
Grass-roots Casale methanol plant

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DISTINCTIVE TECHNOLOGIES FOR METHANOL PLANTS

The Casale Group has a worldwide reputation as the leader in the revamping of existing fertilizer and methanol plants of any kind. More recently, Casale has applied its advanced technologies also to the design of new grass-roots methanol plants with capacity up to 7,000 t/d in a single train. This paper provides an overview of Casale's most distinctive technologies in the methanol field, their application to new methanol plants, and their prominent role in the trend to ever larger single-train plant capacities.

Casale background

The Casale Group has been active in technology development and engineering since 1921, when Dr. Luigi Casale developed one of the first processes for the synthetic production of ammonia, and founded Ammonia Casale. Over the years, the company has diversified and presently the Casale Group is formed of four companies (Ammonia Casale, Urea Casale, Methanol Casale and Casale Chemicals), offering its services in the fields of ammonia, urea, methanol and derivatives production. From the very beginning, the success of the Group was linked to its ability to develop innovations and introduce them to the market. This trend has been preserved and nurtured as central to the company's culture by subsequent management teams.

Casale Group's innovative concepts have found wide acceptance in the market, making a great contribution to the progress of the ammonia, urea and methanol industries. Methanol Casale was established in 1994 to resume the activities in the methanol field and rapidly achieved very successful breakthroughs. At the beginning, Methanol Casale concentrated on revamping synthesis reactors and it soon became leader in the design of methanol synthesis reactors.

As it has gained experience, Methanol Casale has also become a leader in revamping complete methanol plants and in designing new ones. Key achievements in plant upgrading include capacity increase, reduced specific consumption, and improvement in the quality of the raw methanol. Methanol Casale has also recently designed grass-roots plants, including the world's largest plant with a capacity of 7,000 t/d, most of which are already in operation.

These plants incorporate Casale's most advanced technologies, such as the IMC (Isothermal Methanol Converter). This is the ultimate step in terms of converter efficiency, which makes it possible to design very large methanol units, with capacities of 7,000 t/d and more, in a real single train and with a single vessel converter. This paper presents Casale process design for large methanol plants using natural gas as feedstock. Moreover, it focuses on the application of Casale technologies in these plants, their distinctive features and their importance to increase single-train capacities, to lower capital and operating costs, and to improve the plants operability and reliability.

Casale process for large methanol plants

A conceptual analysis of the main process steps involved in the synthesis of methanol is important to understand the basis for Casale's technology applied to large methanol plants.

The production of methanol from natural gas includes three main sections:

- synthesis gas generation
- raw methanol synthesis
- methanol distillation.

It is by optimizing the process scheme for each of these sections, and using its advanced technologies, that Casale can supply the largest single-train methanol plants with best performances and highest reliability. The flowsheet of the Casale advanced methanol process is shown in Fig. 1.

Synthesis gas generation

The first step to methanol production is the conversion of natural gas to a mixture of hydrogen and carbon oxides (syngas), either by catalytic steam reforming, or by catalytic partial oxidation, or by a combination thereof. The three methods yield different qualities of syngas.

The methanol synthesis reaction requires that the amount of hydrogen and carbon oxides in the syngas is properly balanced, to minimize the consumption per unit methanol production rate.

In the *Pure Steam Reforming Process*, the syngas is generated only by reforming of natural gas with steam, according to the steam reforming and shift reactions.

The pure reforming process yields a H_2-rich syngas, therefore not suited for methanol synthesis unless a stream of CO_2 is available to balance it (which is usually not the case).

This scheme is characterized by a large steam reformer or multiple parallel reformers if the capacity is higher than 2,500-3,000 t/d. Moreover, the excess of H_2 in this process route makes it inefficient and unattractive for large plants. The *Pure Autothermal Reforming Process* generates the syngas by partial oxidation of the feed with oxygen from an Air Separation Unit (ASU). Opposite to the steam reforming route, the syngas generated by the ATR process is H_2-poor: to adjust its composition, it is necessary to draw a relatively large purge stream from the loop, and treat it to recover its hydrogen content. The pure ATR scheme requires much oxygen (about 0.7 t/t MeOH), to be produced in a large ASU. The total natural gas consumption is lower than the pure reforming scheme.

