

Methanol Synthesis in a Fixed Bed Recycle-reactor System: Effect of once-Through and Recycle Operation on Activity and Productivity

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Abstract

Methanol is one of the largest scale chemicals and produced on a multi-million-ton scale per year worldwide. Among all organic chemicals, Methanol is the third-largest-scale pure component in production, only being surpassed by ethylene and propylene. Methanol is used for a large number of purposes. It can be used as fuel ingredient, either in pure form or as MTBE, as starting material for the generation of hydrocarbons (MTO and MTG processes), as solvent, as well as precursor for formaldehyde, acetic acid, and dimethyl ether.^[1]

The production of MeOH from synthesis gas is thus an extremely important chemical process. In this contribution, selected results of different MeOH synthesis projects are presented. The target reaction was investigated both in a parallel fixed bed rig using catalysts on a 1 ml scale and in a single-fold sub-pilot plant scale rig with 20 ml of catalyst. In the latter case, both once-through and recycle mode operation were performed. The major process variables were the reaction temperature, the concentration of CO₂ in the feed gas, and the GHSV. The effect of these variables on feed gas conversion and catalyst productivity was studied. One highlight of the study was the generation of MeOH both with high productivity and high gas utilization by operating the sub-pilot rig in recycle mode.

Introduction

Methanol can be produced from synthesis gas according to the following equation:



The initial process was based on zinc-chromium-oxide catalysts that were operated at high pressure (250-350 bar) and temperature (360-380 °C). The state of the art low-pressure process uses Cu-Zn-Al mixed oxide that is operated at 200-300°C and 50-100 bar. While showing a superior activity and selectivity, the latter catalysts are highly sensitive towards catalyst poisons such as sulfur, halogens, and metal carbonyls.

Though stoichiometrically simple, the Methanol Synthesis holds a couple of challenges, if it is to be performed under optimum conditions. Most importantly, the Methanol formation is an exothermic equilibrium reaction. Higher reaction temperatures, which are beneficial for turnover rates, shift the equilibrium to the undesired reactant side. High reaction temperatures also promote catalyst sintering, leading to loss of active surface and catalytic activity. High reaction pressures favor MeOH formation, but demand reactor systems with accordingly higher pressure ratings. A high H₂/CO ratio is also beneficial to achieve high conversion of CO to Methanol, but at the expense of low H₂ utilization and high recycle gas streams. Finally, it is known that equation 1 is in fact a two-step process consisting of CO₂ hydrogenation followed by water gas shift reaction (WGSR).



In the absence of CO₂ and water, reaction rates are very slow. The addition of small level of CO₂ to synthesis gas leads to a pronounced increase in turnover rates, but too high CO₂ concentrations have an adverse effect. The optimum level of CO₂ may be different for different catalysts. For a recent discussion of the reaction mechanism from synthesis gas and CO₂, see [2].

It is thus not a trivial task to run a methanol plant under truly optimum conditions. The major challenge consists in the heat management. Due to the exothermic nature of the process, and its thermodynamically limited turnover, heat removal is an essential requirement. This can be achieved by various means, such as intermittent addition of cold feed gas. Another heat management concept is the operation in two temperature regimes, where the first part of the bed is run at high temperature to achieve high turnover rates, and the second part is run at lower temperature to operate at higher possible Methanol concentration.^[1]

The most important catalyst properties are its intrinsic activity, its ability to convert water and CO₂ and its tolerance towards catalyst poisons. In the field of MeOH synthesis, both the identification of new materials and the optimization of existing materials are challenging and attractive tasks.

In this contribution, a brief overview of a material screening program is given and then compared to the results obtained in a single strand rig with full cold gas recycle operation. The performance of a given MeOH catalyst both in once-through and recycle operation under commercially relevant conditions will be discussed focusing on the impact on activity and productivity in both operation modes.

Screening of MeOH Catalysts in a 32x parallel test rig

Over the past 15 years, hte has developed a powerful and flexible technology platform that allows the execution of research projects from diverse areas. All research projects benefit from the following features of hte's integrated workflows:

- Robust test rig and analytical hardware
- Excellent software for all workflow steps, ranging from experiment definition in our process control software hteControl4 for handling of massive amounts of online analytical data and for managing of flexible and robust data evaluation routines.

