RETROFIT OF A HIGH TEMPERATURE SHIFT REACTOR

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1. ABSTRACT

The Shift section of the oil gasification plant of ULTRAFERTIL was composed of two axial flow high temperature shift reactors.
The flow pattern of the first reactor was changed to the CASALE design, an axial radial type, with the objective of reducing the pressure drop across the catalyst bed, as well as extending the catalyst life.
This paper concerns both the characteristics of this design as well as the management of this change. This involved extensive discussion with CASALE and all the people in charge, operators, engineers and people from maintenance department.
It will be shown the results achieved exceeded expectations and the main reason for this success was the involvement of all concerned working toward a well-defined objective. Understanding the importance of this project and keeping it uppermost in everyone's mind was the key element in the first successful implementation of this new design in a partial oxidation plant in the world.

2. FOREWORD

ULTRAFERTIL is a company located in Brazil that produces almost all types of fertilizers utilized by Brazilian farmers. Besides producing fertilizers and chemicals, ULTRAFERTIL also has it's own mines, from which phosphates and all the raw materials for phosphoric acid and it derivates are extracted to be used in fertilizers. Regarding Nitrogen-based fertilizers, ULTRAFERTIL is the major urea producer in Brazil using a single reactor. It was in this plant, which is integrated with an ammonia plant, located in the city of Araucaria, state of Parana that the retrofit in the High Temperature Shift Reactor was carried out.

The actual production capacity is:

- Ammonia 1350 MTPD (1488 STD) Based on Partial Oxidation Process. Heavy Oil (Residuum Asphalt) is the current feedstock, LURGI DESIGN
- Urea 2000 MTPD (2205 STD) Based on CO_2 Stripping Process Stamicarbon Design

The original (nameplate) capacities were:

- Ammonia 1200 MTPD (1323 STD)
- Urea 1500 MTPD (1653 STD)

This plant, formerly state owned, was privatized in 1993. Since then considerable investments have been made in order to increase production, the reliability and availability. One major improvement was the retrofit of the synthesis converter in 1995 by AMMONIA CASALE S.A.

This paper describes the successful retrofit in the first High Temperature Shift Reactor carried out last year during the planed turnaround.

3. THE PURPOSE OF THE RETROFIT

The gasification process used in ULTRAFERTIL's plants causes more severe operating conditions for the high temperature shift reactors than in the more common steam reforming plants.

The reason for this high severity of operation is that the concentration of carbon monoxide at the shift section inlet is very high, about 50 % vol. dry basis, implying high operating temperatures, and the fact that the shift reaction is carried out in two stages, both with high temperature catalyst. The first shift converter, which is the subject of the revamping presented here, operates with outlet temperatures exceeding 500 °C (932 °F).

The gasification process consists in a gasification reactor, where the feedstock is gasified with pure oxygen in presence of a little steam. The resulting gas is saturated with water first, then more steam is added before proceeding to the shift section to achieve sufficient water content in the gas.

This sequence of operations implies the possibility of having impurities being carried over, and reaching the catalyst bed, increasing the severity of operation for the first shift converter in addition to the high temperature.

As a result, the first converter shift catalyst has a relatively short life, and a significant increase in pressure drop over the operating period.

The main purpose of the retrofit was to significantly decrease the pressure drop over the first high temperature shift reactor. This would allow increased gas flow through the ammonia process loop and increased ammonia production. The feasibility analysis and calculation of the Return Over Investment ("ROI") was based on this increased production.

Another important factor taken into consideration was the expected longer expected life of the high temperature catalyst. In the past the life of this catalyst was about 1,5 years but never longer than 2 years. After the retrofit the catalyst life expected to be at least 2 years and probably longer. The CO slip after 2 years is guaranteed not to exceed 7,66% (volume). Prior to the retrofit, the CO slip after 1,5 to 2 years was more than 8% and sometimes approximately 9%.

Almost one year after the retrofit, the CO slip is averaging only 6,5% and it appears very likely that the process guarantee will be achieved and easily surpassed. It is also important to note that the CO content of the gas entering the first reactor is about 50%.

The performance of the retrofit strongly supports ULTRAFERTIL's intentions of obtaining longer on-stream factors with good efficiency. The goal was to achieve 2,5 years between catalyst changes in the High Temperature Shift Reactor. ULTRAFERTIL has only one high-pressure boiler that supplies steam to the entire plant and when it is shut down the plant must be shut down also. Legal requirements dictate that this boiler be inspected every 2.5 year and ULTRAFERTIL's goal is to extend catalyst life to match the mandatory boiler inspections.

