

Article

Selective CO Methanation in H₂-Rich Gas for Household Fuel Cell Applications

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Abstract: Polymer electrolyte membrane fuel cells (PEMFCs) are often used for household applications, utilizing hydrogen produced from natural gas from the gas grid. The hydrogen is thereby produced by steam reforming of natural gas followed by a water gas shift (WGS) unit. The H₂-rich gas contains besides CO₂ small amounts of CO, which deactivates the catalyst used in the PEMFCs. Preferential oxidation has so far been a reliable process to reduce this concentration but valuable H₂ is also partly converted. Selective CO methanation considered as an attractive alternative. However, CO₂ methanation consuming the valuable H₂ has to be minimized. The modelling of selective CO methanation in a household fuel cell system is presented. The simulation was conducted for single and two-stage adiabatic fixed bed reactors (in the latter case with intermediate cooling), and the best operating conditions to achieve the required residual CO content (100 ppm) were calculated. This was done by varying the gas inlet temperature as well as the mass of the catalyst. The feed gas represented a reformat gas downstream of a typical WGS reaction unit (0.5%–1% CO, 10%–25% CO₂, and 5%–20% H₂O (rest H₂)).

Keywords: CO methanation; ruthenium catalyst; process simulation; adiabatic reactor

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs), also known as polymer electrolyte membrane fuel cells, cogenerate electricity and heat (heated water) from hydrogen or H₂-rich gases (and O₂/air). In order to generate the demanded amount of both heat and electricity, the PEMFCs are mostly combined with a traditional furnace. A connection to the electrical grid is also available to cover the heat and electricity not produced by the fuel cell.

In household applications, renewable energy sources like solar energy, biomass and environmental (geothermal) heat are already often used in power and heat generation systems. PEMFCs are already developed and commercially available for providing power and warm water to households but have to get more efficient and cost-effective in order to be enforced. The H₂-rich gas produced by the steam reforming of natural gas followed by a water gas shift (WGS) unit still contains small amounts of CO at the outlet due to limitation by thermodynamic constraints, typically in a concentration of approx. 0.5%–1% CO [1,2]. These low carbon monoxide contents are too high for permanent application as even traces of this gas poison the PEMFC. Therefore, CO content must not exceed 10 ppm for Pt-anodes and 100 ppm for PtRu-anodes [3,4]. Hence, the carbon monoxide concentration in the feed gas has to be minimized.

CO preferential oxidation (CO-PROX) has been so far the most common process as a fine purification step of the feed gas prior entering the PEMFC [1,5,6]. However, this process needs the installation of a two-step system and an additional, closely controlled, low rate of O₂ supply to prevent the oxidation of H₂ [1,7,8]. Furthermore, during the CO-PROX process, hydrogen oxidation to water

takes place as an unwanted side reaction and heat evolves resulting in a lower efficiency and making the overall reaction strongly exothermic [4,5,9,10]. Selective CO methanation is a promising technique to guarantee the specification for operating gases. This process does not demand an additional reactant and the consumption of additional H₂ through CO₂ methanation can be prevented by choosing the appropriate catalyst.

In our previous paper [11], the activity and selectivity of a 2 wt% Ru supported on γ -Al₂O₃ egg-shell catalyst for CO methanation in CO₂/H₂ rich gases was described and discussed. A kinetic model based on a Langmuir–Hinshelwood approach for both CO and CO₂ methanation was developed. The agreement of the model with measurements in a fixed bed reactor yielded very satisfactory results. Taking these results into consideration, an adiabatic single- and two-stage adiabatic reactor was simulated for household application. This was performed by varying inlet gas temperature as well as catalyst mass. The inlet gas represented a reformat gas downstream of a typical WGS reaction unit (0.5%–1% CO, 10%–25% CO₂, and 5%–20% H₂O (rest H₂)) [2,4,12].

2. Calculations and Methods

The dimensioning of fuel-cell domestic appliances is usually designed to the load demand of an ordinary household. The average electrical energy consumption of a four-person domestic home in Germany is 5000 kWh per year [13]. This is equivalent to 0.6 kW power. A common fuel cell appliance has an electric power of 0.75 kW_{el} and a heat power of 1.1 kW_{th} [14] with a typical efficiency of 80%. This corresponds to a flow rate of 655 L H₂ h⁻¹ (STP), which is equivalent to a total flow rate of 977 L h⁻¹ (STP) for a reformat (outlet of WGS of fuel cell system) consisting of approx. 67% H₂. In this work, this flow rate and gas composition were used as standard case for the modelling of a fixed bed reactor for selective CO methanation. The initial CO content, which may vary at the outlet of the WGS, has a strong influence on the CO conversion and on the temperature profile in fixed bed reactors. Hence, for comparison, calculations were also done for a higher CO content (0.7% and 1%).