Fig. 1 shows a comparison between two of the tested catalyst types as a function of catalyst weight (encoded by the size of the symbols) and the process conditions. The data show an excellent agreement between identical bed configurations (same catalyst, same weight) for both materials. The activity level for CAT2 is generally higher than for CAT1.

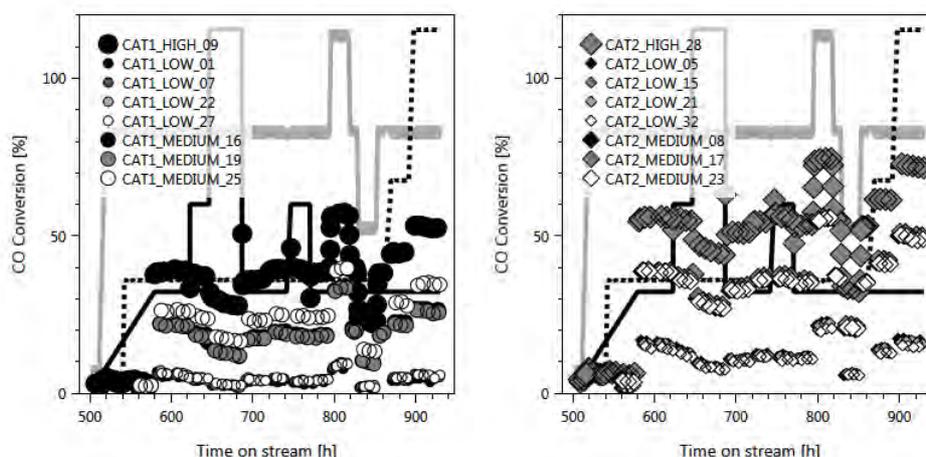


Fig. 1. Course of CO conversion for two catalyst types at various process conditions: temperature (grey line) 180-210 °C, CO₂ concentration (black line) 0-4 vol%, pressure (black dotted line) 50-75 bar.

A closer inspection of the charts reveals that the response of the individual catalysts to changes in process conditions is very similar. In the absence of CO₂ during the initial period of ~ 40 h, the CO conversion was very low with values less than 10 % even for the largest bed of the most active material. Addition of 1 vol% CO₂ led to a massive increase in activity by a factor of ~5. Doubling the CO₂ concentration to 2 vol% had no beneficial effect, and a further doubling of the CO₂ concentration to 4 vol% finally caused a significant drop in activity. The effects of temperature and pressure were as expected. The increase of either temperature or pressure led to an increase in CO conversion.

The effect of reactor temperature and CO₂ concentration is explicitly shown in Fig. 2 for the reactors with the largest and smallest amount of both catalysts.

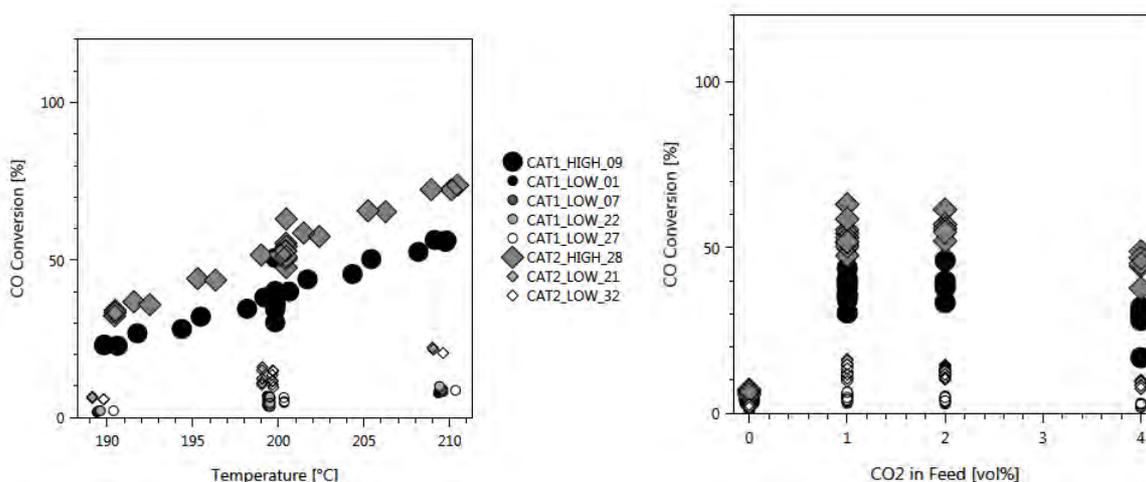


Fig. 2. Plot of CO conversion versus temperature at 1 vol% CO₂ and CO conversion versus CO₂ feed concentration at 200 °C for the largest and smallest beds of both materials.