Another good reason for doing this retrofit, which would justify the investment, was the expected higher suction pressure in the suction of the Synthesis Gas Compressor (due to the lower pressure drop in the shift loop). The savings in steam in the Steam Turbine of the Synthesis Gas Compressor would result in gains that justify the investment (in itself).

Although the increase of ammonia production was the primary justification for the retrofit, either the extended life of the catalyst or the steam savings on the Synthesis Gas Compressor Turbine would also have justified the retrofit.

4. THE MODIFICATIONS TO THE REACTOR

Description of the converter before the retrofit:

The converter consists of a pressure vessel with 3650 mm (143.7 inches) I.D. with a partial opening on the top hemispherical head.

Inside the pressure vessel there is a cartridge hanging on the pressure vessel top flange. The cartridge was provided with a 50 mm (2.0 inches) thick refractory liner attached to the cartridge by means of anchors.
At the center of the cartridge an interchanger is located to pre-heat the gas before entering the axial catalytic bed (see Figure 1).
All the materials of the pressure vessel, cartridge and internals are of low alloy steel.

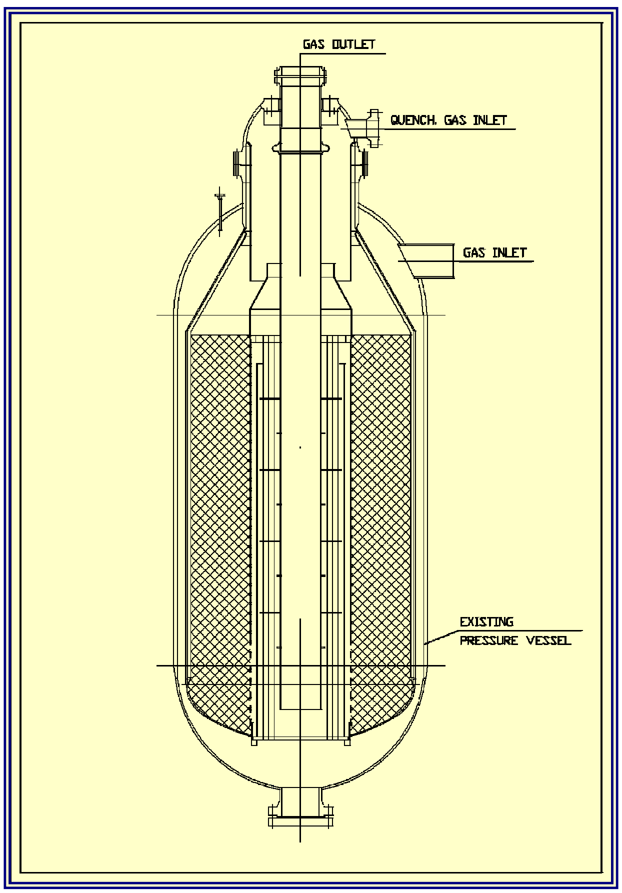

Fig. 1. – The Old Axial Configuration

Description of the New Internals:

The revamp of the converter consists in the "in-situ" modification of the existing unit from an axial bed to the CASALE axial-radial bed.

AMMONIA CASALE has already a long experience in this type of retrofit activity, having modified through the "in situ" modification more then 50 ammonia converters, 8 shift converters in steam reforming plants, and 15 methanol reactors. Also the axial-radial bed has been used widely, in about 150 different reactors, such as ammonia, shift, methanol reactors and pre-reformers.

In an axial-radial catalyst bed the gas distribution is such that most (about 90%) 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 flows downward through a top layer of catalyst in an axial direction, thus eliminating the need for a top cover of the catalyst beds (see Figure 2). This feature is an essential factor for an easy and simple construction of any type of converter internals.

Perforated walls at the inlet and at the outlet control the gas flow through the catalyst, where most of the bed pressure drop is concentrated.

The features of the axial-radial beds lead to several important advantages over the old axial CO shift stages. Among the main advantages to be mentioned are the reduction in pressure drop, the use of smaller size catalyst with consequent better performance of the shift converters and extended catalyst life.

