

Design and Technoeconomic Analysis of Fischer–Tropsch Fixed-Bed Synthesis with Cobalt-Based Catalysts

Christoph Kern* and Andreas Jess*

A multitubular Fischer–Tropsch (FT) reactor with gas recycle and a cobalt-based catalyst is simulated by a 2D fixed-bed model that considers the complex kinetics, all relevant mass and heat transfer aspects, and also the influence of the changing molar flow rate by the FT reaction, of pressure drop, and of formation of steam, which decreases the reaction rate of FT synthesis. Optimal values of gas velocity and single-tube diameter and length are determined by a technoeconomic analysis. The comparison of the data of the FT reactor modeled in this work with data of commercial reactors indicates that the used model reflects reality well and is reliable. A superficial gas velocity of 0.5 m s^{-1} , a tube diameter of 3 cm, and a length in a range of 12–20 m are appropriate for a high production rate of C_{2+} -hydrocarbons with minimal operating costs of the FT unit, even for a large range of the electricity price from 0.06 to 0.3 € kWh^{-1} .

off-gases with a much higher CO_2 . In any case, concentrated CO_2 can serve as carbon source for FT syngas via conversion to CO by reverse water–gas shift (RWGS) ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$), or in future potentially by coelectrolysis of CO_2 and H_2O .

In three recent publications,^[1–3] we presented a model of a multitubular FT reactor with a cobalt-based catalyst without/with gas recycle.^[1,2] The intrinsic rates of formation of methane and of C_{2+} -hydrocarbons (HCs) as well as internal diffusion limitations induced by the low rate of diffusion of dissolved H_2 and CO in the liquid-filled pores of the catalyst are considered by an effectiveness factor. Both aspects were experimentally determined in preceding works.^[1,4–8]

1. Introduction


Fischer–Tropsch synthesis (FTS) is an option to produce fuels like diesel or jet fuel beyond crude oil. Currently, syngas for FTS (CO , H_2) is mainly produced from coal or natural gas, e.g., in South Africa or Qatar. In the future, nonfossil resources may give momentum to FTS: H_2 can be produced by water electrolysis using solar and wind energy. CO_2 can be separated from different sources, whereby flue gases of power plants are today the largest potential source. A promising approach is oxyfuel combustion of natural gas leading to a clean CO_2 -rich flue gas, ideally only consisting CO_2 and H_2O , which makes separation of CO_2 just by cooling an easy task. Other CO_2 sources are off-gases of production of steel and cement, or of chemicals such as NH_3 . In the future, separation from air could be an option, but is more energy-intensive than capturing CO_2 from

The reactor model used here to simulate a cooled single tube is a pseudo-homogenous 2D model. Hence, radial temperature gradients in the bed are considered, as they are needed for an accurate calculation of the performance (axial/radial temperature profiles, CO conversion) of a FT reactor. This 2D approach is in general recommended in the literature, above all for a better prediction of hotspots (thermal runaway) compared to 1D models.^[9–11]

The decrease of the reaction rate of FTS for cobalt-based catalysts by the formation of steam was recently also implemented in the model.^[3] Finally, the influence of the changing molar flow rate by the FT reaction and of the pressure drop (momentum balance) on the reactor performance was also inspected and considered,^[3] as these aspects should be included in FT fixed-bed reactor models but are often disregarded.^[9,11]

This advanced model, which is, to our best knowledge, the rare case or even the first 2D FT-reactor model that covers all of the aforesaid aspects including the radial and axial variation of the catalyst effectiveness (intraparticle mass transfer resistance), was now used to determine favorable design parameters of a technical FT reactor, presented in this article. The overall CO conversion was fixed to 95%, realized by a gas recycle, and unconverted H_2 and CO and the by-product CH_4 are purged. The gas velocity in the tubes and the tube diameter were varied. Economic aspects of the FT reactor and the gas recycle are also discussed, and a favorable combination of tube size and gas velocity is identified by a technoeconomic analysis. Finally, we have compared our results of reactor modeling with data of commercial FT reactors, which is a novel approach rarely or not done in the literature.

C. Kern, A. Jess
Chair of Chemical Engineering, Center of Energy Technology
University of Bayreuth
Universitaetsstraße 30, 95440 Bayreuth, Germany
E-mail: christoph.kern@uni-bayreuth.de; jess@uni-bayreuth.de

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/ente.202301534>.

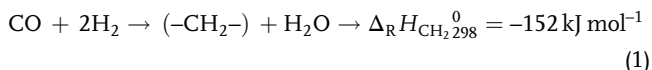
© 2024 The Authors. Energy Technology published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/ente.202301534

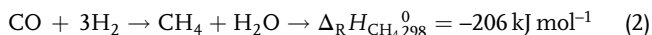
2. Methodology: Kinetics of FTS and Structure of Multitubular FT Reactor Model

2.1. Intrinsic and Effective Reaction Kinetics of FTS

The main reaction of FTS mainly leading to paraffinic C₂₊-HCs is given by



For a reliable kinetic description of FTS, methane formation should be treated separately:



The equations of the intrinsic rates of CO to CH₄ and to C₂₊-HCs for a Co-based catalyst follow Langmuir–Hinshelwood approaches and the already reported kinetic parameters.^[1,4–8] The rate of CO is the sum of formation of CH₄ and C₂₊-HCs, as CO₂ is not formed on a Co catalyst:

$$r_{\text{m,CO}} = -\frac{dn_{\text{CO}}}{dm_{\text{cat}}} = C_a (r_{\text{m,CO,CH}_4} + r_{\text{m,CO,C}_{2+}}) \quad (3)$$

The intrinsic rates $r_{\text{m,CO,CH}_4}$ and $r_{\text{m,CO,C}_{2+}}$ were experimentally evaluated for a Pt promoted (0.03 wt% Pt to facilitate Co reduction) 10 wt% Co/γ-Al₂O₃ catalyst.^[1,4–8] The activity coefficient C_a in Equation (3) considers the Co content and thus the intrinsic activity. C_a is set to one for 10% Co, and a rise of C_a can be realized by a higher Co content.^[1,2] FT catalysts typically contain up to 30 wt% Co ($C_a \approx 3$), and this value is assumed throughout this study.

The inhibition by steam is here also considered, as a high partial pressure ($p_{\text{H}_2\text{O}}$) may be reached at least in the rear part of the tubes. The evaluation of our experiments^[4,8] yielded:^[3]

$$r_{\text{m,CO,H}_2\text{O}} = r_{\text{m,CO}} \left(1 - \frac{c_{\text{H}_2\text{O}}}{472 \text{ mol m}^{-3}} \right) \quad (4)$$

For example, a value of $p_{\text{H}_2\text{O}}$ of 5 bar (120 mol m⁻³ at 230 °C and 30 bar) decreases the intrinsic rate by 25%; for the conditions of this work, this value is reached for a CO conversion per pass above 60% (see supporting information SI 1).

Equation (3) and (4) only reflect the intrinsic chemical rate, but pore diffusion limitations reduce the effective rate compared to the intrinsic for a particle size of millimeters relevant for fixed beds to avoid an excessive pressure drop (here almost proportional to $1/d_p$, see SI 2).

