Supporting information

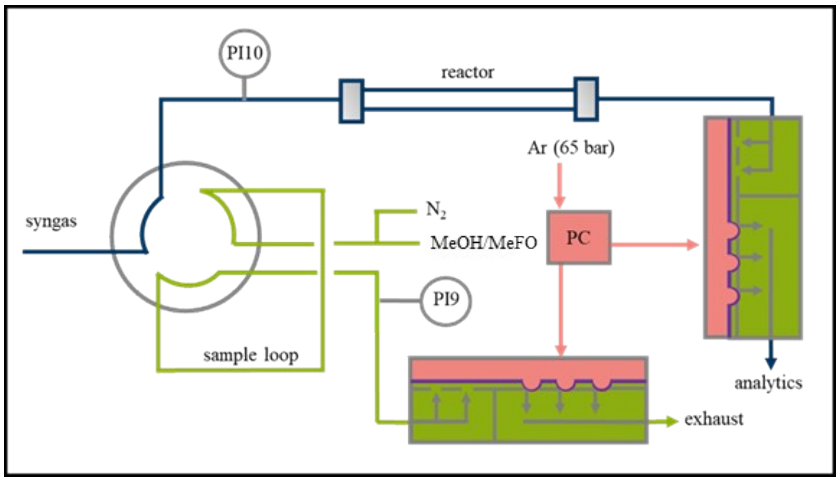

Fig. S1. Schematic drawing of the high-pressure pulse unit (HPPU) containing a 6 port, a 2 position dosing valve equipped with a 1 mL sample loop and two identical back pressure regulators (BPR) connected to a process pressure controller.

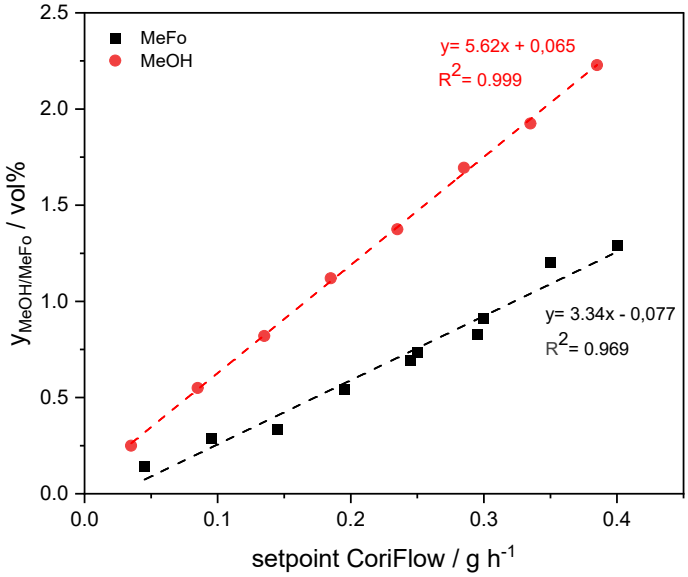

Fig. S2. Calibration of methyl formate and methanol for the high-pressure evaporator system. The evaporator temperature was set to 165°C and the diluting N_2 gas flow was 200 Nml min^{-1}.

