

# The Revamping of Fosfertil Cubatao Ammonia Plant, A Successful Experience

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## Abstract

*In August 2001 Fosfertil started up its ammonia plant in Cubatão, Brazil, after revamping it in order to save energy and increase its capacity.*

*Fosfertil and Ammonia Casale successfully performed this project together.*

*This revamping is also the first industrial application of an axial-radial adiabatic pre-reformer.*

*This paper describes the revamping project, the technologies used and the results achieved.*

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## Introduction

FOSFERTIL S/A, a private Brazilian company, is a Fosfertil subsidiary and controlled by the holding Fertifos administration and participations Inc. and has a large share in the national market of fertilizers, controlling 37% of the phosphate segment and 35% of nitrogenous segment in the Midwest and Southeast region of Brazil.

Fosfertil has four industrial sites in the states of São Paulo (Cubatão and Piaçaguera), Minas Gerais (Uberaba) and Paraná (Araucária), three mining complexes Minas Gerais (Tapira and Patos de Minas) and Goiás (Catalão), and a Maritime Terminal located in São Paulo (Cardoso Island).

Operating in the chemical segment, fertilizer markets and logistic services areas, Fosfertil produces Ammonia, Urea, Nitric Acid, Ammonium Nitrate, Sulphuric Acid, Phosphoric Acid, low and high concentrate Phosphate fertilizer, Methanol and Phosphate rock.

Strategically located in the state of São Paulo, the Piaçaguera Ammonia Plant, which is the subject of this paper, was built in 1970 by Foster Wheeler, and designed for naphtha as feedstock for both process and fuel. Due to the high cost of naphtha, the unavailability of Natural Gas and to the vicinity of a refinery, in 1981 Fosfertil started to use the off-gas from the refinery as fuel and in 1984 as feed.

The problem with this feedstock is its continuous change in composition, which

obliged the plant to maintain a higher than normal steam carbon ratio in order to guarantee a safe run to the primary reformer, but this has consequently caused a high consumption of energy.

The ammonia synthesis converter presented another problem, since it consisted of three separate vessels. After 31 years of operation it had to be replaced due to mechanical reasons.

FOSFERTIL decided to ask Ammonia Casale for a proposal to revamp the ammonia plant. The goal of this proposal, as a first step, was to increase the capacity from 520 MTD (472 STD) to 600 MTD (544 STD), which was successfully implemented and is the subject of this paper. AMMONIA CASALE S.A. was also requested to recommend a second project for further increase capacity to 800 MTD (726 STD).

AMMONIA CASALE S.A. of Switzerland is an independent engineering company that has been operating worldwide for more than 80 years in the field of ammonia and methanol plants.

AMMONIA CASALE had already performed revamping jobs for Fosfertil in its plant in Araucaria, where in 1995 it had successfully revamped the ammonia converter internals and in 2000 the high temperature shift converter.

## Revamping Strategy

AMMONIA CASALE developed a plan to reach the specified goals, after a careful plant survey, which involved the following steps:

- a) To reach 600 MTD (544 STD)
  - Installation of a pre-reformer reactor
  - Modifications to the primary reformer convection section
  - Replacement of the primary reformer burners

- Reduction of the steam to carbon ratio from 3,9 to 3,5.
- Replacement of the ammonia converter vessels with new ones, still in three separate units, but with cold gas flushing, and axial-radial internals

- b) To reach 800 MTD (main items only)

- Revamping of the air compressor
- Revamping of CO shift internals to axial-radial ones
- Revamping of the CO<sub>2</sub> removal section
- Revamping of syngas compressor
- Revamping of feed gas compressor
- Replacement of some heat exchangers
- Installation of an additional Boiler Feed Water Pre-heater

In the following paragraphs only the 600 MTD (544 STD) case will be illustrated in detail.

## Technologies Used

### *Pre-Reforming Reactor Technology*

The first step to be taken in order to be able to reduce the steam to carbon ratio, with consequent reduction of energy consumption and potential for capacity increase in the primary reformer, is to eliminate the fluctuation of composition in the refinery off-gas.