Under all reaction conditions, the CO conversion can be directly correlated with the amount of catalysts. High amounts of catalyst thus give a better gas utilization. However, as shown in Fig. 3, the highest conversion is not necessarily accompanied by the highest productivity. At 190 °C (left), the bed with the largest amount of CAT2 is the one with the highest conversion, and among the ones with the highest productivity. At 200 °C (center) and even more at 210 °C (right), the two beds with the medium amount of CAT2 rival and finally surpass the full bed with respect to productivity. This observation suggests that under conditions of high conversion and thus good gas utilization, the productivity, and thus the utilization of the reactor space and/or catalyst material, is limited. Most likely, the reason for the lower response of the full beds to increased temperature is an incipient thermodynamic limitation.

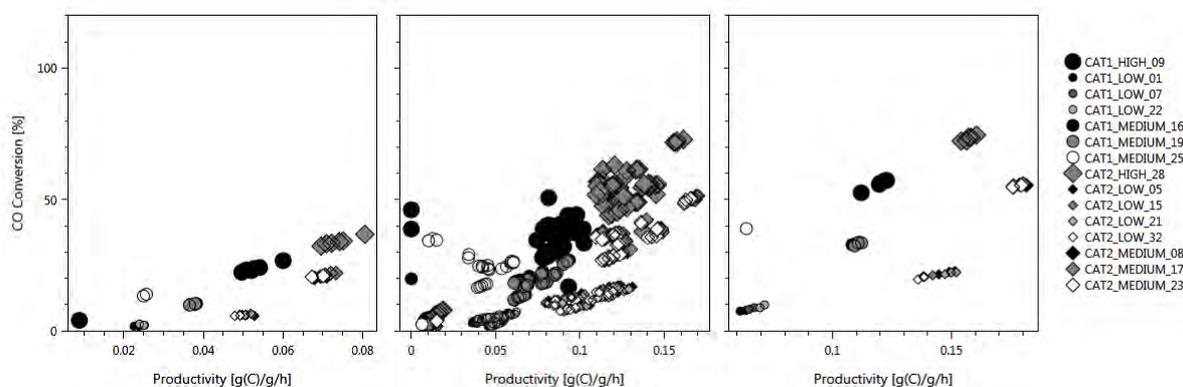


Fig. 3. Plot of the CO conversion vs. the MeOH productivity at 190 °C (left), 200 °C (center), and 210 °C (right).

Screening in a parallel fixed bed test rig is a powerful tool for classification of existing materials and their comparison with new formulations in a broad parameter space. However, its operating mode is limited to once through only. The reaction conditions can be chosen to either achieve optimum gas utilization or optimum productivity, but not both.

Operation of a Methanol Catalyst in a Single Reactor Rig with Full Cold Gas Recycle

An important step in selecting a catalyst for commercial application is its test under conditions that are close to those in a commercial plant. As an extension of its screening work, hte has designed and built a rig that can feed the off gases of a process back into the major feed inlet. A sketch of this rig is shown in Fig. 4. Some of the highlights of the rig are:

- Feed gas modules that can be operated in flow and in pressure controlled mode. The former is used for once-through operation, the latter for recycle operation.
- Coolable condenser (0.6 L volume) with level-controlled, continuous liquid drain off into weighted, larger product vessel (22 L volume) maintained at ambient pressure (not shown in Fig. 4).
- Flow - controlled release of the hot reactor effluent or the cold condenser offgas to the online gas phase analytics.
- For recycle operation (left): gas circulation pump to feed the condenser off gas back into the major feed gas stream.
- For once through operation (right): pressure controller in the major off gas tube.

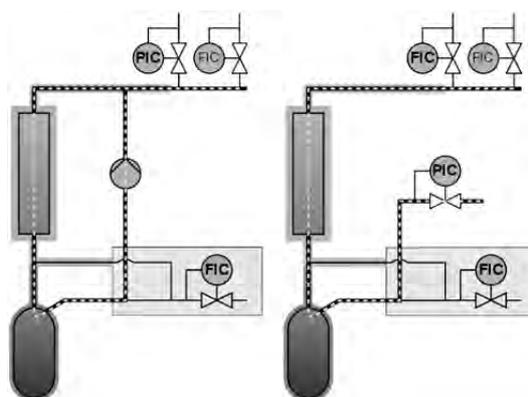


Fig. 4. Simplified rig scheme showing the major gas streams in once-through (left) and recycle mode (right).

