ADVANCED AMMONIA CASALE TECHNOLOGIES FOR AMMONIA PLANTS

Lugano, May 2002
Anvil/paper/conf/amm/NPC-Tehran2002/advanced ammonia technologies

CONTENTS

PART 1. AMMONIA CASALE PROFILE

PART 2. INTRODUCTION

PART 3. AMMONIA CASALE PROPRIETARY TECHNOLOGIES

PART 4. APPLICATIONS OF CASALE TECHNOLOGIES – CASE HISTORIES

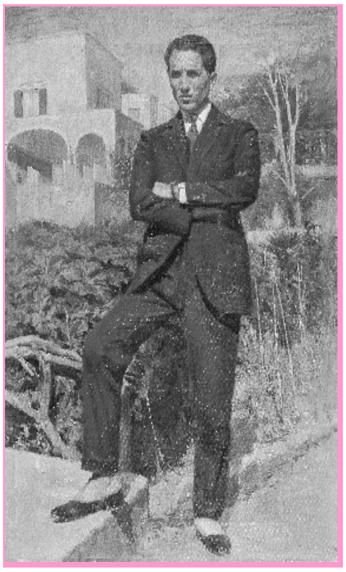
PART 5. COMPLETE PLANT REVAMPING

PART 6. NEW PLANTS

PART 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.



The founder of Ammonia Casale: Dr. Luigi Casale

In the more recent past, activities were mainly devoted to the revamping of existing plants, with more than 130 plants revamped in the last 15 years.
The company is still involved in new plant construction through its licensees.

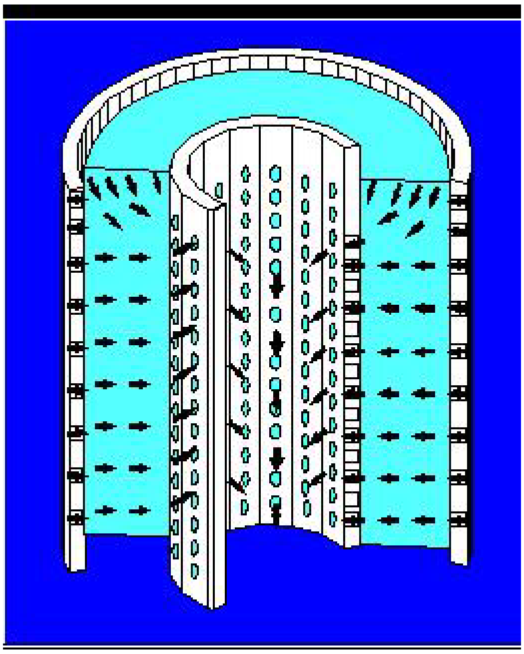
At the present time, Ammonia Casale is a leader in the design of ammonia synthesis reactors and related process loops.

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

TOTAL PLANTS	**128**
Revamping	**111**
Braun	4
Chemico	7
ICI	7
Kellogg	66
Topsoe	6
Various	21
79 IN SITU MODIFICATIONS	
New plants	17
IN OPERATION	**120**

Ammonia Casale Plant Upgrading and New Plant Designs between 1985 and 2001

Plant modernisations represent a very interesting 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.



Casale Axial-Radial Reactor Design

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 rationalised activity.

Process design is now supported by sound insight into the chemistry of the processes, catalyst behaviours, 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, analysing and picturing complex phenomena in a way unachievable with skilled manual calculations, including such tools as computer-aided techniques with applications ranging from chemical process design to fluid dynamics evaluations 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.

The world has changed a lot since the industrial pioneers started out on their paths. New problems are at the forefront and press us for solutions; new needs urge to be fulfilled, often dramatically, such as the quest for a more efficient and environment conscious use of natural resources.

Today's Ammonia Casale has taken up the challenge and, still driven by the same spirit of commitment to excellence and achievement of its founders, offers to the world its most advanced state-of-the-art technology and expertise.

Fragments of History

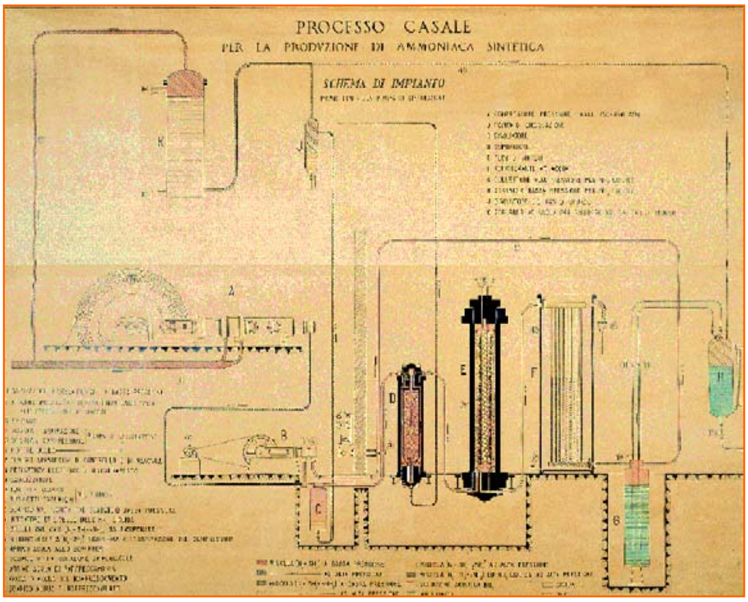
The history of Ammonia Casale is based on success during the pioneering years at the beginning of this century when men sought, and succeeded, to find a way to produce on an industrial scale one of the most important synthetic chemicals: ammonia.

Thanks to the abundant availability of this commodity, mankind was granted practically unlimited access to fertilisers and hence also to food. Synthetic ammonia has therefore contributed, second only to the practice of agriculture, in significantly improving the quality of life of the world population, whereas efforts devoted to researching ammonia synthesis paved the way for many of the industrial chemicals offered today.

At the time Ammonia Casale was founded, synthetic ammonia was only produced in Germany by Badische Anilin und Soda Fabrik (BASF), which had been the first to achieve the industrial production of ammonia in their factories using the Haber-Bosch process.

In 1921 Germany, as well as other European countries, was still suffering from the consequences of war, including the embargo on Chilean guano, the only source of natural fertilizer.

The synthesis of ammonia from elements not only solved a fundamental problem in securing food supply, but also opened a new era for technical chemistry by providing the bases for the development of high-pressure technology.



