CHALLENGES IN DESIGNING SYNTHESIS CONVERTERS FOR VERY LARGE METHANOL PRODUCTION CAPACITY

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1. FOREWORD

It has become common in the last few years to think of methanol plants having capacities of 6'000 MTD or more, which is a capacity double that of the largest methanol plants on stream at present.

In order to efficiently design plants of this capacity it is necessary to develop new designs for the critical pieces of equipment, not just to increase the size of the equipment already in use, or use more of these pieces of equipment in parallel.

Two parts of the methanol process have an important impact on the design of the overall plant, both in terms of global efficiency and size and number of equipment necessary in the plant and they are the synthesis gas generation unit and the synthesis converter.

While for the synthesis gas generation the designers have made significant progress, the synthesis unit seems to be still less developed.

2) EXISTING SYNTHESIS TECHNOLOGIES FOR MEGA METHANOL PLANTS

The methanol synthesis processes disclosed until today for mega methanol plants are:

- The processes based on the use of two synthesis reaction steps in series;
- The processes based on the use of one synthesis reaction step.

Regarding the synthesis converters, the designs proposed are either the use of the same steam-raising tubular reactors foreseen for lower capacities, or the use of newly developed gas cooled reactors, still based on a tubular configuration, in all cases adding more units in parallel for bigger capacity plants.

All the above converters are of axial design, with one exception, i.e. a radial steam raising tubular converter.

3) THE IDEAL METHANOL CONVERTER

Considering the large capacities under consideration, the first requirement of a synthesis converter is its efficiency for the large impact it has on the design of all the loop equipment and on energy consumption. An efficient converter allowing to reach the design capacity with a small recycle ratio makes it possible to considerably reduce the size of all loop equipment, including the converter itself, and the piping size.

To understand how to design an efficient converter it is necessary to examine the thermodynamic aspects of the synthesis reaction, and the following graph gives their representation.

The x-axis indicates the temperatures, the y-axis indicates the methanol concentration, the black line drafted represents the equilibrium concentration, and the red line represents the curve of the highest reaction rates achievable.

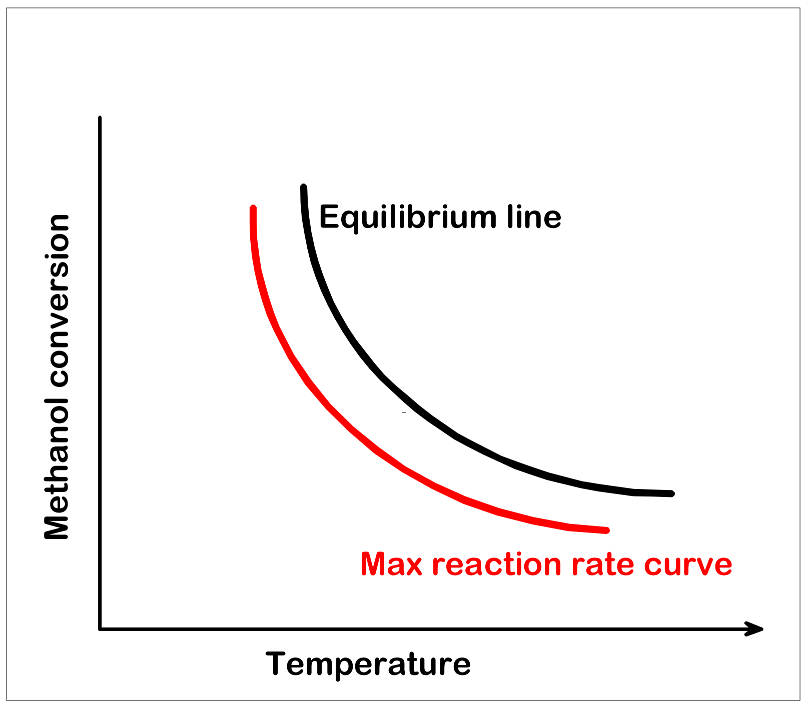


FIGURE 1

The ideal methanol synthesis converter design is the one that always keeps all the catalyst volume operating along the red line, i.e. every point of the catalyst bed has values of temperature and composition corresponding to the highest reaction rate possible. In this case, the converter makes the best use of the catalyst volume available, achieving the highest possible conversion per pass with a given catalyst volume.

