Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Improvement of a multi-tubular Fischer-Tropsch reactor with gas recycle by appropriate combination of axial activity distribution and gas velocity

Christoph Kern, Andreas Jess* (jess@uni-bayreuth.de)

## Supporting Information

*Supplement to Chapter 3*

*Mass balances for CO, $H_2$, and $CH_4$*

For a molar $H_2$-to-CO ratio of 2.2 and a selectivity to $CH_4$ of 20%, which leads to an equal conversion of CO and $H_2$, the mass balances for CO yield the following molar flow rates at the in- and outlet of the reactor and in the recycle and purge gas stream:

$$\dot{n}_{CO,reactor,in} = \dot{n}_{CO,fresh,SG} + \dot{n}_{CO,recycle} \quad \text{(S1)}$$

$$\dot{n}_{CO,reactor,out} = \left(1 - X_{CO,per\,pass}\right)\left(\dot{n}_{CO,fresh,SG} + \dot{n}_{CO,recycle}\right) \quad \text{(S2)}$$

$$\dot{n}_{CO,recycle} = \dot{n}_{CO,reactor,out} - \dot{n}_{CO,purge} \quad \text{(S3)}$$

$$\dot{n}_{CO,purge} = X_{CO,total}\,\dot{n}_{CO,fresh,SG} \quad \text{(S4)}$$

Combination of the equations (7), (S1), (S2), (S3), and (S4) yields all the different dimensionless molar rates of CO related to the given feed rate CO in the fresh syngas

$$\frac{\dot{n}_{CO,reactor,out}}{\dot{n}_{CO,fresh,SG}} = \frac{X_{CO,total}\left(1 - X_{CO,per\,pass}\right)}{X_{CO,per\,pass}} \quad \text{(S5)}$$

$$\frac{\dot{n}_{CO,recycle}}{\dot{n}_{CO,fresh,SG}} = \frac{\left(X_{CO,total} - X_{CO,per\,pass}\right)}{X_{CO,per\,pass}} \quad \text{(S6)}$$

$$\frac{\dot{n}_{CO,reactor,in}}{\dot{n}_{CO,fresh,SG}} = \frac{X_{CO,total}}{X_{CO,per\,pass}} \quad \text{(S7)}$$

$$\frac{\dot{n}_{CO,purge}}{\dot{n}_{CO,fresh,SG}} = X_{CO,total} \quad \text{(S8)}$$

The respective rates of $H_2$ are then simply by a factor of 2.2 higher:

$$\frac{\dot{n}_{H_2,i}}{\dot{n}_{CO,fresh,SG}} = \frac{2.2\,\dot{n}_{CO,i}}{\dot{n}_{CO,fresh,SG}} \quad \text{(with i = } \textit{reactor,out, reactor,in, purge, or recycle}\text{)} \quad \text{(S9)}$$

Finally, the molar flow rates of methane are deduced in a similar manner:

$$\begin{aligned}\dot{n}_{CH_4,reactor,in} &= \dot{n}_{CH_4,recycle} \\ &= y_{CH_4,recycle}\left(\dot{n}_{CO,recycle} + \dot{n}_{H_2,recycle} + \dot{n}_{CH_4,recycle}\right) \\ &= y_{CH_4,recycle}\left(3.2\,\dot{n}_{CO,recycle} + \dot{n}_{CH_4,recycle}\right) \quad \text{(S10)}\end{aligned}$$

$$\dot{n}_{CH_4,reactor,out} = \dot{n}_{CH_4,recycle} + \dot{n}_{CH_4,purge} \quad \text{(S11)}$$

Introduction of Eq. (9) in Eq. (S11) leads to

$$\dot{n}_{CH_4,reactor,out} = \dot{n}_{CH_4,recycle} + 0.2\, X_{CO,per\,pass}\, \dot{n}_{CO,reactor,in} \tag{S12}$$

Combination of Eq. (S8), Eq. (S6), and Eq. (S8) (for the case of $H_2$ in the recycle stream) yields

$$\frac{\dot{n}_{CH_4,recycle}}{\dot{n}_{CO,fresh,SG}} = \frac{y_{CH_4,recycle}}{(1-y_{CH_4,recycle})} \left(\frac{3.2\,(X_{CO,total} - X_{CO,per\,pass})}{X_{CO,per\,pass}}\right) \tag{S13}$$

Insertion of Eq. (10) into Eq. (S13) finally yields:

$$\frac{\dot{n}_{CH_4,recycle}}{\dot{n}_{CO,fresh,SG}} = \frac{\dot{n}_{CH_4,reactor,in}}{\dot{n}_{CO,fresh,SG}} = \frac{0.2\, X_{CO,total}}{(1 - X_{CO,total})} \frac{(X_{CO,total} - X_{CO,per\,pass})}{X_{CO,per\,pass}} \tag{S14}$$

Readjustment of Eq. (9) leads to the dimensionless recycle stream of methane

$$\frac{\dot{n}_{CH_4,purge}}{\dot{n}_{CO,fresh,SG}} = 0.2\, X_{CO,total} \tag{S15}$$

For the recycle ratio $R$ (rate of recycle gas to fresh syngas) we then have:

$$R = \frac{\dot{n}_{recycle}}{\dot{n}_{fresh,SG}} = \frac{(3.2\,\dot{n}_{CO,recycle} + \dot{n}_{CH_4,recycle})}{\dot{n}_{fresh,SG}} = \frac{(3.2 - 3\, X_{CO,total})\,(X_{CO,total} - X_{CO,per\,pass})}{(1 - X_{CO,total})\, 3.2\, X_{CO,per\,pass}} \tag{S16}$$

*Supplement to Chapter 4.1*

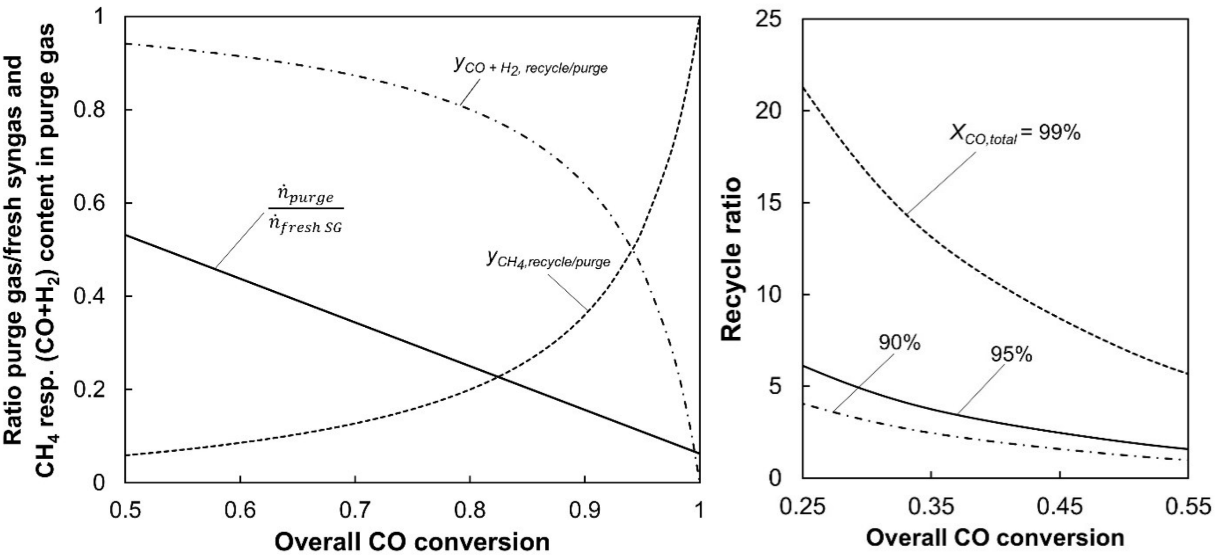


**Fig. S1**: Influence of overall CO conversion ($X_{CO,total}$) on the ratio of purge gas stream to the stream of fresh syngas and on the $CH_4$ and combined $CO/H_2$ content in the recycle and purge gas of a FT reactor (left) and on the recycle ratio $R$ (right) ($CH_4$ selectivity = 20%, $H_2$-to-CO ratio = 2.2).

