# Supplementary Information

## A1 CFD model of the MR

Mesh independence:

| Mesh | #Cells | #Iterations | $CH_3OH$ yield [%] |
|---|---|---|---|
| Coarse | 80,058 | 15,920 | 19.2 |
| Standard | 284,936 | 12,734 | 19.3 |
| Fine | 503,630 | 13,644 | 19.3 |

*Table 1: Mesh independence study of the MR CFD model with residuals of 1e-08.*

## A2 Reaction validation

## A2.1 Gallucci et al. validation[1]

The experimental results by Gallucci et al. in a TR are used to validate the introduced kinetic models. The reaction zone length is 20 cm and the reaction zone diameter is 0.67 cm. The reactor is loaded with 8 g of the CZA type MK-101 catalyst by Topsoe in a packing volume of 7 $cm^3$. The volumetric flow rate at the feed gas inlet is 800 ml/min with $H_2$ to $CO_2$ ratios of 3:1 and 7:1. Gallucci et al. investigate catalytic $CO_2$ hydrogenation at pressures of 20 bar and 24 bar and between temperatures of 200 °C and 263 °C.[1]

Mesh independence:

| Mesh | #Cells | #Iterations | $CO_2$ conversion [%] |
|---|---|---|---|
| Coarse | 11,045 | 302 | 10.2 |
| Standard | 70,584 | 406 | 10.5 |
| Fine | 503,630 | 916 | 10.5 |

*Table 2: Mesh independence study for the reaction validation with data of Gallucci et al. with residuals of 1e-08.*

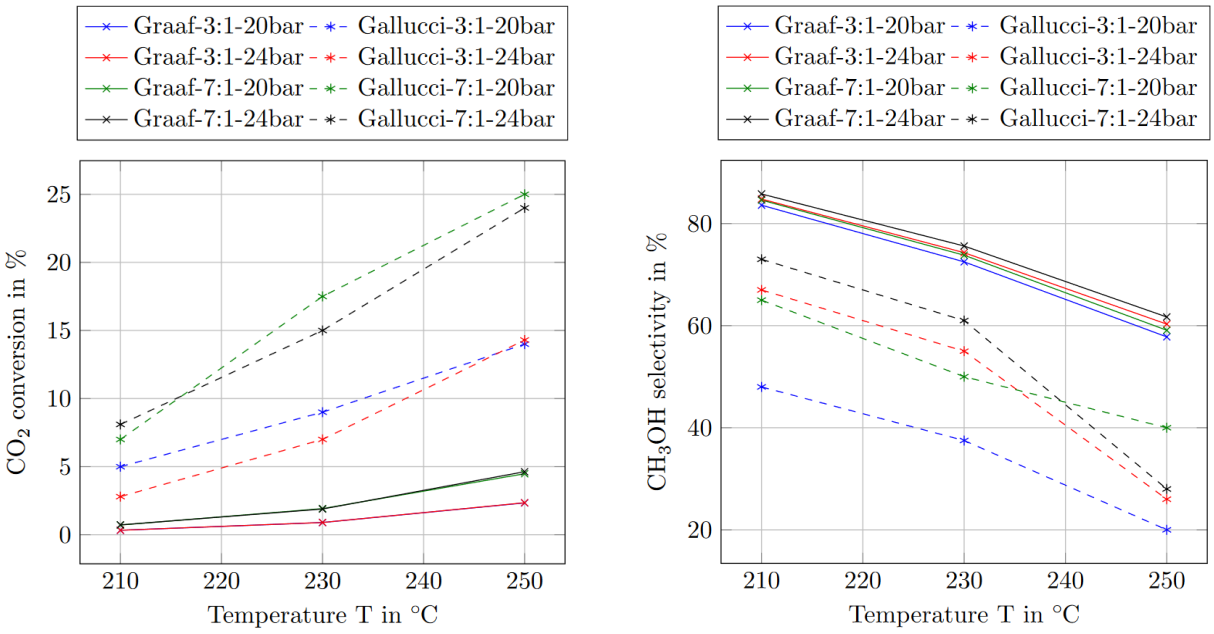


*Figure 1: Comparison of the $CO_2$ conversion and $CH_3OH$ selectivity between the CFD simulation with the reaction UDF based on the kinetic model by Graaf et al. (solid) and the experimental data by Gallucci et al. (dashed).[1]*