First Ammonia Casale Process for Production of Ammonia

At the early stage, because of the relatively low synthesis pressure, water scrubbing was used to yield aqueous ammonia. The Ammonia Casale process, operating at considerably higher pressure than the Haber-Bosch process, was able to obtain direct condensation of pure ammonia already in the first commercial plants, just as is being done today.

Ammonia Casale also greatly simplified reactor design, to improve catalyst life and make catalyst replacement easier.

By 1923 Ammonia Casale technology had been adopted in Italy, France, Japan, Switzerland, Spain and the USA, with more than 15 plants producing altogether about 80'000 tons of ammonia per year. At that time the only competitor was BASF.

Expansion continued at a rapid pace and by 1927, the year of Luigi Casale's sudden death, the process had also been adopted in Belgium, England, Russia, and even in Germany, with an overall ammonia production of more than 320'000 tons per year.

More than 200 plants were built worldwide, based on Casale's first generation technology.

In the mid sixties the concept of single-train energy-integrated ammonia plants, launched by Kellogg and Chemico, constituted a real technical revolution, sustaining the continuously increasing demand and leading to a next generation of advanced process technologies developed by Braun, ICI, Topsoe, Uhde and Casale.

In the early eighties still fast-growing product demand and increases in energy prices were a great challenge for the industry: the existing ammonia plants were in no way optimal regarding energy consumption and investment cost compared to capacity.

As building new plants was in many cases too expensive, modernization of old plants to lower energy consumption and raise capacity levels became a subject of urgent consideration by engineers.

Ammonia Casale upgraded key equipment, such as synthesis reactors, in many plants. New advanced catalysts were also used, improving efficiency along with energy saving and increased capacity. Syngas production units, constituting the front-end of ammonia synthesis plants, were also greatly improved within the same framework of "plant modernization".

It is interesting to note that this particular activity generates an important synergism, as the results of plant modernization are a valuable source of further innovations, leading on to new and original equipment designs, both for new plants and plants still to be modified.
Ammonia Casale's development efforts over the last decades can be measured by the gains in market shares during this period.
In the twenties, 60% of the total world nominal capacity (1.15 million tons per year) was of Casale design and construction. Although the total capacity of new plants designed by Ammonia Casale continued to increase with time, new entries progressively reduced the Casale share of the total market, until the new line of plant modernization activity started during the early eighties, regaining an ever increasing market share for Ammonia Casale, corresponding today to a third of the 130 million tons p.a. world production capacity.

PART 2.
INTRODUCTION

Ammonia Casale has a long tradition of developing and introducing in the market its own proprietary technologies in its fields of activity.

In the last 20 years Ammonia Casale has developed a number of new designs for several of the main parts constituting the ammonia production plants.

These new designs are developed to increase the efficiency and reduce the cost of these parts with respect to the existing designs available from Ammonia Casale itself or from other competitors.

All these innovations can be applied for revamping existing plants to increase their efficiency and capacity, as well as for designing new, better, ammonia plants.

PART 3.
AMMONIA CASALE PROPRIETARY TECHNOLOGIES

3.1 Axial-Radial Catalyst Beds

The axial-radial catalyst bed is the base in most of the technologies used by CASALE in catalytic reactors.

This technology was developed for ammonia converters, and later applied to methanol, shift, formaldehyde and pre-reformer reactors demonstrating to be flexible, economical and efficient.

At present there are more then 400 axial-radial beds designed by CASALE successfully in service.

In an axial-radial catalyst bed the gas distribution is such that most (about 90 percent) of the gas passes through the catalyst bed in a radial direction, resulting in a much lower pressure drop when compared with the axial flow.
The balance passes down through a top layer of catalyst in an axial direction, thus eliminating the need for a top cover of the catalyst beds, *(see figure 1).*

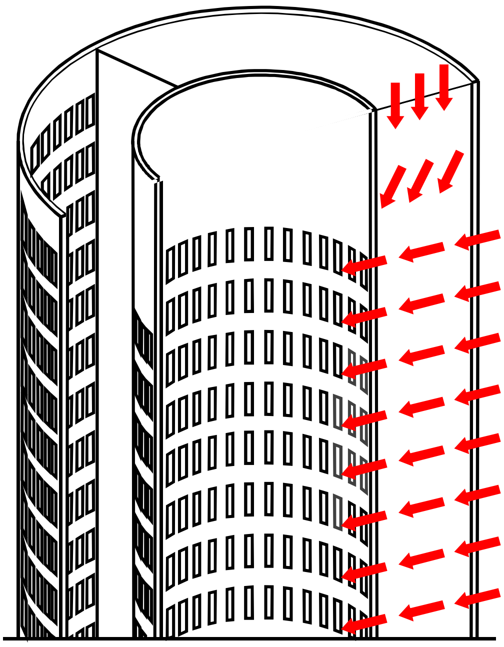


Fig. 1 - Axial-radial Bed, Gas Distribution

Mechanically the bed is very simple, being made only by the two vertical perforated walls and by one bed closed bottom. There is no top cover. This last feature is an essential factor for an easy and simple construction of any type of converter internal.

The materials used for its construction varies depending on the application and can be carbon steel, stainless steel and Inconel, the latter being used for wire mesh only.

3.2 Pre-Reforming Reactor Technology

The pre-reforming reactor proposed by AMMONIA CASALE is designed according to the axial-radial technology for catalyst beds.

The advantages of using this technology for pre-reforming reactors are:

* the low pressure drop achievable;
* the use of small size catalyst;
* the lower operating temperature of the vessel wall when the reaction is exothermic.

The low pressure drop is an important energy saving feature and helps the compressors reaching higher capacities in case of revamping.
When there is no natural gas compressor, if the pressure of the gas is close to the reforming pressure, it is important to minimize the DP in all equipment, especially the added ones, to enable capacity increases without having to install a natural gas blower.

The small-size catalyst has two advantages in comparison with the large- size one:

* a higher sulfur pick-up, that means a longer life since sulfur is the main poison;
* a higher activity.

This means that, with respect to the larger size catalyst, it is possible to reduce the catalyst volume to have the same life or with the same volume to have a longer life.
The lower operating temperature of the vessel wall is due to the fact that the feed gas is colder than the product one, in case of exothermic reaction, and this helps to avoid metallurgical problems due to the high operating temperatures.

