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OVERVIEW OF CASALE GROUP EXPERIENCE: EXAMPLES OF AMMONIA PLANT REVAMPING

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ABSTRACT

This paper presents the approach taken by AMMONIA CASALE to revamp ammonia plants in order to reduce the energy consumption and/or increase their production capacity with a minimum investment cost and the highest benefits.

This approach is based on a number of new technologies developed on purpose by AMMONIA CASALE that are here illustrated.

For each technology presented are also given information on actual implementation

1. INTRODUCTION

AMMONIA CASALE S.A. of Switzerland is an independent engineering company that has been operating world-wide for more than 77 years in the field of ammonia and methanol plants. More recently the range of products has been widened entering also in the field of urea and formaldehyde plants.

For that purpose the company has been split in four, AMMONIA CASALE S.A., UREA CASALE S.A., METHANOL CASALE S.A. and CASALE CHEMICALS S.A., each one taking care of the relevant processes.
All four companies are fully owned by CASALE Holding S.A.

The common targets of CASALE Companies gain substance from the sale of:

* licenses for the exploitation of technologies;
* engineering services;
* equipment and materials;
* complete plant units;
* technical assistance services.

The most outstanding characteristic of all the CASALE Companies is their philosophy of developing new technologies in their field of operation and to market these new technologies.

That is quite different from most engineering contractors that normally obtain licenses from the technology owner. Therefore, the main goal of most contractors is to sell man-hours and materials, from which they obtain their profit.

This leads to the fact that when they tackle a revamping job, the result is a very large project, involving the replacement of many items and a lot of engineering man-hours, rendering it an expensive approach.

On the contrary the CASALE philosophy is to find a way to overcome the existing plant constraints with the smallest effort by applying new ideas and technology, thus reducing amount of items to be replaced to a minimum and the man-hours as well.

The general approach of CASALE to plants revamping is to upgrade the efficiency of the plant's key equipment with innovative technology rather than just increasing the size and/or adding additional equipment.
Most of the technologies have been developed by CASALE to accomplish these goals.

Another unique characteristic of CASALE is that disposing of both ammonia and urea technologies, it is the only company world-wide that can offer integrated packages for revamping both plants, without the difficulties due to the presence of two different engineering companies working in the same plants.

Based on these ideas, CASALE has developed a number of solutions that are here illustrated to revamp ammonia and urea plants for capacity increase and energy efficiency improvements.

2. AMMONIA CASALE S.A.

In the early thirties the CASALE share of total world ammonia production (1 million t/y at that time) was about 60 percent; in the early eighties it was only 8 percent of the total 95 million t/y world production and today is one third of 130 million t/y world production.
Mostly this achievement is thanks to the revamping of synthesis units. The development effort of AMMONIA CASALE is quantified in Table 1.

As shown in the table, although the total capacity of new plants by AMMONIA CASALE continued to increase with time, the new entries reduced progressively the CASALE share of the total market, until the new deal of plant modernization activity started during early eighties, regaining for AMMONIA CASALE an evenly increasing share.

The Company is at the present time a leading licensor of the ammonia synthesis technology. The following international companies are AMMONIA CASALE S.A.'s licensees:

* Chiyoda Corporation	Japan
* Synetix	U.K.
* Linde AG	Germany
* Lurgi	Germany
* Technip	France
* Ube Industries Ltd.	Japan

Table 1: AMMONIA PRODUCING PLANTS CONSTRUCTED OR RETROFITTED BY AMMONIA CASALE S.A. IN COMPARISON TO THE TOTAL WORLD PRODUCTION OF AMMONIA