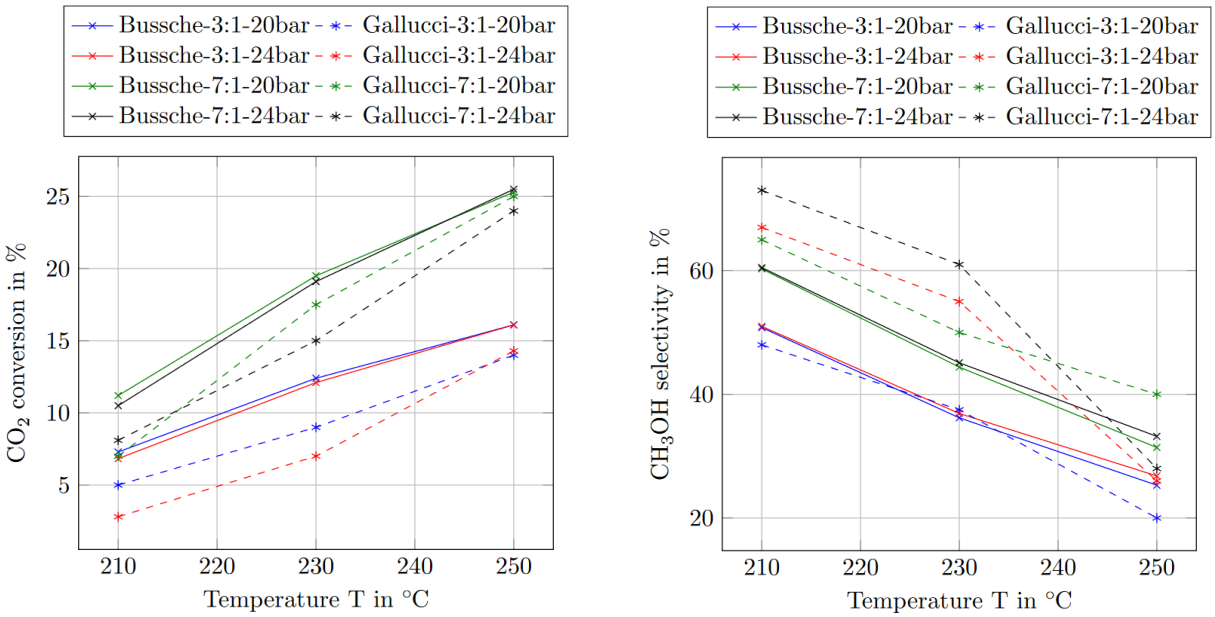


*Figure 2: Comparison of the $CO_2$ conversion and $CH_3OH$ selectivity between the CFD simulation with the reaction UDF based on the kinetic model by Bussche and Froment (solid) and the experimental data by Gallucci et al. (dashed).*[1]