Regarding the operation of an axial-radial pre-reformer, it is to be noted that the temperature profile in the catalyst bed can be measured and followed easily, thanks to the presence of thermocouples in different position along the radial direction in the bed.

Also catalyst loading and unloading is very easy, as the axial-radial bed is completely open on the top granting an easy access to the bed even for small diameter vessels, while for unloading there are drop out pipes provided at the bottom.

The utilization of this reactor enables part of the primary reforming reaction to be carried out (about 10%) outside the primary reformer, allowing the increase of the capacity of existing unit, as well as the reduction of the size of the reformer to be implemented in new plants.

Another advantage of the pre-reformer is that it transforms all higher hydrocarbons to methane, and performs part of the reforming reactions, thus producing some hydrogen. These two actions enable the increase of the preheating temperature of the process gas, and also the reduction of the steam carbon ratio, therefore reducing the energy consumption of the primary reforming section.

3.3 Secondary Reformer Burner

The most common conventional design for the ammonia plants' Secondary Reformer was based on a multiple nozzle burner for injecting pre-heated air into the primary reformer effluent gas. In the common design, the burner is placed at the end of the air feed pipe at the top of a conical combustion chamber. The primary reformer gas flows through an annular tube concentric to the air tube. Mixing and combustion take place into the cone and the combustion product flows down into the catalyst bed (*see Figure 2*).

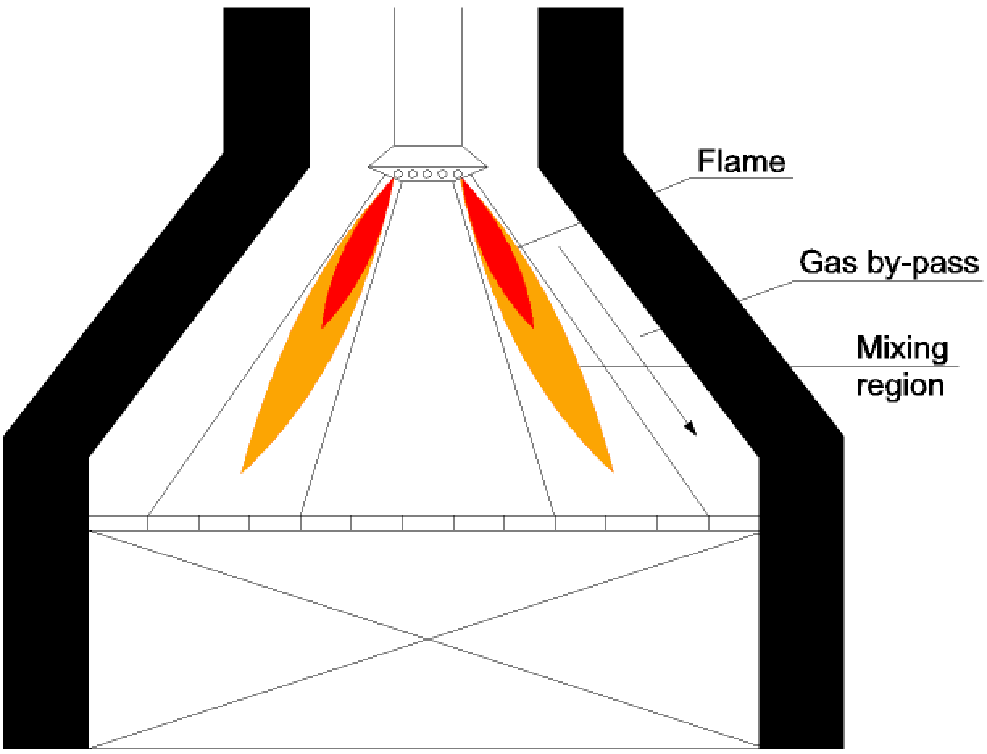


Fig. 2 - Conventional Design of Secondary Reformer Burner

The high temperature on the surfaces exposed to the flames for convection and radiation has always caused problems to the burner.
With the introduction of the air preheat (600°C), in order to reduce ammonia plant energy consumption, the burner surface cooling has become one of the major issues in the secondary reformer design.

In the last 25 years of conventional design to maintain the burner temperatures within reasonable values, the air was forced to flow in complex paths inside the burner head with high pressure losses.

Non-even temperature and composition distribution of the gas also characterized some old burner design with temperature hot spots on the catalyst surface and uneven catalyst gas load.

In the early '70s the flow field and the gas mixing inside the conical chamber were not well understood and the computational fluid dynamics technique, used today for the combustion simulation, were at an early stage of development and not applicable for industrial design.
Nowadays advanced fluid dynamic simulation techniques are more easily available, and with their utilization CASALE has develop an innovative design for Secondary Reformer Burners.

The goal was to develop a simple design capable of withstanding the severe operating condition in a safe, reliable and cost effective manner.

The Computational Fluid Dynamic (CFD) simulations of the velocity, temperature and composition fields inside and outside the burner and in the combustion chamber were performed interfacing a commercial CFD software with "in house" developed combustion subroutines.

During the design of the CASALE Advanced Secondary Reformer Burner these engineering aspects were of major importance:

* low pressure losses of both air and primary reformer stream (much lower than the existing design);
* low temperature of the burner surfaces exposed to the flames;
* an almost perfect mixing in the diffusion flame;
* reduced flame length in order to avoid catalyst impingement for high load operations;
* soot-free combustion;
* homogeneous gas composition and temperature distribution at catalyst bed entrance;
* protection of the refractory lining from the flame hot core.

The recirculation of the reacted gases protects the refractory and the burner from the hot core and also ensures a homogeneous gas and temperature distribution at the catalyst bed entrance (*see Figure 3*).