As it is not possible to improve the feed gas quality from the refinery, the pre-reforming of this gas becomes the best solution.

In fact the off-gas contains mainly hydrogen, methane, and higher saturated and unsaturated hydrocarbons.

The refinery off-gas is a mixture between off-gases from three Petrobras Units - Fluid Catalytic Cracking (FCC), Delayed Coking Unit and Catalytic Reforming Unit - and it is the feed gas used to produce ammonia at Cubataõ.

The refinery off-gas is treated before feeding the ammonia process at the Refinery Off-Gas Treatment Unit (**RogTu**). This treatment consists of saturation of the Olefins into Paraffin by catalytic hydrogenation in a NiMo/CoMo reactor and removal of sulphur compounds by catalytic absorption in a ZnO bed.

Olefins may cause fast coke deposition on the Primary Reformer catalyst; sulphur compounds are poisonous to this catalyst and to

the other catalysts of the ammonia plant. High level of olefins can cause an over temperature at the NiMo/CoMo bed, and a recycle of gas to control this rise of temperature is necessary.

The figure below represents the schematic flow of The Refinery Gas Treatment Unit (**RogTu**) and the next table (Table 1) represents the inlet and the outlet **RogTu** streams analysis.

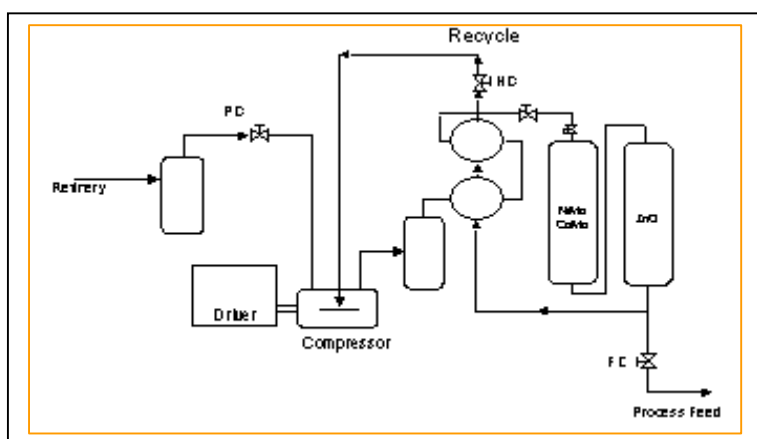


Figure 1: Refinery Off-Gas Treatment **RogTu** Table Unit Gas flow Schematic

Compound	RogTu inlet(%)	RogTu outlet(%)
H <sub>2</sub>	22,65	13,84
N <sub>2</sub>	3,79	4,49
CH <sub>4</sub>	45,44	53,89
CO <sub>2</sub>	0,11	0,13
Ethane	12,92	24,68
Ethene	7,89	
Propane	2,91	1,28
Propene	2,44	
Iso-Butane	0,43	0,70
N-Butane	0,65	0,71
Butene	0,54	
C <sub>5+</sub>	0,23	0,27
H <sub>2</sub> S-PPM	78	< 0,1

Table 1: Comparison between inlet and outlet gas from the Refinery Off-Gas Treatment Unit **RogTu**

The pre-reforming reactors convert the hydrocarbon impurities in this gas to hydrogen, methane, CO and CO<sub>2</sub> only, enabling to maintain the operation of the primary reforming stable, and therefore making it possible to reduce the S/C ratio down from 3,9 to 3,5.

The pre-reforming reactor installed 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 low-pressure drop is an important energy saving feature and helps the compressors reach higher capacities.

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

- higher sulphur pick-up, resulting in a longer life, since sulphur is the main poison;
- greater activity.

This means that, with respect to the larger size catalyst, it is possible to reduce the catalyst volume to achieve the same life or to attain a longer life with the same volume.

