METHANOL CONVERTER AND SYNLOOP DESIGNS FOR GASIFICATION PLANTS

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Abstract

METHANOL CASALE is a well-known designer of high efficiency reactors. In the Methanol Industry it is mostly acknowledged for its ARC design for synthesis converters, which has been widely adopted through revamping or new installations in steam reforming plants during the nineties.

At the beginning of the new century CASALE has introduced a completely new design for reactors, based on the heat removal from the catalyst mass by means of plate exchangers called IMC. This new design has been applied in several new plants and in revamping existing units.

The new IMC design can be developed to suit several different applications. This paper presents the case in which the feedstock for the synthesis loop is obtained from gasification of carbonaceous feedstocks, such as coal or petroleum coke.

1) INTRODUCTION

Today most of the world methanol production is achieved with natural gas as feedstock. In the last several decades, the situation has not changed, and therefore the attention of technology developers, so far, has been focused on these type of plants. Their design has advanced significantly, and their performances have been considerably improved during these decades in terms of energy efficiency, capacity and reliability, and their design still undergoes significant improvements.

In the last few years a new scenario started to appear, in which natural gas resources became more and more difficult to obtain by methanol producers, and the attention switched to the exploitation of new types of feedstock, such as coal and petroleum coke, that are abundant and, so far, less expensive.

Nevertheless, the utilization of these solid feed-stocks implies different technological approaches, both in the preparation of the synthesis gas, and in its utilization to produce methanol.

The differences in the utilization of the gas for the synthesis are what concerns this paper. They are relevant mostly to the composition of the synthesis gas obtained from gasification, that is rich in carbon oxides and low in hydrogen, and may contain several catalyst poisons.

Considering these differences, it is necessary to adopt a specific approach for the gasification plants that covers the design of the synthesis loop, and, even more so, of the synthesis converter.

2) THE SYNTHESIS LOOP IN A GASIFICATION PLANT

The process to obtain synthesis gas in gasification plants from solids with high carbon content, like coal and petroleum coke, consists mainly in the partial oxidation with oxygen at high temperature of these solids. As a consequence, in the most common commercial processes, the gas has a high carbon monoxide content, of about 50%. The gas also contains sulfur and other elements such as arsenic, that poison the methanol synthesis catalyst. The gas has then to undergo further reaction steps to convert part of the carbon monoxide to carbon dioxide. The gas then has to be purified to remove most of the resulting carbon dioxide and then all of the poisons.

The gas composition obtainable can, therefore, be adjusted to the necessity of the methanol synthesis, but, in general, its stoichiometric ratio is lower than two, the inerts content is low and there is the risk that some traces of poison may reach the synthesis loop.

The synthesis loop then has to be designed to take into account and to take advantage of the available gas composition.

This is normally done by providing some features that are not common in natural gas fed plants.
One of these features is a hydrogen recovery unit on the loop purge gas. The recovered hydrogen needs to be added to the make-up gas to increase its stoichiometric number to a value around two.

This is necessary because the synthesis catalyst available today does not like to run with sub stoichiometric numbers, i.e. lower then two. In that situation the selectivity would decrease, augmenting the by-product production, and the operating life would be shorter.