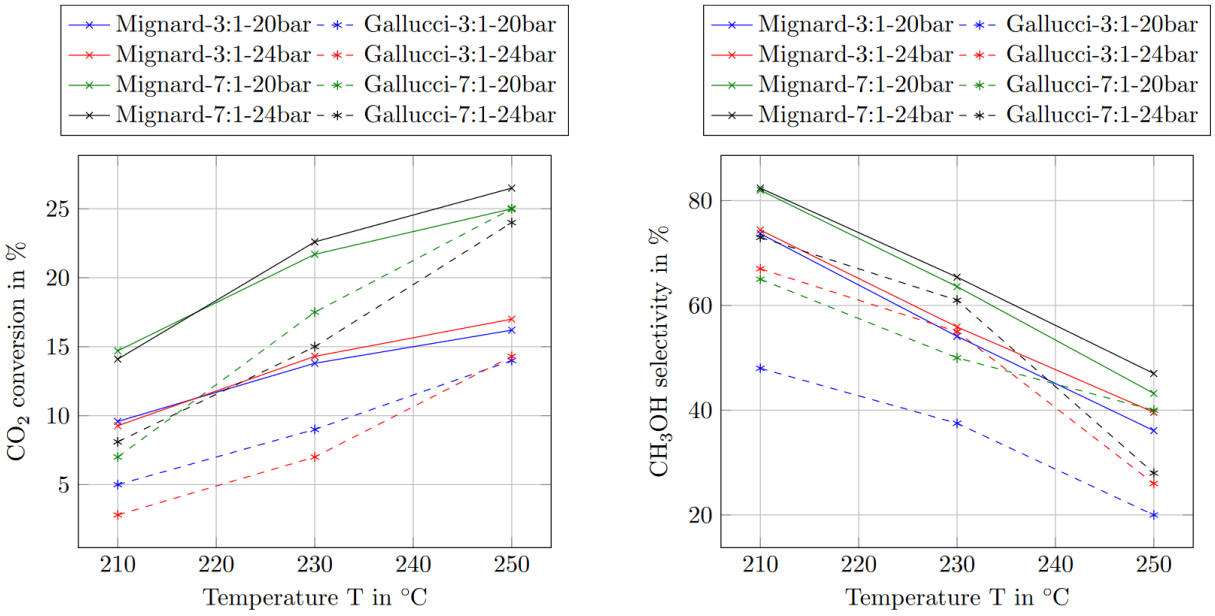


*Figure 3: Comparison of the $CO_2$ conversion and $CH_3OH$ selectivity between the CFD simulation with the reaction UDF based on the kinetic model by Mignard and Pritchard (solid) and the experimental data by Gallucci et al. (dashed).* [1]

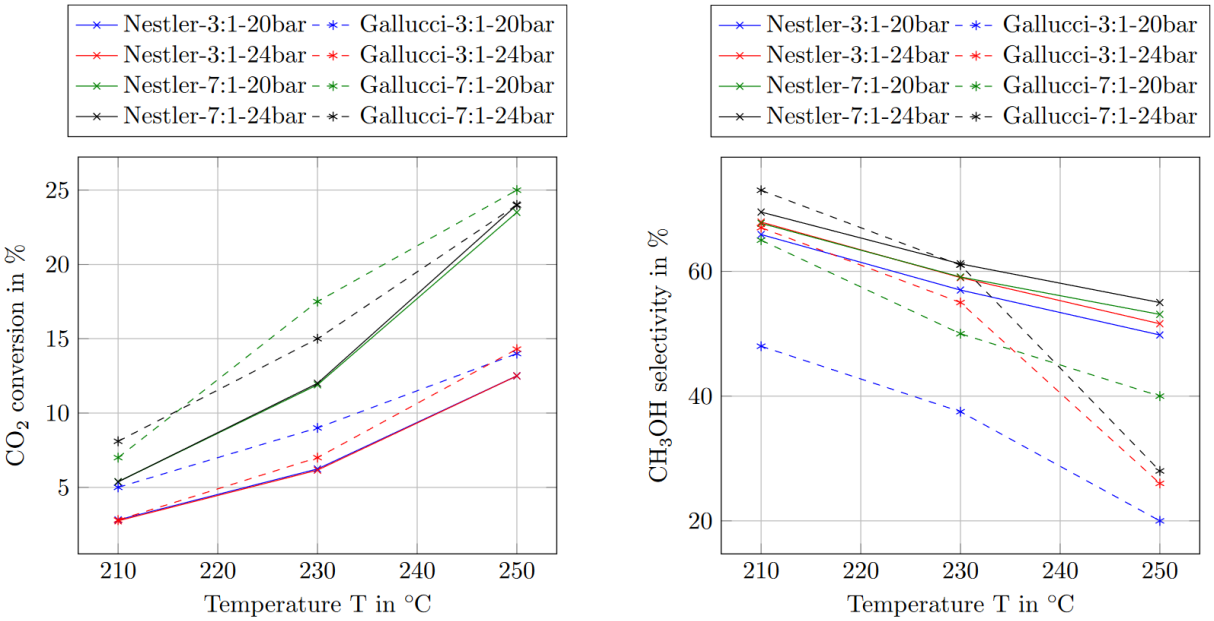


*Figure 4: Comparison of the $CO_2$ conversion and $CH_3OH$ selectivity between the CFD simulation with the reaction UDF based on the kinetic model by Nestler et al. (solid) and the experimental data by Gallucci et al. (dashed).*[1]

## A2.2 Bussche and Froment validation[2]

To assess the accurate integration of the kinetic model, the reaction UDF is additionally validated with simulative data by Bussche and Froment. They investigate methanol synthesis and water gas shift reaction on a commercial $Cu/ZnO/Al_2O_3$ catalyst at pressures up to 51 bar and temperatures between 180 °C and 280 °C. The reactor with a diameter of 0.016 m and a length of 0.15 m is fed with a mass flow rate of $2.8 \cdot 10^{-5}$ kg/s and a $CO/CO_2/H_2$/inert composition of 4/3/82/11 mol%.[2]