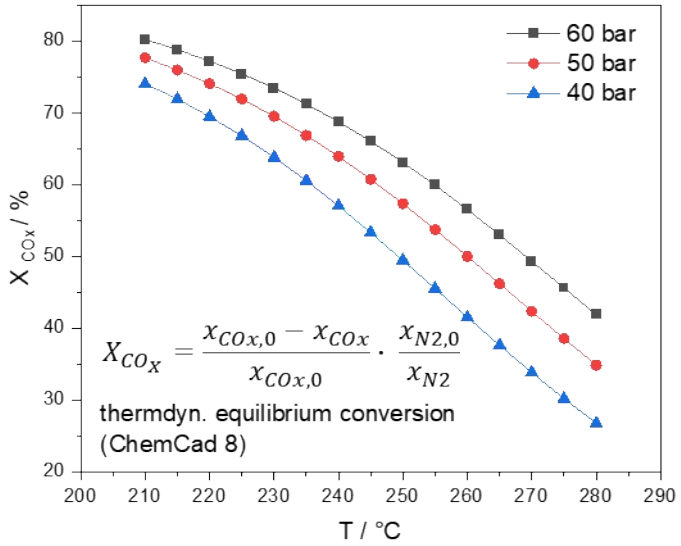

Fig. S3. Thermodynamic equilibrium conversion for methanol synthesis from $CO/CO_2/H_2/N_2$ (13.5 vol%/ 3.5 vol%/ 73.5 vol%/ 9.5 vol%) synthesis gas at 210°C and 60 bar 40, 50 and 60 bar depending on temperature. All calculations were performed using ChemCad 8.

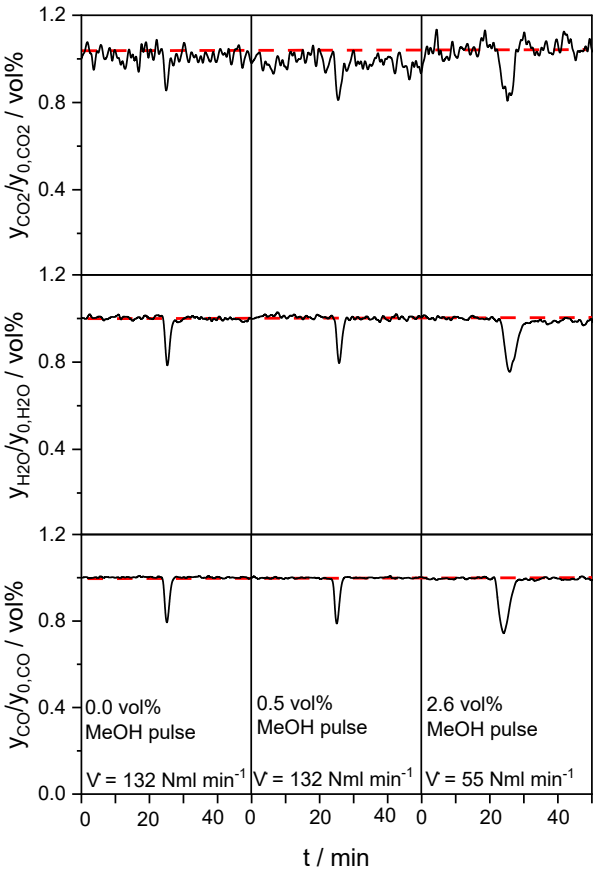

Fig. S4. Recorded mole fractions of CO, CO_2 and H_2O normalized to the initial mole fraction before pulses during the methanol pulse series. Methanol synthesis was performed from $CO/CO_2/H_2/N_2$ (13.5 vol%/ 3.5 vol%/ 73.5 vol%/ 9.5 vol%) synthesis gas at 210°C and 60 bar. The mole fractions of the dosed methanol pulses and the respective gas flow rates are shown below the pulses.