Year	Number of units con-structed or retro-fitted	Total capacity (t/d)	Average capacity (t/d per unit)	Total Cumulative capacity (t/d)	(10^3 t/y)	World production (10^3 t/y)	World capacity (10^3 t/y)	% of the total world capacity
1922-1930	120	4'180	34	4'180	1'400	1'150	2'400	58
1931-1940	9	320	35	4'500	1'500	3'300	5'000	30
1941-1950	12	740	62	5'240	1'700	6'000	6'500	26
1951-1960	38	4'190	110	9'430	3'100	14'700	17'000	18
1961-1970	35	11'270	320	20'700	6'800	49'200	62'000	11
1971-1980	5	1'890	380	22'590	7'500	94'200	95'000	8
1981-1990	50	50'410	1'000	73'000	24'000	117'000	123'000	20
1991-1997	58	62'930	1'070	134'930	44'500	125'000	130'000	34

3. REVAMPING OF AMMONIA PLANTS, 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 was later applied to methanol, shift and formaldehyde 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).*

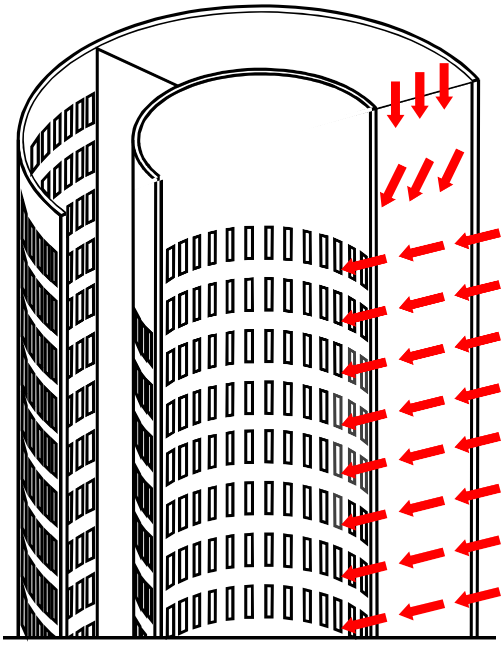

Fig. 1 - Axial-radial Bed, Gas Distribution

Mechanically the bed is very simple, made only by the two vertical perforated walls and by one bed 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 well- known 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 reach 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 allow for 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.

3.3 Secondary Reformer Burner

The ammonia plant Secondary Reformers' conventional design 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*).