The *Combined Reforming Process* (shown in Fig. 2) combines the advantages of the two schemes outlined above, and it is the flow scheme adopted by Casale for the syngas generation in large methanol plants.

All the feed natural gas is pre-reformed. The pre-reformed feed is then split in two fractions, one sent to the steam reforming while the second by-passes the steam reforming. An Auto-Thermal Reformer (ATR) blown with oxygen from an Air Separation Unit (ASU) is installed downstream the primary reformer to process the reformer effluent and the by-pass. The syngas generated by this process is already balanced for methanol synthesis. However, a HRU (Hydrogen Recovery Unit) is provided to further reduce the size of the primary reformer.

The Casale front-end scheme, based on the combined reforming concept, features a smaller ASU than the pure ATR process, thanks to the lower oxygen consumption, and lower gas consumption. The primary reformer is relatively small, and can be built as a single unit for plant capacities higher than 7,000 t/d.

Raw methanol synthesis

The make-up gas is transformed into crude methanol in the synthesis converter, which is the core of the methanol plant. The conversion of syngas to methanol is only partial, due to the equilibrium limitation, hence the reactor effluents must be recycled to the synthesis converter along with fresh make-up gas after separation of the raw methanol product.

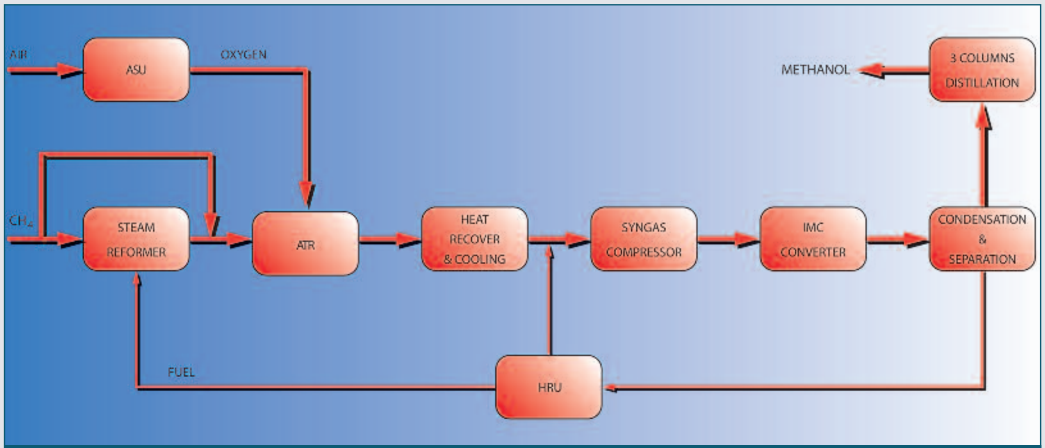

Fig. 1 - Advanced Casale methanol process

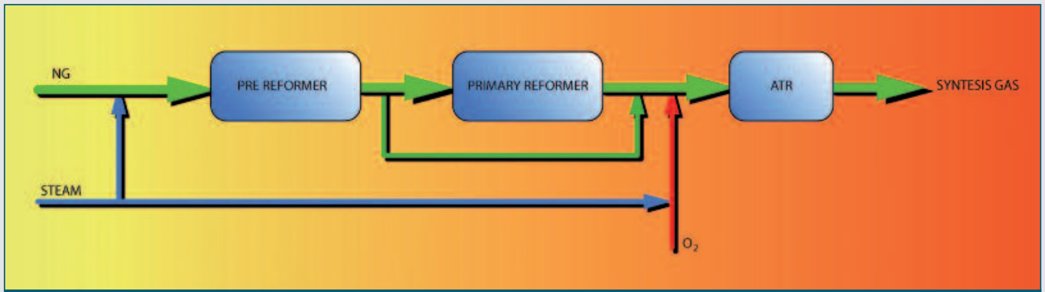

Fig. 2 - Syngas generation by combined reforming

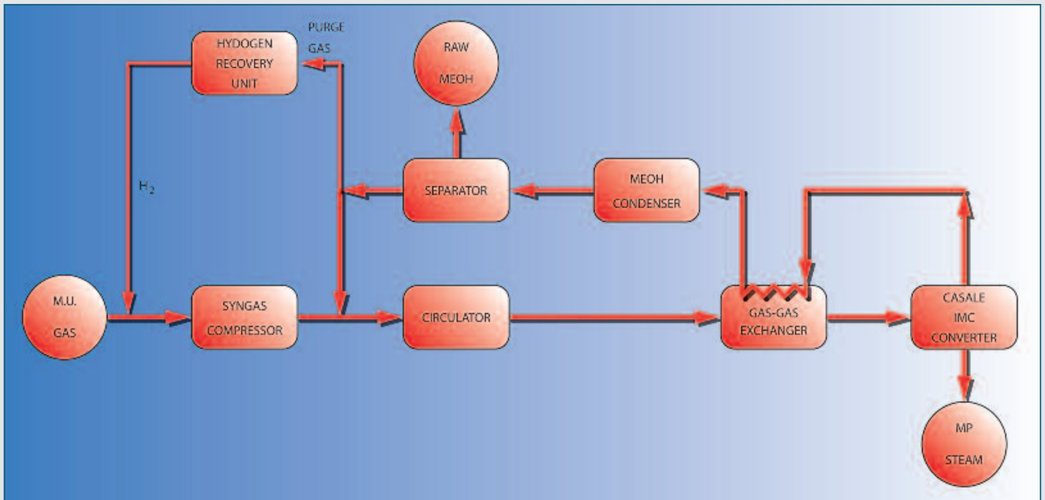

Fig. 3 - Casale synthesis loop

The Casale synthesis loop is very simple, as illustrated in Fig. 3. 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.

The core of the Casale synthesis loop is the IMC (Isothermal Methanol Converter): this is the ultimate converter generation, which achieves a very large methanol capacity with a single vessel converter.

