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CASALE Technologies for Ammonia and Methanol Plants based on Partial Oxidation

by
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for presentation at
NITROGEN & SYNGAS CONFERENCE & EXHIBITION
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Abstract

The production of ammonia and methanol in partial oxidation plants is becoming every day more important. The operating conditions of these plants are, however, more severe than those of the steam reforming based plants. CASALE has in its portfolio the right designs for the shift and the synthesis section, to ensure the best plant efficiency, reliability and availability.

1) INTRODUCTION

Today, most of the world's ammonia and methanol production is still achieved by reforming of natural gas. However, partial oxidation of carbonaceous feedstocks with oxygen is becoming increasingly important, both in the form of coal gasification and partial oxidation of natural gas. Different reasons drive the success of these two alternative routes.

The recently improved attractiveness of coal gasification can be attributed to the increasing price and the decreasing availability of natural gas, the abundance of low cost solid feedstocks, and the major advances in the gasification technologies, including the downstream gas conditioning and synthesis sections.

On the other hand, many forecast that also the partial oxidation of natural gas will gain much importance in the near future, especially in gas-rich countries, since this process allows significantly larger single-train production capacities than the traditional reforming, hence with further improved economies of scale.

The future is bright for these technologies. Nevertheless, they also present significant technical challenges: in fact, all partial oxidation processes yield a much more reactive syngas, which provide the opportunity to reduce equipment size and energy consumption, but otherwise entail more severe operating conditions especially in the CO-shift and synthesis sections of the plant.

Therefore, the necessity arises for adequate technologies and experienced designers, to guarantee the best efficiency, availability and reliability of the partial oxidation ammonia and methanol plants.

CASALE, world leader in the design of converters, has the perfect technologies for the CO-shift, ammonia and methanol synthesis sections in partial oxidation plants.

This paper summarizes the tailor-made solutions that CASALE has introduced to take full advantage of the peculiarities of the synthesis gas generated with this process, while enhancing the plant attractiveness with premium reliability and availability.

2) ADVANCED CO-SHIFT TECHNOLOGY: CASALE AXIAL-RADIAL CONVERTERS

Due to the reaction with oxygen and the high outlet temperature, the partial oxidation plants yield a syngas with a much lower H_2:CO ratio than the traditional reforming plants, i.e. a syngas with more CO. Depending on the desired product, methanol or ammonia, partial or full conversion of the CO is needed: hence the two processes have different needs for their shift section.

The ammonia process requires maximum conversion of carbon monoxide to hydrogen, for maximum ammonia production at a given syngas capacity.
This is generally achieved by carrying out the shift conversion reaction in multiple reactors, (two or three), with intermediate cooling. Staging is also required by the high CO content, which entails a large temperature rise across the converter, especially the first bed. Addition of nitrogen in the stoichiometric amount occurs in the downstream nitrogen wash unit.

The methanol process, instead, requires that only a fraction of the CO feed is converted to hydrogen, to achieve a balance of hydrogen and carbon oxides at the inlet to the synthesis loop. One or two shift converters are usually installed. Removal of the excess carbon dioxide (and H_2S, in coal gasification plants) occurs in the downstream acid gas removal unit.

It is apparent that the best design of the CO-shift section (and converters) holds a great importance for the efficiency and reliability of the ammonia and methanol plants, bearing in mind that it features more converters in series.
Especially for large plants, the shift section should guarantee a low pressure drop during the entire life of the catalyst, to minimize the power consumption of the downstream syngas compressor. Moreover, the shift converters' design must be mechanically robust and adequate to the challenging reaction environment.

The CASALE design for shift converters successfully provides these and other advantageous features, through the application of the renowned axial-radial concept (see Figure 1).

The advantages of the axial-radial over the traditional axial-design converters have been already demonstrated in over 600 beds designed by CASALE to date, in all kinds of services: CO-shift (high and low temperature), sour shift, pre-reformer, ammonia and methanol synthesis.