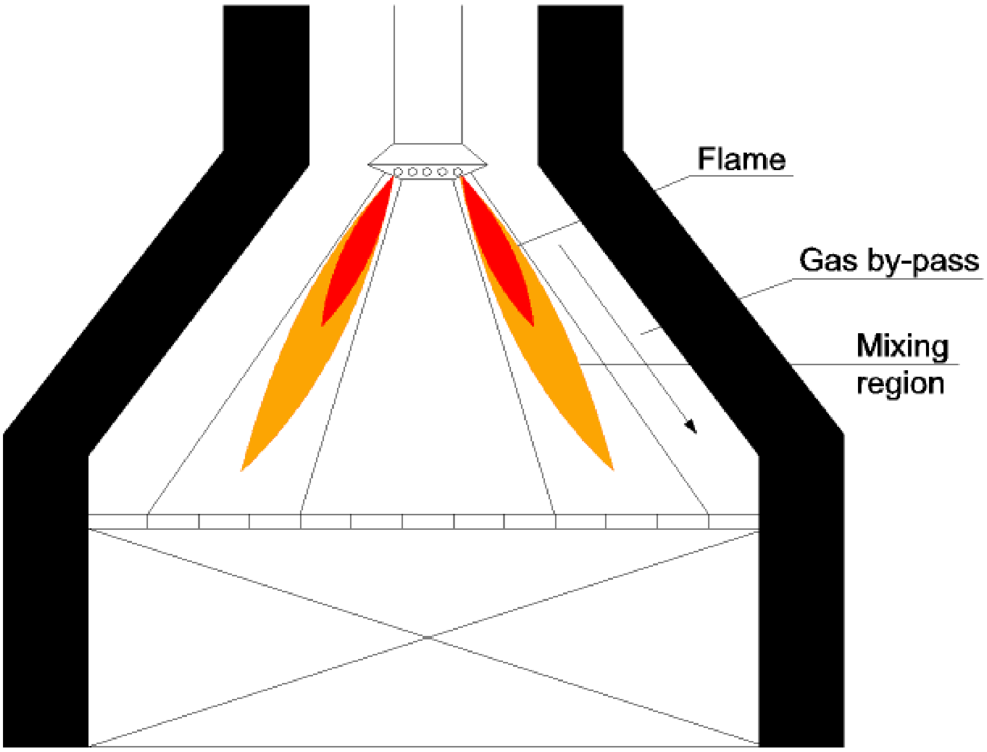

FIG. 2

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 then 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.
* Protections 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*).

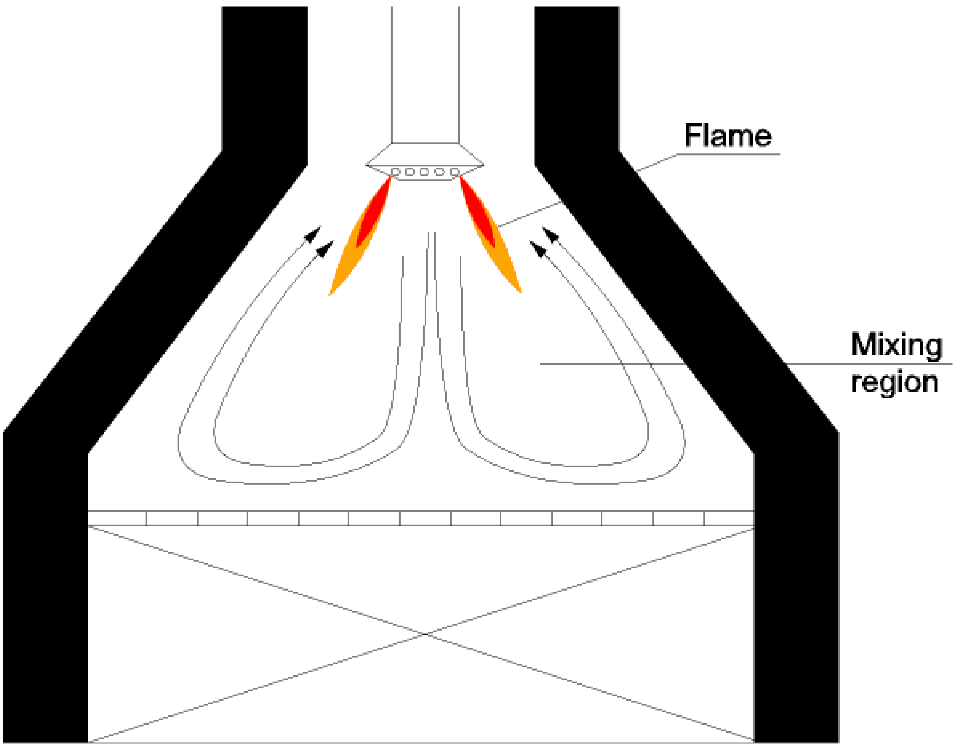

FIG. 3

The performances of the Casale Advanced Secondary Reformer are:

* Pressure loss for the air stream: less then 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

3.4 Shift Converters Revamping

AMMONIA CASALE, based on its long term and successful experience in the field of highly efficient ammonia converters, has completely redesigned the shift converter achieving, in industrial applications, significant improvements.

The new technology 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 revamping of existing shift converters consists in the transformation of existing axial beds into axial-radial ones, by introducing new vertical perforated walls, that are cylindrical and form the inlet and outlet walls, in prefabricated sectors that are assembled inside the existing converter vessel.