The synthesis of methanol is exothermic, limited by the equilibrium. The lower is the temperature, the more favorable the equilibrium methanol concentration. On the other hand, high temperatures promote faster reaction kinetics. An ideal converter follows the maximum rate curve and achieves the highest conversion by removing the reaction heat from the catalyst mass at a controlled rate in the catalyst bed. This is exactly what the Casale IMC plate-cooled converter does.

The Casale IMC synthesis converter and synloop achieve high syngas conversion with low recycle ratio, enabling a smaller size for the loop items.

Distillation section

The crude methanol typically needs to be purified to reach the specification required by the specific application.

To reach AA grade methanol, the final purification is performed in two steps: the topping column separates the lighter compounds from the liquid mixture, while the refining section provides the final separation of water and higher ends from the pure product. The refining section is split in two separated columns, one under pressure and one atmospheric, which is the arrangement achieving the least distillation energy consumption.

The arrangement of Casale three-column distillation is shown in Fig. 4.

Distinctive technologies in large methanol plants

Casale has deeply optimized its methanol process scheme. However, it is the application of its distinctive technologies that allows the outstanding features of the methanol plant in the most efficient and reliable way.

The Casale technologies applied in the new large methanol plants are the Pre-Reformer, the Autothermal Reformer and the IMC Synthesis Converter, all described in this section of the paper.

Pre-reforming reactor technology

Casale's pre-reforming reactor is designed according to the axial-radial technology for catalyst beds, as shown in Fig. 5 and 6.