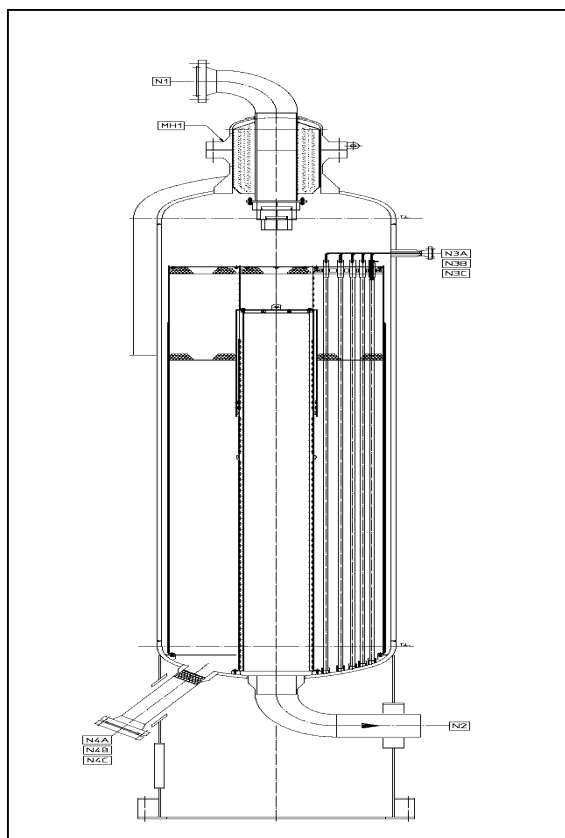
Regarding the operation of an axial-radial pre-reformer, it is to be noted that the temperature profile in the catalyst bed can be measured and followed thanks to the presence of thermocouples in different positions along the radial direction in the bed.



*This picture shows the new installed pre-reformer*

Also catalyst loading and unloading is 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.

Thanks to the pre-reformer installation, it is, therefore, possible to operate the primary reformer smoothly, with stable operating conditions and to reduce the steam carbon ratio to the primary reformer, as the only feed gas is methane plus steam, CO, CO<sub>2</sub> and hydrogen. It is also possible to use the natural gas type catalyst that is more active, and to increase the reforming capacity.



*Axial-Radial Pre-Reformer*

### **Primary Reformer Modification**

The existing primary reformer was a Foster Wheeler design, terrace wall type, with 120 catalytic tubes, 60 in each cell. The convection section has process steam, process air, high pressure steam (100 bar) super heater and boiler feed water coils. Here the following areas of intervention were applied:

*1. Modification of the convection section for reliability improvement*

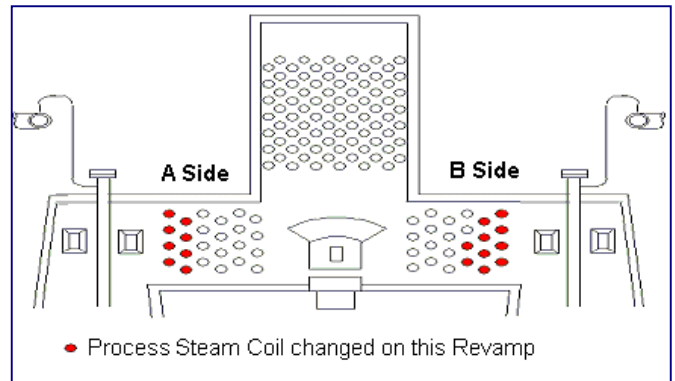
The convection section modification consisted in the replacement of the process steam heater coil due to its age and limitation in design temperatures.

*2. Burners replacement*

***This picture shows the Primary Reformer and the Secondary Reformer***



141,5 mm of external diameter and 9,5 mm thickness, which have an expected lifetime of 100.000 hrs. Before the revamp, the wall temperature was 950 °C (Average) and after revamp, reduced down to 880 °C.



*This drawing shows the coils that were substituted on the revamp*

The burners were replaced due to the poor performance with the off-gas of the old one and naphtha as fuel was no longer used.

The new burners can run with natural gas, or a mixture of natural gas and off-gas, in case this fuel becomes available to the plant in the future.

