Layer management for Methanol Process

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Abstract

Air Liquide Engineering and Construction has a long-standing expertise in methanol (MeOH) production, that includes more than 60 methanol licenses for a total capacity of more than 51 million t/a of methanol production [1], 18 commercial plants licensed with the Lurgi MegaMethanol™ technology and dedicated pilot plants at the Innovation Campus Frankfurt in Germany. Suited to large-scale production the Lurgi MegaMethanol™ process converts syngas derived from any carbonaceous feedstock into methanol and offers minimized production costs at maximum capacity. At the same time, Air Liquide Engineering and Construction offers customers small-scale methanol units that can be integrated into existing industrial complexes. Air Liquide applies its experience to further improve the state-of-the-art methanol synthesis technology via process intensification and new technologies for unconventional feed sources such as stranded gas, unused syngas capacities, CO_2-rich gases and industrial off-gases. Air Liquide Engineering and Construction and Air Liquide Innovation Campus Frankfurt and Clariant have been collaborating for many years and investigated successfully the possibility of improving the utilization of the catalyst volume in the MeOH reactors, e.g. increasing space time yield, and catalyst lifetime by tailoring the arrangement of different catalyst layers (Layer management) according to the changing process conditions over the reaction pathway. The Layer management concept is well known from other applications such as in Clariant's PhthaliMax®/OxyMax® catalysts for production of phthalic anhydride and the FAMAX® series for the production of formaldehyde [2, 3]. Air Liquide Engineering and Construction's reactor systems (water- and gas-cooled reactor) are already a benchmark in the field of per pass conversion and heat management. The utilization of those reactors can be further intensified by applying the layer management technology, while improving the reaction rates over the reaction path by optimizing the temperature profile and selectivity. The potential of the layer management approach for methanol production has been confirmed by studies [4] as well as by pilot-scale test campaigns. Dedicated process modelling tools have been validated and are now being used for the optimization of revamp solutions.

In a first step, this concept is attractive for capacity extension, revamping of an existing methanol plant and for converting off-gases from industries to methanol. This development is another example of successful cross-application technology transfer and joint-development between an engineering company and a catalyst provider working in close collaboration.

Introduction

Air Liquide is represented through its Engineering and Construction and Research and Development entities in this article. The Air Liquide methanol synthesis process covers a wide range of set-ups and conditions with low pressure and Lurgi MegaMethanol™ processes (Fig. 1). In the standard process, only water-cooled reactors are used, while a combination of Water-Cooled Reactor (WCR) and Gas-Cooled Reactor (GCR) are applied in the MegaMethanol™ process. The methanol unit may feature integrated syngas generation to utilize any carbonaceous feedstock. Based on natural gas the Lurgi MegaMethanol™ process offers a 5,000–10,000 t/day capacity with an efficient and cost-effective design due to low recycle ratios. Any unconverted syngas is recycled back into the synthesis loop to increase yield and improve carbon efficiency. The resulting raw methanol product is then distilled further to meet the customers' required specifications.

Since 1969, Air Liquide Engineering and Construction has licensed more than 60 MeOH production plants for a total capacity of more than 51 million t/a. Air Liquide's Lurgi methanol technology is well-known for its reliable performance and efficiency in the market for world-scale capacities, but also has the knowledge and capacity to implement smaller scale units integrated in already existing industrial complexes.

(Photo: stock.adobe.com)