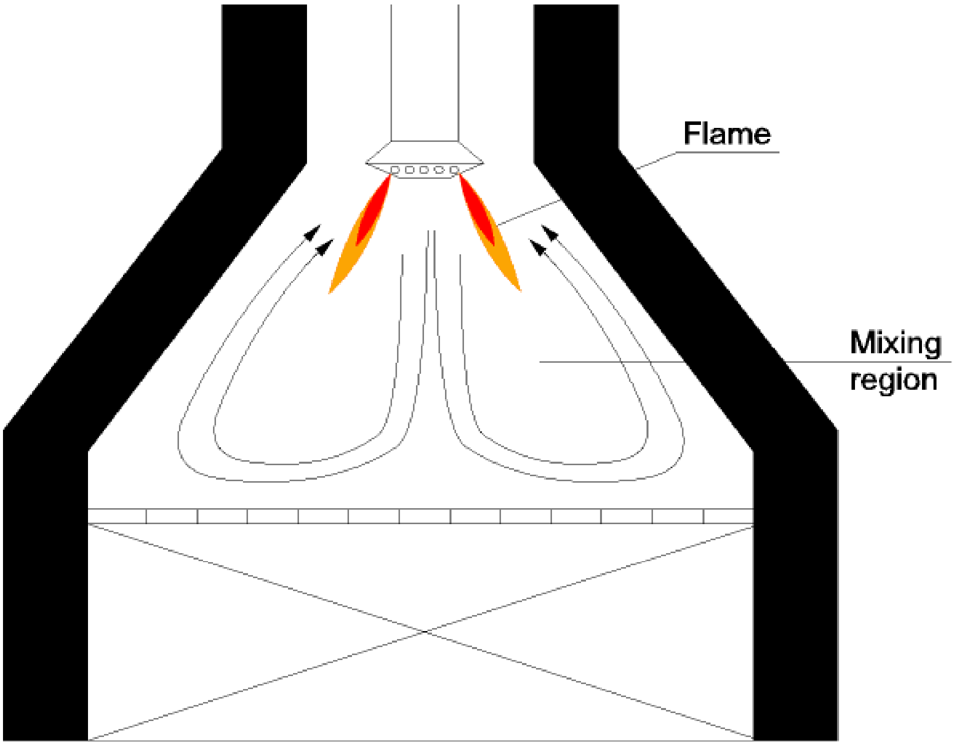


Fig. 3 - CASALE Advanced Design for Secondary Reformer Burner

The performances of the CASALE Advanced Secondary Reformer are:

* Pressure loss for the air stream:	less than 1 bar
* Burner wall temperatures:	700-800°C
* Temperature spread on the catalyst surface:	Uniform within a few Celsius degree range
* Composition spread on the catalyst surface:	Almost Homogeneous

The application of this design on existing plants allows the reduction of the pressure losses of the process air, allowing for an increase in air compressor capacity and for its energy consumption reduction. Furthermore the very even composition achieved at catalyst inlet and the higher amount of reaction taking place already in the gas phase, make it possible to increase the catalyst life, and to reduce the catalyst volume necessary.

These advantages are useful also for new plant design, allowing for a smaller secondary reformer vessel, lower power consumption of air compressor, longer catalyst life and for safer and more reliable operation of the unit.

The burner will be applied in an ammonia plant in Indonesia in June. The following is a picture of it before shipment.

Fig. 4 – CASALE Secondary Reformer Burner

3.4 Shift Converters

The new design developed by Ammonia Casale is based on the use of the axial-radial catalyst bed, described above, and can be applied both to revamping and to new converters.

The new axial-radial configuration has an inherently low pressure drop of the catalyst bed, and this makes it possible to use small-size, more active and more resistant to poisons catalyst.

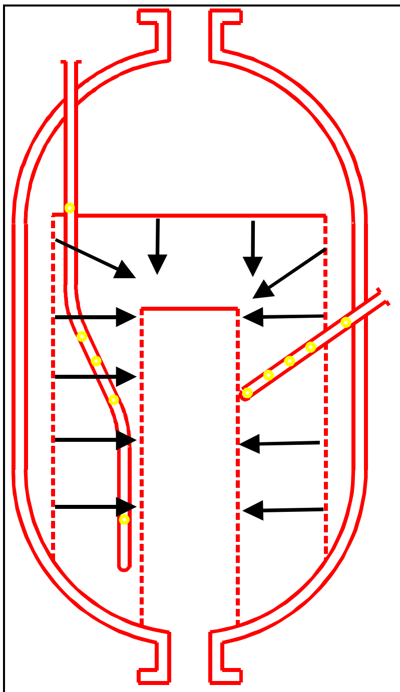


Fig. 5 - Axial-Radial Shift Converter

The new designs has also the following additional features

* protection of catalyst from water droplets carried over from secondary reformer heat recovery train or others;
* possibility to load different volumes of catalyst with no mechanical modifications;
* easy operations.

In case of application to existing plants the existing shift converters can be easily transformed to axial-radial design by introducing new vertical perforated walls, which are cylindrical and form the inlet and outlet walls, in prefabricated sectors that are assembled inside the existing converter vessel.

The advantages achievable with this revamping are the low pressure drop with consequent energy saving, the low pressure drop also helps eliminating the hydraulic constraints having more flow through the front end, allowing for higher plant throughput. The small-size, more active catalyst eliminates the possible constraints due to a fixed catalyst volume that may be insufficient for the new operating conditions of high flow and low steam/carbon ratio, furthermore this catalyst is more resistant to poisons, granting a longer catalyst life with smaller loaded volumes, and also a lower average CO concentration at the outlet, with corresponding higher production with the same process gas consumption.

When applied to new plants the advantages described above translates into the possibility to design smaller, less expensive shift reactors, with a lower pressure drop, lower catalyst volume, lower average CO concentration at shifts outlet along the catalyst life, therefore improving the overall plant efficiency.

3.5 Ammonia Synthesis Converter

The ammonia converter is one of the critical items when planning a revamp for energy saving or capacity increase, and in most cases it is the first item to be revamped thanks to the relatively low cost and very high return. When designing a new plant is also one of the most critical aspect to be considered, in fact an high efficiency converter means lower plant capital cost, and lower energy consumption throughout the plant lifetime.

AMMONIA CASALE is very active in this field and has introduced fundamental innovations in the converter design and revamping, such as the "in-situ" modification of bottle-shaped converters as the Kellogg ones, and the three-bed intercooled configuration that is being used by CASALE for over ten years now.

This activity has been very rewarding and now AMMONIA CASALE has more then 130 converters on stream, out of which about 50 are "in-situ" modifications, and about 30 are three beds intercooled converters (new or revamped) with full bore opening.

The most important ingredients for this success are the axial-radial beds, described above *(see figure 1)*, and the three-bed configuration adopted both for revamping of any kind of converters and for new reactors as well *(see figure 6)*.

These two elements give the highest utilization of the catalyst volume available, thanks to the axial-radial configuration, and the most thermodynamically efficient cartridge configuration, the three-bed interchanger one, with cooling achieved by means of heat exchanger both between 1st and 2nd bed and between 2nd and 3rd bed.