The rig is designed for fixed-bed gas-to-liquid applications. The maximum reactor ID is 25 mm, which allows the testing of >> 100 ml of undiluted catalyst in a 60 cm isothermal zone of the reactor. Smaller ID reactors with 20 and 16 mm are also available. The actual choice of reactor ID and catalyst amount is based on the expected heat evolution, and the preferred GHSV of the target reaction.

It is noted that the available ratio between length and diameter of the catalyst bed is far below that of a commercial reactor, resulting in far lower linear velocity and much less effective convective heat removal. To control the heat evolution in the catalyst particle, a small particle size (300-500 μm) was used, and the catalyst material (20 ml) was diluted with a twofold excess by volume of corundum. The mixture was filled in a 16 mm reactor tube, resulting in a catalyst zone with a height of 35 cm.

Results from Once Through Operation

In a first set of experiments, it was tested whether the catalyst delivered the expected performance in a known process parameter space or not. The CO_2 concentrations was varied between 2 and 6 vol%, the temperature between 210 and 250 $^\circ\text{C}$, and the space

velocity between 3500 and 6500 h⁻¹.

Initially, the interplay between CO₂ concentration (gray thick line) and GHSV (black dotted line) on both the CO conversion and the MeOH productivity was investigated. As shown in Fig. 5, the CO conversion (left) dropped with increasing GHSV and decreasing residence time. The actual level of CO₂ did not have a notable effect. The MeOH productivity (right) was not affected by changing from the low to the medium GHSV. The change to the highest GHSV caused only a small drop in productivity. As for the low GHSV experiments, the level of CO₂ cofeed had little effect on the catalyst activity. These findings clearly demonstrate that the reaction was running under pure kinetic control, where the activity is mainly determined by temperature.

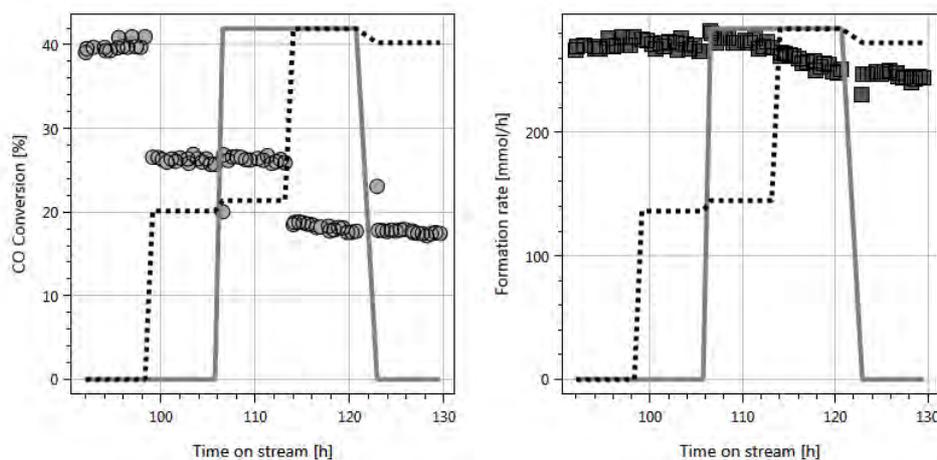


Fig. 5. CO conversion (left) and MeOH formation rate (right) at 210 °C, 2 and 4 vol% CO₂ (grey line), and GHSV 3200-6500 h⁻¹ (black dotted line).

Using a low CO₂ concentration and a high GHSV, the reaction temperature was then varied between 200 and 250 °C. The effect of the various temperature levels on the CO conversion and the MeOH productivity is shown in Fig. 6. While the first five temperature raises led to improvements in activity and productivity, the increments in performance become successively smaller. The temperature increase from 240 °C to 245 °C had hardly an effect on the activity, and a further temperature increase to 250 °C led to a lower activity. This clearly demonstrates that thermodynamically possible MeOH concentration is becoming the rate-limiting factor between 245 and 250 °C. A further improvement in productivity would have only been possible by an increase in the space velocity.