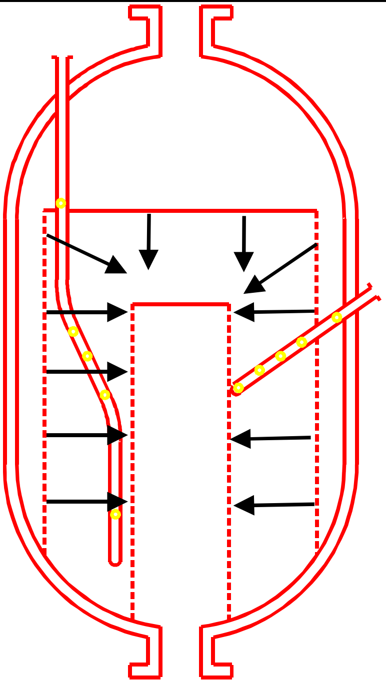

Fig. 4 - Revamped Shift Converter

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 catalyst.

The low pressure drop helps eliminate the hydraulic constraints in having more flow through the front end, while 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.

The main features of CASALE patented design for both HTS and LTS converters which lead to the following advantages, are:

* an axial-radial flow path of the gas crossing the catalyst resulting in a low pressure drop;
* use of small-size, more active and more resistant to poisons catalyst;
* protection of catalyst from water droplets carried over from secondary reformer heat recovery train or others;
* possibility to load different volumes of catalyst easy operation.

Advantages of the Axial-Radial Shift Converters

There are many advantages of the axial-radial technology over the axial one, both when revamping plants for capacity increase and for energy savings, as well as for new converters, and they can be summarized as follows:

Revamping for capacity increase

* no pressure drop limitation due to lower differential pressure within the axial-radial technology;
* no bigger catalyst volume required because of the use of smaller catalyst size with higher activity;
* longer operation at equilibrium with higher product purity (H_2 plants) or higher production rates (NH_3 plants);
* longer operation at equilibrium with the consequence of higher plant capacity;
* longer catalyst life due to higher catalyst activity and poison resistance;
* protection of catalyst from water droplets with the consequence of an extended catalyst lifetime.

Revamping, same capacity

* energy saving, thanks to the lower pressure drop;
* reduced catalyst volume (30-50%) for the same catalyst life;
* same catalyst volume for longer life.

3.5 Ammonia Synthesis Converter

The ammonia converter is, of course, one of the most important items when planning a revamp for energy saving or capacity increase, and in most cases, in fact, it is the first item to be revamped thanks to the relatively low cost and very high return.
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 120 converters on stream, out of which about 50 are "in situ" modifications, and the majority of the others are revamps of full-bore opening converters.
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 converters as well *(see figure 5).*

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.