The kinetics of the CO and CO₂ methanation over a 2 wt% Ru supported on γ -Al₂O₃ can be well described using a Langmuir–Hinshelwood approach for gases in mol kg_{cat}⁻¹ s⁻¹ (for details on the catalyst and the kinetics see [11,15]):

$$-\frac{dC_{CO}}{d\tau} = r_{m, CO} = \frac{k_{CO}(T) c_{CO} c_{H_2}}{(1 + K_1 c_{CO} + K_2 c_{H_2O})^2} \quad (1)$$

$$-\frac{dC_{CO_2}}{d\tau} = r_{m, CO_2} = \frac{k_{CO_2}(T) c_{CO_2} c_{H_2}}{(1 + K_3(T) c_{CO_2} + K_4(T) c_{CO} + K_5 c_{H_2O})^2} \quad (2)$$

$$K_i(T) = K_{0,i} e^{\frac{-\Delta H_i}{RT}} \quad (i = 3 \text{ and } 4) \quad (3)$$

where C_{*i*} (*i* = CO, H₂, H₂O) is the gas concentration in mol m⁻³, τ the modified residence time (in kg s m⁻³), defined as the ratio of catalyst mass to volumetric gas flow at reaction conditions, and k_{CO} and k_{CO₂} represent the rate constants according to the Arrhenius law. K₁ to K₅ are adsorption constants for CO, CO₂ and H₂O, which depend in case of K₃ and K₄ on temperature. The constants for H₂O (K₂ and K₅) and for CO in case of CO methanation (K₁) turned out to be independent of temperature.

The adsorption of CO (K₁ = 23 m³ mol⁻¹, K₄ (190 °C) = 14.6 m³ mol⁻¹) is much stronger compared to CO₂ (K₃ (190 °C) = 0.17 m³ mol⁻¹) and H₂O (K₂ = with 0.3 m³ mol⁻¹, K₅ = 1.1 m³ mol⁻¹), and the active catalyst surface (Ru) is blocked by adsorbed carbon monoxide. Correspondingly, the rate of CO₂ methanation strongly increases with decreasing CO concentration and increasing CO conversion, respectively. The values of all kinetic parameters and reaction conditions are listed in Table 1. Their calculation and validation are presented in our previous paper [11].

Table 1. Simulation parameters of adiabatic fixed bed methanation reactor(s).

Parameter	Value
Catalyst bulk density, ρ_b	500 kg m ⁻³
Activation energy, $E_{A,CO}$	90 kJ mol ⁻¹
Pre-exponential factor, $k_{0,CO}$	3.61×10^7 m ⁶ s ⁻¹ kg ⁻¹ mol ⁻¹
Langmuir (adsorption) constant, K_1	23 m ³ mol ⁻¹
Langmuir constant, K_2	0.3 m ³ mol ⁻¹
Activation energy, E_{A,CO_2}	81 kJ mol ⁻¹
Pre-exponential factor k_{0,CO_2}	2.8×10^4 m ⁶ s ⁻¹ kg ⁻¹ mol ⁻¹
Factor $K_{0,3}$	8.4 m ³ mol ⁻¹
Adsorption enthalpy, ΔH_3	15 kJ mol ⁻¹
Factor $K_{0,4}$	1.15×10^{-13} m ³ mol ⁻¹
Adsorption enthalpy, ΔH_4 ¹	-125 kJ mol ⁻¹
Langmuir constant, K_5	1.1 m ³ mol ⁻¹

¹ Note that formally the adsorption of CO₂ turned out to be surprisingly endothermic in case of CO₂ methanation. Hence, the physical meaning of the constants K_i , denoted here as adsorption constants, is highly questionable, but at least they formally describe the reaction rate(s) quite well.

For household fuel cell systems, the reactor design should be simple and robust. Therefore, an adiabatic fixed bed reactor (or two in series with intermediate cooling) without the need of a complicate cooling system (such as a multitubular reactor with external cooling) was (were) chosen and simulated. The conversion both of CO and CO₂ under steady state conditions was calculated using the rate equations for CO and CO₂ methanation (Equations (1) and (2)) and the following mass balance:

$$-u_s \frac{dc_j}{dz} = r_{m,j} \rho_b \quad (j = \text{CO}, \text{CO}_2) \quad (4)$$

where u_s is the superficial gas velocity, and ρ_b the bulk density of the catalyst. The reaction rates ($r_{m,j}$ in mol_j s⁻¹ kg_{cat}⁻¹) depend on temperature, which changes in axial direction z . The local temperature change (at steady state) and the axial temperature profiles, respectively, were calculated by the following heat balance ($j = \text{CO}, \text{CO}_2$; $n =$ all components of the gas):

$$\frac{dT}{dz} = \frac{\sum r_{m,j} (-\Delta_R H_j) \rho_b}{u_s \sum c_n c_{p,n}} \quad (5)$$

where $c_{p,n}$ is the heat capacity in J/(mol K).

