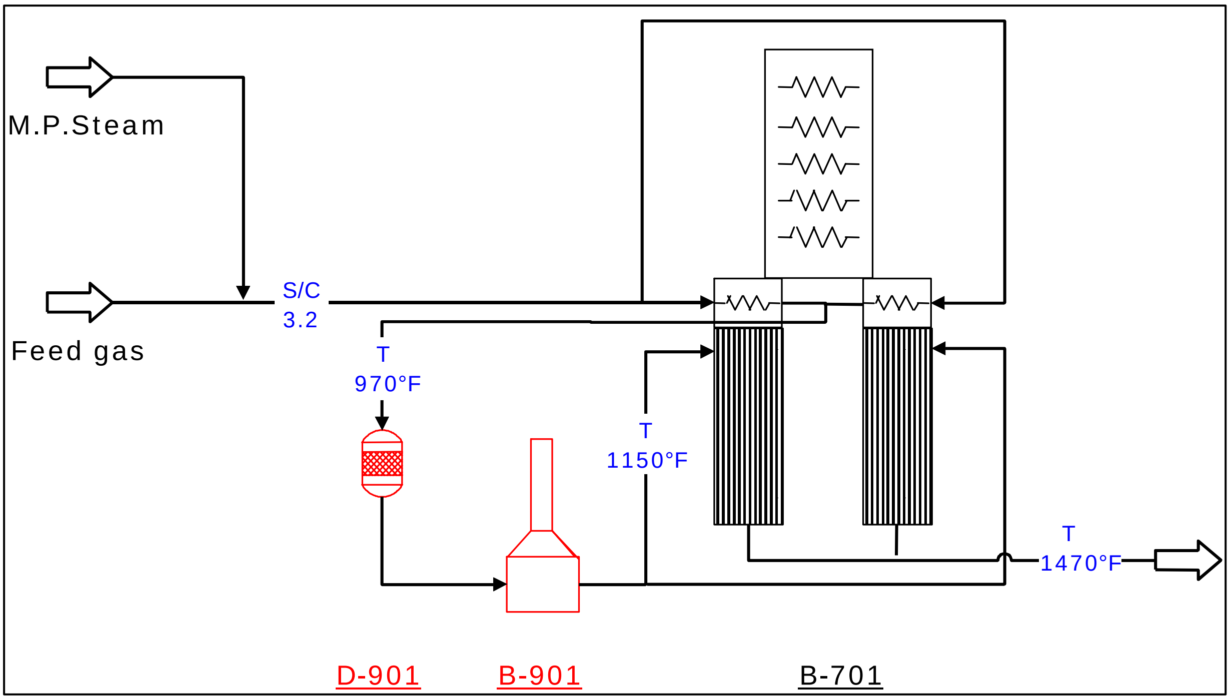

Fig. 5 - Pre-Reformer Arrangement, new items in red.

The radiant box extension was shipped in sections with insulation pre-installed, ready for assembly. The insulation however was damaged in shipping and was replaced on site.

The composition of the fuel gas to the burners was changed with the elimination of the waste gas from the purifier section. The gas from the HRU is much less and the burner tips were changed as a result. The gas turbine exhaust, which supplies oxygen to the burners, was deemed to be insufficient and an auxiliary air blower was installed to supplement the oxygen supply. The exhaust of this blower was tied into the GTE ducting.

Fig. 6 – Photo of the Primary Reformer and Fired Heater

Shift Conversion

The shift converters, both HTS and LTS, were found to be adequate for the revamp and the only change made in this section was the installation of a BFW quench system to control the HTS inlet temperature. This was necessary because of the limitation of the secondary reformer waste heat boiler.

CO_2 Removal

In reviewing the CO_2 removal system the key parameter used for design was the specific energy consumption. , the revamp sought to maintain this at the old rates. To do so, an additional demand was required. This was supplied by installing an additional steam reboiler. In keeping with the increase in reboiler duty, the capacity of the MDEA Regenerator Overhead Condensers had to be increased. This was achieved by installing an additional cooler.
To maintain stripping efficiency, the MDEA strength was increased and the circulation rate was increased. The system hydraulics was reviewed and it was necessary to replace the MDEA Regenerator trays with new high efficiency design trays.