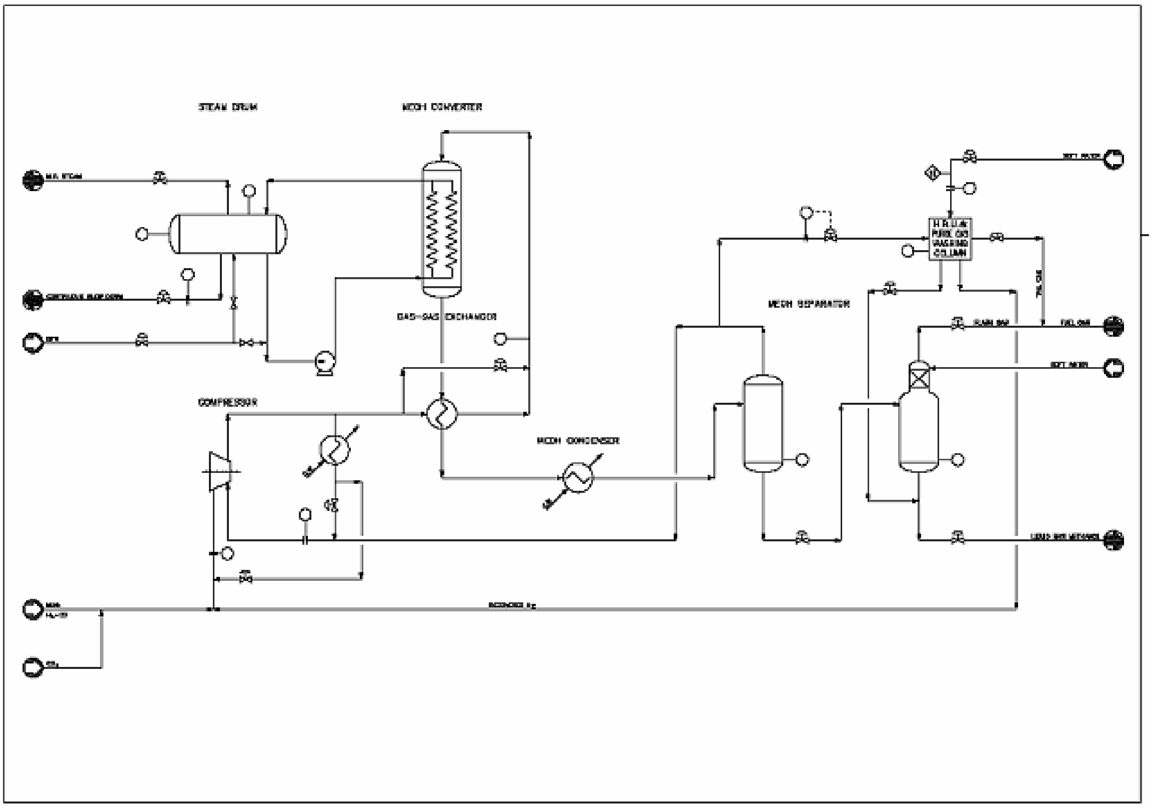
The high carbon monoxide concentration raises also the problem of the formation of carboniles, such as iron and nickel. Once formed they will decompose on the catalyst reducing its activity and promoting undesired side reactions. The formation of carboniles can be avoided by utilizing appropriate types of steel, that are higher grades than in gas based plants, in the areas where carbon monoxide concentration is high and the temperature is roughly in the range of 100 to 200°C.

Another feature characterizing these plants is that it has to be considered the possibility that the make-up gas could contain catalyst poisons, such as sulfur and arsenic. These compounds should be washed away in the gas treatment upstream the synthesis loop, but, there may also be problems due to upset, mal-operation or under performance of some treatment units that may leave more impurities than desired in the gas.
As these poisons are irreversible, it is advisable to protect the catalyst by providing a guard on the make-up gas, which is able to absorb these dangerous substances.

The fact that the make-up gas normally has a low inerts content, and is rich in carbon, on the other hand, makes it possible to achieve high production rates with low recycle ratios and low catalyst volumes, provided that the converter design is appropriate. In fact, as the gas is very reactive it can easily create problems of catalyst overheating and hot spots in the converter.

For this reason it is very important to provide the right reactor, as discussed in the following chapters.
Overall the synthesis loop can be very simple, as illustrated in the flow sheet below It would consist in the synthesis converter, a gas-gas exchanger preheating the reacting gas entering the converter, a condenser to cool down the gas to the methanol condensation temperature, a separator to separate the liquid raw methanol from the unreacted gas, a purge recovery unit to recover hydrogen from the purge gas to correct the stoichiometric number, and the syngas and circulating compressor.
There are six 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 low recycle ratio that can be used, of about 3 implies that these items are also quite small, enabling very large capacities in a single train, much larger then ever achieved so far in any plant of any type, provided, again, that the converter is of the right design.