The reaction rates of CO and CO₂ are almost unaffected by pore diffusion for the given egg-shell catalyst, at least for temperatures below about 230 °C (see [11,15]). Furthermore, the pressure drop over the fixed bed was considered insignificant and a total pressure of 1 bar was assumed. The change of concentration and temperature in radial direction was neglected (plug flow, adiabatic operation).

3. Results and Discussion

The simulation was conducted to calculate the optimum inlet temperature and the corresponding mass of catalyst needed to achieve the demanded residual CO concentration (100 ppm) in the outlet gas. The temperature limit was set at 230 °C in order to avoid the unwanted RWGS reaction (CO₂ + H₂O → CO + H₂O), which was found taking place at temperatures above 240 °C (see [11,15]).

As mentioned above, the inlet gas represents a reformat gas downstream of a typical WGS unit with a CO content of typically less than 1%. The methanation of CO leads to a certain temperature rise and to an unavoidable, but small H₂ consumption (e.g., only 2% for 0.5% CO in the feed gas, see below). An additional rise in temperature and in H₂ consumption is due to the highly undesired CO₂ methanation. Here, the excess H₂ conversion is characterized by the factor $E_{H_2} = X_{H_2}/X_{H_2,min}$,

which is the ratio of the actual H₂ conversion to the minimum conversion, if only CO methanation takes place and the residual CO content of 100 ppm needed for PtRu-anodes is just reached.

3.1. Simulation of a Single Adiabatic Fixed Bed Reactor for Selective CO Methanation

For a feed gas with 0.5% CO (16.5% CO₂, 16% H₂O, and 67% H₂), the target value of 100 ppm CO in the product gas of the methanation reactor corresponds to 98% CO and 2.2% H₂ conversion, respectively. The excess of H₂ conversion is then characterized by the factor $E_{H_2} = X_{H_2}/0.022$.

Figures 1 and 2 and Table 2 show that an inlet temperature of 140 °C is appropriate to avoid too high temperatures (> 230 °C), at least if the mass of the catalyst is limited to values needed for almost complete conversion of CO. 2.9 kg of catalyst (58 g Ru) are required to reach the target value of the residual CO content (100 ppm, i.e., $X_{CO} = 98\%$). The outlet temperature is then 210 °C, which is a reasonable value to limit the RWGS and CO₂ methanation. E_{H_2} is 1.12, i.e., 12% more hydrogen (H₂ conversion of 2.5% compared to 2.2%) is consumed compared to the ideal case without any CO₂ conversion, which is here still rather small and only 0.4%. In other words, only 0.13 mol of CO₂ are converted per mol of converted carbon monoxide.

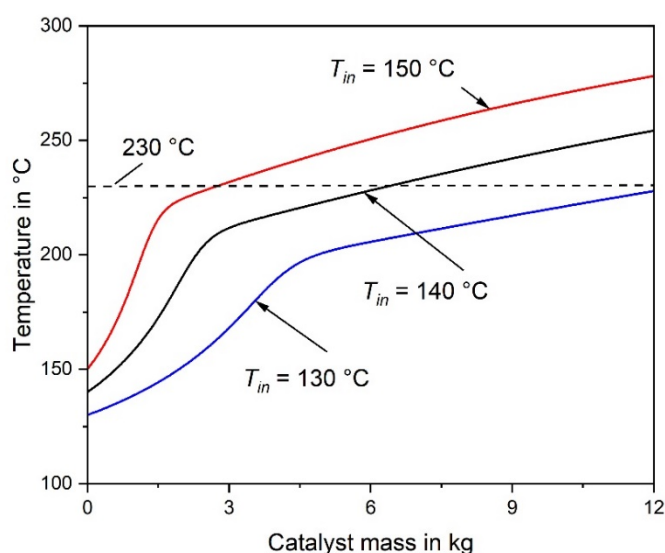


Figure 1. Axial temperature profile of an adiabatic fixed-bed reactor for inlet temperatures of 130 °C, 140 °C and 150 °C (977 L h⁻¹ (STP), feed gas: 0.5% CO, 16.5% CO₂, 16% H₂O, 67% H₂). The adiabatic rise in temperature is $\Delta T = 79$ K (without CO₂ conversion).