The pores are initially filled with liquid HCs until steady-state is reached, and diffusion of CO and H₂ in liquid HCs is then slow. The effective rate of CO based on the pore effectiveness factor η_{pore} and the related Thiele modulus ϕ is

$$r_{\text{m,CO,eff}} = \eta_{\text{pore}} r_{\text{m,CO,H}_2\text{O}} = \frac{\tanh \phi}{\phi} r_{\text{m,CO,H}_2\text{O}} \quad (5)$$

$$\begin{aligned} \phi &= \left\{ \frac{d_p}{6} \sqrt{\frac{\rho_{\text{cat}}}{D_{\text{eff,CO,liq}} \frac{R_{\text{gas}} T}{H_{\text{CO}}}}} \right\} \sqrt{\frac{r_{\text{m,CO,H}_2\text{O}}}{c_{\text{CO}}}} \\ &= C_\phi \sqrt{C_a \frac{(r_{\text{m,CO,CH}_4} + r_{\text{m,CO,C}_{2+}})}{c_{\text{CO}}} \left(1 - \frac{c_{\text{H}_2\text{O}}}{472 \text{ mol m}^{-3}} \right)} \end{aligned} \quad (6)$$

Hence, η_{pore} depends on the (intrinsic) reaction rates and thus strongly on temperature and to a certain extent also on the concentrations of CO, H₂, and H₂O. This has to be considered in a fixed-bed model with strong axial (and for T also radial) gradients of these parameters.

For the particle diameter d_p of 3 mm, as assumed here, C_ϕ is 300 kg^{0.5} s^{0.5} m^{-1.5}.^[1,2] η_{pore} is then less than one above 180 °C, and reaches a value around 0.2 for 240 °C.^[1–3] This leads to a higher molar H₂-to-CO ratio in the particles compared to the bulk phase with a ratio of typically two, and increases unwanted CH₄ formation relative to C₂₊-HCs, as the diffusion coefficient of H₂ in liquid HCs is 2 times higher as of CO. This effect is strong above 240 °C, and the CH₄ selectivity S_{CH_4} then may exceed 20% compared to 10% without diffusion limitations.^[1,5,8] Here, we limited T_{max} to 240 °C, and assumed that S_{CH_4} is constant at 20%. The corresponding stoichiometric H₂-to-CO ratio is then 2.2 (see Equation (1) and (2)). This value is here not only valid for the fresh syngas, but also for the recycle and purge gas, as the H₂ conversion equals the one of CO. External mass transfer limitations are not relevant for FTS (see SI 3).

2.2. Model of Cooled Multitubular Fixed-Bed FT Reactor

The simulation of a tube of the FT reactor was done by a pseudo-homogenous 2D model.^[1–3] Equation (7) and (8) represent the mass and heat balance for a differential tube section (dz) with R1 indicating reaction of CO to CH₄ and R2 to C₂₊-HCs (details in SI 2).

$$\frac{d(c_i u_s)}{dz} = (\nu_{i,R1} r_{\text{m,CO,R1,eff}} + \nu_{i,R2} r_{\text{m,CO,R2,eff}}) \rho_{\text{bed}} \quad (7)$$

$$\begin{aligned} c_p c_g \frac{d(T u_s)}{dz} &= \lambda_{\text{rad}} \frac{1}{r} \frac{dT}{dr} + \lambda_{\text{rad}} \frac{d^2 T}{dr^2} + \left(r_{\text{m,CO,R1,eff}} (-\Delta_{\text{R}} H_{\text{R1}}) \right. \\ &\quad \left. + r_{\text{m,CO,R2,eff}} (-\Delta_{\text{R}} H_{\text{R2}}) \right) \rho_{\text{bed}} \end{aligned} \quad (8)$$

Radial temperature gradients in the fixed bed are considered, and the heat released by FTS is dissipated through the pseudo-homogenous phase (catalyst and gas) within the bed to the tube wall (radial dispersion of heat), through the wall, and finally to the cooling fluid (boiling water). The adiabatic temperature rise by the FT reaction (for $X_{\text{CO}} = 100\%$) is about 1000 K, whereas the allowable rise to avoid thermal runaway is less than 50 K. Hence, efficient cooling is mandatory, realized by small tubes with a high ratio of cooling surface to reaction volume.

The radial heat flux in the bed up to the internal tube wall is governed by the radial effective thermal conductivity λ_{rad} . At the internal tube wall, the heat transfer coefficient $\alpha_{\text{w,int}}$ comes into play, formally considering the thermal resistance very near the wall resulting from the high porosity of the bed at the wall. Heat conduction through the wall, typically a negligible contribution to the overall thermal resistance, and heat transfer from the

external tube surface to boiling water are incorporated. All heat transfer parameters are calculated by literature correlations.^[12–19] Furthermore, the following aspects (details in SI 2) are also considered: 1) The pressure drop Δp_t , calculated by the Ergun equation,^[20] influences the superficial gas velocity (thus residence time), as described in more detail in SI 4; 2) The decline of the total molar flow by the FT reaction, e.g., by 30% for a CO conversion of 50% (pure syngas, 31% CO and 69% H₂), is considered, and leads to a reduced gas velocity u_s and thus a higher residence time compared to disregarding this effect; 3) The heat conductivity λ_{rad} and heat transfer coefficient $\alpha_{\text{w,int}}$ are both enhanced by a rise of the gas velocity. Hence, an axially changing u_s by Δp_t (rising u_s) or by the drop of the total molar flow by the FT reaction (decreasing u_s) changes λ_{rad} and $\alpha_{\text{w,int}}$ in axial direction; 4) The external heat transfer coefficient $\alpha_{\text{w,ex}}$ (tube wall to boiling water) depends on and is enhanced by the radial heat flux (W/m² surface of tube) (see Table S2 (SI 2)). The heat flux varies in axial direction and passes a maximum at the position of $T_{\text{max,axial}}$; 5) Axial dispersion of mass and heat and also radial dispersion of mass were not incorporated, as they are only relevant for much steeper gradients of concentration or temperature over a length of a few particles (see SI 5).

Values of constant main parameter used to model the FT reactor are listed in Table 1; additional data can be found in Table S3, Supporting Information. It was presumed that the recycle gas and purge gas only contain unconverted CO/H₂ and the by-product CH₄. The by-product H₂O and all C₂₊-HCs are (simplifying) considered to be completely separated by cooling as liquids downstream the reactor. This is a certain simplification, as other light HCs such as ethane or ethene, etc. may be not completely separated and are thus also present in the recycle gas.

Details on FT kinetics with Co catalysts, modeling of FT fixed-bed reactors, and on FTS, in general, are outlined in previous publications^[1–3] and the literature cited therein.

Table 1. Values of constant main parameters used to model the FT reactor with gas recycle; additional parameters and data of chemical media and heat transfer in Table S3, Supporting Information.