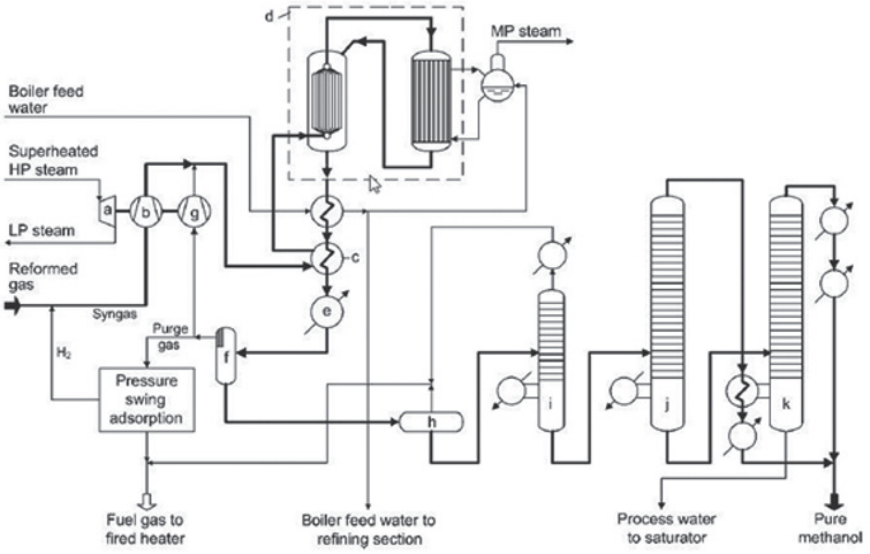

Fig. 1 Process scheme for the Lurgi MegaMethanol™ synthesis process.
a) Turbine for synthesis gas and recycle compressor; b) Synthesis gas compressor; c) Trim heater; d) Reactor; e) Final cooler; f) Methanol separator; g) Recycle gas compressor; h) Expansion vessel; i) pre-run column; j) Pure methanol pressure column; k) Atmospheric methanol column [9]

Air Liquide also applies its experience to further improve the state-of-the-art methanol synthesis technology via process intensification and new technologies for unconventional feed sources such as stranded gas, unused syngas capacities and CO_2-rich gases.

On the design and development of methanol plants, Air Liquide has a long time strategic collaborative partnership with Clariant, who is a leading supplier of syngas and syngas downstream catalysts. In industrial methanol synthesis, synthesis gas (primarily a mixture of CO, CO_2, H_2) is passed over CuO/ZnO/Al_2O_3 catalysts in the methanol reactor with typical catalyst lifetimes of up to six years. Over time-on-stream (TOS) various sources of deactivation lead to a continuous decrease of the intrinsic activity of catalyst loaded in the synthesis reactor.

To overcome deactivation and keep the methanol production rate constant, operating conditions are adapted over time. Typically, more make-up-gas (MUG) and higher recycle ratios are practically applied to sustain the methanol capacity. The solution, however, can only work in a certain range due to the limitation in pressure drop. Additionally, inlet and cooling temperatures are increased to accelerate the reaction rate for maximizing carbon conversion. However, such conditions lead to increased peak temperatures in the catalyst bed and ultimately accelerate by-product formation and catalyst deactivation.

Air Liquide and Clariant adapted and demonstrated layer management for the methanol process. The catalyst library and mathematical model have been built up and the concept has been checked in a dedicated Air Liquide methanol pilot plant at the Innovation Campus Frankfurt site. The present work focuses on finding a way to increase the lifetime production of methanol considering all current design constraints of existing plants by arranging different catalyst layers, which have different activities in the reactor. In this way, this arrangement can mitigate the peak temperature and keeps the catalyst activity and methanol productivity on a high level over the catalyst's lifetime. This configuration is particularly efficient when catalyst aging occurs and can significantly improve the amount of methanol at Middle-Of-Run (MOR) and End-Of-Run (EOR), when deactivation of the catalyst becomes more severe.

Layer management – A cross-application transfer of technology

To increase the productivity and broaden the methanol production portfolio for different feedstocks, Air Liquide and Clariant have joined efforts to develop a more efficient and resilient MeOH process. The Air Liquide reactor systems (Water- and Gas-Cooled Reactor) are already the benchmark for per pass conversion and heat management. Customarily, the reactor tubes are loaded with a single catalyst type only. Apart from the MegaMax® catalyst series for MeOH synthesis, Clariant also offers high performance catalyst solutions for selective oxidations, i.e. the PhthaliMax® product series for the production of phthalic anhydride (PA) and the FAMAX® product series for the production of formaldehyde. For these applications layered reactor concepts are successfully applied and considered state-of-the-art (Fig. 2) [2, 3, 5]. The concept allows optimizing the reaction rates over the reaction path, thus adjusting the temperature profile and selectivity.