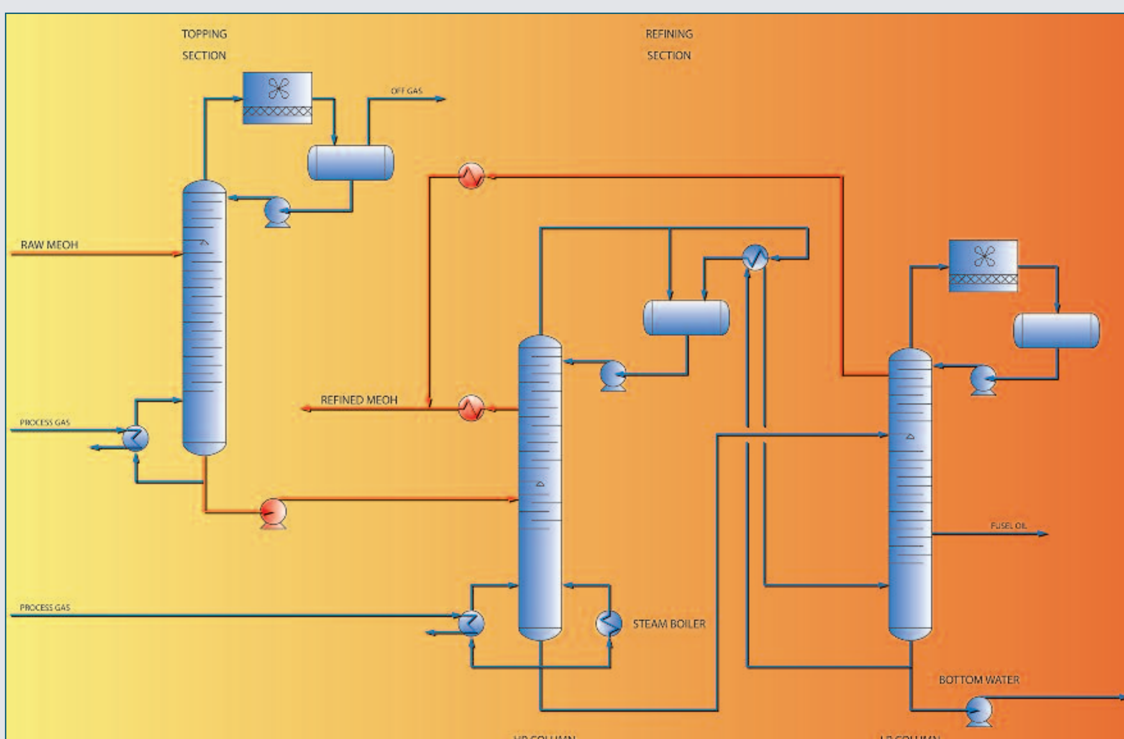

Fig. 4 - Casale three-column distillation

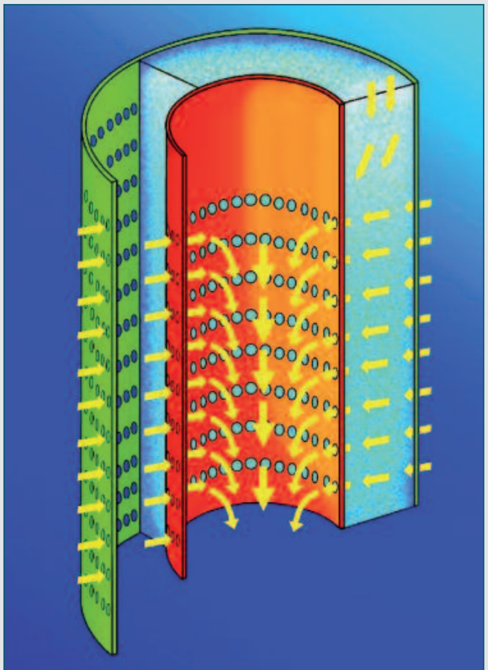

Fig. 5 - Casale axial-radial catalyst bed

Fig. 6 - Casale axial-radial Pre-Reformer

The Casale axial-radial technology is extensively applied in ammonia and methanol plants, having been used in more than 500 (five hundred) catalyst beds.
In an axial-radial catalyst bed as in Fig. 5, most of the gas crosses the catalyst bed in a radial direction, resulting in very low pressure drop. The balance passes down through a top layer of catalyst in an axial direction, thus eliminating the need for a top cover on the catalyst bed.
This layout overcomes the main drawback of axial design, i.e. the limitation in the maximum capacity that can be reached in a single converter, due to the high pressure drop across the bed.
The essential advantages of the axial-radial concept are:
- low pressure drop, stable with time and not controlled by the catalyst bed;
- full utilization of catalyst volume installed;
- possibility to use small size catalyst, more active and more resistant to poisons;
- lower operating temperature of the vessel wall, when the reaction is exothermic (e.g. shift, methanol and ammonia synthesis);
- possibility to design slim vessels, with important capital cost saving especially when high grade construction materials are required, and no size limitations.