Table 2. Basic data of an adiabatic reactor for selective CO methanation at different initial temperatures (977 L h⁻¹ (STP), feed gas: 0.5% CO, 16.5% CO₂, 16% H₂O, 67% H₂).

T_{in} in °C	T_{out} in °C	m_{cat} in kg	X_{CO} in %	X_{CO_2} in %	X_{H_2} in %	E_{H_2}	CO Content at Reactor Outlet
130	200	4.90	98.00	0.38	2.50	1.12	100 ppm
	211	7.40	99.99	0.95	3.10	1.39	< 1 ppm
140	210	2.90	98.00	0.41	2.51	1.12	100 ppm
	220	4.40	99.99	0.90	3.01	1.35	< 1 ppm
150	222	1.80	98.00	0.46	2.64	1.18	100 ppm
	230	2.70	99.99	0.85	3.04	1.37	< 1 ppm

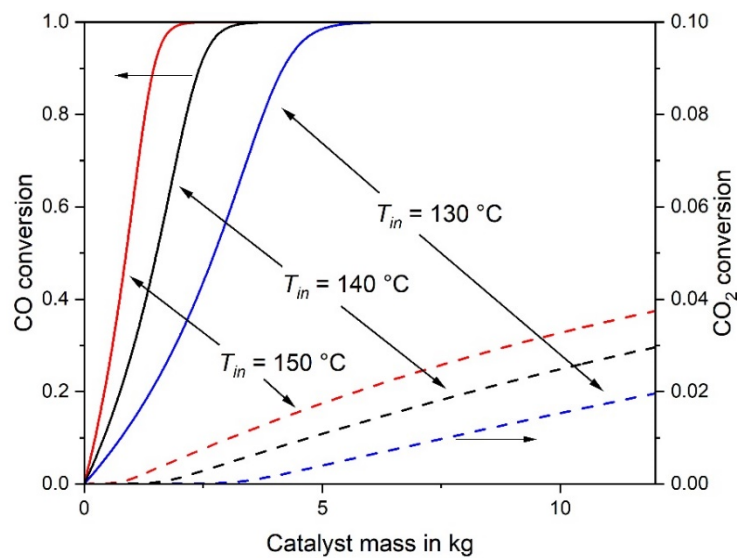


Figure 2. CO and CO₂ conversion of an adiabatic fixed-bed reactor for inlet temperatures of 130 °C, 140 °C and 150 °C (other conditions as in Figure 1).

If the inlet temperature is reduced from 140 °C to 130 °C, the mass of catalyst required for 98% CO conversion undesirably increases from 2.9 kg to 4.9 kg, and the excess of H₂ consumption is almost the same (Table 2). If, vice versa, the inlet temperature is increased from 140 °C to 150 °C, the required mass of catalyst decreases from 2.9 kg to 1.8 kg. Although this seems to be beneficial, E_{H_2} rises from 1.12 to 1.18, which is of course a disadvantage, see also Table 2. Hence, a reasonable compromise has to be made with regard to minimize both m_{cat} and E_{H_2} , whereby the outlet temperature should be always kept below 230 °C. Figure 1 also clearly shows that the size of the reactor and mass of the catalyst, respectively, should not be too high to avoid an unwanted overheating of the catalyst (> 230 °C) as well as an undesired CO₂ methanation and H₂ consumption, e.g., for $T_{in} = 140$ °C and 12 kg catalyst, CO₂ conversion would reach 3% and the corresponding value of E_{H_2} would be 2.3 (H₂ conversion: 5%).

However, to be on the safe side with regard to the maximum residual CO content of 100 ppm, a certain surplus of the reactor size is advisable. Therefore, Table 2 also shows the reactor parameters, if the reactor length and mass of catalyst are by a factor 1.5 larger compared to the parameters for 100 ppm residual CO content. As expected, the CO conversion is then almost 100%, but the CO₂ conversion also increases, which leads to an additional and highly unwanted conversion of hydrogen (higher value of E_{H_2}), e.g., for $T_{in} = 140$ °C, X_{H_2} increases from 2.5% to 3%.

For a feed gas with 0.7% CO, an appropriate reactor set-up is only reached for a very low inlet temperature of 110 °C. The required catalyst mass is then 25.5 kg and equals 1.5 times the minimum mass needed to reach 100 ppm (safety margin). This amount is large compared to 4.4 kg for 0.5% CO in the feed gas (Table 3). The reason is the low inlet temperature (110 °C) required to keep the reactor outlet temperature (224 °C) below the limit of 230 °C. The volume would be 68 liters, e.g., a cylinder with a length of 96 cm and 30 cm in diameter, which is quite large for a household fuel cell system.