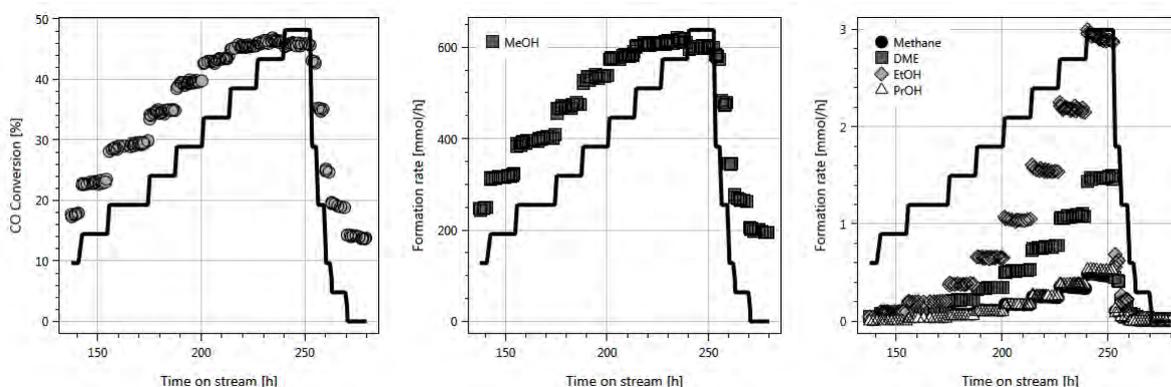


Fig. 6. CO conversion (left), and formation rates of MeOH (center) and side products (right) at 2 vol% CO₂, 6500 h⁻¹ GHSV, and temperatures between 200 and 250 °C (black line).

The effect of the various temperatures on the productivity regarding MeOH and typical side products of the MeOH synthesis (higher alcohols, methane, dimethyl ether) is also shown in Fig. 6. It can be seen that the formation rates of especially EtOH increase with increasing temperature. Methane formation does not play a significant role, even under the harsh conditions at maximum MeOH concentration. It should be noted that even under equilibrium limited conditions, the calculated selectivity to MeOH is still ~99 %.

The experiments described above demonstrate that the MeOH synthesis could be successfully run on a larger scale, with 20 g of catalyst. The experiments also revealed clear limits of a technically attractive parameter space. Using the applied levels of GHSV and CO₂ concentration, a temperature of more than 245 °C is certainly not recommended due to thermodynamically limited MeOH productivity and increased formation of side products. Overall, it was demonstrated that the constraints applied by the once through operation do not allow the reaction to be run with simultaneous good gas utilization and high productivity.

Results from Recycle Operation

The operation in recycle mode instead of once through mode does not only offer a new process variant, but also requires operating the rig in a fundamentally different way.

The only common step in defining the experiments is the definition of the reactor temperatures. The definition of the other parameters, namely, reactor pressure, GHSV, and feed gas composition, differs largely between the two operating modes. In once through mode, the pressure controller at the end of the outlet tube controls the reactor pressure by adjusting the flow rate leaving the reactor system. In recycle mode, one of the gas feed modules is operated in a pressure controlled way and maintains the pressure inside the rig by adjusting the amount of gas that is fed into the rig. The GHSV and feed gas composition in once through mode can be precisely and directly defined by the operator.

In recycle mode, however, the situation is much more complex. The feed gas is passed over the catalyst bed where it is undergoing a change in composition. This composition change is dictated by the catalyst activity and constraints resulting from thermodynamics or stoichiometry. The exhaust gas leaving the reactor is then passed through the condenser where the MeOH is removed from the gas stream. The condenser off gas is then fed back to the main feed line where it is mixed with fresh feed gas. Fresh H₂ is fed in a pressure controlled mode where the flow rate is defined to compensate gas losses through conversion of H₂ and CO to MeOH, by removal of the formed MeOH through condensation, by gas samples taken after the reactor outlet (hot gas analysis, HGA) or after the condenser (cold gas analysis, CGA). Fresh CO and CO₂ are fed in flow controlled mode with flow rates defined by the user. Then, the gas mixture is fed over the catalyst bed again, and the cycle repeats. The mass streams in recycle operation are depicted in Fig. 7.