Only a converter design where the reaction heat is removed directly in the catalyst bed, that is a pseudo-isothermal converter, can obtain this result, as it is evidenced in the following graph, Fig 2. The graph, the same as Fig.1, shows the reaction path of an adiabatic multi-bed quench cooled converter (the blue line). It can be seen that only in one point of each bed the catalyst is operating on the maximum reaction rate curve, evidencing the fact that an adiabatic reactor cannot be the most efficient one.

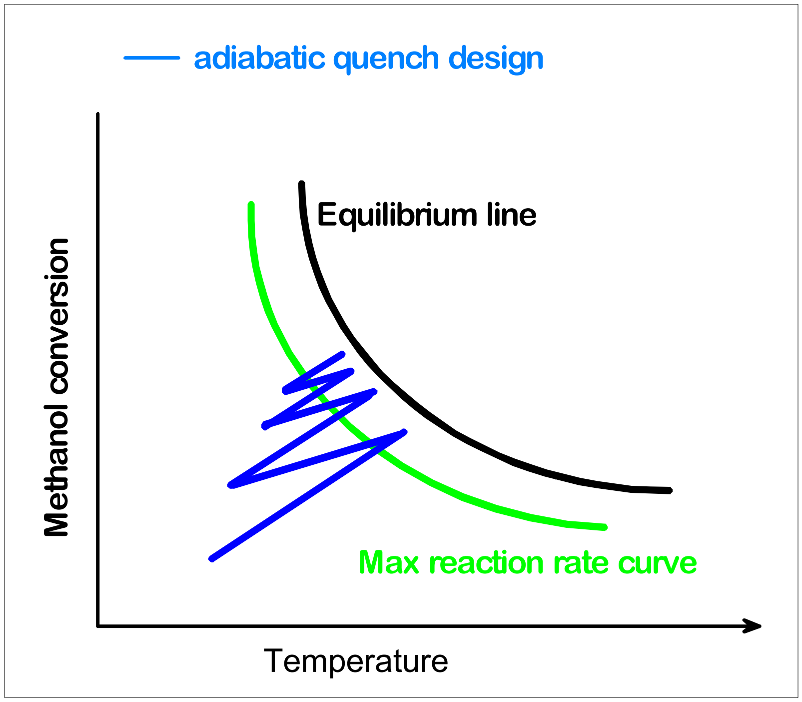


FIGURE 2

Furthermore not only the ideal converter design has to remove the heat of reaction, it also has to remove it according to a desired profile, i.e. it has to remove more heat where the reaction rate is faster, that is at the beginning of the catalyst bed, and remove less heat where the reaction rate is slower, that is at the end of the catalyst bed. In this way the conversion per pass is maximized.

The ideal converter should also have the following features:

- Flexibility during operation, i.e. it must achieve the correct heat removal in different operating conditions, like at catalyst start-of-run, and at catalyst end-of-run, and also with intermediate catalyst life, higher and lower load, different gas compositions, etc.
- A low pressure drop with a pressure vessel not exceeding the maximum diameter allowed for an economical construction and transportation: this means that the converter should be radial.
- An easy access to the converter internals for catalyst loading and unloading, in order to reduce the down time necessary for these operations
- As everything made by men can fail, an easy access to the converter pressure vessel in order to make possible repairs to its internal wall is required and to easily repair or replace parts of the internal heat transfer surface.
- The overall construction should be economical.

Only a complete novel approach can cope with all the above features, which can never be obtained by the conventional “tube cooled” design.

4) A NOVEL APPROACH

Radial gas and or steam rising converters using a new type (for this service) heat transfer surface immersed in the catalyst volume, not requiring tube-sheet, and a new type of temperature control are the key features of the new METHANOL CASALE S.A. design, which achieves all key goals listed above. Modules of plate heat exchangers are the components of METHANOL CASALE S.A. converter internals according to its new advanced design.

Plate heat exchangers have been in use for a long time in the petrochemical industry, and there are many manufacturers producing plates using advanced and well-established production technology.

The plates are normally produced with a fully automated process, with little or no manual intervention. The production process starts normally from a coil of the desired metal sheet, which goes through a sequence of automatic operations such as welding, inflation or printing, assembling and quality control.

The approach is that of a mass production, where, once the production parameters have been set and tested, all the elements are identical, minimizing the possibility of defects, and with a very effective impact on costs.

The plate's geometry is very flexible, enabling the design of converters of any size.

In the new METHANOL CASALE S.A. design, the plates are immersed in the catalyst bed and the cooling fluid flows inside the plates.

Figure 3 illustrates, for the sake of simplicity, a typical axial methanol plate converter gas cooled. The radial design is very similar and will be illustrated ahead.