For a feed gas with 1% CO, a single adiabatic reactor is even inapplicable for CO methanation: The gas inlet temperature should then not exceed 70 °C in order to keep the outlet temperature below 230 °C. This would lead to an unrealistic large reactor with a catalyst mass of about 250 kg which is far beyond the acceptable size for a household fuel cell system. However, this situation can be overcome by using a multi-stage fixed bed reactor set-up as presented in the following section.

Table 3. Simulation results for a single stage adiabatic reactor (0.5%–0.7% CO, 16.3%–16.5% CO₂, 16% H₂O, rest H₂). The mass of the catalyst was assumed to be by a factor of 1.5 larger (safety margin) compared to the amount required to reach a residual CO content of 100 ppm.

Parameter		CO Content in Feed Gas	
		0.5 %	0.7 %
Operating conditions	Inlet temperature	140 °C	110 °C
	Pressure	1 bar	1 bar
	Outlet temperature	220 °C	224 °C
Reactor dimensions	Mass of catalyst	4.4 kg	25.5 kg
	Volume	11.7 L	68.0 L
	Tube diameter/length	20 cm/37 cm	30 cm/96 cm
Outlet gas composition	CO	< 1 ppm	< 1 ppm
	CO ₂	16.5%	16.4%
	H ₂ O	17.0%	17.5%
	H ₂	65.8%	65.2%
	CH ₄	0.7%	0.9%
Conversion	CO	99.99%	99.99%
	CO ₂	0.9%	1.3%
	H ₂	3.0%	4.4%
E_{H_2}		1.35	1.40

3.2. Simulation of a Two-Stage Adiabatic Fixed Bed Reactor with Intermediate Cooling

A single adiabatic fixed bed reactor is inadequate for CO inlet concentrations above 0.7%. An alternative is a two-stage reactor set-up with intermediate cooling by a heat exchanger. The feed gas enters the first reactor with a temperature of $T_{in,1}$, leading to an outlet temperature of $T_{out,1} = 230$ °C (value of T-limit); the gas is then cooled down to the inlet temperature $T_{in,2}$ of the second adiabatic reactor. The gas leaves the second reactor with the desired CO content of 100 ppm (or less), and the temperature at the outlet is still $T_{out,2} \leq 230$ °C. This two-stage concept is applicable for CO concentrations of up to 1% CO, which can be considered as the maximum content relevant for a feed gas from a WGS unit. The simulation results of a feed gas with 0.5% CO are summarized exemplarily in Table 4. The gas enters both reactors with an inlet temperature of 180 °C.

Table 4. Basic data of a two-stage adiabatic reactor set-up for selective CO methanation of a gas with 0.5% CO, 16% H₂O, 16.5% CO₂ and 67% H₂ having a volume flow of $\dot{V} = 977$ L h⁻¹ (STP).

Parameter	1st Adiabatic Fixed Bed Reactor	2nd Adiabatic Fixed Bed Reactor
T_{in} in °C	180	180
T_{out} in °C	230	203
m_{cat} in kg	0.27	0.30
V in L	0.54	0.6
d_r, l_r in cm	5, 28	5, 31
X_{CO} in %	71.21	98.00
X_{CO_2} in %	0.28	0.81
X_{H_2} in %	1.87	3.90
E_{H_2}	-	1.74
Gas composition at reactor outlet	0.15% CO	100 ppm CO
	16.6% CO ₂	16.7% CO ₂
	16.6% H ₂ O	17.1% H ₂ O
	66.3% H ₂	65.6% H ₂
	0.4% CH ₄	0.6% CH ₄

The adiabatic temperature rise by the exothermic CO and CO₂ methanation is depicted in Figure 3. Note that the rise in the rear part of the second reactor is not anymore proportional to the decrease of

the CO concentration. This is the result of the CO₂ methanation, taking place mainly in the rear part, where the CO concentration is low, which enhances the rate of CO₂ methanation, see Equation (2). Figure 4 shows the CO and CO₂ conversion as function of catalyst mass. In the first stage ($m_{cat} = 0.27$ kg) a conversion of 71% CO is reached, and in the second stage (0.3 kg) 98%, respectively.