Parameter	Value
Ultimate CO (and H ₂) conversion $X_{\text{CO,total}}$	95%
Tube length L_t (except Section 4.3)	12 m
Wall thickness s_{wall}	0.3 cm
Molar H ₂ -to-CO ratio (fresh syngas, feed gas of reactor, recycle gas, purge gas)	2.2
Content of CO in fresh syngas $y_{\text{CO,fresh,SG}}$ (rest H ₂)	31.25%
CH ₄ content in recycle and purge gas ^{a)} (rest 14.3% CO and 31.4% H ₂)	54.3%
Ratio of purge gas to fresh syngas ^{b)}	0.109
Total pressure p_{total}	30 bar
Diameter of spherical catalyst particles d_p	3 mm
Activity coefficient C_a of catalyst (corresponding to 30 wt% Co)	3

^{a)}The CH₄ content in the recycle/purge gas depends solely on $X_{\text{CO,total}}$, whereas the content in the feed gas of the reactor (mixture of fresh syngas + recycle gas) also depends on $X_{\text{CO,per pass}}$.^[2] ^{b)}The ratio of the purge gas stream to the stream of fresh syngas CH₄ only depends on $X_{\text{CO,total}}$ (here 95%) and S_{CH_4} (here 20%).^[2]

For a first evaluation of each simulation, the conversion per pass ($X_{\text{CO,per pass}}$) and the production of C₂₊-HCs per tube are used. The tube number, the diameter of the FT reactor, and optimal conditions (T_{cool} , u_s , d_t) for an annual production of 100 000 tons of carbon as C₂₊-HCs were also determined. The tube size d_t (2.5 to 5.5 cm) and gas velocity u_s (0.2–1.6 m s⁻¹) were varied, and appropriate values of T_{cool} and of the recycle ratio R , defined as ratio of recycle to fresh syngas, were calculated. The inlet syngas composition (CO, H₂, CH₄) depends on $X_{\text{CO,per pass}}$ and on R , but the total CO conversion ($X_{\text{CO,total}} = 95\%$) reached in the FT unit was fixed.

The target of T_{max} (center of tube at maximum of axial temperature) was set to 240 °C to limit excessive CH₄ formation, but this value can only be achieved, if T_{cool} , needed to avoid a thermal runaway, is not too low. To ensure safe operation, the maximum value of T_{cool} was set to 5 K below the ignition temperature T_{ig} to keep a sufficient “safety distance”. This is meaningful, as, for instance, fluctuations of conditions such as the gas velocity u_s at the reactor inlet or, even more likely, differences between individual tubes of a reactor with thousands of tubes are probably hard to avoid. For the investigated conditions, a difference of u_s of 0.1 m s⁻¹, such as 0.4 m s⁻¹ instead of 0.5 m s⁻¹, already leads to a 5 K lower value of T_{ig} (see Figure S1, Supporting Information (SI 6)).

For the numerical analysis, the differential equations (DEs) of the mass and heat balance were solved by the program Presto, a reliable solver of DEs (CiT GmbH, Rastede, Germany).

3. Results of Simulation of a Cooled Multitubular FT Reactor with Gas Recycle

3.1. Influence of Tube Diameter and Gas Velocity on Reactor Performance

Figure 1–4 and Table 2 show the influence of gas velocity u_s and tube diameter d_t on CO conversion per pass (Figure 1), on the production rate of C₂₊-HCs (Figure 2), on the pressure drop

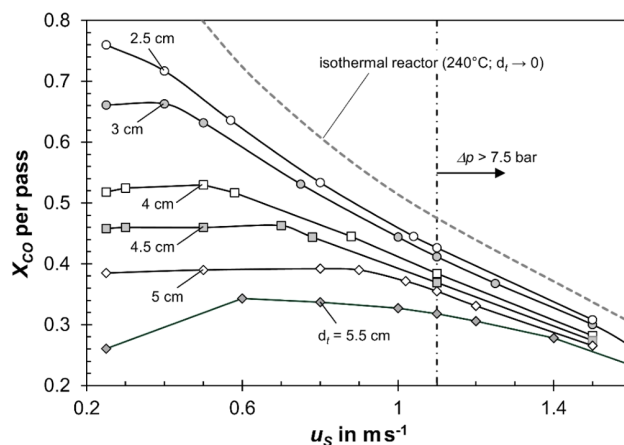


Figure 1. Influence of gas velocity on CO conversion per pass for different tube diameters (conditions in Table 1). CH₄ inlet content depends on $X_{\text{CO,per pass}}$ and recycle ratio R (values in Table 2). The dotted–dashed line indicates high pressure drop of 7.5 bar.

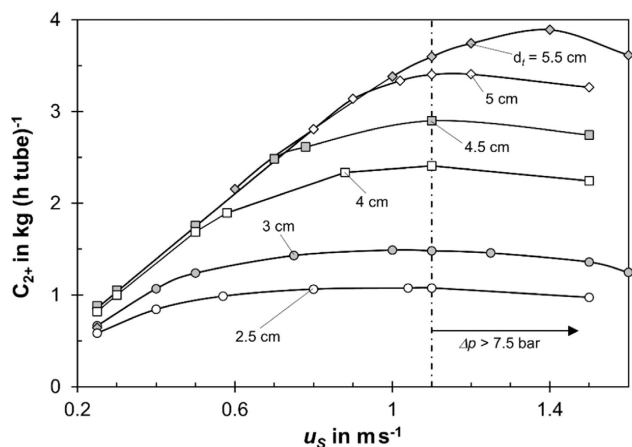


Figure 2. Influence of superficial gas velocity $u_{s,z=0}$ on production of C_{2+} -HCs per tube (other conditions as Table 1). The dotted–dashed line indicates a limiting pressure drop 7.5 bar.

(Figure 3), and on the axial temperature profiles (Figure 4). As already mentioned, the target of a maximum temperature of 240 °C cannot always be realized. For example, d_t should not be higher than 3 cm for $u_s = 0.5 \text{ m s}^{-1}$ (and 5 cm for 1.1 m s^{-1}) to keep a safe distance to a thermal reactor runaway and thus a reliable operation (Figure 4).

For each tube diameter, a minimum gas velocity $u_{s,min}$ is needed to reach the target value of T_{max} (240 °C), e.g., 0.58 m s^{-1} for $d_t = 4 \text{ cm}$ (Figure 5). A rise of $u_{s,min}$ substantially enhances the overall thermal transmittance U_{bed} , representing heat conduction in the bed (λ_{rad}) as well as heat transfer from bed to internal tube wall ($\alpha_{w,int}$) (see Figure 6 (right) and Equation (S15)). U_{bed} mainly depends on u_s , but also to a certain extent on the ratio d_p/d_t .