The know-how gathered from this technology has been transferred to the methanol production process by tailoring the catalyst layers according to the changing process conditions over the reaction path along the reactor. Contrarily to the selective oxidation application, for which hot-spot reduction is the major target, we investigated in particular the possibility of improving the utilization of the catalyst volume in the methanol reactors over the catalyst lifetime, i.e. increasing space-time yield and catalyst life-

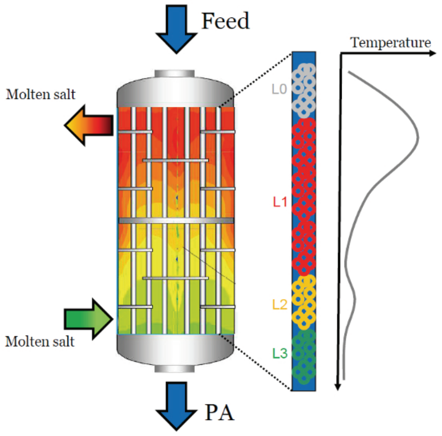

Fig. 2 Illustration of layer management in selective oxidation applications. A schematic temperature profile is shown as inlay [8]

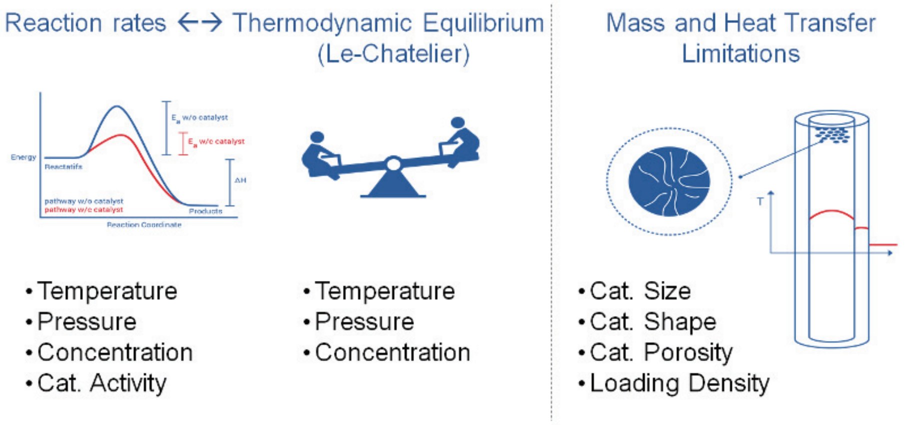

Fig. 3 Layer management for reaction intensification

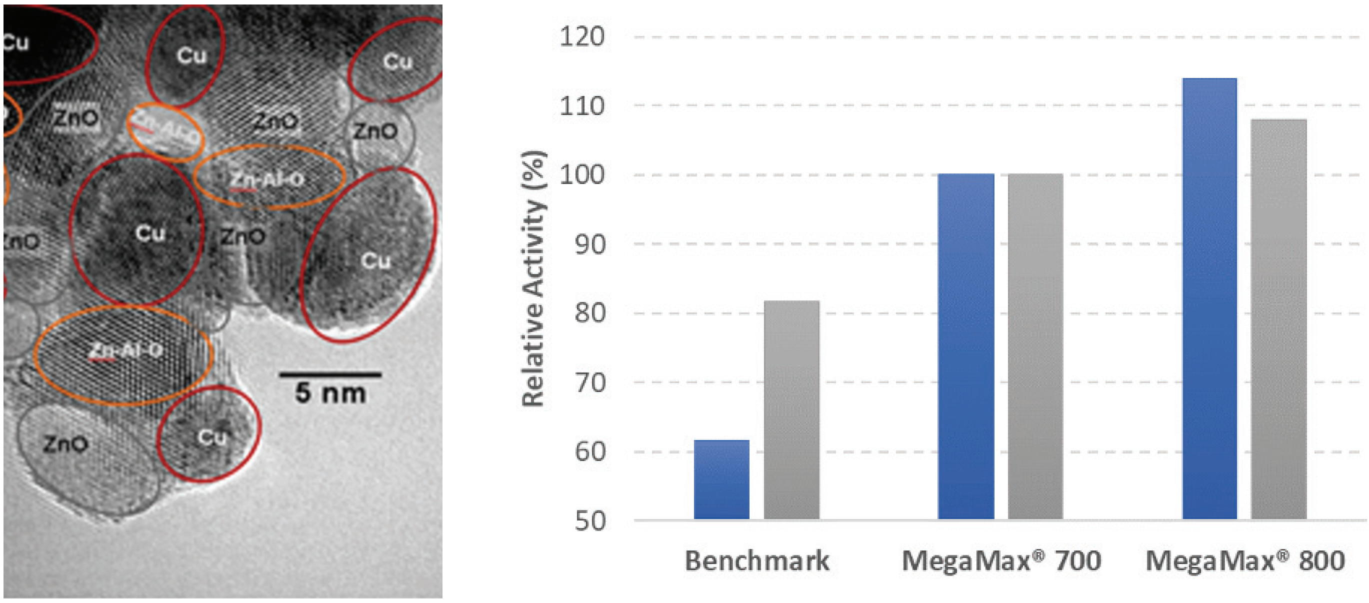

Fig. 4 HR-TEM image of CuO/ZnO/Al2O3 catalyst [6] and evolution of MegaMax® catalyst generations. Blue and grey bar correspond to different operation regimes

time.