*Supplements to Chapter 4.3*

**Tab. S1**: Characteristic data of a multi-tubular fixed bed FT reactor for a uniform activity but different superficial gas velocities $u_s$ with and without gas recycle ($C_a$ = 2; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%, $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C; 913,1369, and 1825 mol/h syngas at reactor inlet for gas recycle and $u_s$ = 0.5, 0.75, and 1 m/s).

| $u_s$ | $n_{SG,fresh}$ in mol/h | $T_{cool}$ in °C | $X_{CO,per\ pass}$ in % | $y_{CH4,reactor,\ in}$ in % | $R$ | **Prod. of $C_{2+}$ per single tube** in $kg_C$/h |
|---|---|---|---|---|---|---|
| 1 | 461 | 223.8 | 40.4 | 40.7 | 2.96 | 1.31 |
| 0.75 | 424 | 221.2 | 47.4 | 37.1 | 2.20 | 1.21 |
| 0.5 | 368 | 216.6 | 56.8 | 31.9 | 1.47 | 1.05 |
| **Only for comparison: cases without gas recycle** ($R$ = 0; syngas: 31.3% CO, 68.7% $H_2$, no $CH_4$) | | | | | | |
| $u_s$ | $n_{SG}$ in mol/h | $T_{cool}$ in °C | $T_{max}$ in °C | $X_{CO}$ in % | $R$ | **Prod. of $C_{2+}$ per single tube** in $kg_C$/h |
| 1 | 1825 | 218.2 | 240 | 33.0 | 0 | 1.81 |
| 0.75 | 1369 | 215.4 | 239.3[a] | 38.8 | | 1.59 |
| 0.5 | 913 | 209.5 | 232.4[b] | 42.8 | | 1.17 |

[a] $T_{ig}$ = 215.4°C. [b] $T_{ig}$ = 214.5°C.

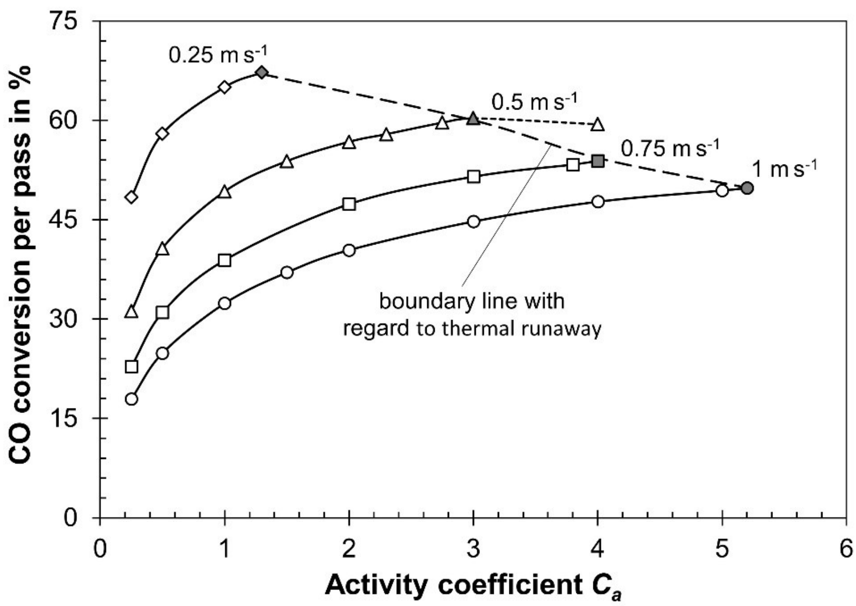


**Fig. S2**: Influence of activity coefficient $C_a$ on the CO conversion per pass for different values of $u_s$ ($p_{total}$ = 30 bar; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C except for 0.5 m/s and $C_a$ = 4 with $T_{cool}$ = 208°C and $T_{max}$ = 235°C). Filled symbols: critical cases with regard to thermal runaway ($T_{max}$ = 240°C).

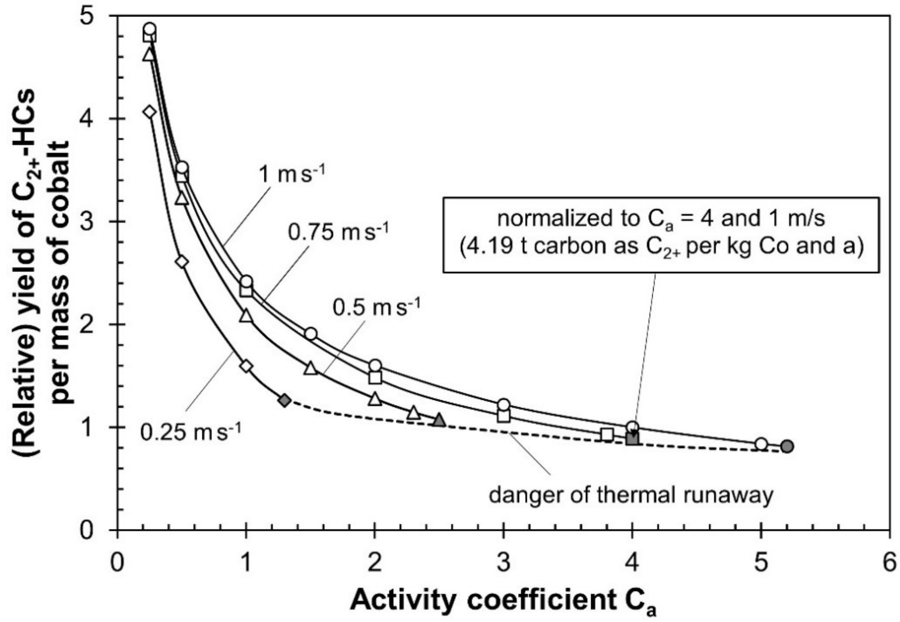


**Fig. S3**: Influence of the activity coefficient $C_a$ on the (relative) yield of $C_{2+}$-HCs per mass of cobalt at different superficial gas velocities $u_s$ ($p_{total}$ = 30 bar; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C). Filled symbols represent critical cases with regard to thermal runaway.