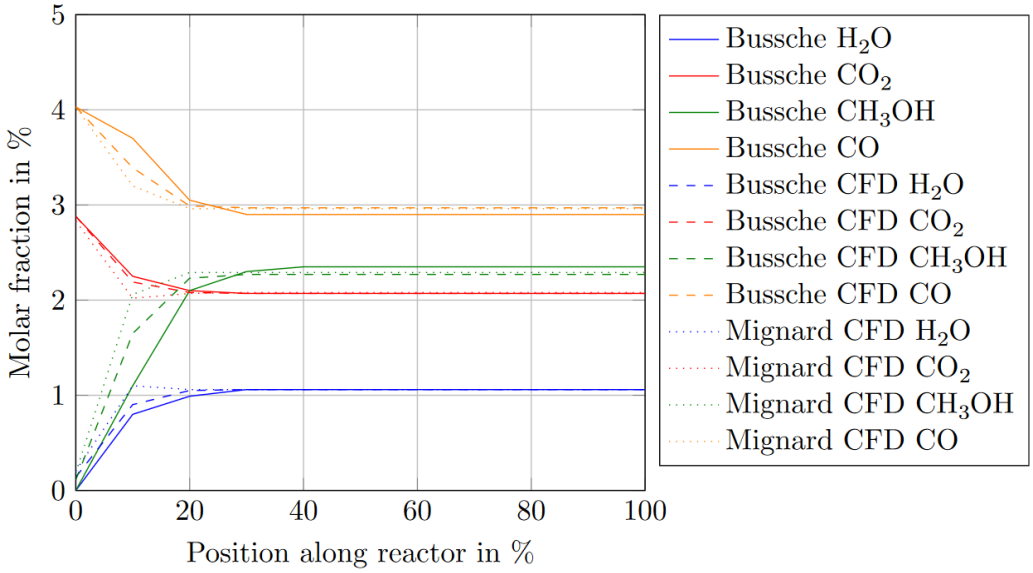


*Figure 5: Comparison of the molar fractions along the reactor of the simulative study by Bussche (solid) with the CFD simulation with the reaction UDF based on the kinetic models by Bussche (dashed) and Mignard (dotted) at 50 bar and 220 °C.*[2]

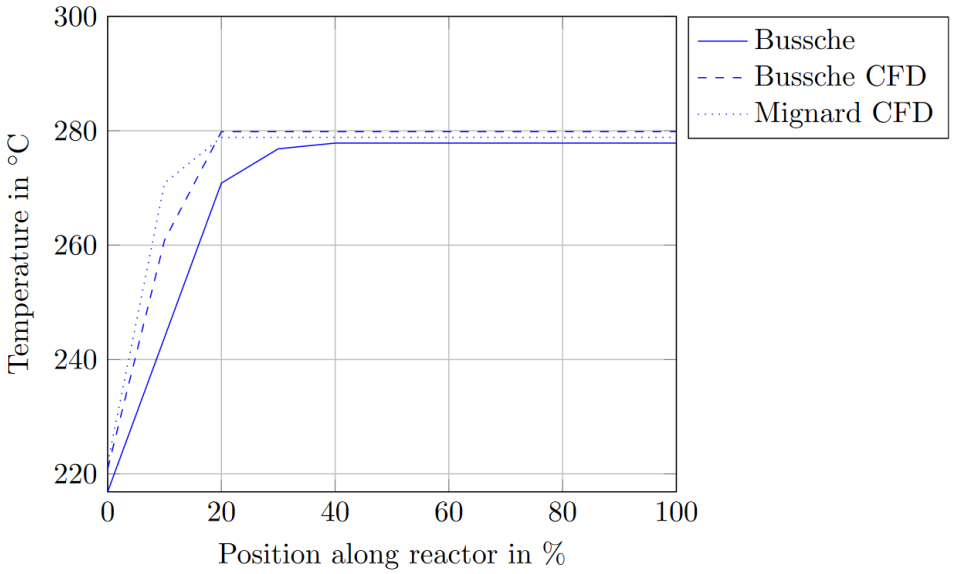


*Figure 6: Comparison of the temperature along the reactor of the simulative study by Bussche (solid) with the CFD simulation with the reaction UDF based on the kinetic models by Bussche (dashed) and Mignard (dotted) at 50 bar and 220 °C.[2]*