In parallel, Air Liquide executed several studies to identify the main parameters for process intensification and optimization of the reaction path in the methanol reactor [4, 5]. Layer management offers a customized approach to improve the most important parameters identified in the study (Fig. 3).

MegaMax® methanol catalyst portfolio as basis for layer management

Clariant is well known for its syngas catalyst portfolio and the Air Liquide methanol process considers Clariant's copper-based methanol catalyst (i.e. the MegaMax® series) as a basis for their design. An extensive research effort and scientific collaboration such as illustrated in high-resolution electron microscopy images (Fig. 4, left) helped in unveilling the intimate interplay of Cu, Zn and Al and understanding the fundamental kinetics of the Cu/ZnO/Al_2O_3 system [6]. Consequently, this allowed Clariant to improve the catalyst preparation route and the production process, resulting in continuously increasing intrinsic activities from one catalyst generation to the next (Fig. 4, right).

To serve the concept of Layer management and allow rapid "in-silico" screening, Clariant has developed a catalyst library [7]. This allows the simulation of various layer management setups (consisting of different shapes and catalyst generations) in a methanol loop model developed jointly with Air Liquide. The model is based on a sophisticated heterogeneous pellet model and uses a proprietary kinetic mechanism. In the layer management concept, each layer can thus be attributed with a different function depending on the targets (i.e. pressure drop, methanol yield, catalyst lifetime, by-products). Moreover, the modelling supports the implementation at industrial scale.

Clariant and Air Liquide developed modelling tools to predict the performance of a methanol reactor loop employing Layer management over the full lifetime of the catalyst. These modelling tools are continuously validated and improved, based on pilot plant data and industrial feedback.

Layer management concept in a nutshell

Various layers of catalysts can be introduced to optimize heat management and local activity