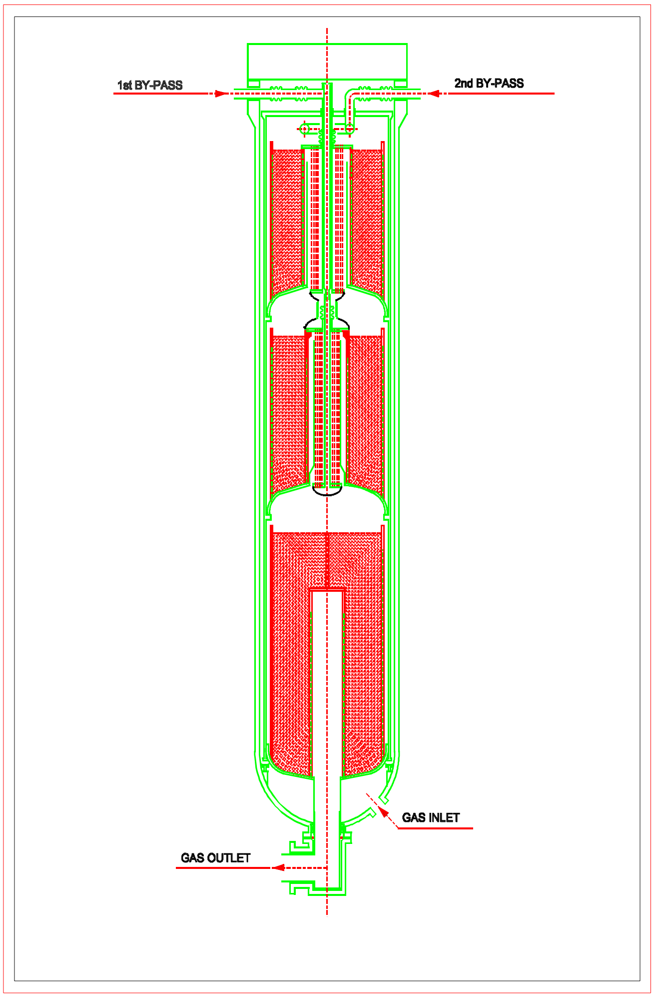


Fig. 6 - <u>CASALE 3-beds 2-interchangers Converter</u>

The design of the cartridge, based on a lay-out with three adiabatic beds and two interchangers, and the use of 1.5÷3 mm size catalyst, makes it possible to obtain a high ammonia conversion with the smallest catalyst volume and a low pressure drop.

A particular feature of the design is its simplicity: the catalyst-containing baskets are easy to be handled and have a low cost. Moreover, the use of a reverse bottom increases the catalyst filling efficiency *(see figure 6)*.

The Casale converters are designed also to have full independent control of the inlet temperature of each catalyst bed, making it possible to run the converter always in the optimal safest conditions, for any operating situation that may happen in the plant life, even if very different from the original design, as it may

happen due to a change in feedstock composition, plant capacity, ambient conditions, etc.
The peculiar design of these converters also enables the recovery of the reaction heat at the highest temperature level, generating high-pressure steam.
Casale has developed in addition to the specific design of the converter internals, a number of different configurations of the converter, in order to fit all possible requirements and to reduce the plant installed cast and its reliability, like the nozzle-to-nozzle connection of the waste heat boiler, eliminating the need for hot high pressure, large size piping exposed to nitrading conditions, the cold wall vessel design, eliminating the problems of vessel cracking due to nitrading and hydrogen embrittlement, the insulated outlet nozzle, again eliminating the problem of high stress at high temperature of this delicate part, exposed to nitrading and hydrogen embrittling environment, etc.

3.6 Catalysts

Ammonia Casale is accepting to operate its plants and equipment with any first class catalyst, and during its long experience has accumulated a unique experience related to the catalysts performances. This experience translates into the possibility of assisting the clients in the catalysts choice.

In addition to this experience the CASALE group markets exclusively a selected Chinese catalyst for ammonia synthesis.

This catalyst is being more widely accepted than ever in the market worldwide, and in fact already 42 charges are in service in CASALE converters, plus several other charges in converters of other technologies.

Of these 42 charges, 9 are in China, the oldest one in service since 1987, 4 are in Asia, 20 are in Eastern Europe, 3 in the USA, 1 in Brazil, 2 in Australia, 1 in New Zealand and 1 also in Iran, Shiraz plant.

The performance of this catalyst is outstanding, and can be considered equal, if not better than the most well known western catalysts.

AMMONIA CASALE, the Company marketing this catalyst, is fully responsible for the quality control, and guarantees the delivery and installation supervision, the reduction supervision and all of the after sales services.

PART 4.
APPLICATIONS OF CASALE TECHNOLOGIES, CASE HISTORIES

4.1 Pre-reforming Installation

Ultrafertil, a fertilizer Company in Brazil, already an AMMONIA CASALE Client, has a 450 MTD nominal capacity ammonia plant based on steam reforming technology and fed by both refinery off-gas and naphtha. The actual load was of about 520 MTD.

The flow rate and composition of the off-gas were changing quite often, reflecting the change in feedstock, load and products range of the upstream refinery. As a consequence the primary reforming run was also unsteady, requiring the use of very high steam to carbon ratio to protect the reforming system from a possible sudden increase in the carbon content of the feedstock.

The Client approached AMMONIA CASALE with the request to increase the plant capacity and reduce the energy consumption, asking for a detailed study to find the best revamping options, with a capacity target of 800 MTD, to be reached in two steps, the first one being 600 MTD.

The primary reformer, running in such conditions, became immediately one of the revamping targets.

The revamping had to deal with the unsteady operating conditions, and with the desire to abandon naphtha as feedstock or fuel, being too expensive.

In these conditions the choice of installing a pre-reformer appeared to be natural, in fact the two main benefits of its installation are:

a) stabilization of the composition of the gas entering the primary reformer;
b) reduction of the duty of the primary reformer.

Point A): the first point is due to the fact that all hydrocarbons entering the pre-reforming are cracked down to methane, and some reforming reaction takes also place. The product is, therefore, methane plus some CO, CO_2 and hydrogen, steam always being present.

The product of the pre-reformer can enter the primary reformer with a much lower steam carbon ration as there is no more danger of carbon deposit on the catalyst. The fact that the only hydrocarbon fed to the primary reformer is methane allows for the use of a normal natural gas catalyst that is more active and gives fewer problems than the naphtha one.