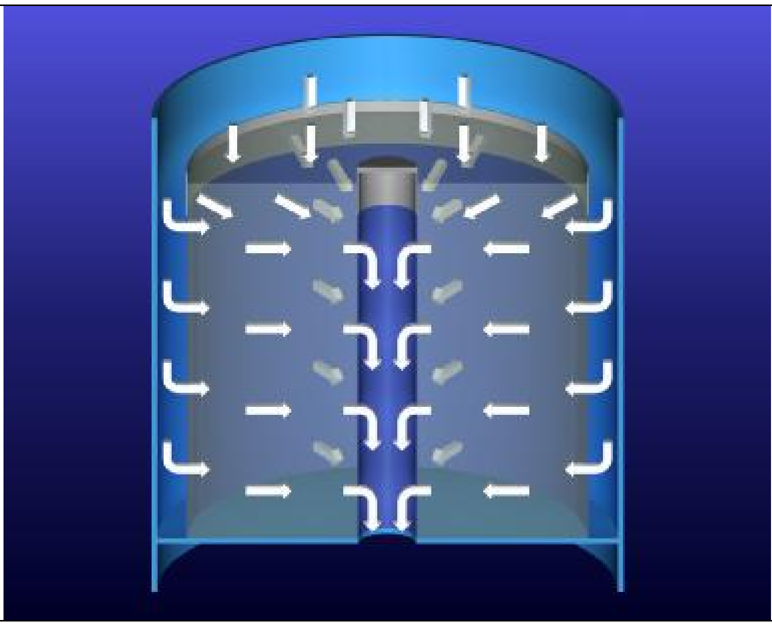

Fig. 1 - CASALE axial-radial catalyst bed

In the axial-radial concept, the distribution of the gas is achieved by the perforated walls, which ensures a low pressure drop, stable with time as the catalyst ages or deteriorates, irrelevant also to caking of the catalyst top layer due to water droplets carry-over. Hence, by ensuring a higher suction pressure to the compressor through the catalyst life, it achieves a higher production rate.

Moreover, since the pressure drop is unaffected by the catalyst, premature change of the catalyst batch is avoided: the life can easily reach and exceed 4 years, even in the case of the first (sour) shift converter, which is the one operating in the most severe conditions.

The major feature of the CASALE axial-radial concept is the low pressure drop, which allows designing the converter with a much slimmer pressure vessel than the axial design would require, and a consequently thinner pressure vessel wall. This can result in significant capital cost saving, especially with regard to the first shift converter. Due to the high operating temperature, an axial bed must be designed either with a SS cartridge, and an annulus for flushing the pressure vessel, or with a refractory lined vessel. Instead, the axial-radial bed with inward flow, keeps the hot gas at the center of the converter, away from the vessel wall, so that only the outlet nozzle is exposed to high temperatures, allowing a much easier, cheaper and robust construction.

Further to the axial-radial design of the converters, the CASALE process design can greatly improve and simplify the heat integration of the shift section.
Intermediate cooling between the converters provides the opportunity to increase the plant efficiency by recovering high-grade heat, e.g. by raising and/or superheating steam. Normally, an external converter feed-effluent exchanger is installed, to control the inlet temperature to the axial shift converter, and a heat recovery is placed at the converter outlet, as shown in Figure 2.. This arrangement requires hot lines at the converter inlet and outlet.

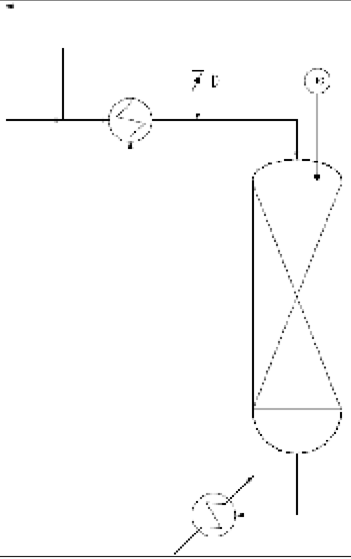

Figure 2 - Heat recovery downstream axial shift converter

The axial-radial design for shift converters, on the other hand, leaves an empty zone at the center of the vessel which can be very conveniently used to place the feed-effluent exchanger, as shown in Figure 3.

This leads to superior performances, and significant mechanical and cost advantages: the pressure drop is lower for the axial-radial bed of the converter and the compact design of the section; hot lines are avoided, since the highest temperatures are confined within the shift converter; finally, the investment cost is lower thanks to the absence of the external gas-gas shell and hot connection piping.