These new burners are John Zink ones. There are 120 burners and 10 auxiliary burners. Burners are GO-SFG-M type, the maximum heat released to these burners is 0,95 MMkcal/h and the maximum capacity pressure is 0,8 bar. Auxiliary burners are PVYD-12-RM, the maximum heat released is 0,625 MMkcal/h and the maximum capacity pressure is 1,5 bar

### 3. Catalytic tubes

The tubes that were operating before the revamp, were Villares “LRE9” with 140mm of external diameter and 16 mm thickness and a lifetime of 65.000 operating hours. Manaurite “XM”, from Manoir, replaced those tubes with



## Ammonia Synthesis Converter

Foster Wheeler designed the ammonia synthesis converter according to a Pritchard scheme. The Converter has three adiabatic beds, each one contained in a separate vessel, with indirect cooling between them, by HP steam generation and feed gas preheating. All the reactor vessels, the connecting nozzles and piping, and the heat exchangers and boilers were refractory lined.

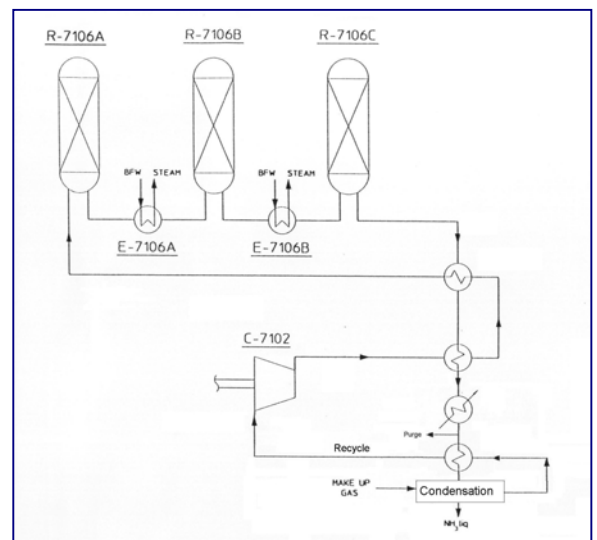
The pressure vessels are a multi layer design, having 11 (eleven) layers. In 1993 the pressure vessels were repaired because of some cracking between the shell and the bottle part. These vessels were at the end of their useable life guaranteed by the repair executors.

The AMMONIA CASALE design proposed maintaining the existing configuration, in order to re-use the intermediate exchangers and boilers that were still in good condition, and replace the old reactor vessels with new ones flushed with cool feed synthesis gas, in order to avoid problems of hydrogen attack and nitrating. This solution was preferred to the replacement of the three reactors with a new one, since the modification to the external equipment has been to be much more expensive.

The new vessel would have, of course, the axial-radial internals, achieving in this way a considerable increase in the performance of the converter, allowing for the capacity increase in all the rest of the synloop.

