

CATCH-ALL SOLUTIONS

Francesco Baratto, Casale, Switzerland, explores the development of processes designed for a range of ammonia plant capacities.

When designing a new ammonia plant it is important to combine the latest technological achievements to obtain the best compromise between investment costs, plant productivity and utility consumption. Research into the optimal plant configuration needs to be performed with a tailored approach to each project, taking note of the specific requirements of the client's needs, climatic conditions, utilities' availability and particular process constraints.

In order to accommodate a variety of customer requirements, Casale has developed a standard for the following capacity ranges:

- A60 for production between 50 and 300 tpd.
- A600 for production between 300 and 800 tpd.
- A2000 for production between 800 and 3000 tpd.
- A3000 for production between 2500 and 3500 tpd.
- A6000 for production between 3500 and 7000 tpd.

Most of these process schemes have been implemented in operational plants.

Of these processes, A2000 is most suitable for world-scale capacity ammonia plants, and is based on a steam reforming route. The main steps are:

- Desulfurisation.
- Primary and secondary reforming.



- High temperature (HT) and low temperature (LT) shift conversion.
- Carbon dioxide (CO₂) removal.
- Methanation.
- Synthesis gas drying.
- Compression.
- Ammonia synthesis.
- Hydrogen recovery.

A6000 is a single-train process suitable for capacities of more than 6000 tpd of ammonia, or 2 million tpy of ammonia. This capacity is three times that of today's typical ammonia plant size, and almost twice that of the current largest single-train ammonia plants.

A6000 reaches the highest single-train ammonia capacity, thus taking full advantage of economies of scale, while still ensuring that all critical items are referenced at the size required and available from multiple vendors.

It also debottlenecks all critical items that limit the maximum capacity in conventional plants, thereby permitting a higher

single-train capacity. This is achieved through the implementation of three design concepts:

- A nitrogen-free front-end based on a pre-reformer, steam reformer and oxygen-blown auto-thermal reformer (ATR). This is known as the 'combined reforming process'.
 - Enhanced CO₂ removal, and purification based on liquid nitrogen wash.
 - Inert-free ammonia synthesis loop with two synthesis converters manufactured by the company.
- The main steps, as shown in Figure 1, are:
- Desulfurisation.
 - Primary and pre-reforming.
 - ATR.
 - Pseudo-isothermal medium temperature (MT) shift conversion.
 - CO₂ removal.
 - Synthesis gas drying.
 - Liquid nitrogen wash.
 - Compression.
 - Ammonia synthesis.

Both the A2000 and A6000 processes are flexible, and the scheme may be adapted to specific market needs and/or customer requirements. Other features are:

- The energy consumption is in the range of 6.5 – 6.8 Gcal/t (23.5 – 24.5 million Btu/short t) on lower heating value (LHV) basis.
- The steam balance can be optimised from zero export to maximum export.
- Able to use any commercially available catalyst, or adopt company products.
- Compact and simple lay-out, with all sections arranged in a way so as to minimise the overall footprint as well as optimise the connections across the different sections of the plant.
- Primary importance is given to the process control, as the safety, reliability, efficiency and economics of the plant depend on it.
- Full life-cycle support by means of Casale's remote plant monitoring and/or customer care services.

Plants based on the A2000 and A6000 process schemes are already in operation in the Middle East, with several more under construction.

In particular two A2000 plants with a capacity of 2050 tpd have been in operation for several years, achieving the targeted energy consumption figure.

In the same region, a Casale methanol plant with a capacity of 7000 tpd is presently in operation. The front-end arrangement is similar to the one expected for the A6000 process scheme.

The combination of this methanol plant with the capability for the plant back-end makes the A6000 scheme a viable industrial-scale process technology. Both the A2000 and A6000 schemes include several technologies at key points of the process.

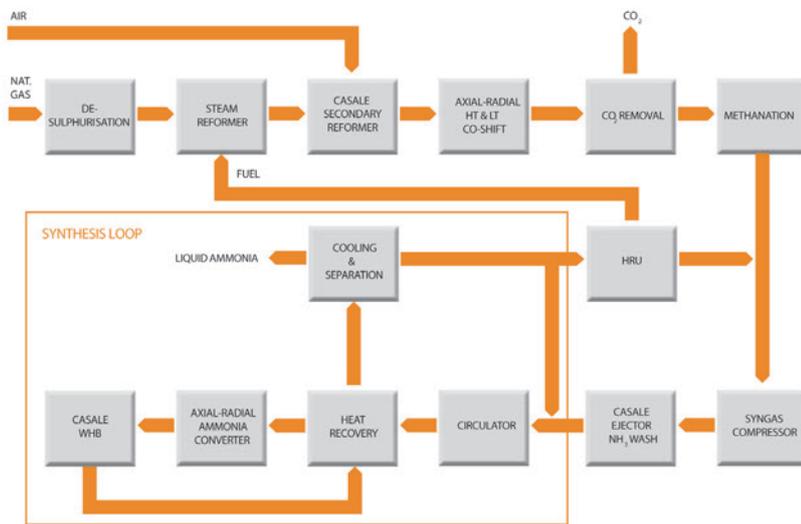


Figure 1. A2000 ammonia process.