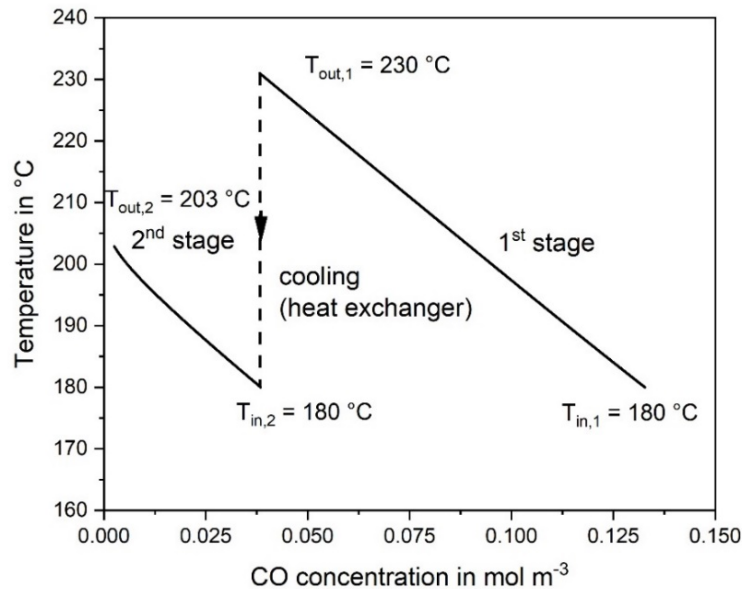


Figure 3. Temperature change vs. CO concentration calculated at reaction conditions in the first and second adiabatic fixed bed reactor; 0.5% CO, 16.5% CO₂, 16% H₂O, and 67% H₂ in the initial gas, $\dot{V} = 977$ L h⁻¹ (STP).

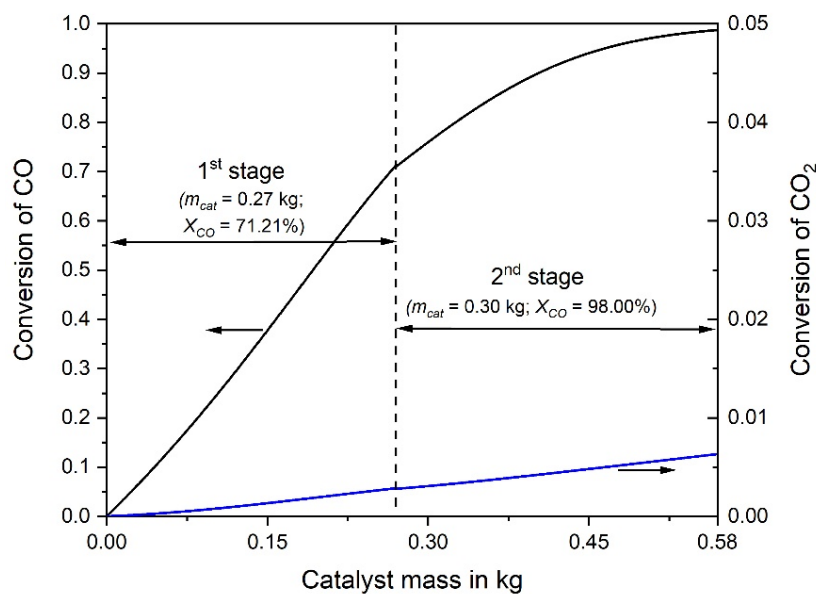


Figure 4. Conversion of CO and CO₂ vs. catalyst mass in the first and second adiabatic fixed bed reactor; 0.5% CO, 16.5% CO₂, 16% H₂O, and 67% H₂ in the initial gas, $\dot{V} = 977$ L h⁻¹ (STP).

The mass of catalyst required for a certain CO-conversion can be calculated based on Equation (4) as

$$\int_0^{X_{CO}} \frac{dX_{CO}}{r_{m,CO}} = \int_0^z \frac{\rho_b}{u_s c_{CO,in}} dz \xrightarrow{\text{yields}} m_{cat} = \dot{V}(T, p) c_{CO,in} \int_0^{X_{CO}} \frac{dX_{CO}}{r_{m,CO}} \quad (6)$$

The integral of Equation (6) (and thus m_{cat} for a given volume rate and CO inlet concentration) can be solved graphically by the plot of the reciprocal CO reaction rate versus the conversion of CO. For a comparison of the single- and the two-stage adiabatic reactor simulation, Figure 5 shows this plot for both cases. Hence, instead of a single reactor with a catalyst mass of 2.9 kg (see Section 3.1) two considerably smaller reactors can be used for the same purpose. The first one has a catalyst mass of 0.27 kg and the second one 0.30 kg, respectively, so in total only 0.57 kg catalyst. It should be noted, that for a final comparison of the single- and two-stage process, e.g., with regard to investments costs, the volume of the heat exchanger needed for the two-stage methanation has to be considered also, but this was beyond the scope of this work.