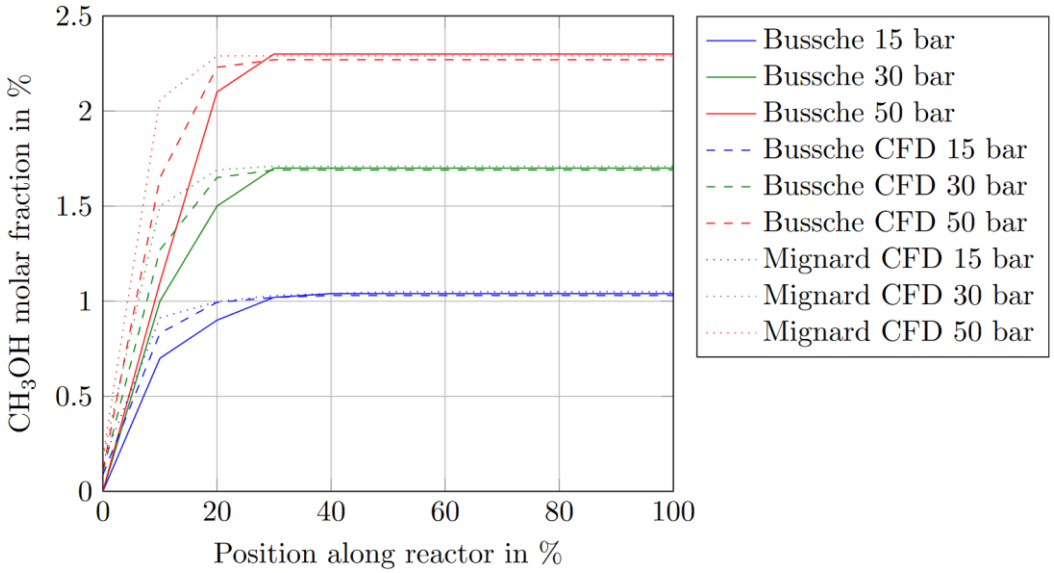


*Figure 7: Comparison of the $CH_3OH$ molar fraction along the reactor of the simulative study by Bussche (solid) with the CFD simulation with the reaction UDF based on the kinetic models by Bussche (dashed) and Mignard (dotted) at 220 °C.[2]*

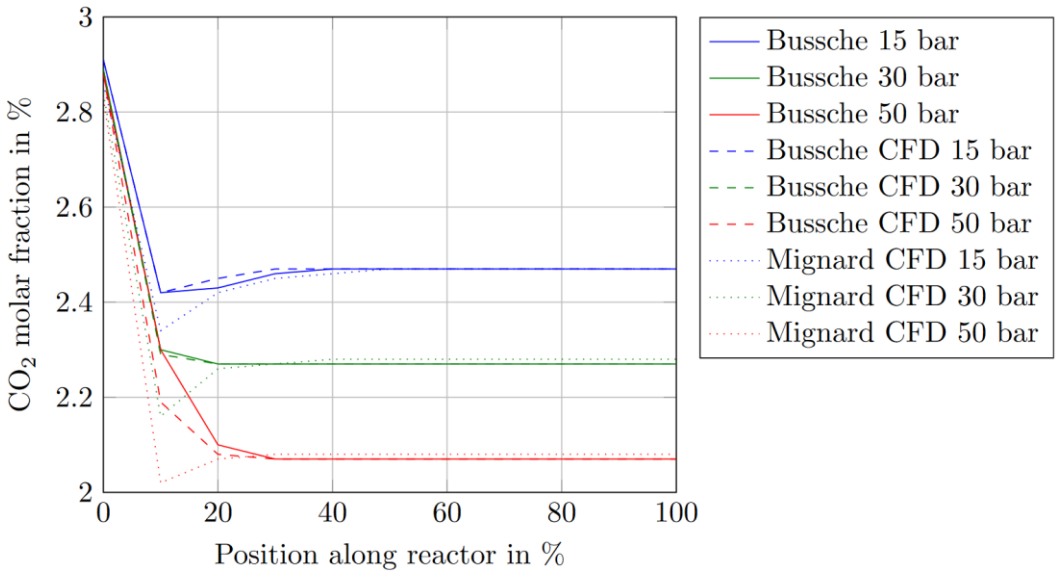


*Figure 8: Comparison of the $CO_2$ molar fraction along the reactor of the simulative study by Bussche (solid) with the CFD simulation with the reaction UDF based on the kinetic models by Bussche (dashed) and Mignard (dotted) at 220 °C.*[2]