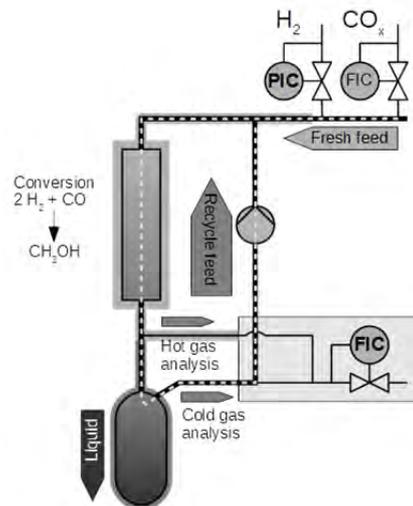


Fig. 7. Feed inlet, recycle, and product outlet routes in recycle operation.

One of the major challenges in recycle operations is to adjust the manually definable process parameters (pressure, temperature, recycle gas flow rate, rate of fresh CO_x feed) in a way that a productive steady state is achieved. In steady state, the following conditions must be met:

- Gas flow equilibrium: The fresh feed rate of the pressure-controlled H₂ must match the rates of H₂ and CO_x that are removed from the system. If this condition is not met, the pressure inside the reactor will not be stable.

- CO_x flow equilibrium: The fresh feed rate of flow-controlled CO_x must match the rates of the CO_x outlet, i.e. the rate by which CO_x is removed from the reactor system. Violating this condition prevents the establishment of a stable CO_x concentration in the reaction feed.

For both conditions, it is essential to have equilibrium between fresh feed gas rates and outlet rates. The fresh feed gas rates can be readily determined. The determination of the outlet rates is less straightforward, as multiple ways for removing H_2 and CO_x from the reaction system exist:

- As such, H_2/CO_x can be purged out of the system through the hot and cold gas analysis.
- Conversion to MeOH, and removal from the system by the continuous drain-off of the liquid MeOH product.

Using the same catalyst as for the previous runs, some additional experiments were performed with the aim of achieving a steady state at various productivity levels. The experiments were set up in the following way: starting with an initial reaction temperature of 220 °C, the CO feed rate was then set to a level close to the MeOH formation rate observed at the given temperature during the once through experiments. It was expected that under these conditions, full conversion of the fresh CO feed should be observed, fulfilling the CO_x flow equilibrium condition. The temperature and fresh CO rate were then increased, and the flow rates of fresh H_2 and CO feed used as qualifier to check whether the system was on the way to a steady state. In Fig. 8 (left side), the process values for the fresh feed rates are shown, as well as the reaction temperature (light gray dotted line), and the recycle gas flow (continuous dark gray line).

For the first two experiments, the existence of a steady state can be quickly deduced from the fact that the rate of fresh H_2 (black line) is quite accurately twice as high as the rate of fresh CO. During the first run at 220 °C, (400 – 425 h), the values are ~9 and ~22 NL/h, and for the second run at 230 °C (425 - 450 h), the values are ~15 and ~32 NL/h. The rate of fresh H_2 was a good indication of full conversion of the fresh CO feed, as the observed 2:1 ratio matched the H_2/CO consumption ratio defined by the reaction stoichiometry. The third temperature level, however, proved to be more challenging. As can be seen by the course of the process values around 450 h, the increase of the CO feed rate to 22 NL/h at 240 °C was not followed by an increase of the H_2 fresh feed rate, but that the latter remained constant at ~32 NL/h. However, after the recycle flow rate was increased from 115 to 170 NL/h and the CO feed rate slightly reduced to 20 NL/h, the H_2 feed rate quickly raised to the level expected for full conversion of the fresh CO feed rate (~42 NL/h). Under these conditions, the rig was operated stable for 2 days.

The reason for this behavior can be deduced by examination of the concentrations of H_2 , CO and MeOH in the hot reactor effluent (Figure 8, right).