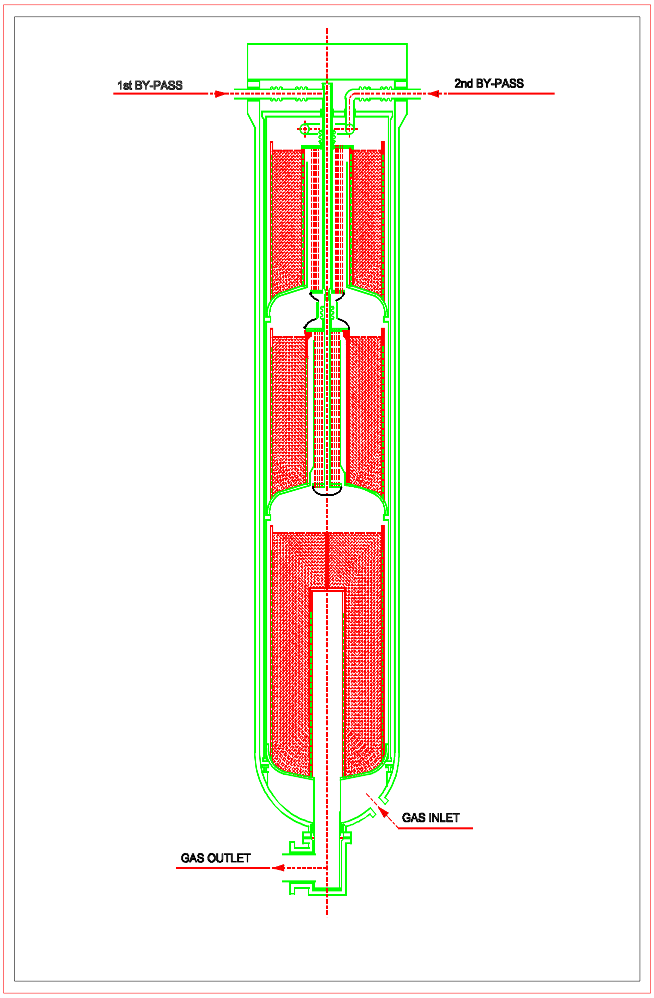

Fig. 5 - CASALE 3-beds 2-interchangers converter

It is possible to use small-size, more active catalyst with the axial-radial configuration, and it is well known that small-size catalyst is more efficient than the large-size one.

Therefore, the design of the cartridge 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 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 5)*.

3.6 Other Main Steps

The CASALE group does not own any proprietary technology for the primary reforming, for the CO_2 removal section and for the compressors.

Nevertheless, within the CASALE group are working technologists that are very skilled in these areas, allowing CASALE to study, design and implement modifications in primary reforming, CO_2 removal section and rotating machinery.

In fact, as it results from the following case histories, CASALE has already studied, designed and implemented revamping on an entire plant, including extensive modifications to the reformer, etc.

3.7 Catalysts

The CASALE group markets exclusively 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 in Iran.

The performance of the Chinese 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.

4. REVAMPING OF AMMONIA PLANTS, 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 consequences 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 then can enter the primary reformer and a much lower steam carbon ration can be taken, 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): the second point is because the reforming reaction taking place in the pre-reformer is not taking place in 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, as the only its feed gas is methane plus steam, CO, CO_2 and hydrogen, it is possible to use the natural gas type catalyst that is more active, and is possible 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 an 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 could not be considered safe any more.

The new converter is based also 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 will be made, to exchangers, pumps and piping.

4.2 Primary Reformer Modification

In '94, due to the rise of methanol prices and to the low price of ammonia, a large ammonia producer in Russia, namely TOAZ, asked METHANOL CASALE to study the possibility to transform one of the 3 GIAP AM 76 ammonia plants into one methanol plant keeping the same production capacity.

AMMONIA
CASALE

At the end of '95 TOAZ decided not to transform one of the existing ammonia plants, but to build a new methanol plant, using as many as existing pieces of equipment possible in its warehouse, originally designed for the eighth ammonia plant.
A new methanol plant with a capacity of 1'350 MTPD (1'477 STPD) was designed by METHANOL CASALE S.A. taking into account TOAZ's requirements not only to maximize the use of the equipment present at site, but also to maximize the manufacturing of the new equipment inside the C.I.S. countries that was done under CASALE's supervision and responsibility.

There are two main features of the new methanol plant:

a) the redesign of the existing ammonia reformer in order to meet the requirement of a new methanol reformer;

b) the new horizontal methanol converter.

In this paper only the transformation of the primary reformer is presented.

4.2.1 Steam Reforming Revamping

The process scheme of the GIAP ammonia reformer, which is very similar to a Kellogg, is detailed in fig. 6 together with the convection section.