For a high gas velocity of 1.1 m s^{-1} (to limit Δp_t), the target of T_{max} of 240 °C can be even reached for a large tube size of 5 cm (Figure 6, left). For a low u_s of 0.4 m s^{-1} , thus less heat dissipation per surface area of tube, d_t is limited to 2.8 cm to reach

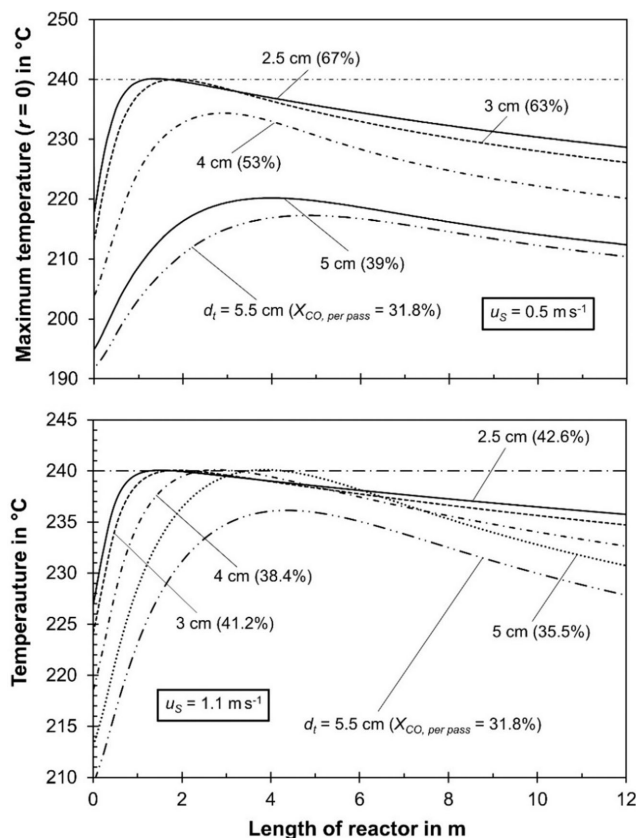


Figure 4. Axial temperature profiles in the center of a single tube of a FT reactor for a constant gas velocity $u_{s,z=0}$ of 0.5 and 1.1 m s^{-1} ; other conditions as in Table 1.

240 °C (Figure 6, left). All values of $u_{s,min}$ and other parameters to reach T_{max} are listed in Table 3 (see Figure S2–S9 in SI 7).

A pressure drop above 7.5 bar, already 25% of the initial pressure, is probably too high, and u_s should not exceed 1.1 m s^{-1} (Figure 3), particularly, as formation of C_{2+} -HCs per tube for

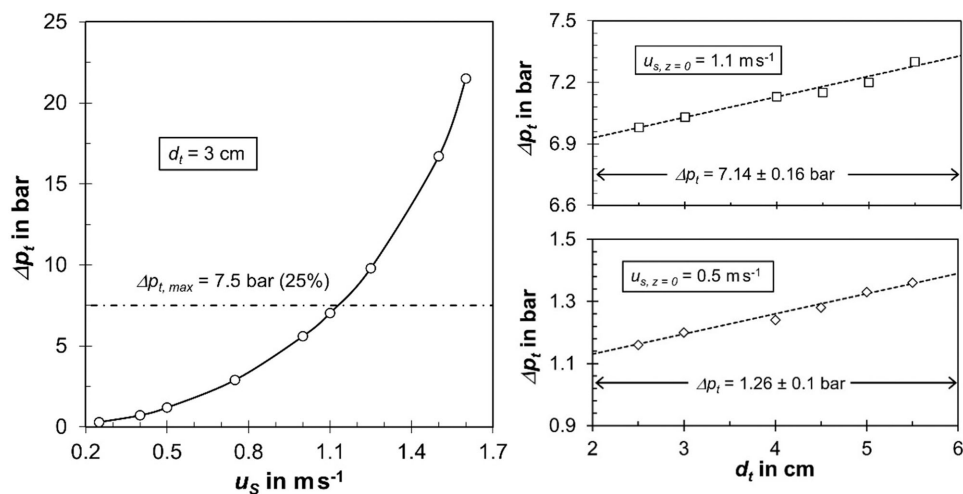


Figure 3. Impact of gas velocity $u_{s,z=0}$ on pressure drop of reactor (conditions in Figure 1).

Table 2. Characteristic data of FT reactor (single tube) for different values of d_t and u_s ($u_s \leq 1.1 \text{ m s}^{-1}$ to keep $\Delta p_t < 7.5 \text{ bar}$; other conditions in Table 1).

d_t [cm]	$u_{s,z=0}$ ($u_s, z=12$) [m s^{-1}]	T_{cool} [$^{\circ}\text{C}$]	T_{max} [$^{\circ}\text{C}$]	$X_{\text{CO,per pass}}$ [%]	$\gamma_{\text{CH}_4, \text{ reactor, in}}$ [%]	R	Production of $\text{C}_{2+}\text{-HCs}^{\text{c)}$	
							per tube [$\text{kg}_C \text{ h}^{-1}$]	per [kg_C cat. [$\text{kg}_C \text{ h}^{-1}$]
2.5	0.4 (0.27)	214.6	240	71.1	22.6	0.71	0.844	0.149
2.5	0.8 (0.72)	223.8	240	53.4	34.2	1.71	1.065	0.188
2.5	1.1 (1.23)	227.0	240	42.6	39.6	2.69	1.078	0.191
3	0.4 (0.29)	209.2	238.1 ^{a)}	66.3	26.4	0.95	1.069	0.131
3	0.75 (0.66)	219.4	240	53.1	34.4	1.73	1.430	0.176
3	1.1 (1.24)	224.2	240	41.2	40.2	2.86	1.482 ^{b)}	0.182
4	0.5 (0.40)	204.0	234.4 ^{a)}	53.0	34.4	1.73	1.688	0.117
4	0.88 (0.86)	215.1	240	44.5	38.7	2.48	2.336	0.161
4	1.1 (1.25)	218.6	240	38.4	41.4	3.22	2.409	0.166
5	0.5 (0.43)	195.0	219.5 ^{a)}	39.0	41.2	3.14	1.750	0.077
5	0.8 (0.77)	206.0	234.3 ^{a)}	39.2	41.1	3.11	2.809	0.124
5	1.1 (1.27)	213.2	240	35.5	42.7	3.67	3.403	0.150
5.5	0.6 (0.54)	195.7	221.8 ^{a)}	34.3	43.1	3.87	2.155	0.079
5.5	0.8 (0.78)	201.8	228.4 ^{a)}	33.7	43.4	3.98	2.808	0.103
5.5	1.1 (1.28)	209.5	236.2 ^{a)}	31.8	44.1	4.35	3.598	0.131

^{a)}Target of $T_{\text{max}} = 240 \text{ }^{\circ}\text{C}$ cannot be reached regarding thermal runaway (see also Figure S2 and S3 in SI 7); ^{b)}Example of C balance: For $u_s = 1.1 \text{ m s}^{-1}$ and $d_t = 3 \text{ cm}$, the total molar feed rate (fresh syngas + recycle gas) per tube is 2006 mol h^{-1} , i.e., 375 mol CO/h (18.7%). For $X_{\text{CO,per pass}}$ of 41.2% and 80% selectivity to $\text{C}_{2+}\text{-HCs}$, the production rate of $\text{C}_{2+}\text{-HCs}$ (carbon) per tube is then 1.48 kg h^{-1} ($=375 \text{ mol h}^{-1} \times 0.012 \text{ kg mol}^{-1} \times 0.412 \times 0.8$); ^{c)}Production rate of $\text{C}_{2+}\text{-HCs}$ related to carbon, i.e., the rate of HCs is by factor 1.17 higher ($=M_{\text{CH}_2}/M_C$).

a given tube size is then not or only to a small extent ($d_t = 5.5 \text{ cm}$) further enhanced (Figure 2).