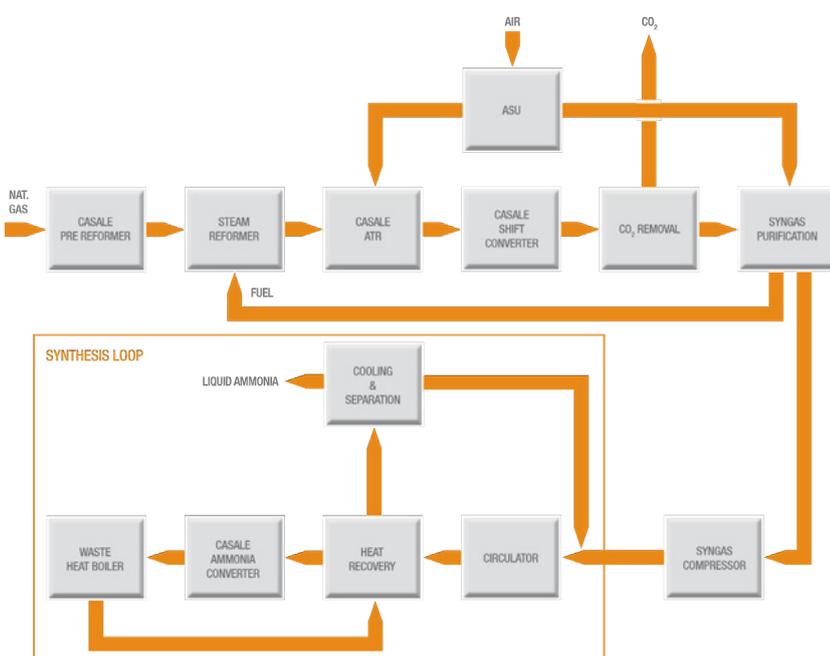


Figure 2. A6000 ammonia process.

Pre-reformer

An axial-radial pre-reformer performs a significant role in the A6000 scheme. All the mixed feed (desulfurised natural gas [NG] and steam) is treated in the pre-reformer, achieving the following benefits:

- Protection against coke formation: the pre-reformer has the main function of destroying the higher hydrocarbons in the natural gas, stabilising the feed and avoiding coke formation upstream the reformer and ATR.
- Safe reduction of the steam/carbon (S/C) ratio.
- Safe increase of the re-heating temperature of the pre-reformed stream, which no longer contains higher hydrocarbons.
- Saving of costly catalyst tube surface, debottlenecking of maximum steam reformer capacity: steam reforming of CH_4 partially occurs in the pre-reformer – this feature, combined with the substantial pre-heating of the pre-reformed gas, reduces the radiant duty and the cost of the reformer tubes.

Top-fired primary reformer

For large units, the top-fired reformer, having fewer burners and a much more compact construction, is a logical and cost-effective choice. The top-fired reformer's main features are:

- Compact design and small number of burners (in comparison with a side-fired reformer) even for large units.
- Less complex burner piping layout and easier integration of combustion air pre-heating system for maximum thermal efficiency (in comparison with a side-fired reformer).
- Easier and faster start-up.



Figure 3. Primary reformer in a 2050 tpd ammonia plant.



Figure 4. Oxygen blown ATR for 7000 tpd methanol plant.

- Easier convection section cross-section for combustion air pre-heater layout (in comparison with a side-fired reformer).
- Suitable for high capacity plants.

Secondary reformer

The secondary reformer is a critical item in the ammonia plant since any malfunction or deviation from the design will compromise the performances of the overall plant. The function of the secondary reformer is the final conversion of the hydrocarbons into hydrogen and carbon oxides and its performance is therefore evaluated on the basis of the residual methane content at the outlet.

The theoretical minimum methane slip is determined by the chemical equilibrium of the reforming reaction: the more efficient the reformer design is, the closer the actual methane slip is to the equilibrium value. In the company's design, the approach to the equilibrium is minimised due to the optimal distribution of the temperature and composition at the inlet of the catalyst bed, thus avoiding the generation and the propagation of any hot spot or composition difference along the catalytic layer.

The optimal distribution of the reacting gas is achieved by an advanced design of the burner, which is responsible for the mixing of the combustion reactants and for the temperature, composition and velocity profiles of the stream leaving the flame chamber and entering the catalyst zone.