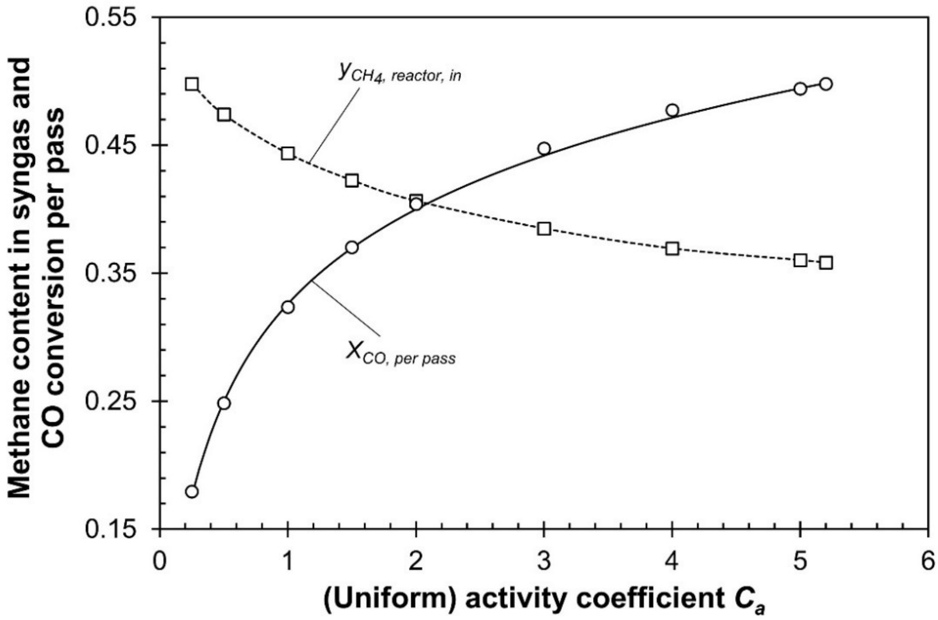


**Fig**. **S4**: Influence of (uniform) axial activity $C_a$ on methane content in syngas entering the FT reactor and on the CO conversion per pass ($p_{total}$ = 30 bar; $u_s$ = 1 m/s; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

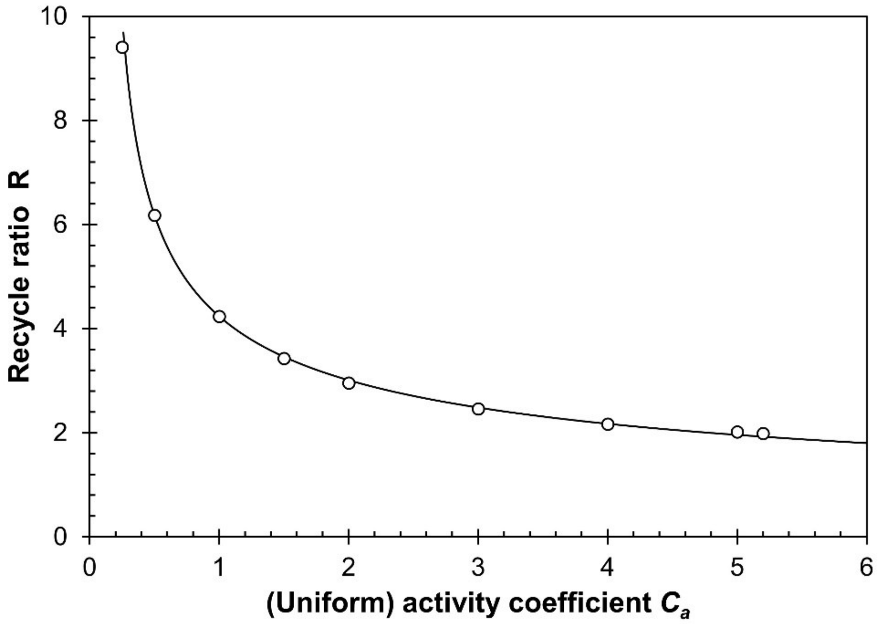


**Fig. S5**: Influence of (uniform) axial activity $C_a$ on recycle ratio of FT reactor ($p_{total}$ = 30 bar; $u_s$ = 1 m/s; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

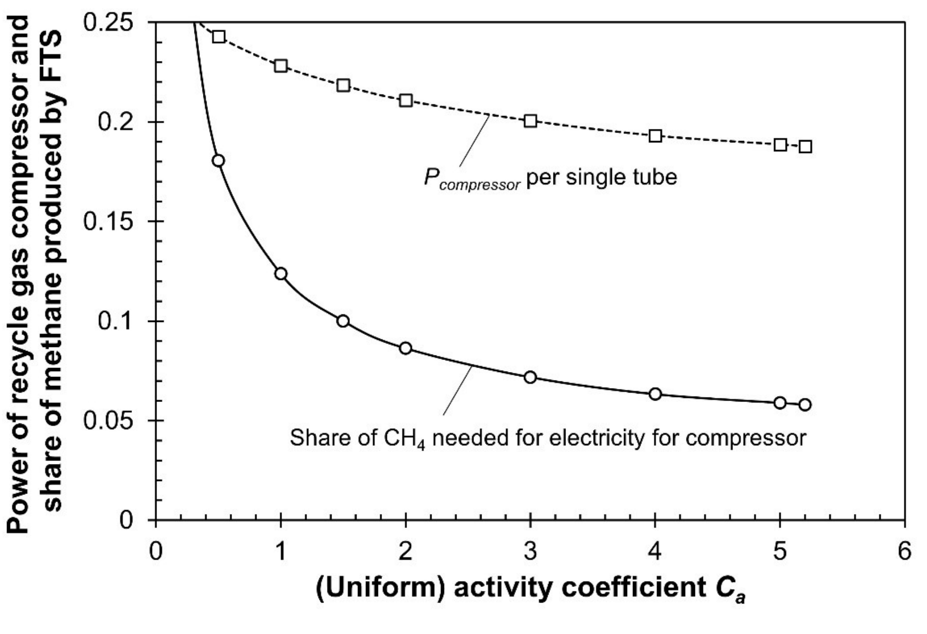


**Fig. S6**: Influence of (uniform) axial activity $C_a$ on the power of the recycle gas compressor and on the share of methane produced by FTS needed to drive the compressor (as a simple measure for the electrical energy need for gas recycling assuming an efficiency of power production of 40%) ($p_{total}$ = 30 bar; $\Delta p$ = 6 bar; $u_s$ = 1 m/s; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

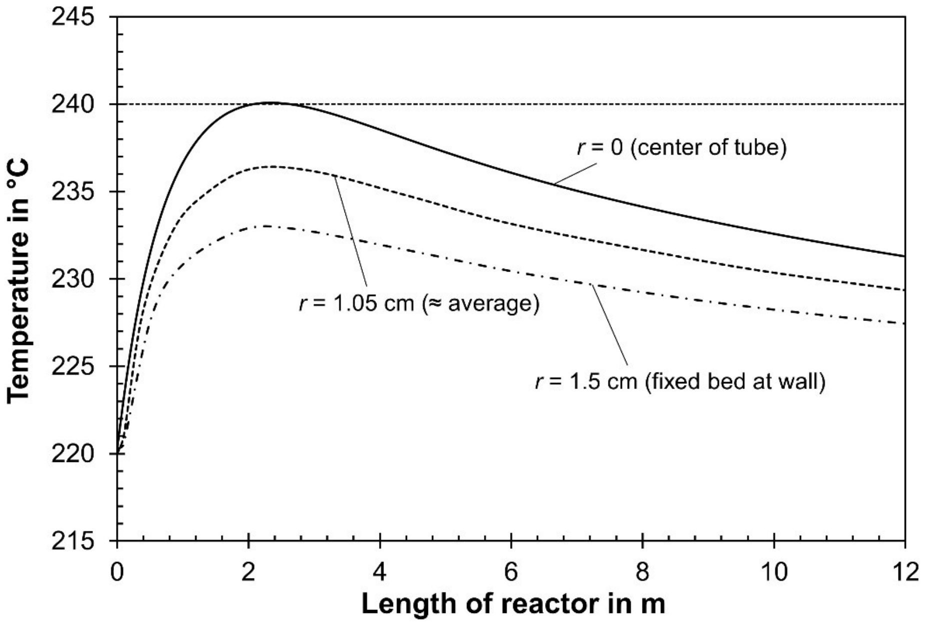


**Fig. S7**: Axial temperature profiles in the center of the single tube ($r$ = 0), at the position $r$ = 1.05 cm, and in the fixed bed directly at the wall ($r$ = 1.5 cm) ($C_a$ = 3; $p_{total}$ = 30 bar; $u_s$ = 1 m/s; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