Figure 7 shows the influence of d_t on $X_{\text{CO,per pass}}$ and production of $\text{C}_{2+}\text{-HCs}$ per tube for the target of T_{max} of $240 \text{ }^{\circ}\text{C}$ and u_s of 0.5 or 1.1 m s^{-1} . An increase of u_s (better heat removal) enhances the production of $\text{C}_{2+}\text{-HCs}$ (Figure 7, right), but this effect weakens for a high d_t as T_{max} ($240 \text{ }^{\circ}\text{C}$) is not any more reached to avoid a runaway. The limits are 3.4 cm for 0.5 m s^{-1} and 5.2 cm for 1.1 m s^{-1} (Figure 7, left). Hence, $X_{\text{CO,per pass}}$ drops by a rise of d_t (lower T) and u_s (lower residence time), which increases the recycle ratio R . A high gas velocity yields a high pressure drop, and Δp_t and R boost the capacity and energy need of the recycle compressor.

3.2. Dimensions of a FT Reactor for an Annual Production of 100 000 Tons of Liquid Fuels

The dimensions of multitubular FT reactors for the annual production of 100 000 tons of $\text{C}_{2+}\text{-HCs}$ (related to carbon; 8000 h a^{-1}) are listed in Table 4 for different tube diameters for $u_s = 0.5 \text{ m s}^{-1}$ and $L_t = 12 \text{ m}$. The dimensions, e.g., case 2 in Table 4, are impressive. The reactor has 10 090 tubes, a heat exchange area of almost $14\,000 \text{ m}^2$, and the combined tube length is 121 km. The weight of the empty reactor (steel tubes) is 300 tons and 400 tons with catalyst charge. The energy released by the reaction is 59 MW (power of six large wind turbines; not directly comparable, but illustrative). On average, 4.2 kW of heat per m^2 tube surface area is transferred to the cooling water, and 2700 tons of water are evaporated per day of operation

(20 bar, $213 \text{ }^{\circ}\text{C}$) compared to only 450 tons of water formed as by-product of FTS. Only a negligible share of 2% of the reaction heat is dissipated as sensible heat by the small difference of 13 K between out- and inlet gas temperature ($=226\text{--}213 \text{ }^{\circ}\text{C}$, Figure 4 (top) for $d_t = 3 \text{ cm}$).

4. Technoeconomic Analysis of a FT Reactor with Gas Recycle and Cobalt as Catalyst

4.1. Influence of Tube Diameter and Gas Velocity on Capex of FT Reactor

The results presented so far are difficult to evaluate economically, although Figure 7 (right) shows that a high gas velocity combined with a large tube diameter is favorable for a high production rate of $\text{C}_{2+}\text{-HCs}$ per tube. But is this really the best choice for a multitubular FT reactor? A first attempt to answer this question is given in Table 5, where not only production data per tube for different tube diameters and a low and high value of u_s are listed, but also the external heat transfer area per tube $A_{t, \text{single, ext}}$. The capital costs of a single tube and thus of a multitubular reactor, respectively, depend on $A_{t, \text{single, ext}}$ with a scaling factor of 0.68, i.e., $\text{capex} \approx A_{t, \text{single, ext}}^{0.68}$ (SI 8). The production of $\text{C}_{2+}\text{-HCs}$ per tube relative to $A_{t, \text{single, ext}}^{0.68}$ is therefore a measure of the production rate relative to (only) capital expenditures of the FT reactor (last column in Table 5). It is then obvious that for $u_s = 0.5 \text{ m s}^{-1}$, a tube diameter of 4 cm is the best choice, and for $u_s = 1.1 \text{ m s}^{-1}$ d_t should be 5 cm (Table 5). The latter case outperforms the first with regard to production per capex of reactor

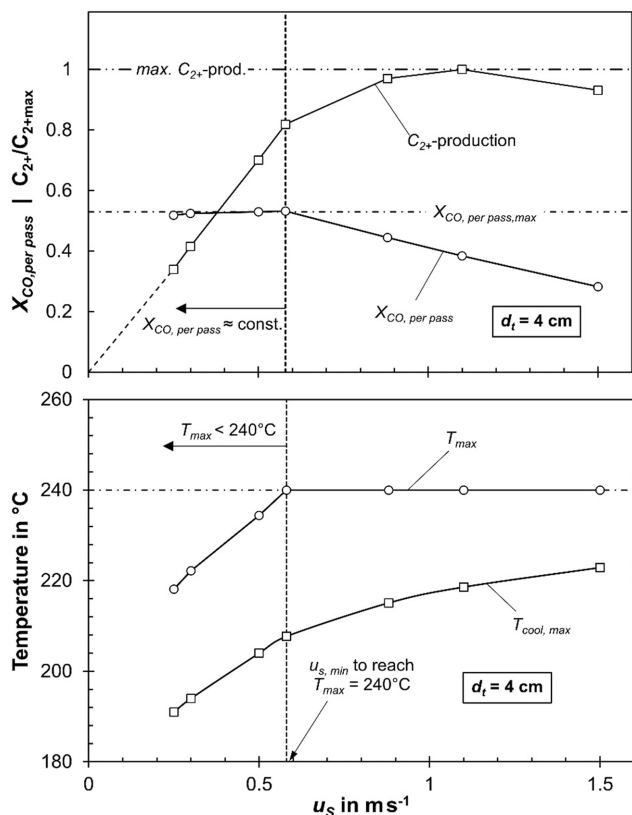


Figure 5. Impact of u_s on $X_{CO,per\ pass}$ and production of C_{2+} -HCs per tube relative to maximum (top) and on T_{cool} and T_{max} (bottom) for $d_t = 4\text{ cm}$ ($T_{max} \leq 240^\circ\text{C}$; other conditions in Table 1). The target of 240°C is not reached for $u_s < 0.6\text{ m s}^{-1}$ regarding runaway.

by 76%, but the recycle ratio is more than doubled (3.67 compared to 1.73) and Δp_t drops by a factor 6 (Table 5; Figure 3). The capital related and variable costs (electricity) of the recycle

compressor are strongly related to R and Δp_t , but were not yet counted; this is done in Section 4.2 to get a better picture.

4.2. Influence of Tube Diameter and Gas Velocity on opex of FT Reactor with Gas Recycle

To identify an appropriate combination of tube size and gas velocity, a technoeconomic analysis of the core of the FT unit was done based on the literature data and the following assumptions: 1) As investment-related items, only the reactor and the recycle compressor are here counted. The total invest for this core unit was calculated based on these two items, including costs for erection, piping, engineering, and so on (see SI 8). The capital-related fixed operating costs include the provision for investment recovery, maintenance, overhead, and insurance. A rule of thumb is that the annual fixed costs are 25% of total capex;^[12] 2) The variable opex are mainly (here only) related to the electricity need of the recycle compressor, and depend on the recycle ratio, pressure drop, and price of electricity; 3) The annual production rate of C_{2+} -HCs is 100 000 tons (carbon related, 8000 h operation). The production rate of C_{2+} -HCs, mainly paraffins, is then 117 000 tons a^{-1} ($M_{CH_2}/M_C = 1.17$); 4) The opex related to the FT catalyst were neglected, although the mass of catalyst (see below) rises for a given production rate of liquid fuels with increasing tube diameter. The reason is the lack of reliable data, and an estimation also indicates that the catalyst-related operating costs are around 6% of the total to run the FT reactor and gas recycle (see SI 8); 5) Other items of the power-to-liquid (PTL) plant such as costly compressors for CO_2 and H_2 , heat exchangers, RWGS reactor, and upgrading of FT products by cracking and distillation are not counted, as they do not depend on design or size of FT reactor and gas recycle, as long as the feed rate of fresh syngas and production rate of HCs are constant.