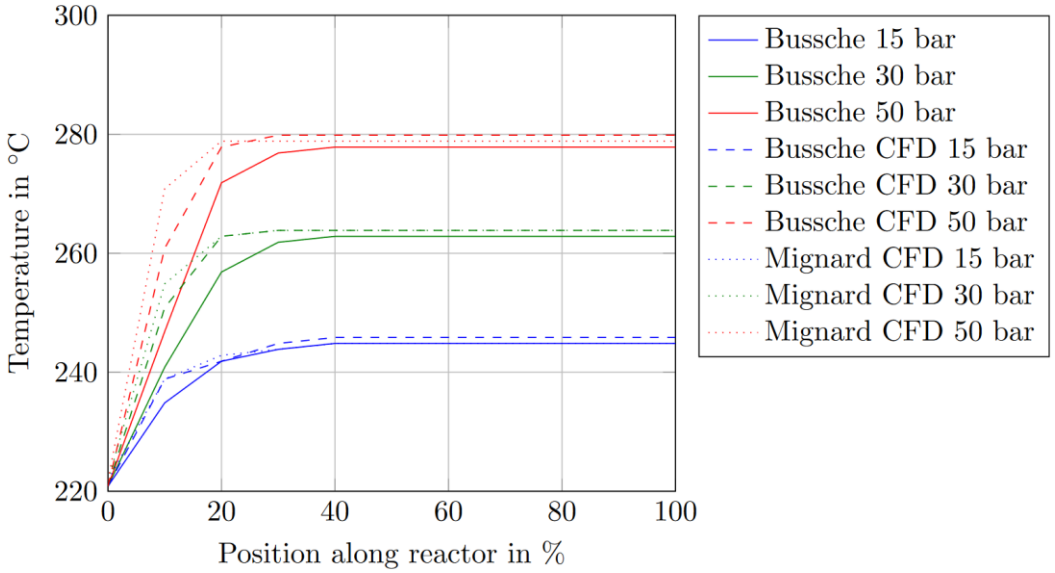


*Figure 9: Comparison of the temperature along the reactor of the simulative study by Bussche (solid) with the CFD simulation with the reaction UDF based on the kinetic models by Bussche (dashed) and Mignard (dotted) at 220 °C.*[2]

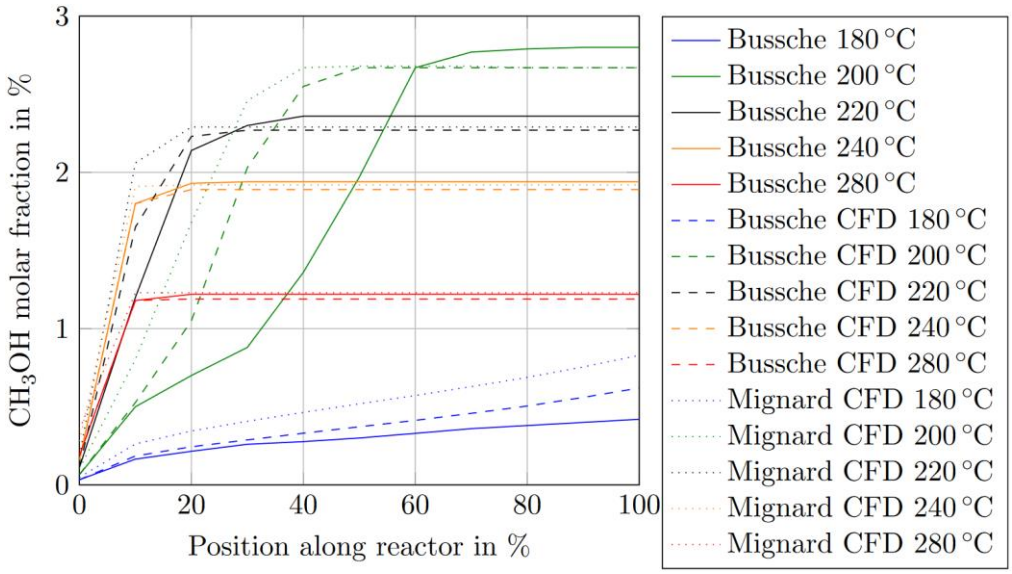


*Figure 10: Comparison of the $CH_3OH$ molar fraction along the reactor of the simulative study by Bussche (solid) with the CFD simulation with the reaction UDF based on the kinetic models by Bussche (dashed) and Mignard (dotted) at 50 bar.*[2]