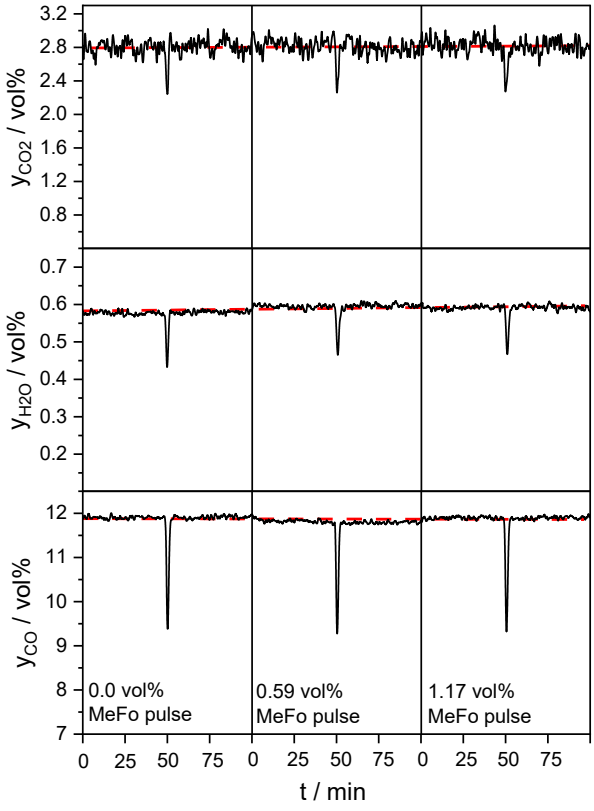

Fig. S5. Recorded mole fractions of CO, CO_2 and H_2O during the methyl formate pulse series. Methanol synthesis was performed from $CO/CO_2/H_2/N_2$ (13.5 vol%/ 3.5 vol%/ 73.5 vol%/ 9.5 vol%) synthesis gas at 210°C and 60 bar. The mole fractions of the dosed methyl formate pulses are shown below the pulses.

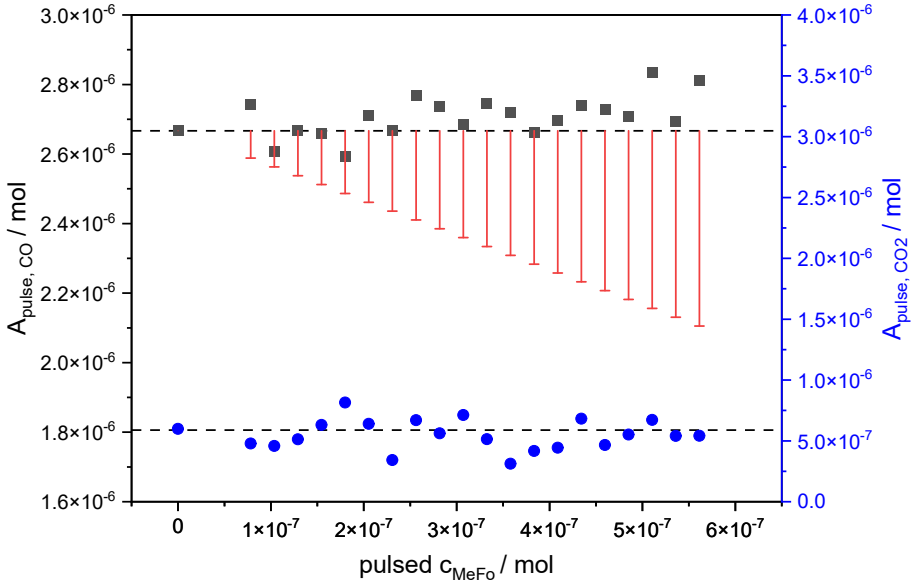

Fig. S6. Molar amounts of CO (black squares) and CO_2 (blue dots) detected as responses to methyl formate pulses and the missing molar amount of CO per pulse in red.

Table S1. Partial pressures of methanol in the 1 ml sample loop at 60 bar.

pulsed n_{MeOH} / mol	pulsed n_{N2} / mol	pulsed $n_{MeOH+N2}$ / mol	p_{MeOH} / bar
3.66E-07	3.01E-05	5.92E-03	0.72
4.09E-07	3.01E-05	5.92E-03	0.80
4.61E-07	3.00E-05	5.92E-03	0.91
5.14E-07	3.00E-05	5.92E-03	1.01
5.92E-07	3.00E-05	5.92E-03	1.16
5.77E-07	2.99E-05	5.92E-03	1.13
6.19E-07	2.99E-05	5.92E-03	1.22
6.63E-07	2.98E-05	5.92E-03	1.30
7.05E-07	2.98E-05	5.92E-03	1.39
7.48E-07	2.97E-05	5.92E-03	1.47
7.91E-07	2.97E-05	5.92E-03	1.56