3) OVERVIEW OF THE CASALE CONVERTER DESIGN

The type of converter that is proposed by METHANOL CASALE for this type of service is the "**IMC**", that stands for **I**sothermal **M**ethanol **C**onverter. This reactor design is characterized by the fact that the catalyst bed is cooled by hollow plates immersed in the catalyst, containing a cooling fluid (normally boiling water or synthesis gas). The **IMC** converter can also use a combination of the above, like boiling water and synthesis gas, in the same pressure vessel.

This type of reactor is an innovation introduced by METHANOL CASALE, a well-established designer of high efficiency reactors. In the methanol industry it is mostly known for its **ARC** design for synthesis converters, which had been widely adopted through revamping or new installations in steam reforming plants during the Nineties.

At the beginning of the new century METHANOL CASALE introduced this completely new design, based on the heat removal from the catalyst mass by means of plate exchangers. This new design was applied for the first time in a methanol synthesis converter in 2002.

Cooling Plate

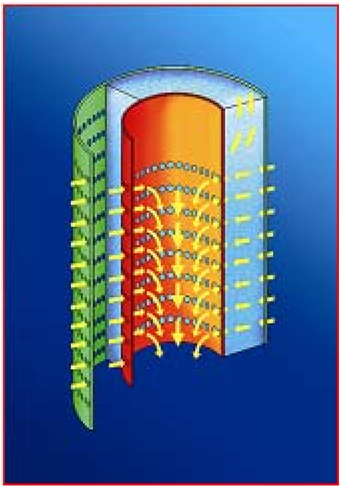
METHANOL CASALE had then applied this new design in several other plants, either new or existing through revamping. At present there are already 5 **IMC** converters in operation, with capacities ranging from 400 to 3’400 MTD, while 6 more are under construction with capacities from 1’350 to 7’000 MTD. It is to be evidenced that out of these six converters and synthesis loops under construction, five are in coal or pet coke gasification plants.

4) THE STEAM RAISING PLATE COOLED CONVERTER

In the case of gasification plants, the amount of carbon monoxide and dioxide present in the synthesis gas is very significant. Normally the concentration of these gases is of about 15%v for CO and of 5%v for CO_2 at reactor inlet. These high concentrations of carbon oxides imply that the converter must be provided with an heat sink, to control the reaction temperature. This heat sink is normally boiling water generating medium pressure steam, that is around 30 bar. This pressure is selected because its corresponding temperature level matches the operating temperature in the catalyst bed well, and the steam produced can be usefully utilized in the plant in turbines

As mentioned above the plate-cooled converters, make use of cooling plates immersed in the catalyst mass for heat removal. The boiling water enters the converter shell and is distributed at the bottom of the plates. It then flows inside the plates from the bottom to the top. The mixture water/steam is collected in a manifold and exits the converter.

The construction of the converter internals is conceived so that there is no tube sheet, 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 dimpled, 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 plates are surrounded by the catalyst mass where the process gas is flowing. The process gas flow can be axial or axial-radial. In the latter case very large capacities in a single vessel with a low pressure drop, can be obtained.

It is to be underlined that METHANOL CASALE is part of the CASALE GROUP, which includes AMMONIA CASALE. Together these companies are using axial-radial catalyst beds in synthesis converters, and also in other types of applications, since more than twenty years, and have successfully designed and built more than 500 different axial-radial beds. Their experience in designing these types of catalyst beds is, therefore, unmatched and unique.

Axial-Radial Flow Catalyst Bed

The long and wide experience of the company, focused on these types of applications, explains the important advantages that comes from the use of the **IMC** design, and the accuracy with which every detail of the converter is studied.

As a matter of fact there are several advantages that can be achieved utilizing the plate-cooled steam-raising converters in gasification based plants instead of the old tube-based approach.

The new CASALE design overcomes the traditional limitations of size, allowing much higher production rates in a single converter. This is due to the fact that there is no tube-sheet, the plates are connected through manifolds. The catalyst is outside the plates, making a larger cross section area available for the process gas flow in axial converters. The gas flow in the catalyst can be axial-radial, and the catalyst bed cooling can be achieved with a combination of water and gas, leading to the lowest temperature at converter exit, improving the conversion per pass.