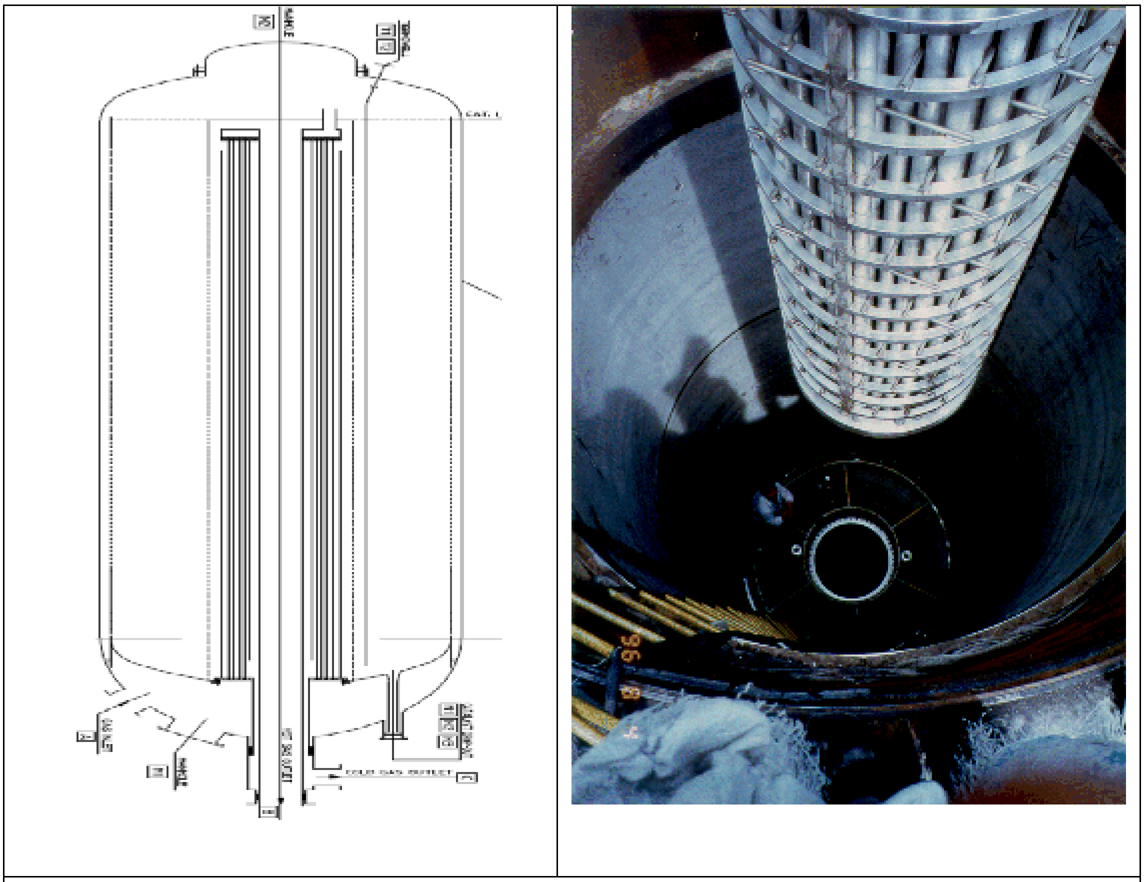

Figure 3 - Axial-radial shift converter and internal heat exchanger

CASALE Shift Converters: A Successful Experience

CASALE's experience with axial-radial shift converters is a successful one, as it has always been for the other services to which this concept had been applied in the past.
The axial-radial bed concept has already been applied to 22 shift converters, including HTS and LTS in steam reforming plants, HTS in POX plants and Sour Shift converters, while 11 more are under construction.

Out of these 22 units in operation, two are HTS in partial oxidation plants, while three are sour shifts, first and second converters.
The two HTS in POX plants are revamps of existing axial units (see Figure 4). The revamping, in both cases had been done to reduce the old units pressure drop, and to avoid that the pressure drop would depend on the age of the catalyst.