Point B): reforming reaction starts and proceeds to a certain extent in the pre-reformer, reducing the load on the radiant section of the primary reformer.

Thanks to the pre-reformer installation, it is, therefore, possible to operate the primary reformer smoothly, with stable operating conditions, to reduce the steam carbon ratio to the primary reformer (since the only feed gas is methane plus steam, CO, CO_2 and hydrogen. This holds true also for the use of the non-reactive natural gas type catalyst and to increase the reforming capacity.

4.1.1 Other Plant Modifications

Other main plant modification in order to reach the higher capacity and lower energy consumption goals are:

FIRST STEP, 600 MTD

* modification to the existing primary reformer convection section;
* replacement of reformer burners;
* NH_3 converter replacement with a high efficiency one.

The NH_3 converter had to be completely replaced because of metallurgical reasons, the pressure shells of the old one had shown extensive cracking and its operation could no more be considered safe.

The new converter is based on the well-known AMMONIA CASALE axial-radial technology.

SECOND STEP, 800 MTD

* reformer tubes replacement;
* shift converters revamping;
* CO_2 converter revamping;
* feed gas, air and synthesis gas compressors revamping;
* new purge gas recovery unit.

Also other minor changes to exchangers, pumps and piping are planned.

The plant is now on stream after revamping since July 2001 and the main performance achieved are the following:

Table 1 – Pre-reformer Summary Performances

		Process guarantees	**Test run**
Conversion of C_2H_6	%	*> 85*	98.7
Conversion of C_{3+}	%	*> 95*	100

Table 2 - Synthesis Loop Summary Performances

		Process guarantees	Test run
Converter capacity (total of the 3 reactor)	MTD	*600*	> 616
Ammonia concentration at 3rd converter outlet	%	*15.8*	> 16.08
Converter pressure drop	bar	*2.8*	2.8

FIG. 7 - New Axial-Radial Pre-reformer in Ultrafertil Cubatao

FIG. 8 - <u>New Ammonia Synthesis Converters at Ultrafertil Cubatao</u>

4.2 Shift Converters

4.2.1 Shift converter industrial experience

AMMONIA CASALE has already on stream nine axial radial shift converters. The first four shift converters revamped in 1995 and 1996 were two HTS and two LTS in two Kellogg ammonia plants in the P.R. of China.

Then other axial radial shift converters were one HTS started up in October 1998 in the USA, at the AGRIUM plant in Borger, Texas, one HTS in China, started up in September 1999, one HTS in Brazil in Ultrafertil Araucaria ammonia plant, and one HTS and one LTS in Samad ammonia plant in Saudi Arabia.

The Agrium converter runs according to the following parameters:

			Prior to Revamp	**Axial-Radial Revamp**
	Plant Capacity	[stpd]	1450	1600
	Catalyst Volume	[m³]	38	42
	Catalyst Size	[mm]	9 × 6	6 × 3
SOR	Inlet Temperature	[°C]	360	343 (1)
	Pressure Drop	[bar]	0.8	0.45 (1)
	CO Leakage, dry	[vol.%]	2.45	2.20 (1)
EOR	Inlet Temperature	[°C]	372	370
	Pressure Drop	[bar]	1	0.45
	CO Leakage, dry	[vol.%]	3.0	2.95
	Catalyst Lifetime	[years]	6	6 - 7

(1) Test-run value

4.3 Ammonia Converter Industrial Experience

AMMONIA CASALE has revamped and started up more than 100 converters of different type with capacities ranging from less then 300 MTD to more then 2000 MTD.

As an example of this activity, the revamping the revamping of four 1'000 STP M.W. Kellogg ammonia converters at CFI Industries, Louisiana, USA is here illustrated.

These converters were already revamped by AMMONIA CASALE in '86 adopting the 1st generation of internals (4 beds, 3 quenches), and then at the end of their catalyst life they were revamped again adopting new and more efficient internals: 3 beds, quench and interchanger.

In the following Table 3 the achieved performances of these converters have been indicated.

TABLE 3

Operating data AMMONIA CASALE revamping for Kellogg ammonia converter 1st generation: 4 beds, 3 quenches, 2nd gen.: 3 beds, quench interchanger.

CASE		ACSA-MWK 4 beds	3 beds retrofit
Ammonia production	[MTD]	1287	1475
Catalyst age	[years]	10	10
Inerts concentration at 105-D inlet	[mol%]	9.8	7.7
NH_3 concentration at 105-D inlet	[mol%]	2.6	1.4
Temperature at 105-D inlet	[°C]	139	148
NH_3 concentration at 105-D outlet	[mol%]	14.4	16.9
Pressure at 105-D outlet	[bar a]	137	138
Temperature at 105-D outlet	[°C]	299	371

As mentioned above, Ammonia Casale has also on stream converters running in excess of 2000 MTD, one in Germany, at Hydro Agri plant in Brunsbuettel, running at 2050 MTD since 1989, and one in US, in PCS plant in Augusta , running at about 2100 MTD since 1996.

PART 5.
COMPLETE PLANT REVAMPING

AMMONIA CASALE has recently completed the revamping of 1000 MTD ammonia Plant based on M.W. Kellogg's technology of the AL-JUBAIL FERTILIZER COMPANY (SAMAD), located in Al-Jubail, Kingdom of Saudi Arabia.

The plant was put into operation in Al-Jubail in March 1983.
It is a natural gas based plant, i.e. using natural gas for feed and for fuel.
The plant, before revamping was operating at a capacity of about 1170 MTD after converter internals revamping by Topsøe (S-200) in 1989 and addition of a membranes-type Hydrogen Recovery Unit.

The production increase to 1300 MTD was the main goal of the project. Further targets were the energy saving, the cooling water consumption reduction and the reliability improvement.
A second step of capacity increase up to 1800 MTD has been also considered, and may be taken into consideration in a short while. 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 for September 2001. Turnaround took place in January 2002. All modifications have been implemented during the period of a standard shut-down. Start-up followed immediately after.

Since every modification to machinery results in very expensive interventions and a reharping of the almost new primary reformer tubes in the short-term would have been uneconomical, CASALE minimum investment revamping option was prepared according to the following guidelines:

- Avoid revamping or replacement of the main rotating equipment;
- No modifications 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;
- Plant shall be able to operate when new sections are isolated;
- Possible trip of new sections shall not involve the trip of the existing plant.