As it can be seen the plates are in immersed in the catalyst bed, the cooling gas enters from a nozzle on the top and is distributed to the plates. Inside the plates the gas flows downward and after having been preheated it is collected to a central raiser pipe, from where it reaches the top of the catalyst bed. There the gas flows downward in the catalyst bed, and then exits from the bottom central nozzle.

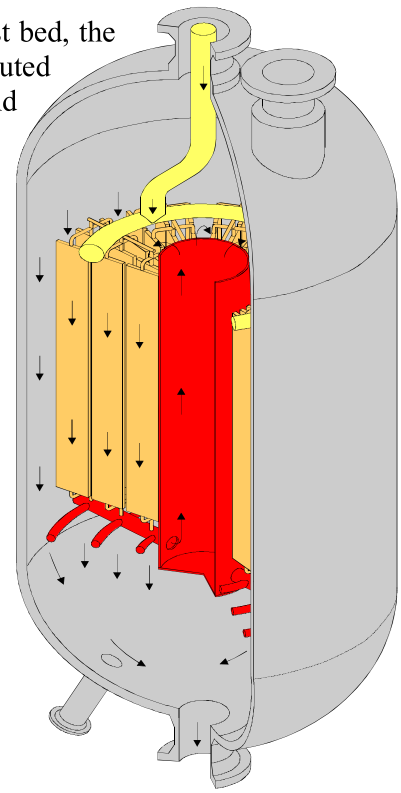


FIGURE 3

4.1 Mechanical Advantages

This type of construction (shown in Fig. 3) has already several of the optimal mechanical characteristics required, in fact:

- It does not have a tube sheet. Therefore the only mechanical limitation is the maximum diameter of the pressure vessel.
- The catalyst bed is continuous, supported by a bottom layer of inert material. Therefore it can be easily loaded from the top, and unloaded from the bottom through drop-out pipes, minimizing the downtime for catalyst replacement.
- The plates are connected in modules (groups of plates) and each module can pass through the manhole. The central raiser pipe is large enough to be accessed by a man, assuring in this way an easy access to all parts of the reactor, allowing the replacement or repair of any item that could fail during operation, i.e. the pressure vessel, the plates or the internal pipes.
- Thanks to the absence of a tube sheet and to the automated production of the plates, the overall construction is very cost effective.

4.2. Process Advantages

As mentioned in Chapter 3, the new converter has to achieve the control of the temperature profile in the catalyst bed so that the catalyst mass can work as close as possible to the line of maximum reaction rate. This situation is illustrated in Fig. 4, where the red line represents the desired operating curve of the converter, and I.M.C. stands for Isothermal Methanol Converter.

The problem in achieving this temperature profile in a gas-, cooled converter, or a water-cooled one, whether the cooling fluid is co-current or counter-current with the gas in the catalyst, is that the temperature difference between the gas in the catalyst and the gas inside the plates, or tubes, is not the same along the converter.

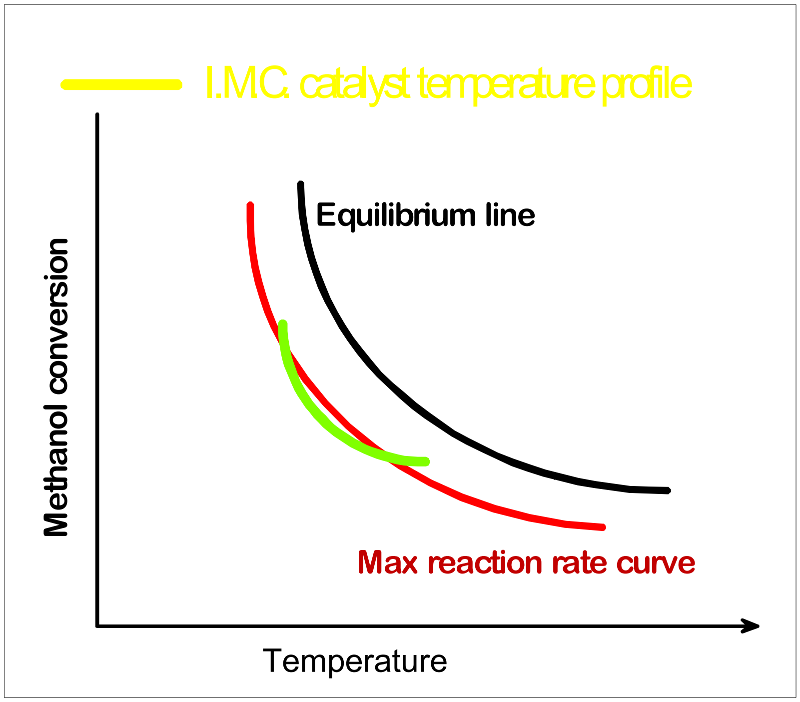


FIGURE 4

In fact if the flow is co-current, there is a large temperature difference between the cold cooling gas at the inlet of the plates, or tubes, and the gas entering in the catalyst, while the temperature difference at the opposite end, i.e. between the preheated fluid exiting the plates or tubes, and the reacted gas leaving the bed, is much smaller, even ten times smaller.