Casale axial-radial design ensures a perfect gas distribution on the reacting side, controlled by perforated walls (the inlet and outlet collectors). Since the gas distribution is controlled by the walls and not by the catalyst bed, it is not affected by the catalyst aging, catalyst uneven loading, poor distribution or deterioration. At the same time, the gas pressure drop is low and stable throughout the life of the catalyst.
Another advantage of the axial-radial design, specific for pre-reformers, is that the small-size catalyst has higher sulphur resistance and higher activity: as a consequence, the catalyst volume is reduced for the same life, with consequent cost saving.
The axial-radial pre-reformer is a distinctive element in Casale's scheme for new large methanol plants, achieving several important benefits.
The pre-reformer protects the plant against coke formation in the primary reformer feed preheat coil and catalyst tubes inlet, by destroying the higher hydrocarbons contained in the natural gas, stabilizing the feed and avoiding coke formation upstream the reformer and ATR: this increases the plant reliability. Moreover, steam reforming of the feed partially occurs in the pre-reformer, thereby reducing the load on the primary reformer.
The pre-reformer also allows reducing the steam/carbon ratio, which lowers the energy consumption, and to increase the pre-heating temperature of the pre-reformed stream, with consequent further reduction of the radiant duty (and cost) of the primary reformer.

Fig. 7 - Casale ATR burner

The first Casale axial-radial pre-reformer is successfully in operation since 2000 in a revamped plant in Brazil. Three more units were installed in the following years, both in ammonia and methanol plants.

Auto-Thermal Reformer Technology (ATR)

The ATR is characterized by a special Casale design to achieve a perfect mixing between oxygen and gas, obtaining a very good combustion. The combustion chamber design of the Casale ATR unit is conceptually very simple. The oxygen stream is introduced at a high velocity axially at the top of the combustion cylindrical chamber. The process gas is introduced from one side at the top of the cylindrical chamber, before the burner tip. The high velocity of the oxygen increases mixing between the two and reduces the flame length since the combustion reaction takes place instantaneously after mixing. A short flame avoids impingement on the catalyst surface that would result in destroying its top layer with consequent performance decrease and high-pressure drop.

The fluid-dynamic field inside the combustion chamber is designed to protect the refractory lining from the high temperature core of the flame, preventing hot spots on the lining surface.

The burner is provided with a water-cooling system derived from the well-proven system adopted in the more demanding Casale POX burner. This design, which is in service in methanol and ammonia plants, has the following features:

- high reliability and long durability, with several years of operation with no deterioration;
- high efficiency of conversion of methane to syngas, thanks to the uniform field of temperature and composition;
- longer lasting performances of the catalyst, thanks to the short flame length avoiding impingement and damages on catalyst surface;
- total absence of soot formation, as evidenced by the analysis and inspections on ATR catalyst and downstream equipment;
- wide flexibility: it has been successfully operated at temperature conditions, composition and flow rates far from the design ones.

The first unit of the Casale ATR was put in service since November 2001 in a Methanol plant in China. The picture in Fig. 7 was taken during burner installation. Since then, several others have been installed or are under construction.