Synthesis Gas Compressor

The LP stage of the compressor was found to be suitable to the capacity increase. This was primarily due to the significant increase in suction pressure, caused by the decommissioning of the purifier section.

The HP stage was limiting with the increased volumetric flow and had to be retrofitted. A new rotor was installed.

Synthesis

The plant is fitted with two ammonia converters operating in parallel. The revamp of the synthesis section demanded a very significant efficiency improvement because of:

- The large capacity increases and
- The higher concentration of inerts in the circulating gas due to the front-end transformation.

This entailed the retrofit of the converter internals with Ammonia Casale isothermal design. This new design allowed a significant reduction in the circulation flow and consequently a considerable decrease in the specific duties of the exchangers. The lower recycle flow resulted in a smaller heat recovery in the synthesis waste heat boiler. To overcome this, a BFW pre-heater was installed. Additionally, the increased ammonia conversion in the synthesis loop translated into no additional load on the refrigeration system, which in turn meant no modification to the refrigeration compressor.

The Isothermal Ammonia Converter (IAC) design abandons the use of multiple adiabatic catalyst beds, commonly used in the ammonia industry for the pseudo isothermal design, and offers a higher conversion per pass. The new design is based on the use of plates immersed in the axial-radial catalyst bed to remove the reaction heat while it is formed.

As indicated in the diagram above, the temperature profile achieved in the catalyst bed follows the line of maximum reaction rate, so obtaining the highest possible conversion per pass from a given catalyst volume.

The use of plates for cooling, allows the design of a pseudo isothermal converter without tubesheets, eliminating the size restriction and simplifying the construction of the internals and the operation of catalyst loading and unloading. In addition, the non-adiabatic beds are axial-radial, featuring a low pressure drop and allowing the use of small size, high activity catalyst.

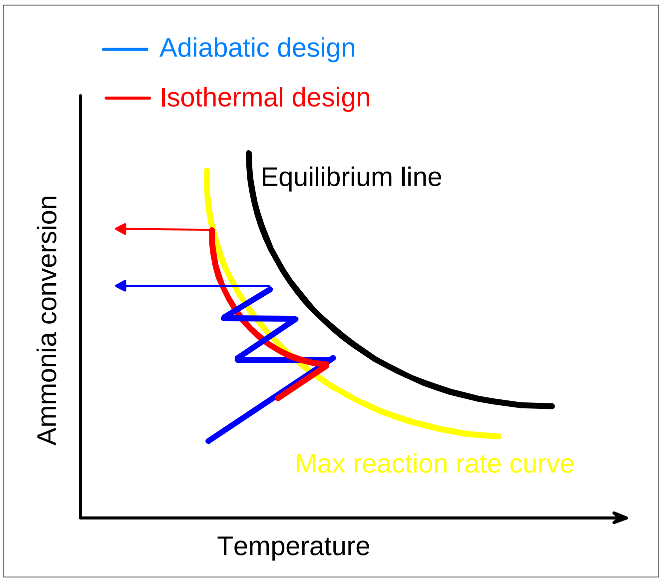

Fig. 7 - Temperature Profile of the IAC.

Fig. 8 - Photo of the Converter Basket being lifted into place

Purge Gas Treatment

With the change in front end operating philosophy, the concentration of inerts in the loop was significantly increased, resulting in a much higher purge gas flow from the loop. To recover the hydrogen in the purge, a Hydrogen Recovery Unit, HRU, has been installed. The hydrogen product is recycled back to the synthesis gas compressor and the rejected or waste gas is used for dryer regeneration and sent to the primary reformer burners as fuel.

Fig. 9 - Photo of the Refurbished HRU

Steam System

HP steam generation has increased, but no equipment modifications were necessary.

4. CONCLUSIONS

The cases described here above are only examples of the different and possible schemes of the modification than can be applied to any ammonia plant to improve its performances.

The Casale approach is to customize the revamping to the real needs of the plant taking into proper consideration the age of the equipment and its problems, in order not only to improve plant performances, but also to solve some "ageing" problems in order to extend the plant life and ageing is a big concern in the ammonia plant of former USSR countries.

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