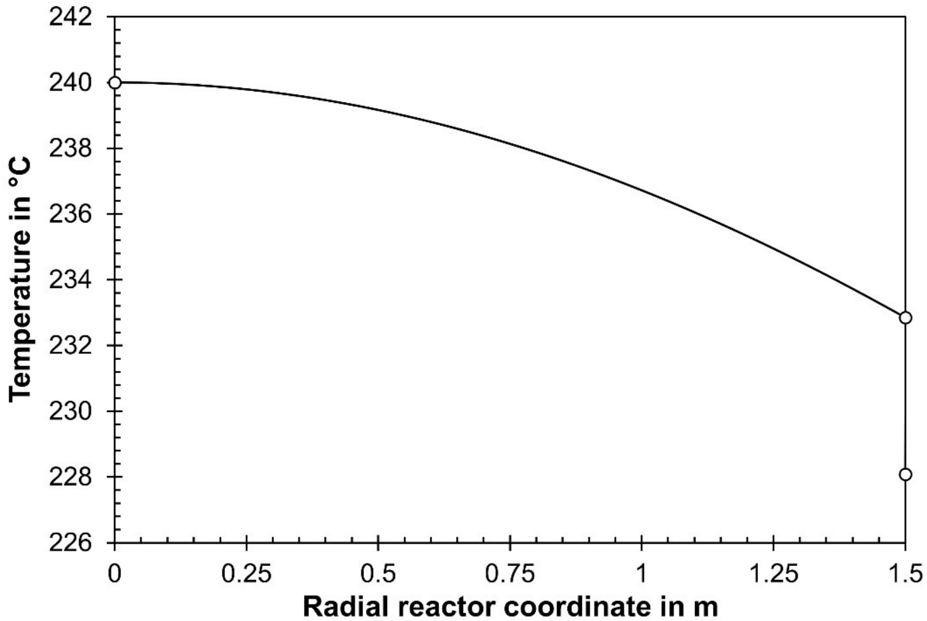


**Fig. S8**: Radial temperature profile at the position of the axial temperature maximum ($z$ = 2.2 m) ($C_a$ = 3; $p_{total}$ = 30 bar; $u_s$ = 1 m/s; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

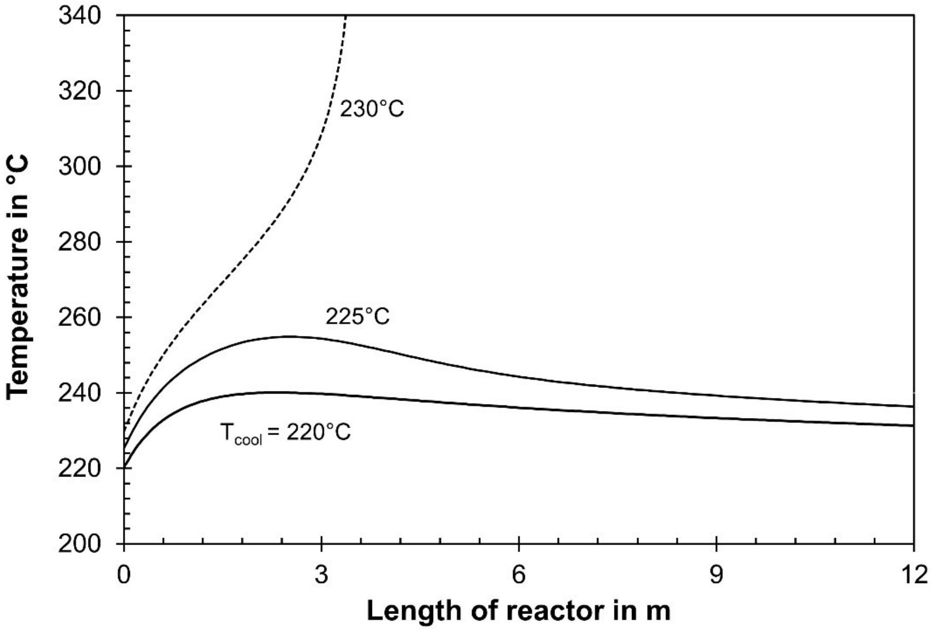


**Fig. S9**: Axial temperature profiles in the center of the single tube ($r$ = 0) for three different cooling temperatures. For $T_{cool}$ = 230°C (dashed-dotted line), thermal runaway occurs ($C_a$ = 3; $p_{total}$ = 30 bar; $u_s$ = 1 m/s; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

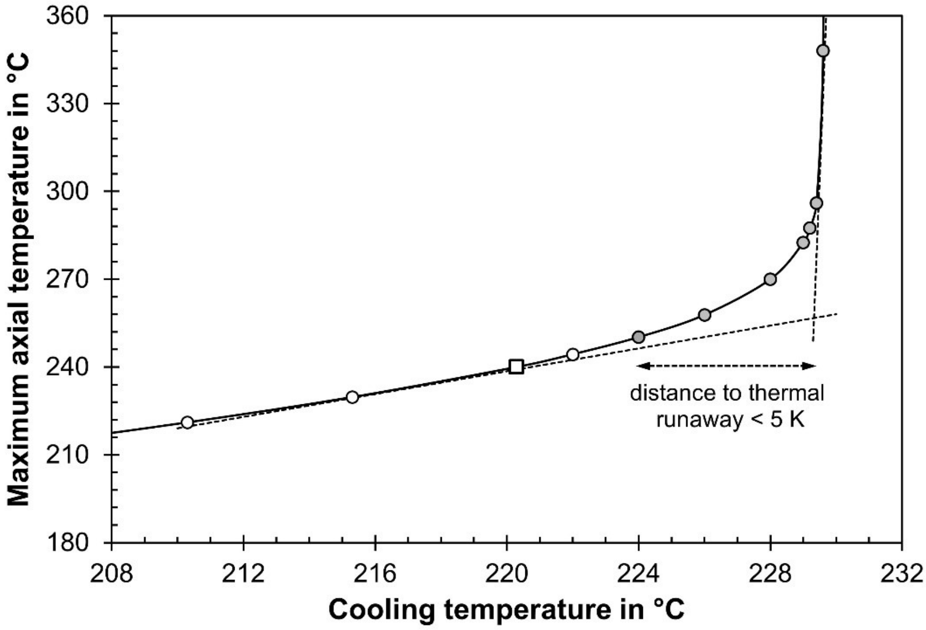


**Fig. S10**: Influence of $T_{cool}$ on $T_{max}$ (center of tube) at axial position of around $z$ = 2 m, where maximum axial temperature is reached (see Fig. S9). Thermal runaway occurs for $T_{cool}$ of about 230°C; hence, $T_{cool}$ should be 225°C ($C_a$ = 3; $p_{total}$ = 30 bar; $u_s$ = 1 m/s; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%; molar $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

