

## **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**

Synthesis gas can be produced from a variety of carbon sources and many processes are commercially available using synthesis gas as intermediate for the production of hydrocarbons, mainly in the chemical and petrochemical industry [1]. In this contribution, we will focus on the industrially relevant methanol synthesis [2] with a commercial methanol synthesis catalyst to maximize methanol productivity and synthesis gas utilization in gas recycle operation.

Methanol synthesis was studied in a broad parameter space ( $\text{CO}_2$  ranging from 0 – 6 vol.-%, GHSV 3150 – 13000  $\text{h}^{-1}$ , temperature 200 – 250 °C) in once-through and in gas recycle operation mode. hte used a bench scale test system with 60 mL catalyst volume in a 16 mm ID reactor tube to evaluate performance of a commercial  $\text{Cu/ZnO/Al}_2\text{O}_3$  catalyst. All experiments were carried out at 40 bar(g) pressure level. While using gas recycle operation mode, pressure could not be controlled via back-pressure regulation valves and a more sophisticated process control was needed. Hydrogen was used as pressure regulator gas to compensate volume contraction while carbon-containing feed gases ( $\text{CO}_x$ ) had to be controlled to compensate the carbon release via liquid methanol drainage and to avoid  $\text{CO}_x$  accumulation in the recycle stream. We demonstrated stable operation in gas recycle mode that can be applied while liquid methanol was the main product released from the system. Stable operation was achieved over 900 h time-on-stream in both operation modes and typical characteristics of methanol synthesis could be demonstrated. Productivity is mainly driven by temperature increase up to thermodynamic equilibrium conversion in once through operation mode. In contrast, productivity could be further increased by overcoming thermodynamic limitations in full-recycle operation due to removal of liquid products from the product stream while sending unconverted cold gas back to the reactor inlet. High production rates of about  $1 \text{ g}_{\text{MeOH}}(\text{g}_{\text{Catalyst}} \cdot \text{h})^{-1}$  were achieved at stable process control and heat management. Accumulation of undesired by-products like ethanol, methane, and DME were observed at higher temperature in both operation modes. Net  $\text{CO}_2$  production could be clearly assigned to water-gas shift reaction with increasing temperature while  $\text{CO}_2$  concentrations of > 2 vol.-% in the feed stream did not show significant effect on CO conversion at all.

### **References**

- [1] M. Marchionna, DGMK Tagungsbericht (2015-2), ISBN 978-3-941721-56-2
- [2] Alfred Haas et al., DGMK Tagungsbericht (2008), ISBN 978-3-936418-81-1