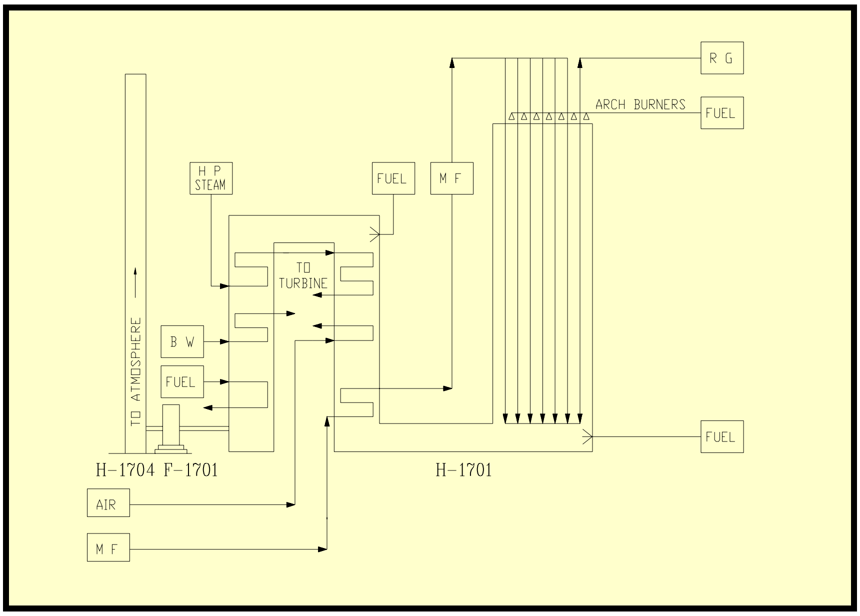

Fig. 6 - Existing Reformer Process Scheme

In order to reach the guaranteed 1'360 MTD methanol, the new reformer configuration required the process design modifications as per Fig. 7.

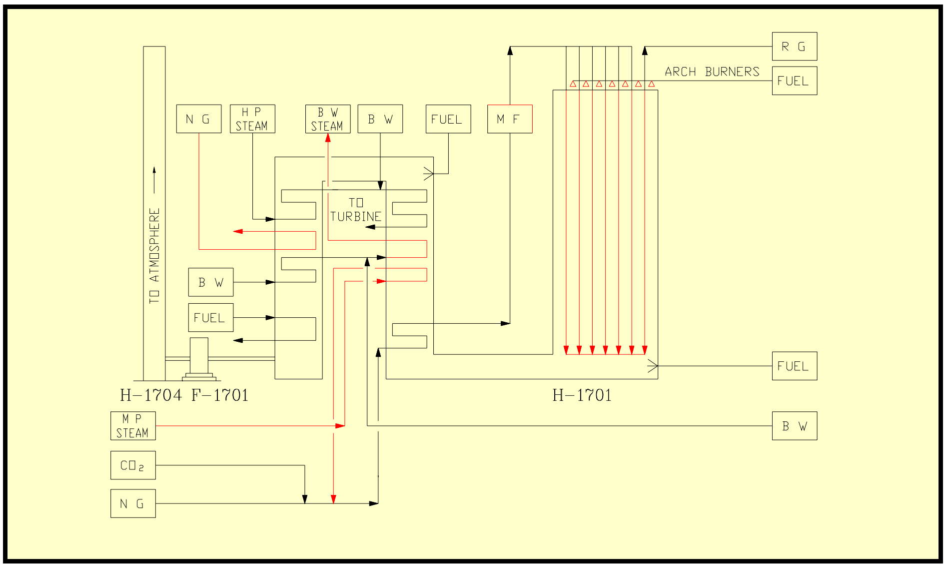

Fig. 7 - Retrofitted Reformer Process Scheme

The main revamping features were the following:

* Increase of reforming catalyst quantity from 20.8 m^3 to 37.6 m^3 by changing catalyst tubes;
* Increase of radiant heat liberation from 170'000'000 kcal/h to 227'000'000 kcal/h by modification of roof burners;
* Addition of one BFW heater/boiler convection coil;
* Addition of one natural gas preheater convection coil;
* Utilization of existing air preheater convection coil to heat MP process steam;
* Addition of inline de-superheater between 1st and 2nd stage H.P. steam superheaters to control the temperature at H.P. turbine inlet.