The overall heat transfer coefficient along the converter remains about the same, as well as the amount of heat transfer surface per cubic meter of catalyst.

The heat released by the synthesis reaction per cubic meter of catalyst is more at the beginning of the bed and less at the end, compensating partially for the difference in temperature ‘differential’.

As a whole, the amount of heat removal capability required in a co-current design is different from point-to-point along the converter, being considerably smaller at the entrance of the bed then at the exit.

For a counter-current design, the difference of temperature between the cooling gas and the catalyst bed is large at the end of the bed, where the cooling fluid is cold, and small, theoretically zero, at the bed entrance, where the cooling fluid is already preheated.
Here the fact that the reaction rate is faster at the bed entrance, i.e. the amount of heat to be removed per cubic meter of catalyst is higher at the bed entrance, increases the difference in the heat removal requirement between the bed inlet and the bed exit.

It is clear that with a standard design it is not possible to follow an ideal temperature profile in the catalyst bed. A new approach is necessary.

The use of the plates makes it possible to feed different quantities of cooling fluid at different heights, thus enabling the removal of different quantities of heat in different parts of the converter, achieving the goal of running the whole catalyst bed with a temperature profile corresponding to the one with the highest possible reaction rate.

The amount of cooling fluid fed to the different parts of the plates can be controlled by the plant operators with normal control valves, so that it is possible to modify the temperature profile in the catalyst bed adapting it to the specific needs, i.e. fresh catalyst or spent catalyst conditions or other requirements, as if it was a quench type converter.

This design, therefore, presents the same operating flexibility of a quench converter with the high efficiency of an ideal pseudo isothermal design with indirect cooling.

The graph of Fig. 5 shows the temperature profile in the catalyst bed obtained with the Casale design, where the cooling fluid is co-current with the reacting gas.

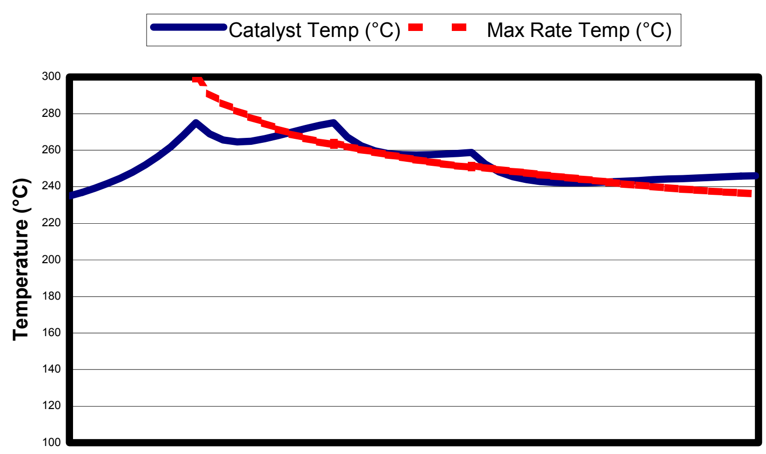


FIGURE 5

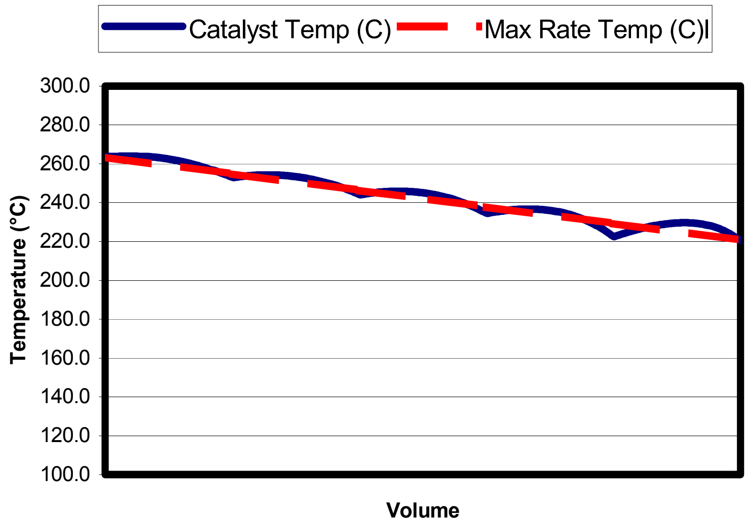


FIGURE 6

The Figure 6 shows the same graph for a counter-current design.