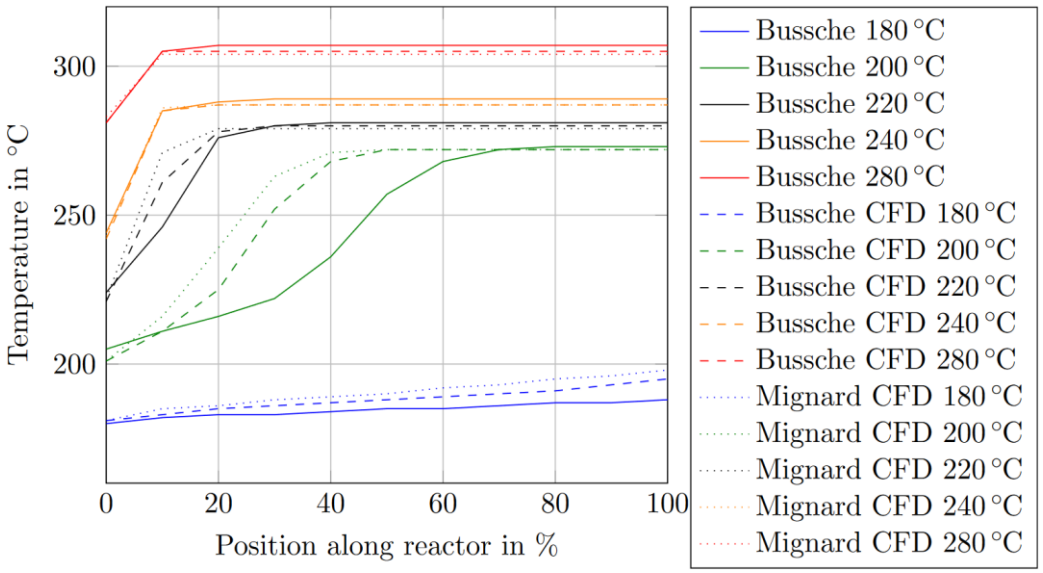


*Figure 11: Comparison of the temperature along the reactor of the simulative study by Bussche (solid) with the CFD simulation with the reaction UDF based on the kinetic models by Bussche (dashed) and Mignard (dotted) at 50 bar.*[2]

## A3 Permeation validation[3]

The NaA zeolite membrane developed by Li et al. is employed in the pilot MR making the agreement between the experimental results by Li et al. and the permeation model a vital objective. Li et al. investigate the separation of the quinary $H_2O/CO_2/CO/H_2/CH_3OH$ gas mixture with a composition of 1.77±0.14/23.52/0.98/73.50/0.23±0.02 mol% at operating conditions of 21 bar and 200 °C, 21 bar and 250 °C, and 38 bar and 250 °C. The NaA zeolite membrane by Li et al. has a thickness of 3 µm to 4 µm and is synthesized on a ceramic hollow-fiber support with an inner diameter of 0.75 mm and an outer

diameter of 1.5 mm. The membrane has an effective length of approximately 50 mm. The feed gas has a volumetric flow rate between 200 mL/min and 500 mL/min at standard temperature and pressure conditions. The permeate side is swept with helium (He).[3]

Mesh independence:

| **Mesh** | **#Cells** | **#Iterations** | **$H_2O$ permeance [$10^{-7}$ mol/m$^2$sPa]** |
|---|---|---|---|
| Coarse | 113,666 | 2,287 | 1.60 |
| Standard | 575,175 | 720 | 1.60 |
| Fine | 1,857,960 | 8,008 | 1.60 |

*Table 3: Mesh independence study for the permeation validation with data of Li et al. with residuals of 1e-08.*

## References


[1] F. Gallucci, L. Paturzo and A. Basile, Chemical Engineering and Processing: Process Intensification, 2004, 43, 1029–1036.

[2] K. Bussche and G. Froment, Journal of Catalysis, 1996, 161, 1–10.

[3] H. Li, C. Qiu, S. Ren, Q. Dong, S. Zhang, F. Zhou, X. Liang, J. Wang, S. Li and M. Yu, Science, 2020, 367, 667–671.