4.2.2 New Catalytic Tubes

In order to accommodate the increased heat duty and to increase the volume of the catalyst, new catalytic tubes were designed.
The new tubes were increased in diameter from 114 mm to 121 mm and decreased in thickness from 21 mm to 12 mm.
The decrease of thickness was possible thanks to the use of new material 25Cr 35NiNb microalloy, which has proven its reliability in industrial application in the last ten years.

4.2.3 Increase of Burners Heat Liberation

The existing burners were designed for a total heat liberation of 188'000'000 kcal/h, while the new required heat liberation is 227'000'000 kcal/h.
Therefore, the existing burners were simulated in the new conditions to check if they were suitable for the new capacity and if the new flame did not impinge on the catalytic tubes.
The check revealed that only the burner nozzle had to be resized and replaced for the new conditions.

4.2.4 Modification of Convection Section

The new process design of the methanol plant has required the following retrofitting of the reformer convection section:

Process steam heater

The existing air preheater has been utilized to heat process steam before mixing with natural gas and no modifications were required in this coil.

New BFW heater/boiler

A new BFW heater has been inserted between the process steam heater and the 2nd stage steam superheater.
In this coil the BFW is heated up to boiling point and a part of it is evaporated.

H.P. steam desuperheater

A new H.P. steam desuperheater was inserted between 1st and 2nd stage steam superheaters to control the steam temperature at inlet of H.P. steam turbine.
The desuperheater is characterized by a steam stud with atomizer which produces fine water drops.

Natural gas preheater

The new natural gas preheater is installed between the 1st stage steam superheater and the BFW preheater.

4.3 Burner for Partial Oxidation with Oxygen

CASALE CHEMICALS was asked in '97 to design and supply a new burner for a plant producing CO in southern Italy, the goal being to increase the production capacity by 100 percent, to improve the reliability of the burner and reduce the soot formation.

The burner was design according to the new CASALE technology and now is in service since December 1998 with excellent results.
The operating conditions are more severe than those of ammonia plant secondary reformers, as the production of the desired gas is made through partial oxidation of hydrocarbon with pure oxygen.

The burner operates with an average temperature of the main recirculating gases of about 1'300°C, that is 300 to 400°C over the mean temperature of the secondary reformer recirculation.

It has been recently inspected after 13 months of operation and it showed no signs of deterioration whatsoever, while the burners previously installed had to be repaired or replaced about every 12 months.

The design process parameters have been met in terms of pressure drop and uniformity of temperature and composition, i.e. soot formation.

4.4 Shift Converters Revamping

4.4.1 Shift converter industrial experience

AMMONIA CASALE has revamped six 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.

The last shift converters revamped were one HTS started up in October 1998 in the USA, at the AGRIUM plant in Borger, Texas and one HTS in China, started up in September 1999.

The Agrium converter runs according to the following parameters:

			Prior to Revamp	**Axial-Radial Revamp**
	Plant Capacity	[stpd]	1450	1600
	Catalyst Volume	[m^3]	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

4.5 Ammonia Converter Industrial Experience

AMMONIA CASALE has revamped and started up three out of four 1'000 STP M.W. Kellogg ammonia converters at CFI Industries, Louisiana, USA and the last one is due on stream next spring.

These converters were already revamped in '86 adopting the 1st generation of internals (4 beds, 3 quenches) and now at the end of the catalyst life have been revamped again adopting new and more efficient internals: 3 beds, quench and interchanger.

In the following Table 2 the achieved performances of these converters has been indicated.

Table 2: 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

5. CONCLUSION

Proven technologies are made available by the CASALE Companies for the revamping of a whole ammonia production complex.

Thanks to the wide range of the technologies available within the CASALE companies combined with their wide experience, CASALE can handle not only capacity increase projects (up to very large increases), but also just energy reduction projects or project dealing with increasing of plant reliability or with plant optimization.

These revamping projects can be done also in the downstream urea plants with a single point of responsibility with several advantages for the Clients.