The 1300 MTD ammonia production has been selected since this value was positioned at the very limits of the existing syngas compressor suction capacity and of the refrigeration compressor capacity.

The modifications implemented are the following:

Feed gas desulphurisation

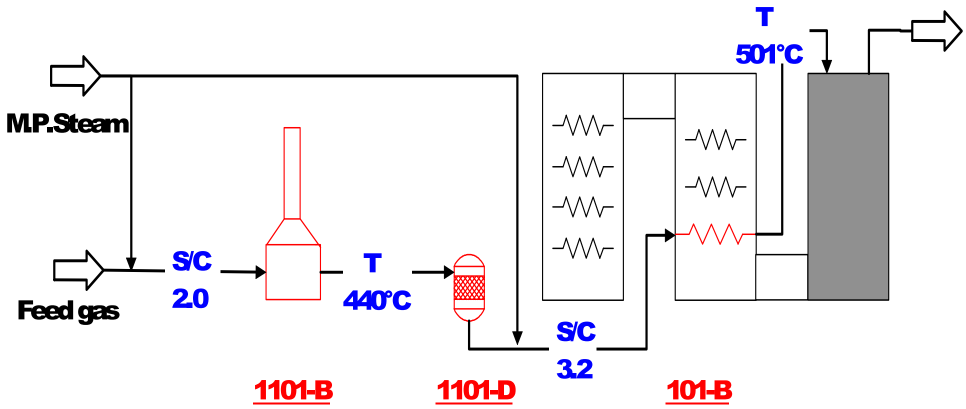
The desulphurization section and the feed gas compression were suitable for the new operating conditions and needed no modifications.

Prereforming and Primary reforming

The Primary Reformer of the SAMAD Ammonia Plant is a typical Kellogg top-fired unit with 416 catalytic tubes arranged in 8 rows. The reformer tubes were replaced in 1997 using HK40 material (the same as per original design) and the tubes thickness is also identical to the original design.

The heat flux to the primary reformer without replacing the reformer tubes could only be marginally increased   Therefore, to increase the capacity of the reformer up to the level needed for the capacity expansion, the steam to carbon ratio had to be decreased from 3.7 to 3.2.

Having a high concentration of higher hydrocarbons in natural a pre-reformer unit was installed to allow for safe S/C reduction.
Prereformer feed has to be preheated to about 440°C, therefore a fired heater was installed for this scope, as illustrated below.



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

* safe reduction of the S/C ratio;
* increased superheating of steam without interventions on steam superheating coil;
* increased process air preheating;
* mixed feed coil replacement could be avoided (only a mechanically simple tube rows removal will be necessary);
* BFW preheating level could be maintained;
* flexibility for every possible change in natural gas composition.

Process Air

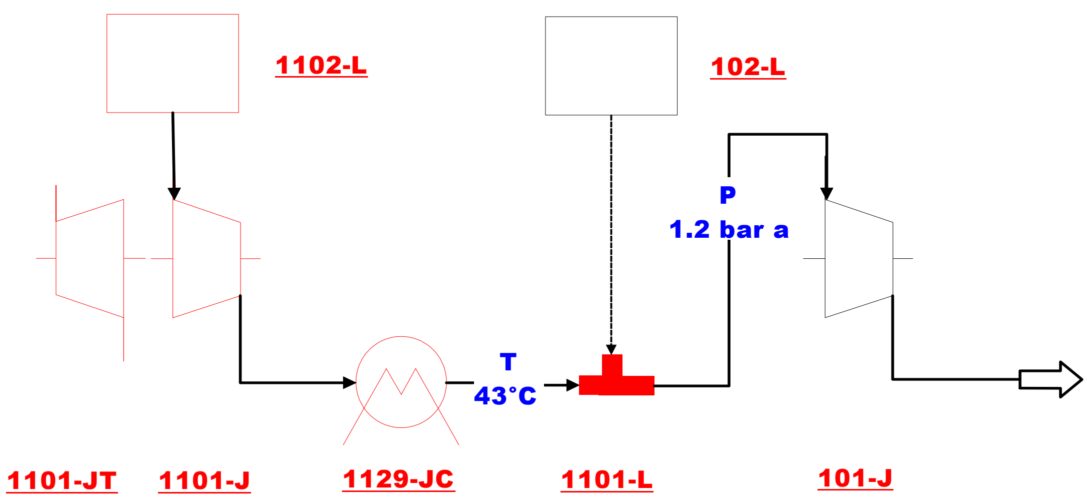
The section was designed to provide in normal conditions sufficient process air for a production of 1000 MTD of ammonia.
In 1989 after the first plant revamping the plant production has been ranging between 1170 and 1220 MTD of ammonia. The air compression section that was constantly operated at its maximum suction capacity limited the production.
For the capacity increase the section needed to be debottlenecked.
The intervention consisted in the addition of a booster on the suction of the air compressor. The booster was sized so as to be suitable also for the major expansion planned in the future.

The following modifications have been implemented in the air compression section:

- ∗ installation of a new intake air filter;
- ∗ addition of 1101-J air booster driven by 1101-JT back-pressure steam turbine;
- ∗ addition of 1129-JC aftercooler downstream the new air booster;
- ∗ installation of a flow deviator to connect air booster to existing air compressor.

The performance of 101-J existing compressor have been also improved by the replacement of 129-JC first interstage cooler; the remaining intercoolers will be replaced in near future.

SIMPLIFIED PROCESS SCHEME



Secondary reformer

No modifications were necessary to the secondary reformer and to its burner. The downstream waste heat boiler 101-C was replaced for maintenance.

Shift converters

The shift converters had a relevant pressure drop, 0.5 bar for H.T. Shift and 1 bar for L.T. Shift. These high values were due to the axial design of these converters and to the large catalyst volumes installed. Their retrofit with CASALE axial-radial internals was necessary to reduce the pressure drop.

The pressure drop after revamping is about 0.3 bar each, that will correspondingly increase the suction pressure of the syngas compressor. This pressure increase is very important to allow this machine 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 catalyst life;
- longer catalyst life;
- catalyst protection against water droplets.

5.1 Synthesis Gas Purification System

Carbon Dioxide removal

The CO_2 from the ammonia synthesis gas was scrubbed using Union Carbide licensed MEA Amine Guard (AG II) system. The CO_2 content of purified gas was satisfactorily low (around 120 ppm) but corrosion problems were observed.