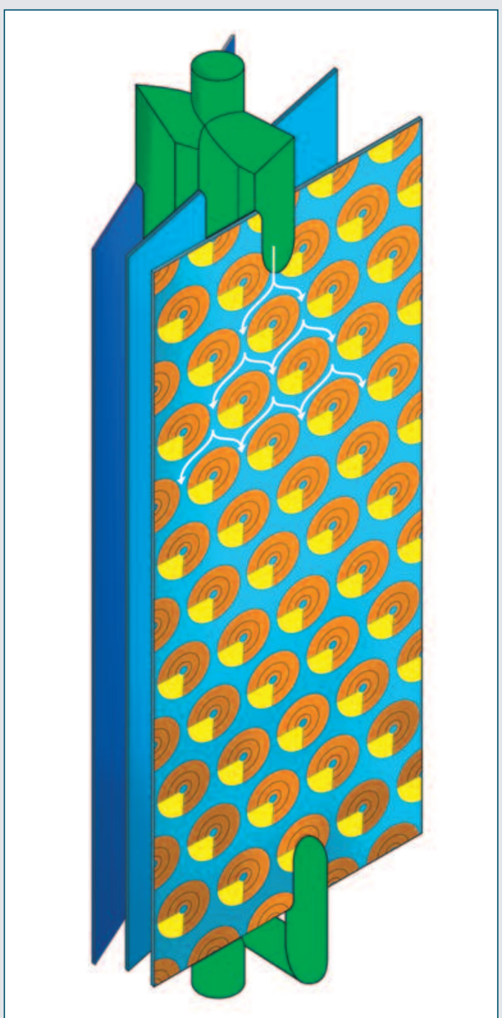

Fig. 8 - Casale IMC converter plates

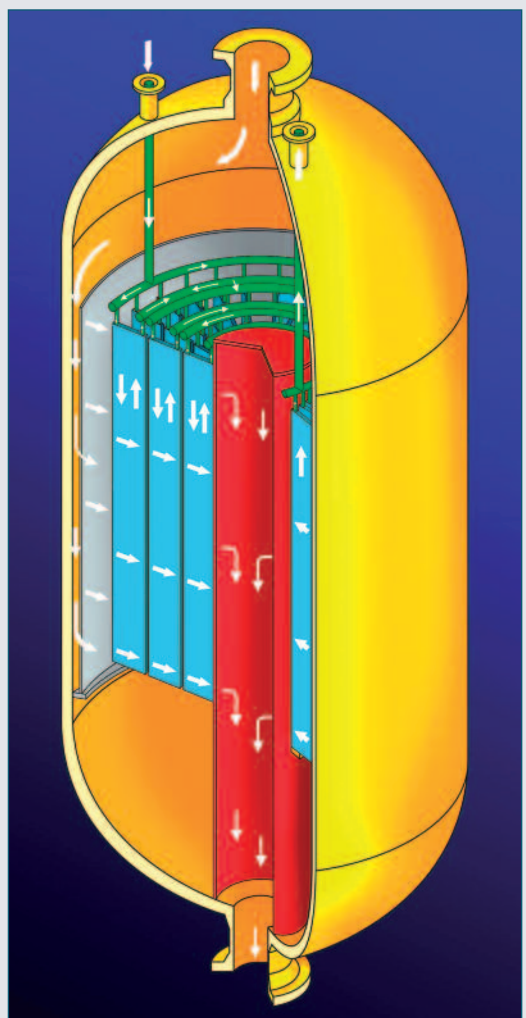

Fig. 9 - Casale axial-radial IMC converter

Isothermal Methanol Converter (IMC) Synthesis Technology

The synthesis converter in the Casale process is designed according to its most advanced methanol converter design: the IMC (see Fig. 8 and 9).

The IMC is a pseudo isothermal converter in which the heat transfer surfaces are plates, and the catalyst is loaded outside the cooling plates. The Casale IMC design was first applied to methanol synthesis in 2002, and has achieved important successes in the last ten years.

The IMC design has the following main characteristics:

- the heat removal from different parts of the catalytic bed can be adjusted independently, enabling a perfect control the temperature profile in the catalyst mass, and operation of the converter according to the highest reaction rate temperature profile;
- heat can be removed directly from the catalytic bed, without the need of tube sheets;
- the catalyst bed is continuous, supported by a layer of inert material, so it can be easily loaded from the top and unloaded from the bottom, through drop-out pipes;
- the converter can be designed with

Casale axial-radial flow configuration, to benefit of the features of this superior technology.

Thanks to the above features, it is possible to reach the maximum efficiency for given operating conditions and reaction volume, to minimize the size and number of the loop equipment and pipes, and optimize the energy consumption and size of the front-end. The construction of the converter internals is conceived so that there is no tubesheet, therefore there is no constraint in the converter size, and the construction is light, consisting of a normal pressure vessel containing the catalyst bed and the plates.

The plates are obtained in an automatic production process consisting in their welding with a laser controlled by a computer. This results in a very high quality consistency, where the manual input is minimal.

The advantage of the IMC design is to overcome the traditional limitations, allowing much higher production rates in a single converter, to introduce a new concept in reliability and catalyst handling, and to allow a better temperature control in the catalyst mass, increasing the operating life of the catalyst charge. Alternative configurations of IMC can be designed, since the flow path can be axial or axial-radial, while the cooling fluid flowing inside the plates can be the fresh converter feed gas, water or other heat transfer fluid. A combination of different fluid is also possible.