Axial-radial HT and LT shift converters

The technology commonly used has the gas flow in an axial direction, from top to bottom, with the consequent limitations due to the inherently high pressure drops. In particular, when designing a new unit, the following alternatives are only possible with the axial design:

- Acceptance of a high pressure drop, due to the high gas velocity, to limit the diameter of the vessel.
 - Increase the diameter of the reactor and, accordingly, its cost to reduce the gas velocity and its pressure drop.
- Therefore, the fluid-dynamical inefficiency of these equipment increases either the syngas compressor power consumption or the investment costs for the shift converters.

The company's technology for shift converters is based on a different concept: the axial-radial design of the catalytic bed.

The main features of the design for both HT and LT shift converters are:

- An axial-radial flow path of the gas crossing the catalyst, resulting in a low pressure drop, whatever the diameter of the reactor.
- Use of a small size, and thus more active, catalyst, which is also more poison-resistant.
- Protection of the catalyst from water droplets carried over from the secondary reformer heat recovery train or other elements.
- Safe operability due to steady pressure drop.
- Lower CAPEX due to the slimmer vessel.

The radial concept can be applied to shift converters in revamping as well as in new plants.

The isothermal design for shift converters integrates the company's traditional design for shift converters with plate-cooled isothermal catalytic beds.

In the isothermal reactor, the catalytic bed is cooled by means of the exchanger plates vertically immersed inside the

catalytic mass. The reaction heat is removed by heat exchange with a cooling fluid flowing inside the plates.

CO₂ removal

Various absorption systems are available for the removal of CO₂ from synthesis gas. The two main processes used worldwide are the activated MDEA® and carbonate processes. Casale has experience with both these processes, in revamping as well as for new plants; however for new plants the activated aMDEA® process, licensed by BASF (OASE®), is preferred.

Ammonia wash drying of the syngas to the synloop

The ammonia wash system is an easy and simple way to remove water and CO₂ traces from syngas before feeding it into the ammonia loop.



Figure 5. Ammonia washing ejector.



Figure 6. Direct connection between converter and hot heat recovery exchanger.

In this way, syngas can be directly feed to the ammonia reactor, lowering energy consumption.

The ammonia wash system itself consists of a vapour-liquid contactor, suitably designed to promote the closest contact between the two phases. Since the purity required to the vapour stream leaving the new unit is extremely high, the contactor allows the ideal mass transfer between the two phases. To allow close contact between liquid ammonia and water, an ejector is installed.

Ammonia synthesis loop

In the last 10 years, the company's ammonia loops have been chosen for a number of new projects (with a capacity range from 600 to 2000 tpd), most of them in China.

The design for ammonia synthesis converters is based on:

- Optimal thermodynamic catalyst distribution in multi-bed cartridge and maximum filling of catalyst inside the cartridge, i.e. maximum volume of catalyst loaded, with consequent high conversion.
- Highest efficiency of each bed, particularly of the axial-radial technology, which allows the complete utilisation of the catalyst volume and maximises the use of the reactor's volume.
- An axial-radial flow of the gas stream through the catalyst bed at much lower pressure drop than before.

The ammonia synthesis catalyst AmoMax® is designed for the company's reactors, and has evolved from the wustite-based catalyst AmoMax 10. It is able to provide approximately 30% more efficiency than a standard catalyst.

Designs have also been developed for heat recovery exchangers downstream the ammonia synthesis converter, which is the most critical exchanger of the loop. High pressure boilers, medium pressure boilers, steam superheaters and boiler feedwater (BFW) heaters are all proven in running plants.

As shown in Figure 6, the first exchanger is directly connected to the synthesis converter with a flange-to-flange connection. This solution saves on usage of the HT piping which would be required to connect the reactor with the downstream exchanger.

This feature of the proposed layout avoids the installation of pipe subjected to high temperature operating conditions: in fact, the conditions of syngas leaving the converter (at more than 440°C) are conducive to a nitriding attack.

To protect the connection section from the effects of nitriding, the converter outlet internal tube is made from the same material of internals (which is resistant to nitriding) and an insulation layer to keep the temperature of pressure components below the nitriding threshold.

The advantages of the synthesis loop are:

- Higher performances with lower circulation rate, lower energy consumption and smaller equipment, piping, machinery.
- Higher reliability.
- Optimised layout.
- Lower CAPEX.

Conclusion

Selecting the right process scheme in a revamping operation is a key factor in obtaining the best trade-off between investment cost and performance. In turn, what makes a process scheme effective is the use of advanced, efficient and reliable technologies provided by a licensor and deployed at critical points of the process. **WF**