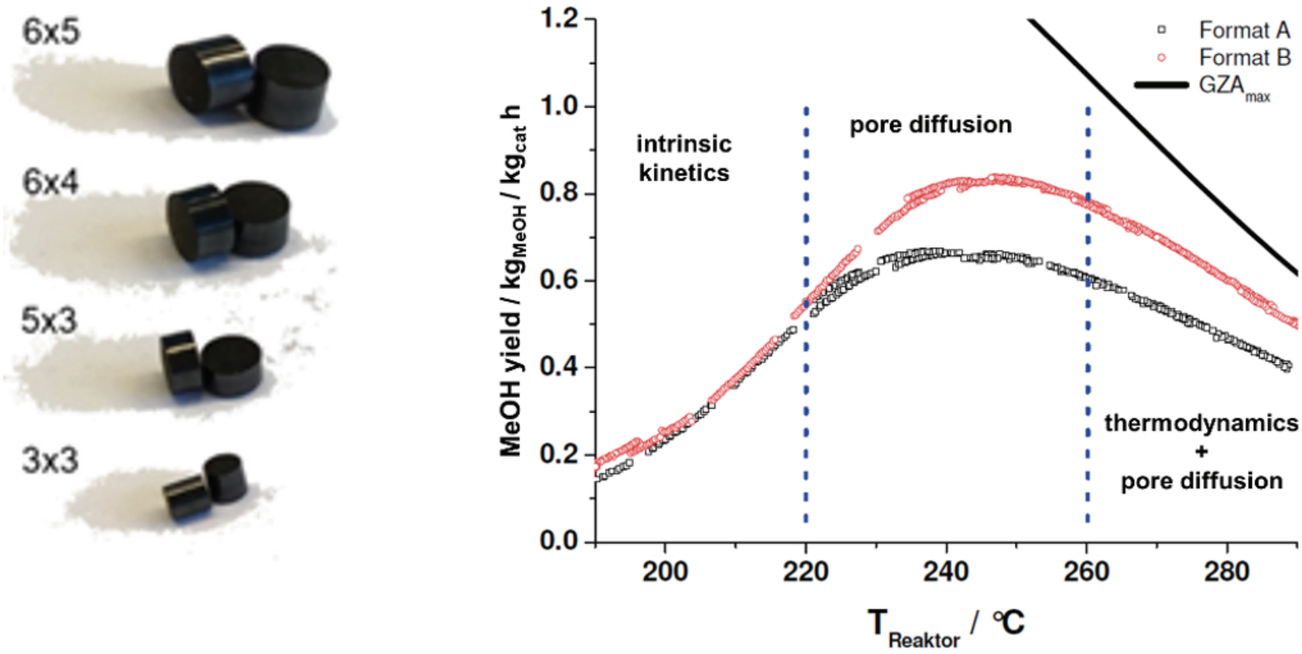

Fig. 5 Various catalyst formats (left) and activity test results illustrating the influence of two different catalyst formats in different operation regimes (right) [7]. The solid line represents the thermodynamic equilibrium limit.

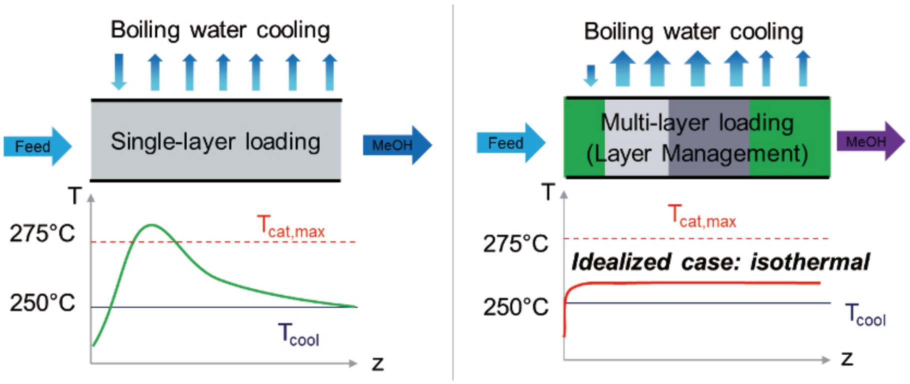

Fig. 6 The Concept in a nutshell – WCR single-layer loading vs. layer management

	Standard Loading	Layer Management
Per pass conversion (%)	93.3 ± 0.5	89.7 ± 0.3
Space time yield (kg MeOH/Lcat/h)	1.0 ± 0.1	2.1 ± 0.1

Tab. 1 Evaluation of maximum potential of Layer Management in pilot plant.

inside the tubular reactor. The properties of each catalyst layer are tailored to the local conditions along the reaction pathway (Fig. 6). Catalyst deactivation in industrial processes deactivation is unavoidable in commercial methanol plants, so that an industrial catalytic process cannot be designed or optimized without considering catalyst aging over the lifetime. Therefore, understanding and being able to predict catalyst deactivation behaviour is crucial to determine the lifetime-yield and catalyst turnover [10]. Based on temperature profiles of commercial plants an activity profile can be deduced using an optimization approach. As can be anticipated, the result is a sigmoidal activity profile (Figure 7).

The potential of layer management

A first set of experiments to prove the concept in Air Liquide's pilot unit had positive results. In fact, it was shown that under very specific conditions the maximum potential of Layer management could lead to the use of about half of the amount of catalyst used in state-of-the-art processes (Tab. 1). Therefore, layer management has the potential to significantly modify the state-of-the-art of new methanol plants. It would then support optimized designs of grass root plants and new processes (such as CO_2 applications). Nevertheless, in a first step for the commercialization of layer management, the focus is put on revamp and capacity extensions of existing plants considering all constraints and conditions of existing plants.

Concept for commercialization

Commercialization is envisioned through refill solutions, which meet the constraints of existing facilities and stepwise exploit the potential of Layer management. The first layer management reference has been in commercial operation since August 2018. In this case, the successfully achieved target was to optimize pressure drop in the GCR of a large-scale methanol plant. However, the main objective of layer management for refill cases – besides pressure drop optimization – is longer lifetime of the catalyst and more accumulated methanol production over the lifetime. Regarding layer management for existing methanol processes one of the critical important factors to be considered is the pressure drop. Hence pressure drop is a significant constraint to equip plants with layer management and it will impact the operating conditions of the whole synthesis loop.