Figure 4 - Revamping of a POX HT shift converter in Brazil

The three sour shift converters are in operation in coal gasification plants in China already four years now.

Among the 11 units under construction, three are sour shifts in coal gasification plants, two are the first and second converter in a new plant in the U.S.A., while the third is in China, and it is a first converter.

3) ADVANCED METHANOL SYNTHESIS TECHNOLOGY

Compared to the methanol plants based on reforming, the synthesis gas produced by partial oxidation, after conditioning, is much more reactive. It has a stoichiometric ratio generally lower than two (i.e. a slight excess of carbon oxides) and very low inerts concentration. In coal gasification plants, it may also contain some traces of poison, which should be prevented from reaching the synthesis loop.

Hence, the synthesis loop and converter must be designed adequately, to benefit of the advantageous gas composition, but also to ensure the proper resistance to the challenging environment.

CASALE has developed and refined an advanced design for the synthesis loop and converter in partial oxidation plants, which is perfect for the task: it provides several key features to cope with the peculiar operating conditions, the combination of which allows the best efficiency and reliability.

The main feature is obviously the CASALE Isothermal Methanol Converter (see Figure 5), characterized by the fact that the catalyst bed is cooled by hollow plates immersed in the catalyst, containing a cooling fluid.

In partial oxidation plants, the reactivity of the synthesis gas is very high, hence the converter must be provided with an adequate heat sink, to control the reaction temperature. This heat sink is boiling water at about 30 bar, that matches well with the operating temperature in the catalyst bed. Moreover, the steam produced can be usefully utilized in the plant steam turbines.

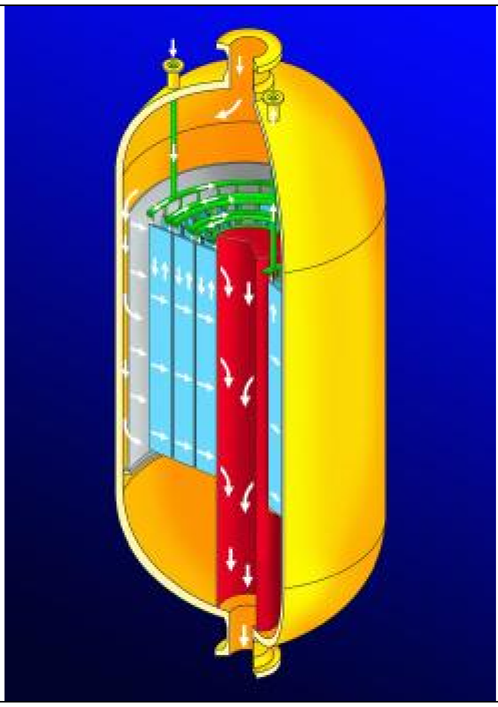

Figure 5 - CASALE Isothermal Methanol Converter

These CASALE IMC converters are perfectly suited for the partial oxidation application, for the very effective cooling of the catalyst, the reliable and simple mechanical construction, the absence of tube-sheets, as well as the easy catalyst loading and unloading. Provided with axial-radial design of the catalyst bed, the IMC converters are suitable for very large capacities in a single vessel.

This design is well-proven already for capacities exceeding 3’000 MTD in a single unit.

A tremendous advantage of the IMC design is the control of the temperature profile in the catalyst, which allows the increase of the conversion per pass in the reactor, the reduction of the peak temperature of the catalyst, and the optimization of the design of the equipment external to the reactor.

Secondly, a Hydrogen Recovery Unit is provided on the loop purge gas, to recover hydrogen back to the make-up gas, and optimally balances the make-up gas for methanol synthesis. An excess of carbon oxides would, in fact, compromise the catalysts selectivity and operating life.

The high carbon monoxide concentration entails also the potential formation of carbonyls, such as iron and nickel. Once formed, they decompose on the catalyst reducing its activity and promoting undesired side reactions. The CASALE design is resilient to formation of carbonyls by utilizing appropriate, higher grade types of steel, in the areas where carbon monoxide concentration is high and the temperature is roughly in the range of 100 to 200°C.