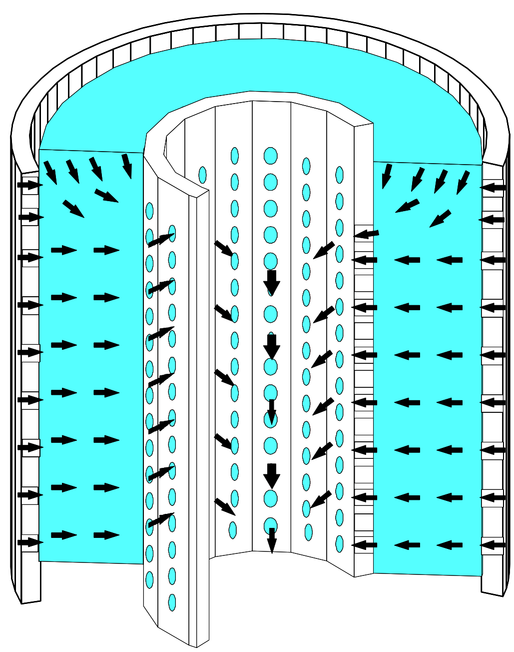

Fig. 2 - Axial-radial Distribution Concept

The modification of the existing equipment into an axial-radial catalyst bed is obtained by the installation of two new cylindrical walls, one external, near the pressure vessel wall, and one internal in the existing converter shell (see Figure 3).

In addition also new thermocouples bundles are installed to monitor the temperature not only at bed inlet and outlet, but also in intermediate positions.

The materials used for the new internals is AISI 304.

It is important to underline that no welding was done on the existing pressure vessel; so all risks of metallurgical nature were avoided.

From the mechanical point of view, the design of the new internals had to consider some problems, principally:

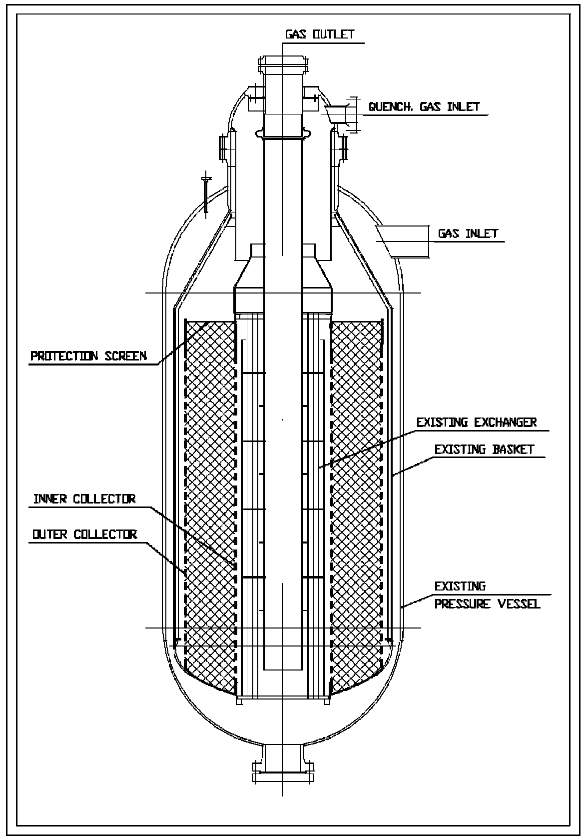

Fig. 3 – New Axial-Radial Configuration

- Absence of supports for the new collectors.
- Presence of refractory that limited the internal diameter of the cartridge (hence limit to the volume of the catalyst).

According to CASALE technology, an outer collector and an inner collector allowing an axial-radial flow characterize the new internals; these two perforated collectors are to be inserted in panels through the top converter partial opening, and then assembled together inside the converter.

The inner collector is connected without any weld to the bottom ring of the cartridge.

The outer and inner collectors are connected to the cartridge in way that allows a free thermal expansion in radial direction with respect to the cartridge.

The existing exchanger was re-used, although it was well-known that it was not in good condition. For this reason, ULTRAFERTIL is planning on changing this exchanger during the next shut down.

The thermowells have been modified in order to measure the new temperature distribution resulting from the axial-radial flow. For this purpose the existing thermowell nozzles were re-used and replaced the portion of thermowells inside the cartridge.

Thanks to the low pressure drop of the axial-radial configuration it has been possible to load smaller size catalyst, namely 6x3 mm tablets instead of the 6x6 mm or 6x9 mm normally used in the axial configuration.

The smaller size catalyst is more active, as evidenced by the low reaction strike temperature at bed inlet, as reported in chapter 7, and has a longer operating life.

5. RESULTS ACHIEVED

The results achieved were better than expected, mainly regarding the pressure drop, which had a value guaranteed by CASALE of 1.1 bars [16 PSI], although the expected value was 0,9. This value before was in between 1,5 and 2,5 bar [21.8 and 36.3 PSI] (Start of run and End of run). The pressure drop today is in the range of 0,6 to 0,8 bars [8.7 to 11.6 PSI], according to the load, and this value has been stable since the start-up. One year after the retrofit the value of the CO slip is in an average of 6,5 volume %. During the start-up, this value was in the range of 5,9 to 6 %. It appears certain that after 2 years this value can be lower than the value predicted by CASALE (7,66%). These good results enable ULTRAFERTIL to get the expected increase of capacity in it's Ammonia plant, and moreover, to keep the average capacity in a higher value than expected, due to the good conditions of the Shift Section in the ammonia plant.