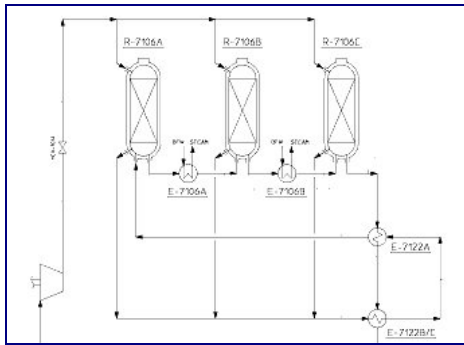


*This photograph shows the three new converters and the HP waste heat boilers*



*Loop schematic before revamp*

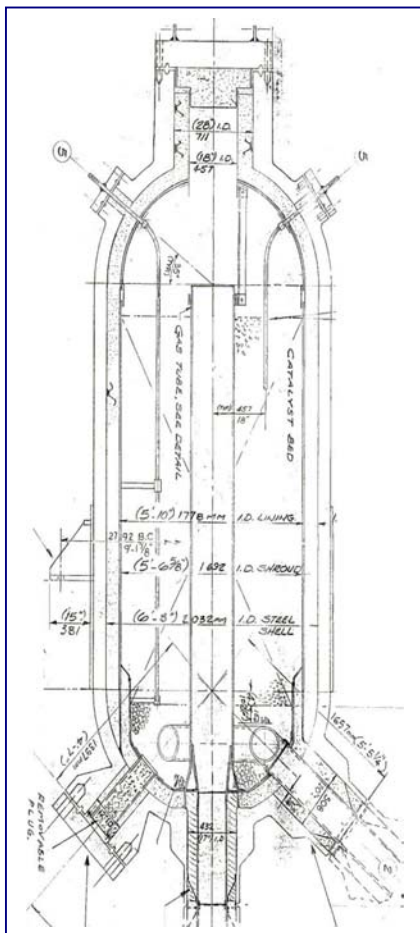




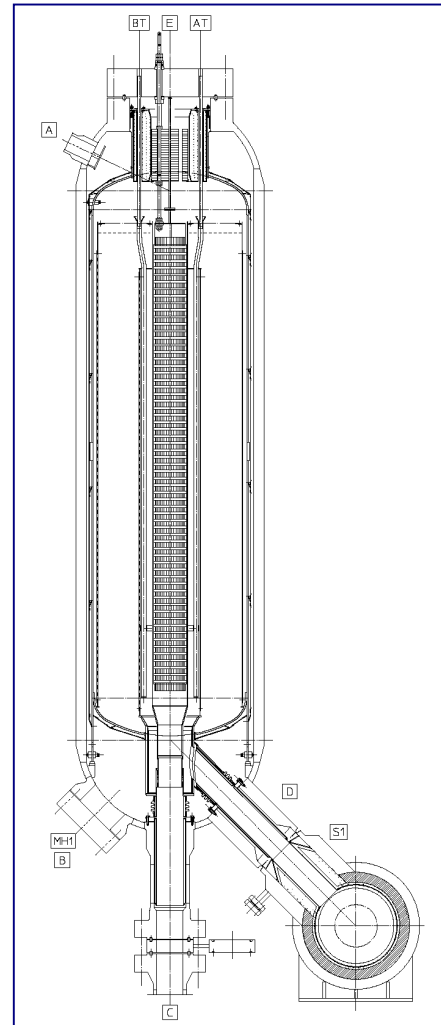
*Loop Schematic after revamp*

The main advantages achieved after revamping are:

- Pressure drop decrease
- Conversion per pass increase
- Heat recovery increase
- Reliability increase



*Original Ammonia Converter*



*New Axial-Radial Ammonia Converter*

## Goal of Fosfertil in this Project

Fosfertil studied several alternatives such as acquiring a new high capacity ammonia plant or buying a used ammonia plant, or revamping its existing one.

The high price of the raw material for the new plant and the high cost of dismantling, transporting and assembling the used plant made both of these options unfeasible, revamp was the best option that fitted with Fosfertil objective. The objectives were:

- To guarantee the operational continuity of the ammonia plant by changing the synthesis reactors that had been repaired in the past due mechanical problems and the maintenance warranty period of which had almost expired;
- To take advantage of this event to look for the plant modernization, mainly synthesis loop;
- Reduction of the energy consumption of the ammonia plant;
- Increase to the maximum possible capacity with the smallest investment in the first step and for 800 ton/d (726 STD) in the future;
- Reduction of the amount of ammonia imported to supply the Fosfertil Group and the internal market.

Among all of the consulting technology companies with knowledge in ammonia plant revamping, Ammonia Casale offered Fosfertil the most attractive economical alternatives.

The scope of the work was:

- Study by Ammonia Casale and Fosfertil to develop the improvements to be implemented to get the best return on investment;
- Basic engineering by Ammonia Casale;
- Design of synthesis and pre reformer reactor vessel by Ammonia Casale;

- Detailed engineering by Engevix Engenharia S/C Ltda/Inepar (Consortium), Brazil;
- Synthesis and pre reformer reactor vessels fabricated by Confab Industrial S/A;
- Synthesis and pre reformer internals by Ammonia Casale Design and VRV manufacturing;
- Internal's assembly by Confab Industrial S/A under Ammonia Casale supervision;
- Field assembly by Alston Industries S/A under Ammonia Casale supervision.
- To reduce the shut down time, Fosfertil decided to take out the old vessels without taking out the catalyst (inert with nitrogen). Fosfertil required an engineering study for the installation of the new burners to the original Foster Wheeler design, which used a real model of the burners supporting structure to simulate this installation.
- The shut down was concluded on time as the revamping time schedule predicted. The downtime period took over 45 days to change the converters.
- The catalytic pre-commissioning and reduction were concluded on time as the time schedule predicted, although some difficulties appeared, like the problem experienced to keep the circulation gas under the specification of CO+CO<sub>2</sub> (100 ppm) to the pre-reformer catalyst.