The power of the recycle compressor, $E_{recycle}$, is calculated assuming isothermal compression and 90% efficiency (η_{comp}) with gas constant R_{gas} , recycle ratio R , and pressure at inlet p_{in} :

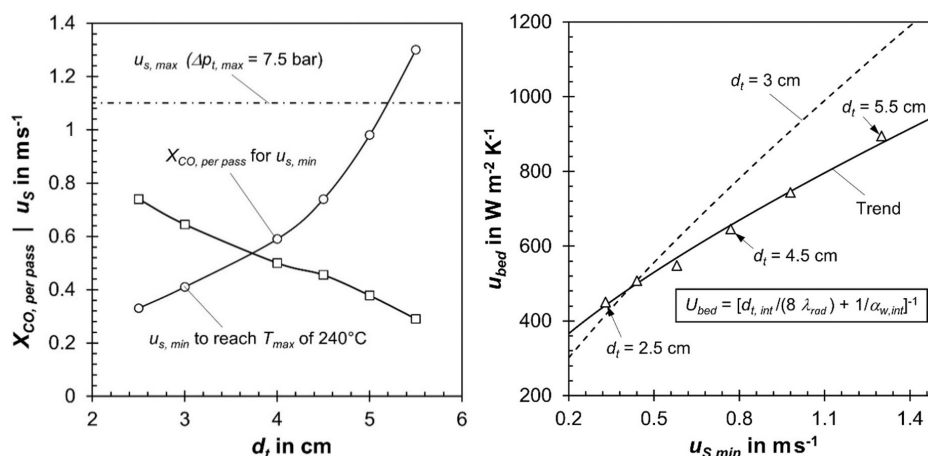


Figure 6. Left: Impact of d_t on $u_{s,min}$ and $X_{CO,per\ pass}$ to reach T_{max} of 240°C . Right: Influence of $u_{s,min}$ on thermal transmittance U_{bed} ; note that d_t varies. For comparison, U_{bed} is shown for $d_t = 3\text{ cm}$ (dashed line), indicating the influence of u_s on U_{bed} and also the positive effect of a smaller tube size d_t on the heat removal (here $U_{bed} \approx 1/d_t^{0.4}$).

Table 3. Minimum superficial gas velocity to reach the target of a maximum axial temperature (center of tubes) of 240 °C in a multitubular FT reactor for a tube diameter in a range of 2.5–5.5 cm (other conditions in Table 1; details in Figure S2–S9 in SI 7).

d_t [cm]	$u_s, z=0$ ($u_s, z=12$) [m s^{-1}]	T_{cool} [°C]	T_{max} [°C]	$X_{\text{CO, per pass}}$ [%]	$\gamma_{\text{CH}_4, \text{ reactor, in}}$ [%]	R	$\text{C}_{2+}\text{-HCs per tube}$ [$\text{kg}_c \text{h}^{-1}$]	Δp_t [bar]
2.5	0.40	215	240	71.7	22.6	0.71	0.84	0.68
3	0.45	211		65.3	27.1	1.00	1.17	0.93
4	0.58	208		53.2	34.3	1.72	1.97	1.67
4.5	0.74	209		45.2	38.4	2.41	2.54	2.93
5	0.98	211		37.7	41.7	3.33	3.27	5.55
5.5	1.40	215		27.8	45.7	5.29	3.89	13.6

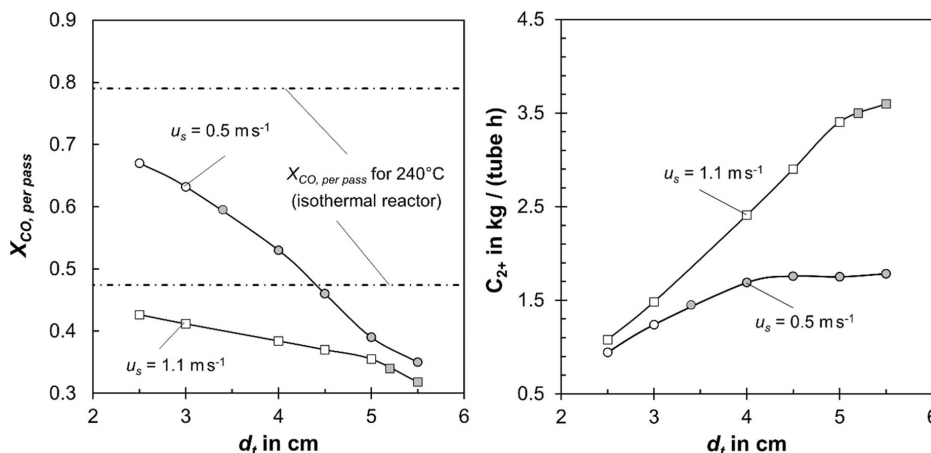


Figure 7. Left: Influence of d_t on $X_{\text{CO, per pass}}$ for T_{max} of 240 °C (if possible) for $u_{s, z=0}$ of 0.5 and 1.1 m s^{-1} . Right: Production of $\text{C}_{2+}\text{-HCs}$ /tube (conditions: Table 1). Gray symbols indicate where T_{max} is not reached. Horizontal dashed–dotted lines: border cases of isothermal operation ($d_t \rightarrow 0$) at 240 °C for $u_s = 0.5$ (lower line) or 1.1 m s^{-1} .

Table 4. Dimensions of FT reactors for production of 100 000 tons of $\text{C}_{2+}\text{-HCs}$ /a (only related to carbon; 8000 h year^{-1} of operation) for $u_s = 0.5 \text{ m s}^{-1}$ and $L_t = 12 \text{ m}$.