For large methanol plants, the most suitable type of IMC converter is the axial-radial converter, with boiling boiler feed water inside the plates, such as the picture shown in Fig. 10. The bed is axial-radial. Several plate-shaped heat exchangers are dipped in the catalyst mass, in multiple rounds, and crossed by water, which is heated at the expense of the reaction side generating medium pressure steam (approximately 25-35 bar). A pump circulates the water/steam mixture through the cooling plates.

The catalyst temperature is controlled by changing the saturated steam pressure according to the process requirements (i.e. catalyst deactivation).

The fluid in the plates is boiling water, flowing axially. Since the water is saturated, there is no concern about cross-flow between gas side and cooling side, as the water-steam temperature is the same in every section of the plates. The plates distribution system is designed to achieve the desired distribution with any operating condition. The Casale loop arrangement proposed for large capacity methanol plants features a single, axial- radial, steam generating converter, entailing two major benefits: the reaction heat is entirely recovered to generate steam, maximizing the synloop heat recovery, and the gas only crosses one axial-radial catalyst bed, therefore the converter pressure drop is well below 1 bar. Another advantage of the Casale synloop is that, since the converter diameter is only marginally influenced by the circulation (at a given capacity and make-up condition), the loop recycle ratio can be optimized to maintain a low syngas consumption both with fresh catalyst (SOR) and "spent" catalyst (EOR). Other designs with axial converters, instead, are forced to use low recycle ratios to contain the vessels size, and may suffer a penalty in capacity at EOR.

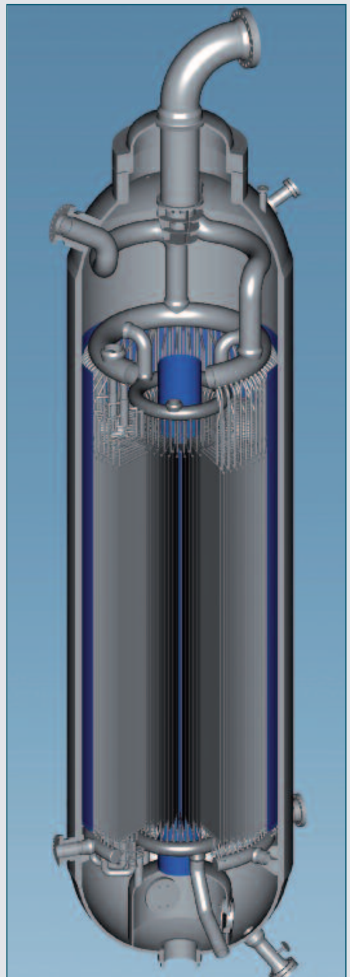

Fig. 10 - Casale IMC for large methanol plants

Conclusions

Thanks to its innovative design and its distinctive technologies, the Casale Advanced Methanol process has outstanding performances, such as a total energy consumption lower than 6.7 Gcal/MT of produced methanol (including the ASU).

The efficiency of the plant is also reflected in the minimum consumption and size of the utilities plant, particularly the cooling towers. Another important feature of the Casale scheme is that the size of all the main plant items is not critical for the construction and/or the supply of a plant with capacity of 7,000 t/d or more, especially as regards the steam reformer, the Air Separation unit and the syngas compressor. With Casale IMC design, even more than 10,000 t/d can be achieved in a single pressure vessel. These outstanding features of the Casale technology make it economically attractive to build plants with very large capacity, 7,000 t/d and higher, in a real single line.

Through the continuous development of its technologies, Casale has been able to develop innovative processes for methanol grass-roots plants. Casale is ready to respond to the future market demand with its advanced process and technologies, specially conceived for plants with very large capacity.

RIASSUNTO

Tecnologie proprietarie per gli impianti di sintesi di metanolo

Il Gruppo Casale è leader mondiale nell'ambito della modernizzazione d'impianti per la sintesi di metanolo e fertilizzanti, grazie all'applicazione di conoscenze specifiche e tecnologie proprietarie. Recentemente, Casale ha applicato queste tecnologie anche alla progettazione di nuove unità, tra cui l'impianto di sintesi metanolo di maggior capacità al mondo, da 7.000 t/d. L'articolo descrive le principali tecnologie del Gruppo Casale applicate alla sintesi del metanolo, evidenziandone il ruolo primario nel consentire la costruzione d'impianti di taglia sempre maggiore, per seguire le esigenze di questo particolare mercato.