The BASF aMDEA process was best suited for revamping the MEA unit by a simple solvent swap, keeping the existing section configuration. There was no need of any equipment modification.

The aMDEA solvent family has proven to be non-corrosive thanks to the nature of their components (no use of primary and secondary amines). Corrosion inhibitors are unnecessary and no solvent degradation is observed.

The specific energy consumption was decreased from 36'900 to 30'700 kcal/kmol CO_2. Thanks to this energy saving it was possible to reduce the S/C ratio. This reduction resulted also in a significant saving in the sea cooling water fed to the stripper overhead condenser.

Moreover, since there is no solvent degradation, there is no need for solvent reclaiming. Consequently, the existing reclaimer could be removed. Since no reclaimer is operated no nasty residuals causing waste disposal problems are present. Furthermore, the solvent itself is biodegradable.

Methanator

No modifications were required to the heat exchangers and to raw syngas separator. Also the 106-D methanator was suitable for the new operating conditions.

5.2 Ammonia Production System

Compression of purified synthesis gas

The reduction of the steam to carbon ratio and the revamping of the shift converters internals allowed an increase in the plant throughput without appreciably increasing the system pressure drop.

The only modification to the syngas compressor was the replacement of the recycle wheel by a new one that allowed the synloop to be operated at the maximum discharge pressure achieved by the M.U.G. stages at the increased suction flowrate.
The new recycle wheel was designed for the lower recycle flow rate and lower head necessary with the revamped synthesis converter internals.

With the new wheel the loop operated at a higher pressure and this reduced the power requirement in the 103-J machine as well as in the 105-J machine.

Synthesis

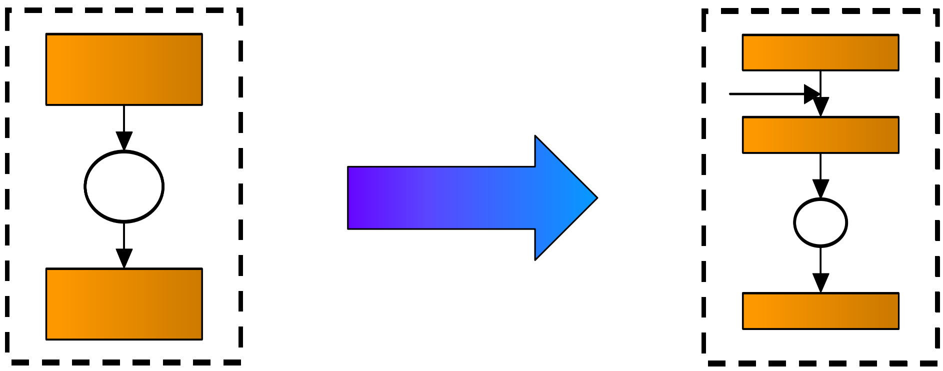
The main modifications regarding the ammonia synthesis loop were the converter internals retrofit and the recycle wheel replacement with a smaller one. These two interventions allowed the 105-D synthesis converter to reach higher performances, thus resulting in a higher ammonia outlet concentration and temperature. The increased outlet temperature made necessary the replacement of the converter outlet pipe and the replacement of the BFW preheater 123-C.

The benefits achieved by these modifications were:

- reduction of the power consumption in the 103-J machine, that allowed avoiding the revamping of this compressor and of its driving turbine;
- reduction of the loop chillers duty, necessary to avoid the revamping of the existing 105-J compressor (refrigerant ammonia compressor).

Ammonia Converter

The ammonia converter was revamped to a two bed-intercooler design in 1989 using Haldor Topsøe technology.
The performance of the converter was further enhanced by installing the CASALE technology, transforming the internals to a three bed-quench-intercooling design.



The cartridge configuration was changed to a modern axial-radial design with intermediate cooling. The new cartridge configuration was 3-bed with one quench between the first and the second bed and one interchanger between the second and the third bed.
Due to the better converter performance and higher operating pressure the temperature at converter outlet is higher and above the design values for the existing converter outlet pipe and 123-C exchanger. For the above reason it was necessary to replace the outlet pipe with one with improved metallurgy.

Refrigeration
The higher performance of the synthesis loop after converter revamping allowed a significant reduction of the chillers specific duties, thanks to this improvement, the plant capacity increase has been born by the 105-J ammonia compressor and by its steam driver without any modification.

5.3 Performances of the Revamped Plant

The following table 4 gives a summary of the main plant performances compared to the Base Case (i.e. before revamping).

Table 4

Description		**Base Case**	**Revamped**
Production:	MTD	1170	1312
	ENERGY CONSUMPTION		
Total specific cons.	Gcal/MT_{NH3}	9.77	9.23
	SEA COOLING WATER		
Specific	m^3/MT_{NH3}	416.0	388

consumption

PART 6.
NEW PLANTS

For new plants Ammonia Casale has available all the advanced and proven technologies and know how illustrated above. These elements allow the design of the most efficient, reliable and less expensive plant according to a standard scheme based on steam reforming of natural gas. For the plant parts where Casale has no proprietary technologies, like primary reformers and CO2 removal, Casale works together with the best supplier like BASF, Linde, KTI-Technip, Foster Wheeler, etc

Ammonia Casale in the recent years has installed 13 new ammonia synthesis loops, with capacity ranging from 400 MTD to 1350 MTD, in new grass root ammonia plants, in countries like Greece, US, India, Australia, Egypt, China, etc. These projects have been performed with licensees such as Linde, KTI, Technip, but also directly with local contractors in China.

Ammonia Casale has, therefore, the experience, accumulated in more then 80 years of existence, collaborating with major contractors, but also operating directly and in revamping existing plants, to supply the design of complete new efficient, low cost and reliable plants. As a matter of fact Ammonia Casale has developed together with Lurgi, also a completely new scheme for a non conventional ammonia plant, based on well proven technologies owned by the two partners, that enables the design of very large capacity plants, with single trains of 4000 MTD, characterized by a very low investment cost, simple design and lay out, high efficiency, ease of operation.

AMMONIA CASALE S.A.

A MEMBER OF CASALE GROUP

CASALE GROUP

AMMONIA CASALE

UREA CASALE

METHANOL CASALE

CASALE CHEMICALS

Via Sorengo, 7 - 6900 Lugano (Switzerland)
Tel.: +41.91.960.72.00 - Fax: +41.91.960.72.91/2
web site: www.casale.ch e-mail: ammonia@casale.ch