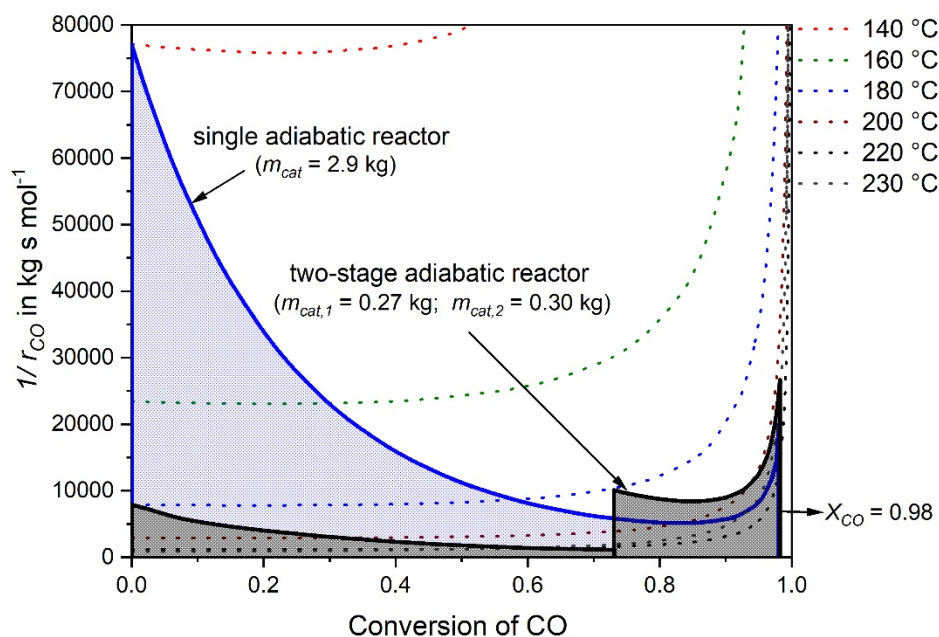


Figure 5. Reciprocal reaction rate of CO versus conversion of CO for a feed gas with 0.5% CO, 16.5% CO₂, 16% H₂O, 67% H₂ (rest N₂) and $\dot{V} = 977 \text{ L h}^{-1}$ for two scenarios, a single adiabatic fixed bed reactor and a two-stage adiabatic fixed bed reactor with intermediate cooling.

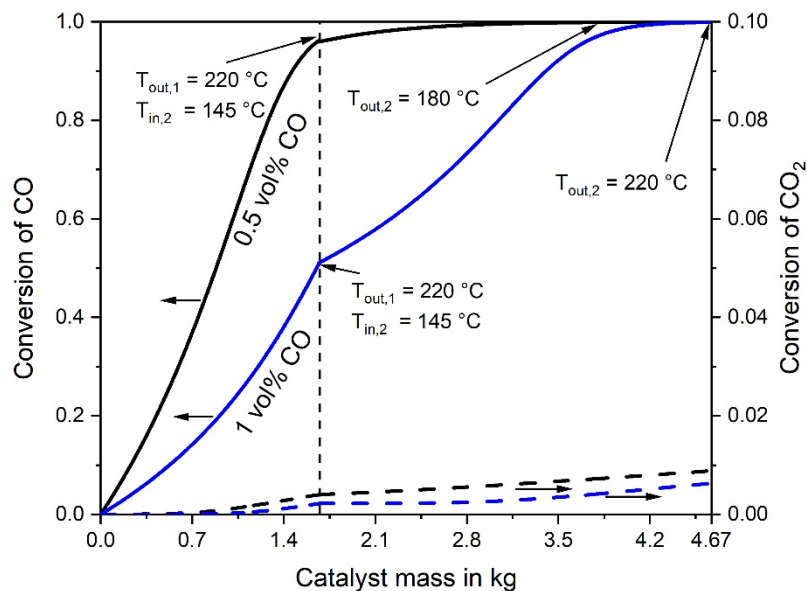
3.3. Flexible and Safe Operation of the Two-stage Adiabatic Fixed Bed Reactor

The two-stage adiabatic reactor was further modified to ensure temperatures below 230 °C and CO concentrations at the outlet of the second reactor below 100 ppm. The modifications allowed to regulate temperature changes, CO concentration variations in the feed gas from 0% to 1% and a potential drop of catalytic activity. Here, the reactor outlet temperature was set at $T_{out} = 220 \text{ °C}$ (compared to 230 °C as before in the “standard” simulation), i.e., 10 °C below the critical temperature (onset of CO formation by RWGS).