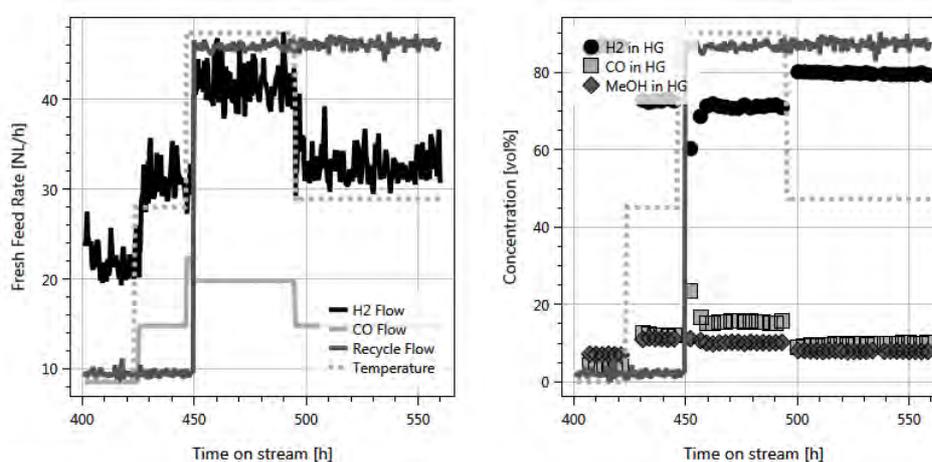


Fig. 8. Interplay between the flow rates of fresh H_2 and CO, the reaction temperature, the flow rate of the cold recycle gas, and the composition of the hot reactor effluent.

Firstly, it can be seen that the temperature increase at 450 h initially leads to a drop in H₂ and to an increase in CO concentration. This observation is in agreement with incomplete conversion of the fresh CO feed, which was already deduced from the process data. Secondly, the MeOH concentration in the effluent remains nearly constant at ~10 vol%. Obviously, the thermodynamically limited MeOH concentration was initially a rate-limiting factor. The increase in the flow rate of the (essentially MeOH-free recycle gas) led to an increase in gas velocity through the catalyst bed, which allowed at constant MeOH concentration a higher rate of MeOH to be formed and thus a higher rate of CO to be consumed.

In Fig. 9, the productivities of MeOH and of the major side products are shown. At 240 °C and high recycle gas flow, a formation rate of 900 mmol/h MeOH was observed, which is ~50 % higher than the highest MeOH formation rate under once-through conditions. The observed MeOH formation rate closely matches the measured CO feed rate, indicating an excellent gas utilization. It should be noted that the essentially constant MeOH concentration in the hot reactor effluent suggests that the MeOH formation rate might still be thermodynamically limited. Using an even higher recycle gas flow, the catalyst would most likely have been able to consume even more CO and produce correspondingly more MeOH. Interestingly, methane was observed to be the most important side product, while it was the least important under once-through conditions. The reason is not an increase in methane selectivity, but a more efficient increase of the low-volatile methane in the circulating gas atmosphere.

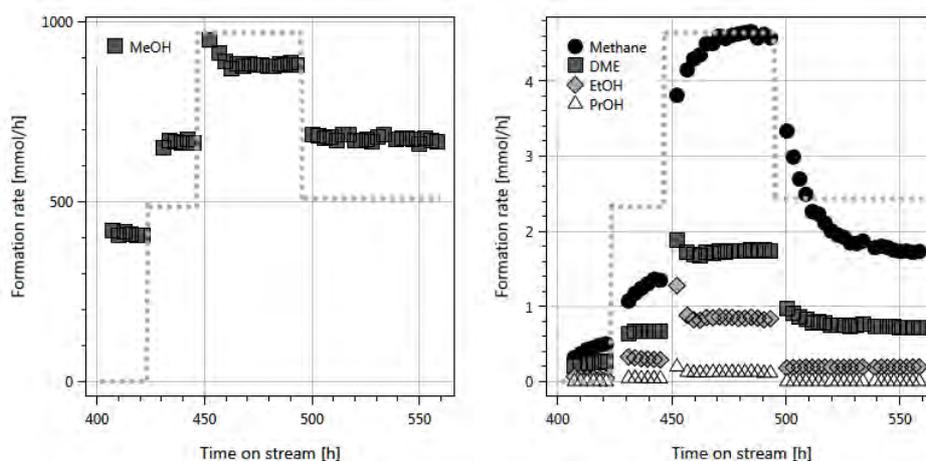


Fig. 9. Formation rate of MeOH (left) and side products (right) in recycle operation (reactor temperature, grey dotted line).

Summary

The MeOH synthesis is an industrially highly relevant process that is run on a large scale and that is expected to see substantial growth in the future.^[3] At hte, screening of catalysts and process optimization can be supported in parallel fixed bed reactors measuring the kinetics and activity in a broad parameter space with small amounts of catalysts. Selected catalysts can also be tested at a larger scale under cold-gas recycle conditions at maximum productivity or equilibrium conditions to study long-term stability of the catalyst and to generate batches of liquid product for further analysis.

References

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