Nos.	d_t [cm]	Number of tubes n_t	d_{reactor}^a [m]	m_{cat} [tons]	$A_{t, \text{ reactor, ext}}$ [m^2]
1	2.5	13 256	4.7	75.0	15 491
2	3	10 090	4.8	82.2	13 694
3	4	7405	5.2	107.2	12 842
4	4.5	7114	5.7	130.3	13 679
5	5	7167	6.3	162.1	15 132
6	5.5	6921	6.7	189.4	15 917

^aAssuming an (external) cross-sectional area of all tubes of 57% of cross-sectional area of reactor (see Table 7).

$$E_{\text{recycle}} = \frac{\dot{n}_{\text{recycle}} R_{\text{gas}} T_{\text{in}}}{\eta_{\text{comp}}} \ln \left(\frac{p_{\text{in}}}{p_{\text{in}} - \Delta p_t} \right) = \frac{R \dot{n}_{\text{syngas, fresh}} R_{\text{gas}} T_{\text{in}}}{\eta_{\text{comp}}} \ln \left(\frac{p_{\text{in}}}{p_{\text{in}} - \Delta p_t} \right) \quad (9)$$

Adiabatic compression even for a pressure drop of 7.5 bar ($p_{\text{in}} = 30 \text{ bar}$) only leads to a temperature rise from 20 to

46 °C and an only 4% higher energy demand compared to isothermal operation. So compression can be here almost regarded as isothermal, and the electricity consumption relative to the case of $d_t = 3 \text{ cm}$, $E_{\text{recycle, rel}}$, for a given rate of fresh syngas $\dot{n}_{\text{syngas, fresh}}$ and thus a constant production rate of $\text{C}_{2+}\text{-HCs}$ by a certain number of tubes is

$$E_{\text{recycle, rel}} = \frac{R_i}{R_{d_t=3 \text{ cm}}} \frac{\ln \left(1 - \frac{\Delta p_{t,i}}{p_{\text{in}}} \right)}{\ln \left(1 - \frac{\Delta p_{t,d_t=3 \text{ cm}}}{p_{\text{in}}} \right)} \quad (10)$$

For a certain gas velocity, Δp_t only slightly depends on d_t (Figure 3, 8). The small rise with increasing d_t is related to the drop of conversion from 67% to 34% for 2.5 cm to 5.5 cm. This leads to a smaller decline of the total molar flow by the FT reaction, thus to a slightly higher u_s along the tubes and a higher Δp_t . The compressor's electricity demand is dominated by the ratio $R_i/R_{d_t=3 \text{ cm}}$, Equation (10), and rises with d_t (Figure 8, left; details in Figure S10, Supporting Information).

Figure 9 depicts the impact of d_t on mass of catalyst and capex of reactor and recycle compressor relative to the case of $d_t = 3 \text{ cm}$ and $u_s = 0.5 \text{ m s}^{-1}$. The capex of the compressor depend on the electricity need by a scaling factor of 0.82 (see SI 8). All costs—except capex for $d_t < 4 \text{ cm}$ —increase with d_t (Figure 9). The relative capital expenditures of the reactor were calculated by the heat

Table 5. Production rate of C₂₊-HCs for different tube diameters and gas velocities of 0.5 and 1.1 m s⁻¹.

d _t [cm]	u _{s, z=0} [m s ⁻¹]	X _{CO,per pass} [%]	R	A _{t, single, ext} ^{a)} [m ²]	(A _{t, single, ext}) ^{0.68} [m ^{1.36}]	Production of C ₂₊ -HCs	
						per tube [kg _C h ⁻¹]	per (A _{t, single, ext}) ^{0.68} [kg _C h ⁻¹ m ^{-1.36}]
2.5	0.5	67.0	0.91	1.17	1.11	0.94	0.85
3.0		63.2	1.10	1.36	1.23	1.24	1.01
4.0^{b)}		53.0	1.73	1.73	1.45	1.69	1.16
5.0		39.0	3.14	2.11	1.66	1.75	1.05
5.5		34.5	3.84	2.30	1.76	1.81	1.03
2.5	1.1	42.6	2.69	1.17	1.11	1.08	0.97
3.0		41.2	2.86	1.36	1.23	1.48	1.20
4.0		38.4	3.23	1.73	1.45	2.41	1.66
5.0		35.5	3.67	2.11	1.66	3.40	2.05
5.5		31.8	4.35	2.30	1.76	3.60	2.04

^{a)} Assuming a constant wall thickness of 3 mm regardless of internal single-tube diameter; ^{b)} Values in last column are a measure of production rate relative to capex of reactor (best values in bold), as explained in the text (conditions in Table 1 and 2).

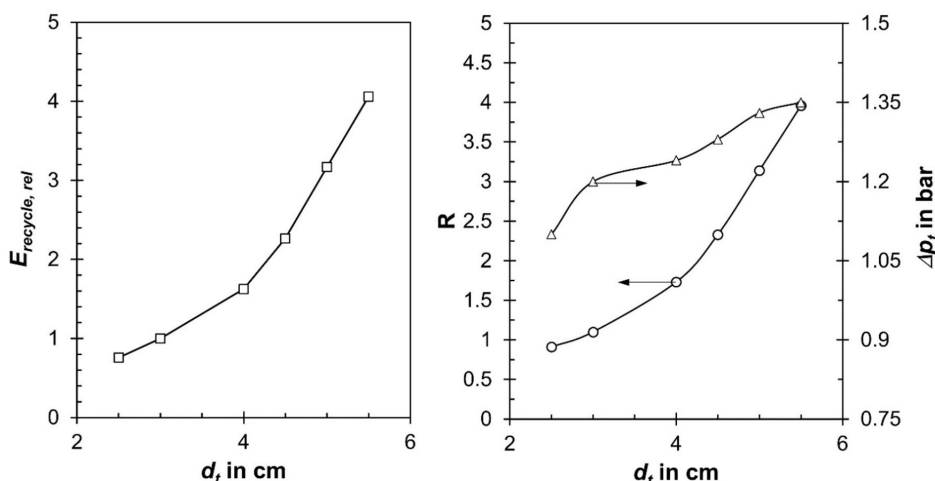


Figure 8. Influence of d_t on energy demand of recycle compressor relative to case of $d_t = 3$ cm (left), and on recycle ratio R and pressure drop (right). Conditions: constant production of HCs by respective number of tubes; $T_{\text{max}} = 240$ °C, $u_{s, z=0} = 0.5$ m s⁻¹; other conditions in Figure 1. E_{recycle} is 151 kW for $d_t = 3$ cm, and 10 090 tubes are then needed to produce 100 000 t C₂₊-HCs (as carbon) per year (8000 h).

exchange area of all tubes $A_{t, \text{reactor, ext}}$ with a scaling factor of 0.68 (SI 8).

Figure 10 shows absolute values of opex per ton C₂₊-HCs for d_t of 3 cm. Four electricity prices were inspected: 0.16 € kWh⁻¹ (average industrial electricity in Germany between 2014 and 2021^[18]), a high price of 0.3 € kWh⁻¹ (Germany 2020^[21]), a low value of 0.06 € kWh⁻¹ (advised price for German companies until 2030 financed by state subsidies), and electricity without charge.

The optimal gas velocity is in a narrow range of 0.4–0.5 m s⁻¹, favoring a slightly lower value for a high price of electricity (Figure 10, dotted line). For u_s of 0.5 m s⁻¹ and a low price of 0.06 € kWh⁻¹, 55% of the operational expenditures are capital related (49% reactor, 6% compressor) but already 45% are related to electricity costs (Figure S11, Supporting Information).

Side note: For a higher electricity price of, e.g., 0.16 € kWh⁻¹, the numbers are different. The total operating costs rise from 60 € ton⁻¹ C₂₊-HCs (only carbon counted) for 0.06 € kWh⁻¹ to 110 € ton⁻¹ (Figure 10), and 72% and not “only” 45% are then related to the electricity costs.