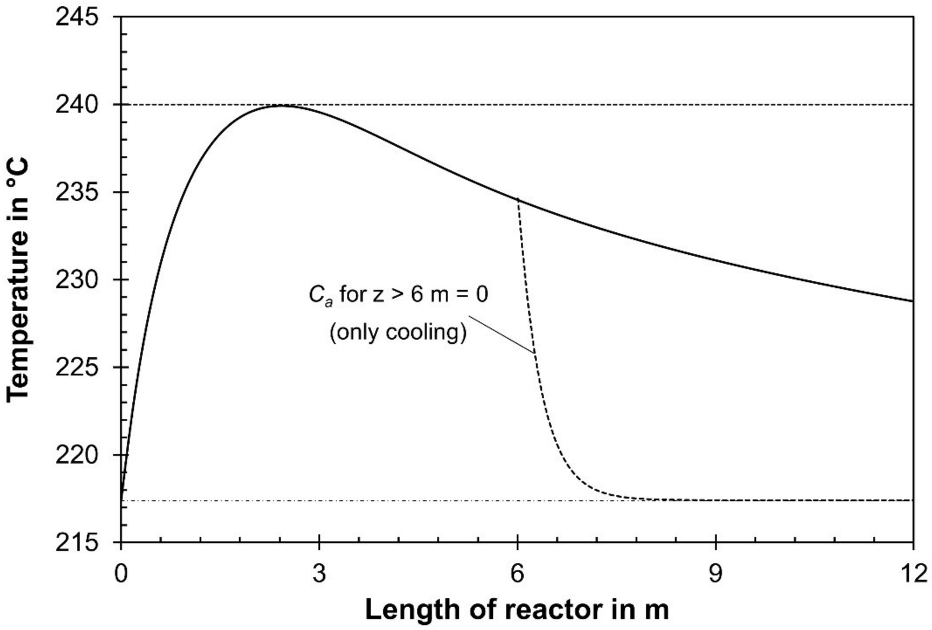


**Fig. S11**: Axial temperature profile in a single tube of a FT reactor with constant catalytic activity ($C_a$ = 4). The dotted line indicates the T-profile for the hypothetic case of no activity in the second part of the tube ($C_a$ = 4 for $z$ > 6 m) to show the high intensity of cooling in a multi-tubular FT-reactor ($p_{total}$ = 30 bar; $u_s$ = 1).

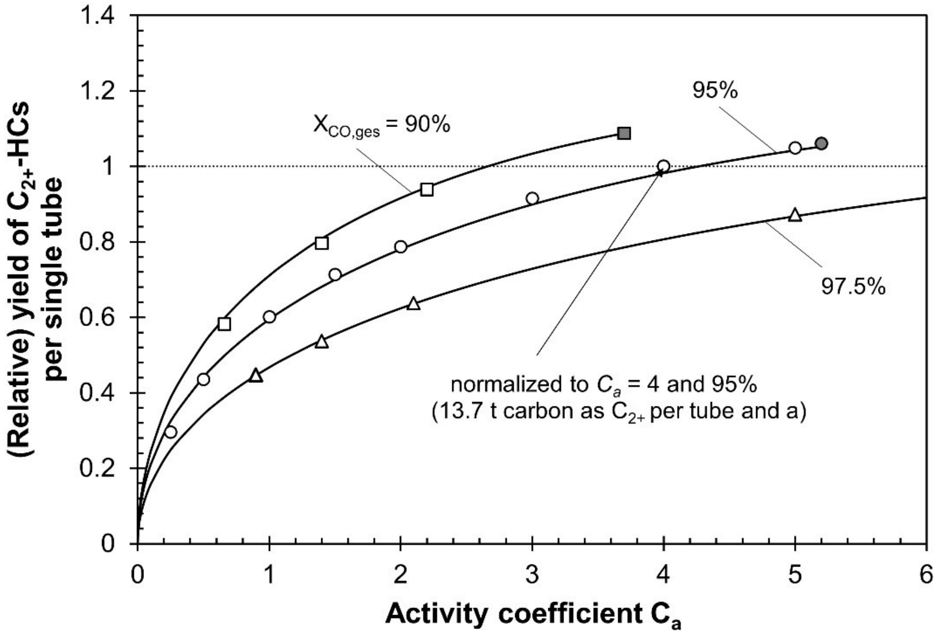


**Fig. S12**: Influence of activity coefficient $C_a$ on the (relative) yield of $C_{2+}$-HCs per single tube for three different values of the overall CO conversion $X_{CO,total}$ . A relative yield of one equals 13.7 t of carbon as $C_{2+}$-HCs per tube and year, reached for a uniform activity $C_a$ of 4 ($p_{total}$ = 30 bar; $u_s$ = 1 m/s; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C). Filled symbols represent critical cases with regard to thermal runaway.

**Tab. S2**: Characteristic data of a cooled multi-tubular FT reactor for different uniform axial activities $C_a$ and an overall CO conversion ($X_{CO,total}$) of 90% and 97.5% ($p_{total}$ = 30 bar; $u_s$ = 1 m/s; $CH_4$ selectivity = 20%, $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C; $u_s$ = 1 m/s; 1825 mol/h syngas at reactor inlet).

| $C_a$ | $n_{SG,fresh}$ in mol/h | $T_{cool}$ in °C | $X_{CO,per\ pass}$ in % | $y_{CH4,reactor,\ in}$ in % | **R** | **Production of $C_{2+}$ per single tube** in $kg_C$ per h | $n_{purge}$ in mol/h |
|---|---|---|---|---|---|---|---|
| $X_{CO,total}$ = 90% | | | | | | | |
| 0.66 | 360 | 229.2 | 25.24 | 28.9 | 4.06 | 0.95 | 71 |
| 1.4 | 494 | 224.2 | 33.2 | 33.2 | 2.70 | 1.31 | 105 |
| 2.2 | 581 | 220.5 | 38.1 | 38.1 | 2.14 | 1.54 | 134 |
| 3.7[a] | 674 | 215.4 | 43.21 | 43.2 | 1.71 | 1.79 | 167 |
| $X_{CO,total}$ = 97.5% | | | | | | | |
| 0.9 | 256 | 231.4 | 34.71 | 61.0 | 6.14 | 0.74 | 25 |
| 1.4 | 308 | 229.2 | 40.3 | 59.0 | 4.94 | 0.89 | 32 |
| 2.1 | 364 | 227.7 | 45.2 | 56.8 | 4.01 | 1.04 | 39 |
| 5 | 499 | 220.7 | 54.8 | 51.5 | 2.66 | 1.43 | 59 |
| 8.3[b] | 580 | 213.3 | 59.2 | 48.4 | 2.15 | 1.66 | 73 |

[a] Limit $C_a$ value with regard to runaway: $T_{ig}$ = 220.3°C, i.e. $T_{cool,max}$ = $T_{ig}$ - 5 K = 215.3°C.

[b] Such a high value of $C_a$ is unrealistic for a real FT-catalyst.