The process advantages achievable with this new design are then:

- The possibility to actually obtain the ideal temperature profile in the catalyst, reaching therefore the highest conversion with the lowest catalyst volume.
- The possibility to control and adjust the temperature profile in the catalyst bed, therefore achieving the optimal temperature profile in conditions different from the design ones.

4.3 The Axial-Radial Design

Additional advantages may be obtained (see Fig 7) with the use of the well-known axial-radial configuration for the catalytic bed, which greatly simplifies the converter internals' lay-out.

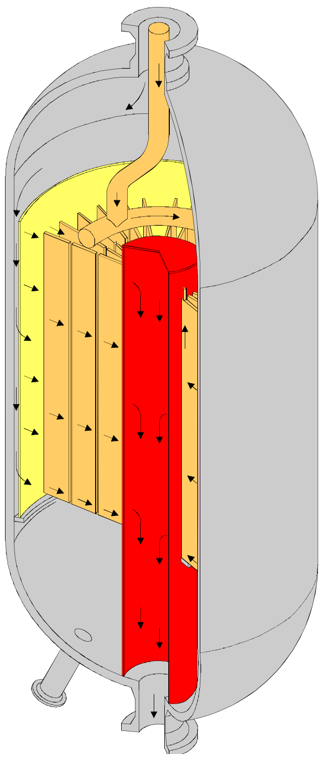


FIGURE 7

The mechanical construction of the axial-radial design is similar to the axial converter, mainly it is added only an additional outer collector to collect/distribute the gas to the catalyst bed.

The flow in the radial design differs because in the catalyst mass the gas crosses the catalyst from one side to the other instead of from top to bottom.

In the plates the flow has to be parallel to the flow in the catalyst, therefore from one side of the plate to the other. It is then necessary to utilize a different plate design, as illustrated in Fig 8.

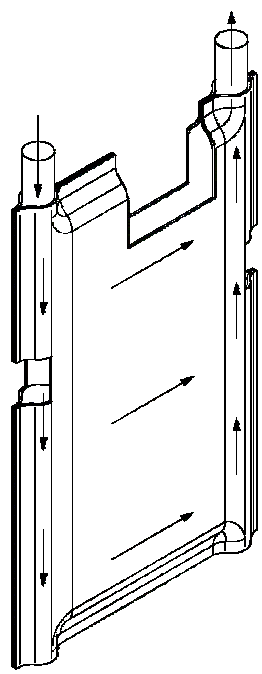


FIGURE 8

All the mechanical and process advantages described for the axial case are present also in the axial-radial one.

The axial-radial design allows the use of more economical lower diameter converter vessels while keeping a low gas pressure drop.

These features of slim vessels and low pressure drops, enable reaching very high capacities in a single vessel converter, such as 5000 or 6000 MTD, with the highest performances in terms of low recycle ratio and high carbon efficiency.

The possibility of designing a large capacity synthesis loop with a single vessel converter, having the best performances achievable in terms of low pressure drop, high carbon efficiency and low recycle ratio, is unmatched until now. This design, therefore, considerably reduces the overall cost of the synthesis loop, improving the performance of the plant also in terms of flexibility of operation, mechanical reliability, and reduced shut-down time for catalyst replacement.

4.4 Typical Size of a 5'000 MTD Converter

To evidence the features of the new Casale design, a single vessel 5000 MTD converter may be expected to have the following key parameters:

a) main size : 10/12 m T.L. 6/7m diameter
b) operating pressure : 80 bar, using standard available catalyst
c) overall pressure drop : less then 2 bar

Such a single vessel converter may incorporate also different types of catalyst cooling, such as gas and water-cooling, at the same time.