In coal gasification plants, the make-up gas could contain poisons for the synthesis catalyst, such as sulfur and arsenic. These compounds should be washed away in the gas conditioning upstream the synloop. However, the CASALE design usually includes a guard to absorb these dangerous substances from the make-up gas, in the event of upset, mal-operation or under-performance of the upstream treatment units.

The low inerts concentration, balanced syngas and high $CO:CO_2$ ratio, on the other hand, provide partial oxidation plants a tremendous opportunity to achieve high production rates with low recycle ratios and catalyst volumes. Of course, the converter design must be adequate: in fact, as the gas is very reactive it can easily create problems of catalyst overheating and hot spots in the converter.

The CASALE synthesis loop is very simple, as illustrated in the flow sheet (Figure 6).. It features a single synthesis converter, a gas-gas exchanger to preheat the converter feed, a methanol condenser, a liquid methanol product separator, a hydrogen recovery unit from the purge gas, a syngas compressor and a circulating compressor.

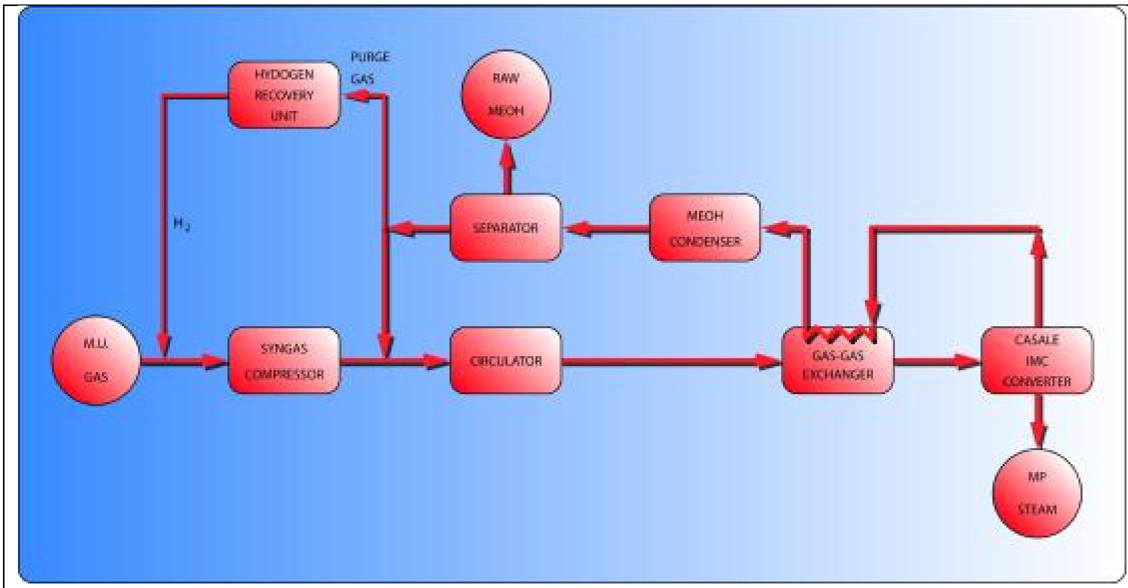

Figure 6 - CASALE methanol synthesis loop from partial oxidation gas

There are seven main items overall, to which a guard bed may be added on the make-up gas, for protection from possible spikes in poisons content.

The efficient CASALE synthesis converter and synloop achieve high syngas conversion with very low recycle ratio, enabling a smaller size for the loop items: CASALE can achieve very large methanol capacities in a single train, up to 10’000 MTD or more.

CASALE Experience With IMC Converters

Two CASALE Isothermal Methanol Converters are already in operation in coal-based gasification plants in China, with design capacities of 1350 MTD and 2000 MTD, all with very satisfactory results.

Eight more IMC converters from coal gasification are in various phases of engineering, construction and commissioning, the biggest with a 3’000 MTD methanol capacity, and all of them are single-vessel converters. The next start-ups are scheduled in early 2010.

4) ADVANCED AMMONIA SYNTHESIS TECHNOLOGY

Similar to the methanol synthesis loop, also the ammonia synthesis section in partial oxidation plants has peculiar features that should be considered and exploited in the design.