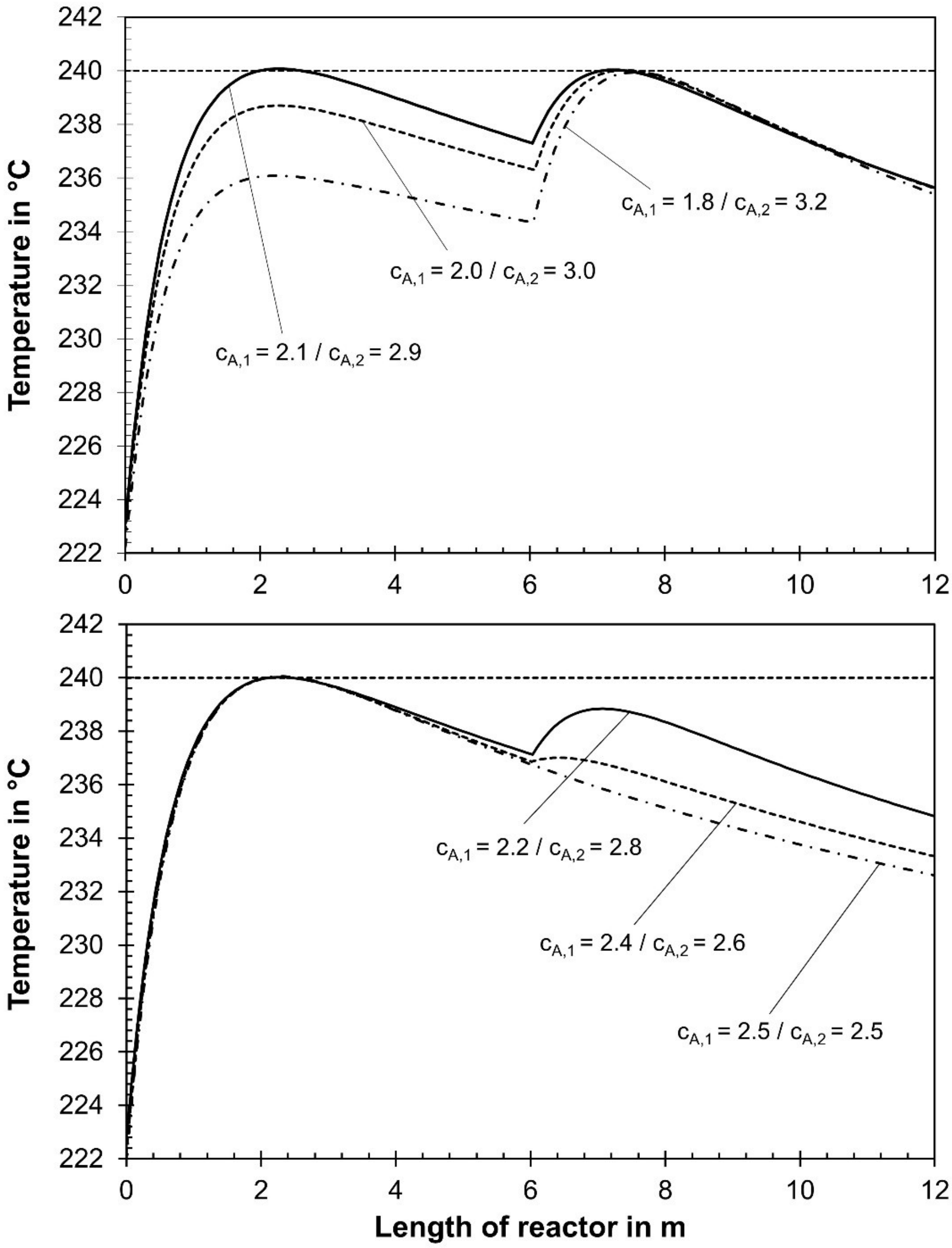


**Fig. S13**: Axial temperature profiles in a two-zone FT reactor with two catalytic zones of equal length (6 m) for different values of the activities $C_{a,1}$ and $C_{a,2}$ and a constant mean activity $C_{a,mean}$ of 2.5. The corresponding values of the yield of $C_{2+}$-HCs are shown in Fig. S11 ($p_{total}$ = 30 bar; $u_s$ = 1 m/s; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

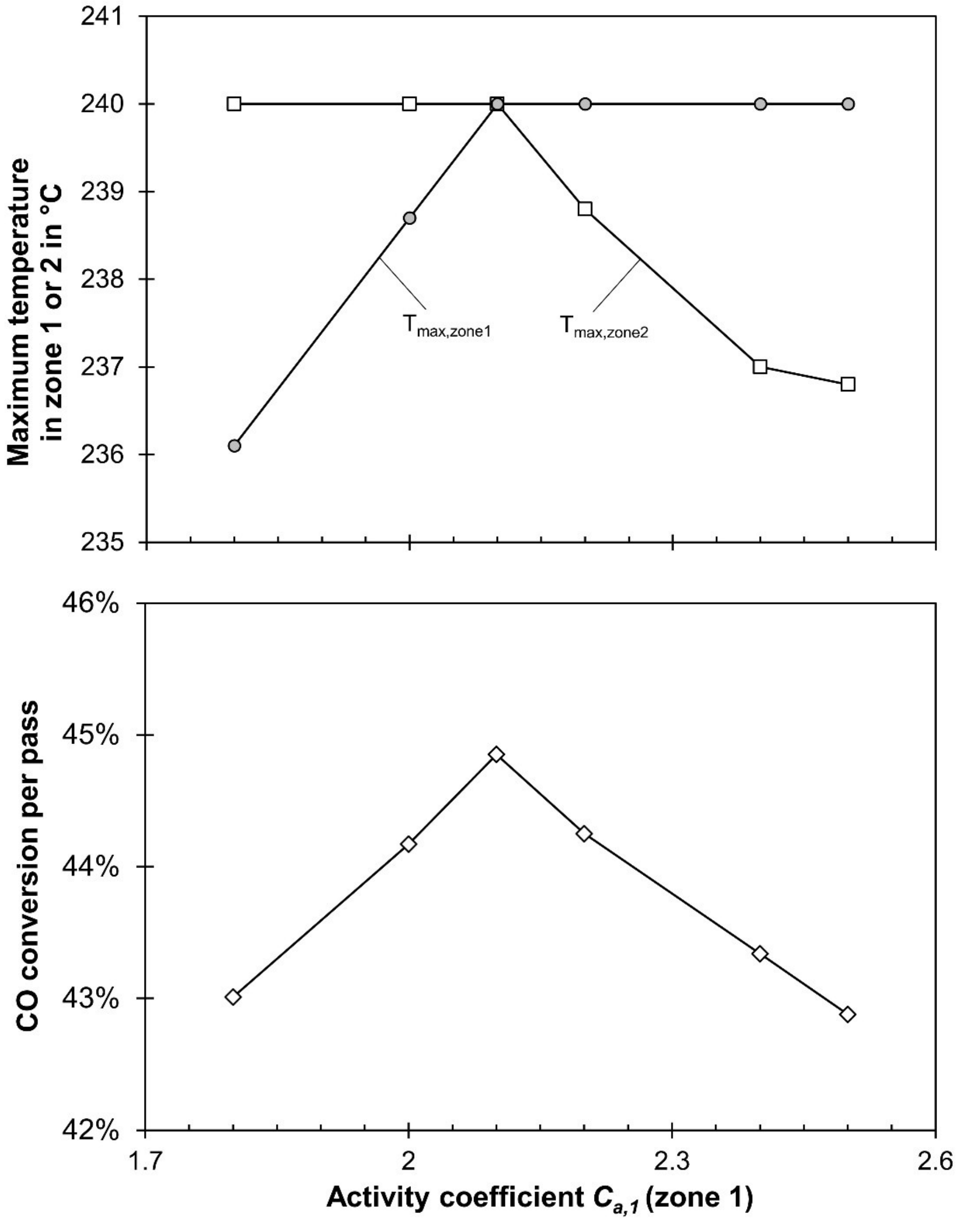


**Fig**. **S14**: Maximum axial temperatures in both zones of a two-zone FT reactor (top) and CO-conversion per pass (bottom) for a variation of $C_{a,1}$ and a constant value of $C_{a,mean}$ of 2.5, i.e. $C_{a,2}$ = 5 - $C_{a,1}$ ($p_{total}$ = 30 bar; $u_s$ = 1 m/s; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2).