5.0 INDUSTRIAL EXPERIENCE

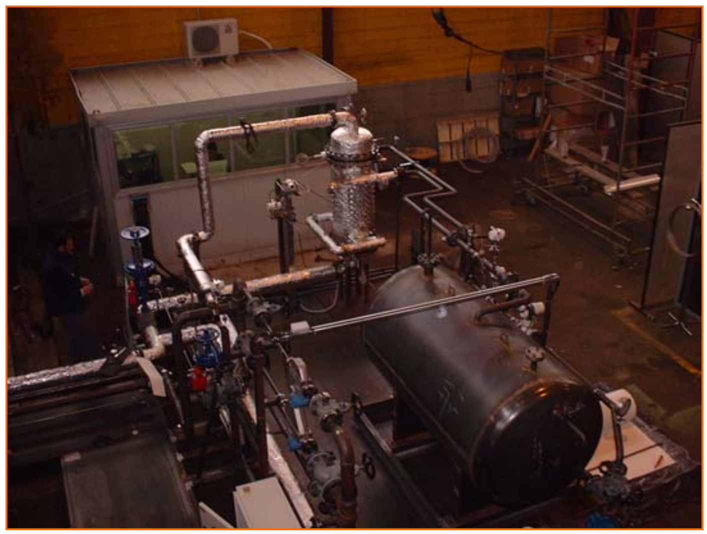
The concepts explained in this paper have been checked extensively in computer simulations and these simulations have then been used to design a test unit, dedicated to the measurement of the heat transfer phenomena.

This unit is on stream since April 2002, and the data collected have been used to fine tune the theoretical models.

Furthermore, METHANOL CASALE S.A. has received the first contract for revamping an existing methanol synthesis converter with this new technology.

The new internals have been already installed and the converter it is in service since late November 2002.

The performances obtained are excellent, confirming in every aspect the concepts used for the design, demonstrating their validity.



Heat Transfer Testing Unit

The plant where the converter internals have been installed is in Russia. Its old converter design was with adiabatic beds and quench cooling. The feedstock is acetylene off-gas enriched with hydrogen coming from an ammonia plant.

The converter size is about 4 meters in diameter by 8 meters of length (catalyst volume equivalent to a 1000 MTD production converter operating at 80 bar), and all the new internal parts have been introduced, during a normal turnaround for catalyst replacement, through the top manhole, and then assembled inside.

This type of retrofit, called ‘in situ’, was pioneered, for other projects, by AYMMONIA CASALE S.A. and METHANOL CASALE S.A. more than fifteen years ago.

The performance test run has already been made, exceeding all guarantees, and even the expectations.

In addition to the excellent performances achieved, the converter has demonstrated other operating advantages:

- The catalyst reduction has been smooth and easy, without temperature peaks, thanks to the controlled heat removal performed by the converter internals.
- The converter has demonstrated to be easily controlled, and very flexible, operating also in conditions far from the design, maintaining always an optimal temperature profile. In fact, due to plant problems it has been run with a stoichiometric ratio at converter inlet as low as 2.1, instead of the design value of 3.5, without showing any tendency to hot spots formation, and allowing to adapt the catalyst bed temperature profile to the new conditions.
- The temperature control also ensures the lowest by-product formation, which was in fact well below the expected value, and a longer catalyst life.

At this point we can state that the new design is industrially proven, not only in terms of process performances, but also of the practical operability and of the possibility to transform an existing adiabatic converter to pseudo-isothermal one, even if the pressure vessel has only manhole openings.

6.0 ACHIEVEMENTS

Conclusions

Designing methanol synthesis converters for mega plants needs a novel approach and stretching the existing design does not solve the problems posed by the size of the new plants.

Keeping this in mind, METHANOL CASALE S.A. has introduced a new design, based on several different and innovative concepts; such as the use of cooling plates and temperature control along the catalyst bed, converter internals made by detachable modular components, and the axial-radial gas distribution in the catalyst. The new design is now successfully proven in the industry.

Announcement

At last, but not the least, based on a recent study carried out by PIDEC, as an Iranian Engineering Contractor to acquire advanced process technologies needed for the Industrial Development Program of Iran and for the same program in the Regional States in the Middle East and Central Asia, proposals were made for conclusions of License Agreements with AMMONIA CASALE S.A. and METHANOL CASALE S.A, so that PIDEC could act as our **"Exclusive Licensee"** (approved contractor) for future Ammonia and Methanol Projects inside and outside Iran. Based on relevant experiences of this Iranian Company (PIDEC), particularly in the area of Design and Detail Engineering, Supply of Equipment and Project Management for Commissioning of the Grass Root Projects, we both concluded **"Exclusive License Agreements"** for both Ammonia and Methanol Technologies, which have come into effect, as of 10 months age.