Firstly, the ammonia make-up gas is free of inerts, due to the low outlet methane from the POX or coal gasifier. Moreover, if the H_2/N_2 ratio is adjusted in a nitrogen wash unit, this section condenses out all residual methane and argon, thus producing an inert-free synthesis gas.

This fact is positive because high conversion per pass can be achieved, and no purge (or a very small flow rate) needs to be drawn from the synthesis loop.

However, special care in the design of the synthesis converter and heat recovery exchangers in the synloop is also required, because a higher operating temperature may be reached within the converter and at its outlet.

The CASALE technology for this section of the plant relies on the ammonia synthesis converter with three adiabatic beds with two interchangers, as shown in Figure 7..

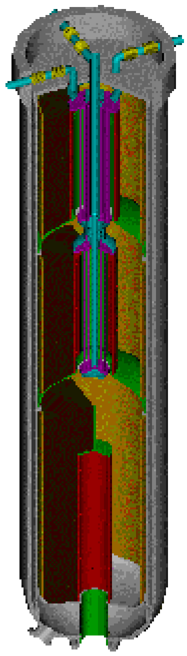

Figure 7 - CASALE ammonia synthesis converter

The three catalytic beds have axial-radial flow, to minimize the nozzle-to-nozzle pressure drop.
The CASALE design for the ammonia synthesis converter has already proven its performance and reliability, on the grounds of the following key concepts:

- the axial-radial flow in the catalyst beds ensures an optimal distribution of the gas in the catalyst, avoiding any hot spots, and full utilization of the catalyst;
- the temperatures in each of the beds is controlled independently, to keep the converter optimized in any operating conditions;
- the materials of construction used for the internals, i.e. SS 321 and Inconel 600, are chosen for their resistance to nitrading and hydrogen attack;
- all the internal parts are connected with sliding joints, allowing unrestricted differential thermal expansions, and are free from leakages due to material aging;
- the pressure vessel is flushed with cool gas, ensuring that it is not subject to embrittlement due to nitrading, which may lead, in the long run, to cracking;
- the converter effluent is directly conveyed to the downstream exchanger, which is be lip-sealed to the converter, thus eliminating the hot converter outlet pipe, and allowing the use of safer horizontal exchangers.

Altogether, the ammonia synthesis loop for partial oxidation plants is not significantly different from the reforming plants, except for the better overall performances (lower recycle rate, no purge, higher specific heat recovery) and the higher grade materials required inside the synthesis converter.

The selection of the most suitable heat recovery in the ammonia synthesis section of a partial oxidation plant is mainly driven by the overall steam balance. The low recycle rate and high converter outlet temperature allow for high-grade heat recovery, such as steam superheating. In this regard, CASALE has its own proven design for steam superheaters, waste heat boilers and boiler feed water preheaters.

CASALE Experience with Ammonia Synthesis Converters

CASALE is by far the most successful ammonia synthesis converter designer supplier in the world.

CASALE has supplied 150 three-bed converters (new and revamped units), several with capacities exceeding 2’000 MTD.

Moreover, CASALE has supplied or is supplying 25 ammonia synthesis converters for synthesis loops from coal gasification, with capacities ranging from 625 to 2030 MTD.

6) CONCLUSIONS

Producing ammonia and methanol from partial oxidation is very promising, but it requires a different technological approach than the one adopted for traditional reforming plants.

CASALE has developed dedicated solutions to minimize the cost and energy consumption of the CO-shift section, and to take full advantage of the reactivity of the make-up gas in the synthesis sections, while at same time ensuring the best availability and reliability.

Application of the CASALE axial-radial design to the shift converters enables to minimize the section pressure drop and stabilize it with time. Moreover, the slimmer pressure vessel design reduces the capital investment, while the inward gas flow limits the hot temperature zone within the converter except for the outlet nozzle. Equipping the shift converter with an internal heat exchanger generates further cost reduction, mechanical reliability improvement and a flow-sheet simplification.

The CASALE ammonia and methanol synthesis loops are simpler and smaller in size than the traditional reforming units.

The CASALE ammonia and methanol converters cope effectively with the more active gas, higher temperature and the low circulation, thereby providing a significant increase in the plant efficiency, reliability/availability and single train maximum capacity.