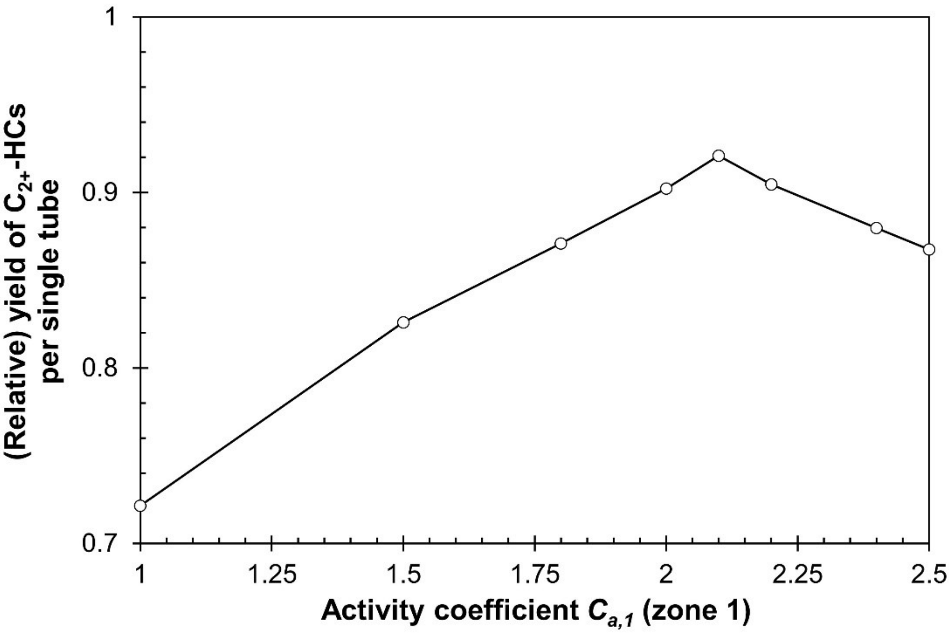


**Fig. S15**: FT reactor with two zones of equal length (6 m): Influence of $C_{a,1}$ on (relative) yield of $C_{2+}$-HCs per tube ($C_{a,mean}$ = 2.5; $C_{a,2}$ = 2 $C_{a,mean}$ - $C_{a,1}$; conditions in Fig. S10). A relative yield of one equals 13.7 t of carbon as $C_{2+}$-HCs per tube and a, reached for a uniform activity $C_a$ of 4. Maximum yield is reached for $C_{a,1}$ = 2.1 and $C_{a,2}$ = 2.9, corresponding to case that $T_{max}$ = 240°C in both zones (see Fig. S10).

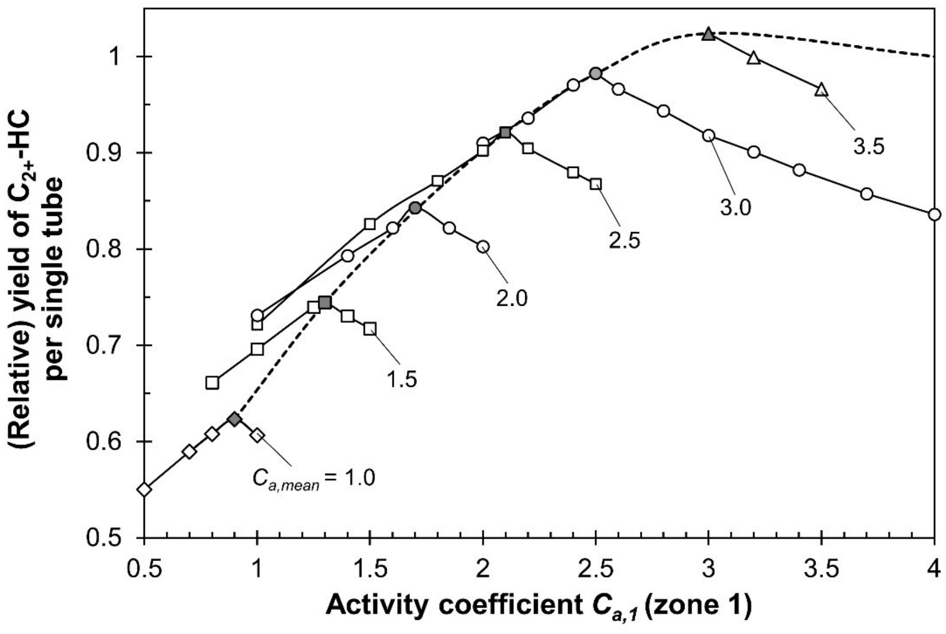


**Fig. S16**: Two-zone reactor (tube) with two fixed beds of equal length (6 m): Influence of activity coefficient $C_{a,1}$ on relative yield of $C_{2+}$-HC per tube for different mean activities $C_{a,mean}$. A relative yield of one corresponds to 13.7 t of carbon as $C_{2+}$-HCs per tube and a, reached for a uniform activity $C_a$ of 4. Filled symbols represent maximum yield reached in each case. Dotted line connects optimum values of for each $C_{a,1}$ (30 bar; $u_{s,\,z=0}$ = 1 m/s; $CH_4$ selectivity = 20%; molar $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

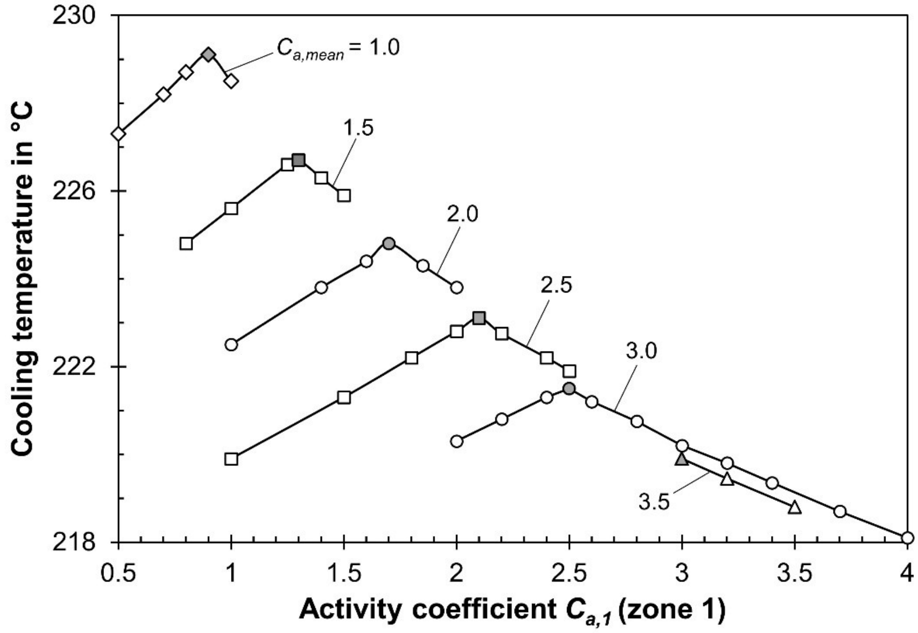


**Fig**. **S17**: Two-zone FT reactor with zones of equal length (6 m): Influence of activity coefficient $C_{a,1}$ on $T_{cool}$ for different mean activities $C_{a,mean}$. Filled symbols represent case that maximum yield is reached, see also Fig. S16 ($p_{total}$ = 30 bar; $u_s$ = 1 m/s; $CH_4$ selectivity = 20%; $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C).