Therefore, the aim is to find a solution to improve the methanol production by using the layer management concept within the design restriction of pressure drop. Therefore, this work presents a smart Layer management concept leading to an improvement of methanol production merely by an optimization of the catalyst bed design and operating conditions. Case studies were taken into consideration to evaluate the benefit of layer management on existing plants. All plant specific constraints (i.e. pressure drop, recycle compressor, steam temperature...) are considered in the simulations and an optimum solution for the specific plant is developed. In most methanol plants recycle ratio, reaction temperature and pressure drop in the methanol synthesis loop are increased over time to compensate for deactivation of catalyst. With Layer management loop efficiency will be increased, thus the loop can be operated at milder conditions. This results in increased energy efficiency and extended catalyst lifetime. If more synthesis gas can be made available, Layer management is a solution for increased capacity.

Model and Concept Validation with Pilot Plant

One of the strengths of Air Liquide's experts is in generating data in a pilot plant, translating the data into a form that can be used to scale-up results. The process development unit (PDU) consists of a reactor with steam jacket, two separators at different pressure levels and a recycle loop to feed unconverted gas back to the inlet of the reactor as depicted in Figure 8. The comparison of one of the experiments and the respective modelling results are shown in Figure 9. It can be seen that the temperature profile and the conversion obtained from the model are in line with the experimental observations. In the experiment, no unusual catalyst deactivation was observed for the Layer management arrangement during the test duration (up to 1000 h). The experiments confirm the validity and accurateness of the model developed by Air Liquide with the support of Clariant.

Modelling case study – Demonstration of lifetime yield benefit

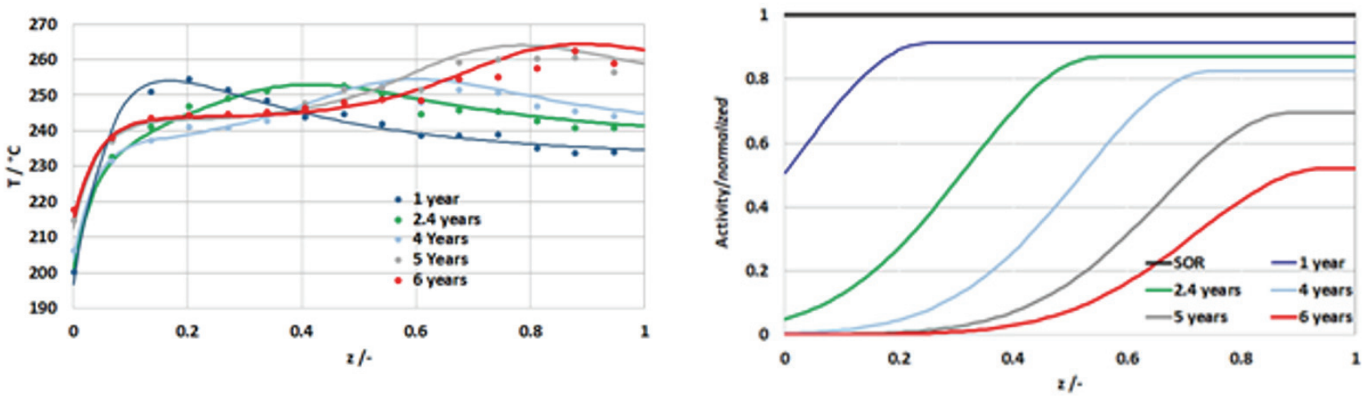

Fig. 7 Temperature and activity profile over the reactor length in commercial reactors for different times-on-stream (TOS). SOR = Start-of-Run.