*This photograph shows the Assembly of the New Converter*

## Plant Performances After Revamp

### *Operating condition of the Pre- Reformer*

	<i>Inlet and Outlet Streams</i>	
Inlet Temperature, °C (°F)	436 (817)	420 (788)
Outlet Temperature, °C (°F)	460 (860)	440 (824)
Steam/Carbon Ratio	2,2	2,7
ΔP, bar (psi)	0,3 (4,35)	0,32 (4.64)
Expected Life, years	> 2	2,2

Compound	Pre Reformer inlet(%)	Pre Reformer outlet(%)
H <sub>2</sub>	13,84	17,38
N <sub>2</sub>	4,49	2,68
CH <sub>4</sub>	53,89	73,26
CO <sub>2</sub>	0,13	6,68
Ethane	24,68	
Ethene		
Propane	1,28	
Propene		
Iso-Butane	0,70	
N-Butane	0,71	
Butene		
C <sub>5</sub> +	0,27	
H <sub>2</sub> S-PPM	< 0,1	

### *Pre-Reformer Inlet and Outlet Streams*

#### **Primary Reformer after Pre-Reformer installation**

- Reduction of 20°C (36°F) at the outlet temperature of the catalytic tubes;
- Reduction of Steam/Carbon ratio from 3,9 to 3,5;
- Reduction of outside wall temperature from 950°C (1742 °F) to 880 °C (1616 °F) of the catalytic tubes that lengthens their durability;
- Reduction of ΔP on catalytic side of the tubes of about 1 bar (14,5 psi);

- Use of standard NG catalyst for the Primary Reformer;
- Stable operation thanks to the stabilization of the Primary Reformer feed.

#### **Synthesis Loop**

- Reduction of ΔP on converter of about 3 bar (43.5 psi);
- Use more efficient catalyst with  $\phi$  1,5 – 3,0 mm (0,06 " ~ 0.12 "); “

- Reduction of the operation pressure from 165 (2393 psig) bar to 145 bar (2103 psig);
- Increasing the conversion from 10% to 14% in NH<sub>3</sub> at converter outlet flow.

### **Final Results\***

After more than two years of operation it is now possible to list the benefits achieved over a long period of time.

These benefits are:

- Average Production : 614 MTD (557 STD)
- Maximum Production : 634 MTD (575 STD)
- Reduction on Imported Steam: 12 %
- Reduction on gas Consumption: 11,59%
- Reduction on Energy Consumption: 10,55%

\* Comparative with reference to the year 2000

### **Conclusions**

From the above explanation regarding the revamping of Fosfertil's ammonia plant, we can conclude that:

- Pre Reformer installation was a good solution to:
  - ✓ Stabilize the Feed Gas composition of the Primary Reformer
  - ✓ Reduce the Steam/Carbon ratio from 3,9 to 3,5
  - ✓ Increase the capacity by about 15%
  - ✓ Increase life of catalytic tubes
  - ✓ Reduce the maintenance costs
  - ✓ Reduce the final cost of production
- Synthesis Loop revamp was an excellent way to :

- ✓ Reduce the operation pressure by about 20 bar (290 psi)
- ✓ Reduce the  $\Delta P$  by 3,0 bar (43,5 psi) with the installation of Axial-Radial internals
- ✓ Increase the conversion efficiency and performance of the converters
- ✓ Increase the capacity at the rest of the Synthesis Loop

Finally we conclude that the Fosfertil Ammonia Plant Revamp by Ammonia Casale was a complete success.

Lugano, July 2004

Anvil/paper/conf/amm/meetings/Aiche 2004/Cubatao Aiche 2004 paper