*Supplements to Chapter 4.5*

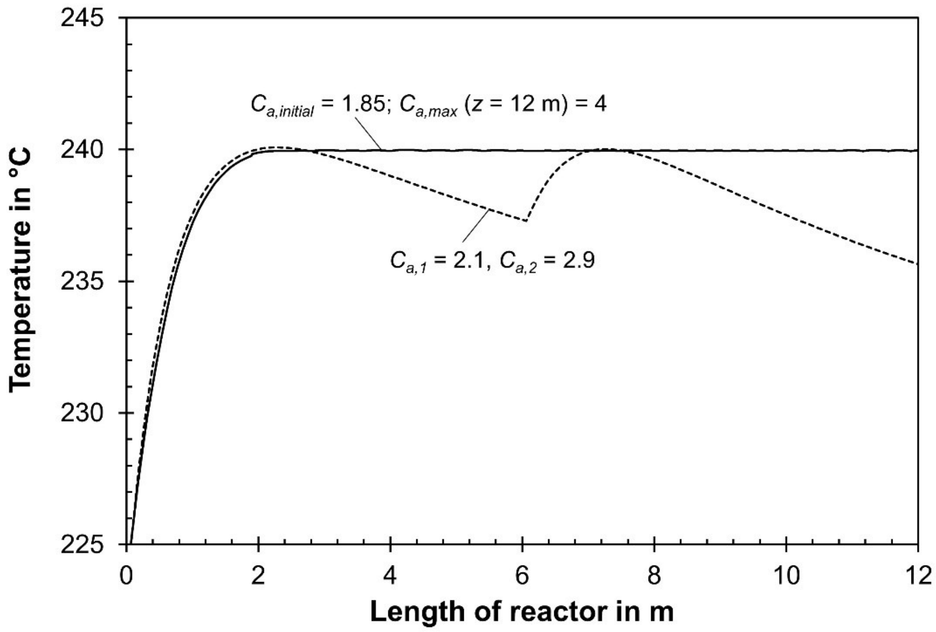


**Fig. S18**: Axial temperature profiles at $r$ = 0 (center of tube) in a single tube of a FT reactor for two zones of equal length (6 m) with $C_{a,1}$ = 2.1 and $C_{a,2}$ = 2.9 (dashed line) and for a reactor with $C_{a,initial}$ = 1.85 until $T_{max}$ of 240°C is reached (at z = 2.45 m) and thereafter a continuous increase of $C_a$ to keep the temperature (240°C at $r$ = 0) constant ($p_{total}$ = 30 bar; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%, $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C; $u_{s,\, z=0}$ = 1 m/s). Further data in Tab. S3.

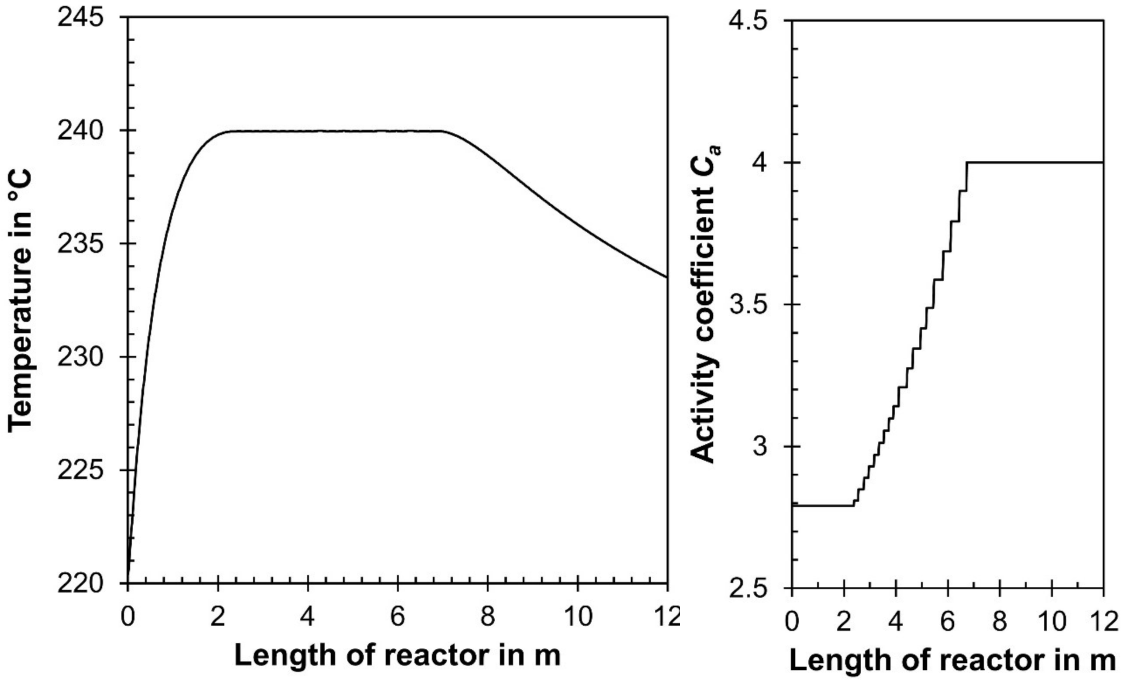


**Fig. S19**: T-profiles ($r$ = 0) and grading of activity in a single tube for $C_{a,initial}$ = 2.79 until 240°C is reached (z = 2.5 m) and then a rise of $C_a$ to keep the temperature (240°C at $r$ = 0) constant until $C_{a,max}$ of 4 is reached at $z$ = 6 m (30 bar; $X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%, $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C; $u_{s,\, z=0}$ = 1 m/s; further data in Tab. S3).

**Tab. S3**: Data of reactor for two activity distribution: $C_{a,initial}$ until 240°C is reached and then rise of $C_a$ to keep $T$ at 240°C ($r$ = 0); two-zone reactor for optimal $C_a$ values ($X_{CO,total}$ = 95%; $CH_4$ selectivity = 20%, $H_2$-to-CO ratio = 2.2; $T_{max}$ = 240°C; $u_{s, z = 0}$ = 1 m/s).

| $C_{a,mean}$ | $C_{a,1}$ (z < 6 m); $C_{a,2}$ (6 m < z < 12 m) | | $X_{CO, per pass}$ in % | $T_{cool}$ in °C | $R$ | **Production rate of $C_{2+}$-HCs per tube** in $kg_C$ per h |
|---|---|---|---|---|---|---|
| | $C_{a,1}$ | $C_{a,2}$ | | | | |
| 1.5 | 1.3 | 1.7 | 38.1 | 226.7 | 3.27 | 1.22 |
| 2 | 1.7 | 2.3 | 41.8 | 224.7 | 2.77 | 1.38 |
| 2.5 | 2.1 | 2.9 | 44.9 | 223.1 | 2.45 | 1.51 |
| 3 | 2.5 | 3.5 | 47.0 | 221.5 | 2.23 | 1.61 |
| 3.5 | 3.0 | 4.0 | 48.5 | 219.9 | 2.10 | 1.68 |
| $C_{a,mean}$ | **Optimal $C_a$ distribution** $C_{a,initial}$ and rise of $C_a$, if $T_{max}$ is reached ($z$ ≈ 2.5 m) | | $X_{CO, per pass}$ in % | $T_{cool}$ in °C | $R$ | **Production rate of $C_{2+}$-HCs per tube** in $kg_C$ per h *(improvement rel. to two-zone reactor)* |
| | $C_{a,initial}$ | $C_{a,max}$ | | | | |
| 1.5 | 1.18 | 2.11 ($z$ = 12 m) | 38.9 | 227.3 | 3.16 | 1.25 (+*2.6%*) |
| 2 | 1.54 | 3.03 ($z$ = 12 m) | 43.0 | 225.4 | 2.65 | 1.43 (+*3.3%*) |
| 2.5 | 1.85 | 3.93 ($z$ = 12 m) | 46.1 | 223.9 | 2.33 | 1.57 (+*3.6%*) |
| 3[a] | 2.23 | 4 ($z$ > 9.6 m) | 48.7 | 222.3 | 2.08 | 1.70 (+*5.0%*) |
| 3.5[a] | 2.79 | 4 ($z$ > 6.7 m) | 49.8 | 220.4 | 1.98 | 1.75 (+*3.9%*) |

[a] In these two cases, the limiting value of $C_{a,max}$ = 4 (catalyst with about 40 wt.-% Co) is reached at $z$ = 9.6 m and 6.8 m, respectively. Hence, $T$ decreases thereafter and reaches 237°C and 234°C at $z$ = 12 m.