Using this reactor design, the inlet temperature could be regulated (increased by about 10 K) to a certain degree depending on the catalyst activity and inlet CO concentration. The basic data of a two-stage adiabatic reactor set-up for selective CO methanation of a gas with 1% CO are listed in Table 5; the inlet temperatures are 150 °C (reactor 1) and 145 °C (reactor 2) to limit the outlet temperature of both reactors to 220 °C (Table 5). Figure 6 shows the influence of the catalyst mass on the CO and CO₂ conversion, both for an inlet CO content of 0.5% and 1%. The simulation with the low CO inlet content (0.5%) already leads to a CO conversion of about 95% in the first reactor, and a very low outlet CO content of less than 2 ppm is reached in the second one, even at very low temperatures ($T_{in,2} = 145 \text{ °C}$, $T_{out,2} = 180 \text{ °C}$). In this case, the inlet temperature could be set even higher, e.g., to about 200 °C, without the danger to exceed the temperature limit of 220 °C. For 1% CO in the feed gas, the conversion in the first reactor is only about 50%, but almost full CO conversion is achieved in the second one (final CO content of 8 ppm) (Table 5).

Table 5. Basic data of a two-stage adiabatic reactor set-up for selective CO methanation of a gas with 1% CO, 16% H₂O, 16% CO₂, 67% H₂ having a volume flow of $\dot{V} = 977 \text{ L h}^{-1}$ (STP).

Parameter	1st Adiabatic Fixed Bed Reactor	2nd Adiabatic Fixed Bed Reactor
T_{in} in °C	150	145
T_{out} in °C	220	220
m_{cat} in kg	1.67	3.0
V in L	3.35	6.0
d_r, l_r in cm	10.43	20, 76
X_{CO} in %	51	99.93
X_{CO_2} in %	0.22	0.85
X_{H_2} in %	2.45	5.30
E_{H_2}	-	1.15
Gas composition at reactor outlet	0.5% CO	8 ppm CO
	16.1% CO ₂	16.2% CO ₂
	16.8% H ₂ O	17.7% H ₂ O
	66.1% H ₂	64.9% H ₂
	0.5% CH ₄	1.2% CH ₄

**Figure 6.** Conversion of CO and CO₂ vs. catalyst mass in the first and second adiabatic fixed bed reactor. Feed gas with 0.5% or 1% CO (16% CO₂, 16% H₂O, and about 67% H₂), $\dot{V} = 977 \text{ L h}^{-1}$ (STP).

Thus, the two-stage fixed bed reactor set-up could be used for the selective methanation of CO with gases containing CO concentrations up to 1%. Even in case of a drop of the catalyst's activity, the temperature can be increased by 10 K (even for a feed gas with 1% CO) in order to keep the outlet concentration below 100 ppm and the maximum temperature below 230 °C. The catalyst mass (volume) would then be in total 4.7 kg (9.4 L), which is still a reasonable value for a household fuel cell system.

4. Conclusions

A fixed reactor for application in a typical domestic home (four-person household) was simulated based on the kinetics of CO and CO₂ methanation. First, a single adiabatic fixed bed reactor was simulated for CO concentrations of 0.5%, 0.7% and 1% CO, respectively. The outlet temperature limit was set to 230 °C in order to exclude the RWGS reaction taking place at temperatures above 240 °C. The optimum inlet gas temperature was calculated for a maximum CO concentration of 100 ppm. The simulation showed that a single adiabatic reactor was suitable for up to a maximum inlet content of CO of 0.7%. For 0.5% CO in the feed gas, an inlet temperature of 140 °C resulted in a final outlet

temperature of 220 °C, which was sufficiently below the critical value of 240 °C. The mass of catalyst needed in this case was about 4.4 kg for a rate of the feed gas of 977 L h⁻¹ (STP), which can be regarded as typical for a fuel cell system of a domestic home.

For a feed gas with 1% CO, a single adiabatic fixed bed reactor turned out to be inapplicable for the selective CO methanation. The outlet temperature went too high (>240 °C) for realistic inlet temperatures (>100 °C), i.e., at an outlet temperature of 230 °C, the mass and volume of the catalyst bed were much too high if a residual CO content of 100 ppm should be reached. For this reason, a two-stage adiabatic fixed bed reactor with intermediate cooling was simulated considering an outlet temperature limitation of $T_{out} = 230$ °C. Using this device, even a feed gas with up to 1% CO could be used. Here, the resulting total mass of the catalyst was only 3.6 kg to reach the goal of less than 100 ppm CO.

However, to account for a certain decline in the activity of the catalyst and to ensure still concentrations below 100 ppm CO, the outlet temperature was lowered to $T_{out} = 220$ °C. This enables a temperature increase of about 10 K in case of a drop of the activity with time on stream. Again, a two-stage adiabatic reactor was simulated, which is applicable for varying CO concentrations of up to 1% CO. The total mass of the catalyst is then 4.7 kg (compared to 3.6 kg for an outlet temperature of 230 °C), which is still a reasonable value for a household fuel cell system.

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