The main result of this retrofit was the significant decrease of the pressure drop of the first reactor. This enabled ULTRAFERTIL to increase ammonia to the desirable value, and this alone justified the investment. Another benefit achieved from the lower pressure drop was the resulting higher pressure improved the operation of the next sections of the plant including the physical absorption CO_2 removal system (Rectisol Process) and N_2 Wash Removal. The higher pressure at the suction of the synthesis gas compressor lowered the steam consumption of its turbine driver.

The expected increased lifetime of this reactor by 0,5 to 1 year is a very important additional benefit and represents a significant improvement to ULTRAFERTIL.

6. THE "SURROUNDINGS' MODIFICATIONS" MADE IN THE PROCESS AROUND THE REACTOR, THE RISK ANALYSES MADE AND THE GOOD RELATIONSHIP BETWEEN CASALE AND ULTRAFERTIL DURING THE FINAL PHASE OF THE DESIGN

These modifications were very important for the success of the whole project and they had played an important role in this retrofit. The driving force that guided ULTRAFERTIL to do the "Surroundings' Modifications", which was a risk analysis of the whole modification. ULTRAFERTIL had a very good experience with this big change. To accomplish this modification successfully a team of operations and engineering personnel was assembled that were very experienced and familiar with the operation of the High Temperature Shift Section. Internal meetings were held that evaluated all aspects of the project with a very defined goal, which was: "We were not allowed to fail in this design."

A Hazop analysis observed all the upset conditions, i.e. more flow, less flow, back flow, more pressure, less pressure, alteration of the composition of the gas, higher steam to gas ratio, lower steam/gas ratio, presence of condensate inside the reactor in shutdowns, carryover of condensate to the steam.

All the past experiences that have caused, or could have potentially caused considered in the Hazop were carefully considered and solutions were found to avoid them. This resulted in adopting many small changes to improve the reliability of this retrofit, such as:

1) Avoid the entry of condensate into the reactor, mainly during shutdowns.

- We have changed the exit position of the 100 bar (1450 PSI) saturated steam from the main header, which is used to control the temperature of the steam used for the shift reaction. ULTRAFERTIL moved this branch connection to the top of the main 100 header. Previously it was from the bottom of the main header.
  We also put one more Steam Trap in this line.

- We have also put some extra drains inside the Shift Section, in order to facilitate the draining procedures before and after shutdowns.

2) Avoid operating the section with a lower Steam to Gas ratio.

- In a Partial Oxidation Plant, usually more than one of the Gasification Reactors are present. These reactors have operating on-stream factors lower than the rest of the entire ammonia plant, and in case of a shutdown, the operators have to actuate them in order to adjust to the new conditions for the whole plant. At ULTRAFERTIL there are three reactors on line, the load will be reduced in one third. In these cases, the operators have to adjust the conditions of the shift reactors. ULTRAFERTIL added some new alarms, besides the one alerting the operators before the steam/gas ratio becomes too low, (that in our case happens before the steam-to-gas ratio decrease), so they can correct some operating conditions in time, before the steam/gas ratio becomes even lower.

3) All operating procedures were carefully reviewed, especially those required to avoid any possibility of steam condensate inside the reactors and, of course the evaporation of this condensate inside the reactors during start-up. Measures to maintain the appropriate steam/gas ratio to the reactor were also revised. These new procedures enable complete control of the pressure and temperature increases inside the HT reactor during the heating up of the unit after long and short shutdowns.

ULTRAFERTIL considered these modifications very important to the success of the whole project, and without them, probably the results would not be as good as we are getting now.

7. CONCLUSIONS

This retrofit, the first one for Partial Oxidation Plants, was very successful, and is providing ULTRAFERTIL with a smooth operation of this very important section of an ammonia plant. After one year we are operating the reactor with an inlet temperature lower than 340° Celsius (644 °F). We started up with 325° Celsius (617 °F), which is a clear indication of the good stability of this design. Regarding the catalyst lifetime we are expecting 2,5 years, which is in accordance with the maximum operating time without planned shutdowns in our ammonia plant. The lower pressure drop made it possible to increase the gas flow and the average ammonia production as well. The stability of the reactor after one year, made ULTRAFERTIL more confident to guarantee the ammonia production in a higher average value. So, it is important not only to produce more, but also to produce more in an extended time.