The CASALE design dramatically improves the reliability of the converter internals, introducing the concept of the automatic, computer controlled manufacturing of the plates, and drastically reduces the number of connections between the plates and the water and steam collectors and distributors, with respect to the designs based on tube cooling. Every plate is pressurized, during the forming process, at pressures much higher than the operational one, making sure that all the plates are free from any mechanical defect.

This design also enables easy catalyst handling and converter maintenance. The space above the catalyst bed, for the axial and also for the axial-radial case, is essentially empty and fully accessible, allowing an easy and effective loading of the catalyst from the top. The catalyst unloading is done from the bottom, where drop out nozzles are provided. Once the drop out nozzles are opened the catalyst flows out. The operation of catalyst loading has been, of course, proven in the converters that are on stream, while the catalyst unloading has been recently successfully performed in the first IMC converter that went on stream in 2002. After five years of operation the catalyst flowed out completely in few hours, reducing the down time for the turnaround by days, with respect to the old design.

The new CASALE **IMC** design also enables a good temperature control in the catalyst mass. This aspect is very important for gasification based plants, where, due to the high concentration of reactants, it is necessary to avoid the presence of hot spots in the catalyst beds. The **IMC** design achieves this goal thanks to the efficiency of the reaction heat removal.
The plates surface density per unit of catalyst volume is in fact very high and uniform. This fact ensures the highest performances of the converter in terms of conversion per pass, enabling the generation of steam at the highest pressure level, and increases the operating life of the catalyst charge, as there are no hot spots formed in the bed.

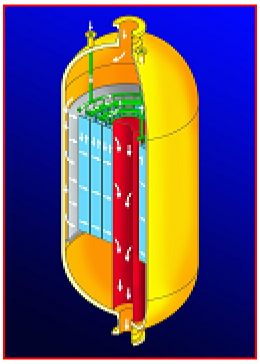
5) CASALE EXPERIENCE WITH IMC CONVERTERS

All these advantages are proven in the industry.

As mentioned above there are already five **IMC** converters in operation and all of them running fine. Two of these five units are of special importance as a reference for these types of plants.

One of these two is applied in the Metafrax plant in Gubakha, Russia. The plate cooled steam raising converter design has been applied there for the first time in a revamping project aimed at capacity increase.

This plant is a natural gas based one, but the plate cooled converter is installed on the fresh make-up gas as a once-through unit, receiving a gas with a high carbon oxides content, similar to that of a synthesis loop in a gasification plant. The converter is producing about 850 MTD of methanol and 30 to 40 t/h, (SOR and EOR respectively), of 32 bar saturated steam. It is on stream since August 06, the test run has been already performed and the performances obtained are excellent.



The other converter is the first axial-radial plate cooled one. It is on stream in the AMPCO plant in Equatorial Guinea. Its capacity is of 3'400 MTD, and is the result of an “in situ” modification of an existing converter.

This means that the revamping consisted in removing the old internals from the existing pressure vessel, and in installing the new axial-radial plate cooled ones. This has been achieved by introducing the new internals in prefabricated parts through the top manhole, and assembling them inside the vessel, during a turnaround.

Axial-Radial Plate Cooled Converter

The converter was originally a four-bed three-quenches design, and, without modifying the pressure vessel, it has been revamped to a new configuration featuring two axial-radial beds, each one cooled with plates. Also this converter is on stream, since July 06, and its performances are excellent.
It is to be noted that the axial-radial flow in the plate cooled converter can be adopted also for gas cooling, a feature never achieved with tube cooling. This possibility can be useful for large capacity gasification plants to improve the converter conversion per pass, in combination with steam raising.

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6) CONCLUSIONS

Producing methanol from gasification of coal or petroleum coke requires tailor made solutions that can differ significantly from those so far used in the more common gas based plants, to take full advantage of the peculiarities of the synthesis gas generated with this process.

The synthesis loop can be made simpler and smaller, provided that the synthesis converter can cope effectively with the more active gas at the low circulation. The converter design developed and proven recently by METHANOL CASALE is achieving this goal, it is proving to maintain its promises in the plants where it is being used, and, from every point of view, whether regarding efficiency, reliability and/or capacity, it is a leap ahead of the older designs available based on tube cooling.