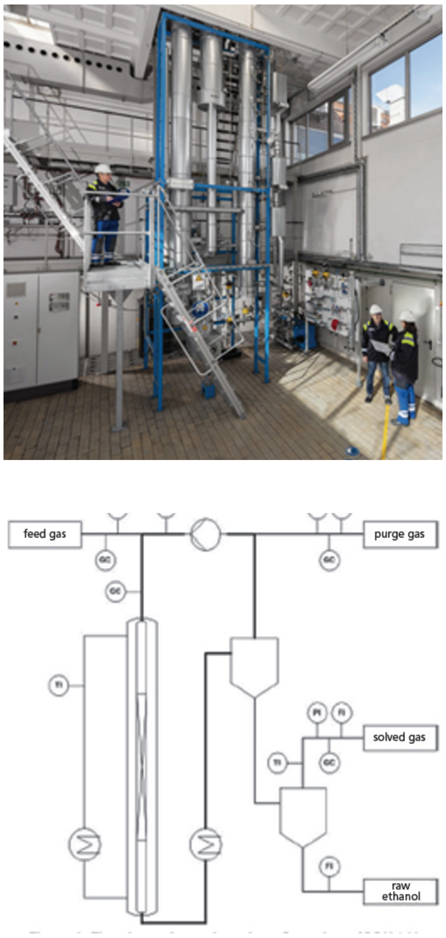

Fig. 8 Pilot plant at Air Liquide's Innovation Campus Frankfurt

Based on the validated model and the commercial deactivation behaviour, it is possible to make reliable lifetime yield prediction and optimize the reactor layout. In a modelling case study, it could be shown that a benefit in methanol yield can be achieved especially at middle-of-run (MOR) and end-of-run (EOR), when local deactivation of the catalyst layer becomes important and the per pass conversion decreases (Fig. 10). This opens the possibility to extend the operation lifetime and contributes significantly to the lifetime production of the catalyst.

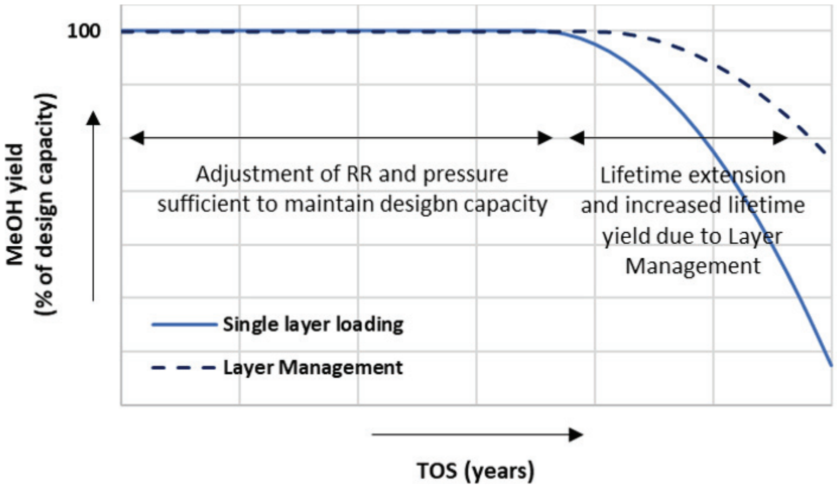

Fig. 10 Prediction of methanol yield over lifetime for single-layer loading vs. Layer Management.

Conclusion

Clariant and Air Liquide have been collaborating in the field of MeOH synthesis for many years and have successfully investigated the possibility of improving the interplay and overall performance of catalyst and reactor. The development of Layer management for methanol synthesis is another example of successful cross-market technology transfer and joint-development between an engineering company and a catalyst provider working in close collaboration. The potential of layer management can be seen as a game changer for future methanol production providing compacter and more resilient design. This concept allows for a vast range of tailor made refill improvements that can improve the catalyst usage in all existing units for e.g. debottlenecking. In the context of circular economy, different feed sources such as stranded gas, unused syngas capacities and CO_2 rich gases, layer management is a flexible tool to offer optimized methanol synthesis set-ups for a wide range of specific plants.

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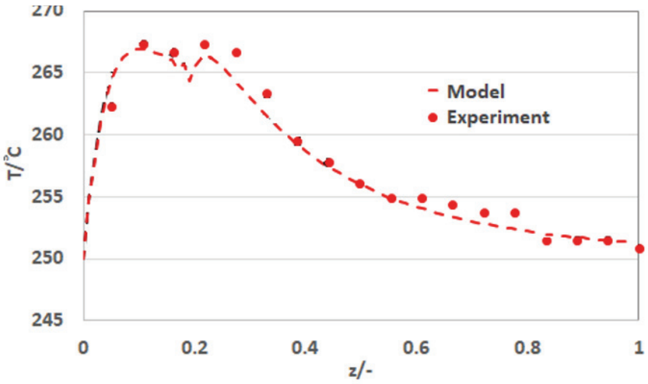

Pilot plant	Experiment	Model
Tmax (°C)	267.3	266.9
Tout (°C)	250.9	251.3
XCO, pp (%)	81.5	81.6
XCO2, pp (%)	32.2	31.2

Fig. 9 Pilot plant experimental results for Layer Management and validation of model predictions. In this experiment, the top 20% of the reactor were filled with a different catalyst than below