Returning again to the case of electricity costs of 0.06 € kWh⁻¹. For a higher gas velocity than 0.5 m s⁻¹, e.g., 1.1 m s⁻¹, the CO conversion drops and the recycle ratio increases (Table 4). This leads to much higher costs for the gas recycle of 112 € ton⁻¹ liquid fuel (as carbon) compared to only 33 € for 0.5 m s⁻¹ by a more expensive compressor and above all higher electricity costs (Figure S11, Supporting Information). On the other hand, the number of tubes decreases with rising gas velocity, about 8400 tubes for 1.1 m s⁻¹ compared to around 10 100 tubes for 0.5 m s⁻¹ (Figure S12, Supporting Information). Hence, the

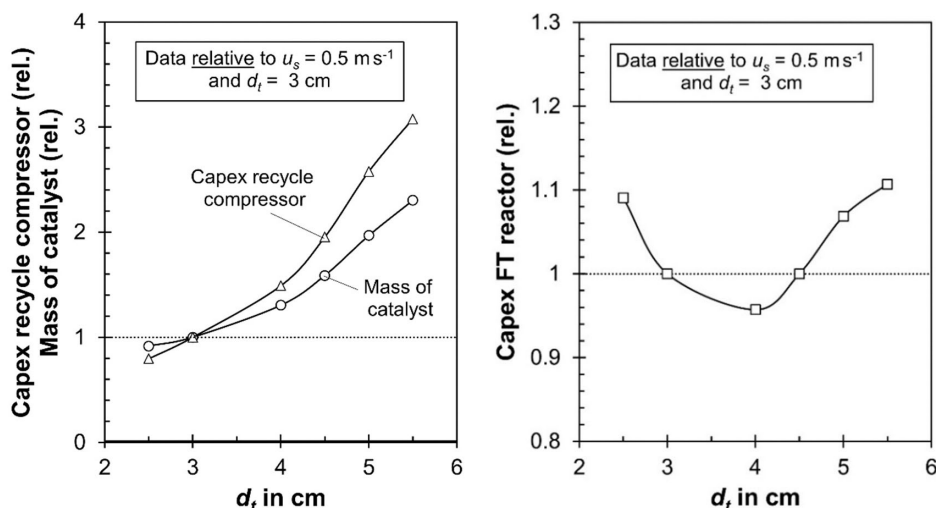


Figure 9. Left-right: Impact of tube size on mass of catalyst, capex of reactor, and recycle compressor for a gas velocity of 0.5 m s^{-1} (base case: $d_t = 3 \text{ cm}$; conditions in Figure 8).

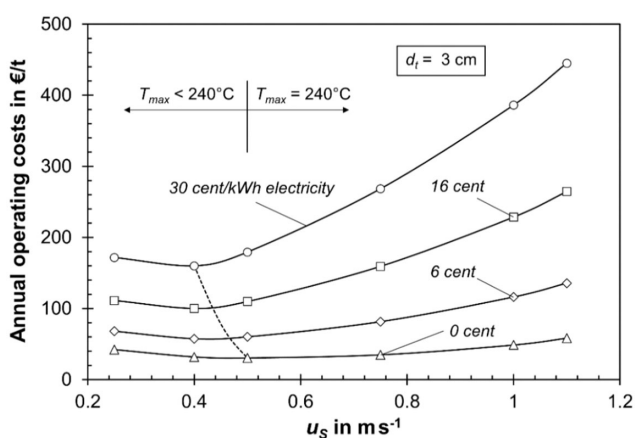


Figure 10. Annual operating costs of core unit of FT plant (reactor with gas recycle) for a constant tube diameter of 3 cm (100 000 tons of C as C_{2+} -HCs/a; 8000 h a^{-1} operation). Dotted line indicates optimum of operating costs (details in text and Figure S1 11, Supporting Information, for 0.06 € kWh^{-1}).

capex of the FT reactor (and thus the operating costs) are 11% lower ($= 1 - (8434/10\,090)^{0.68}$), but this positive effect is far from equalizing the much higher costs related to the gas recycle (Figure 4, 10). In total, the overall operating costs are more than doubled, 136 € ton^{-1} of liquid fuel (as carbon) for a gas velocity of 1.1 m s^{-1} compared to 60 € for 0.5 m s^{-1} .

For other tube sizes, the trends shown in Figure 10 are similar (Figure S13–S18, Supporting Information), but the level of the overall opex rises with d_t , e.g., to 83 € ton^{-1} C_{2+} -HCs for $d_t = 4 \text{ cm}$ (electricity price 0.06 € kWh^{-1}) for the then optimal u_s of 0.58 m s^{-1} compared to 60 €/t for $d_t = 3 \text{ cm}$ and $u_s = 0.5 \text{ m s}^{-1}$ (see also Figure S16 and S17, Supporting Information). Consequently, the lowest opex are reached for the smallest tube considered here with d_t of 2.5 mm. The costs are then 51

€/t C_{2+} -HCs (electricity still at 0.06 € kWh^{-1}), 15% lower compared to 3 cm (see Figure S13 and S14, Supporting Information). Nevertheless, a tube size of 3 cm is still the better choice, as the tube-to-particle size ratio for $d_t = 2.5 \text{ cm}$ of 8 is then less than 10, which is regarded as limit^[12] to avoid undesirable wall effects (bypass, slippage), and the reactor model used here is then probably also not anymore very reliable.

To take stock: For the “optimum” case of tube with 3 cm diameter and a gas velocity u_s of 0.5 m s^{-1} , the annual production costs are 6 million € for 0.06 € kWh^{-1} electricity and an annual production of 100 000 tons of carbon as C_{2+} -HCs, hence 60 € ton^{-1} . The costs rise strongly, if the electricity price is higher, 110 € ton^{-1} for 0.16 € kWh^{-1} and even 179 € for 0.3 € kWh^{-1} .

As already mentioned, these operating costs are only related to the FT reactor and recycle compressor, including electricity consumption. Total production costs of a PTL plant are obviously higher, as discussed in some more detail in SI 8. For example, a minimum viable selling price is 1000 € ton^{-1} of liquid fuel using a FT process based on steel mill gas.^[22]

For syngas based on renewable H_2 and CO_2 (separated from off-gases of the chemical industry, etc., and converted to CO by RWGS), much higher production costs are expected. According to Tremel et al., the costs for syncrude (year 2014) are 2000 € ton^{-1} with electricity costs of syncrude (year 2014) for electricity costs of 0.09 € kWh^{-1} .^[23] 64% of the costs are related only to H_2 production by electrolysis, 8% to CO_2 , and only 28% (560 €/t) to the whole FT plant, including items neglected here such as syngas compression, RWGS, and product upgrading.^[23] If we consider syncrude as diesel or jet-fuel (0.85 kg L^{-1}), the production costs are 1.7 € L^{-1} . Similar costs are given by Machhammer and Janisch for power-to-synthetic diesel production by FTS based on electricity from onshore wind power located in Germany and Chile.^[24] The estimated leveled costs of electricity and diesel oil are 0.06 € kWh^{-1} and 2.7 € L^{-1} for Germany and only 0.03 € kWh^{-1} and 1.6 € L^{-1} for Chile.

4.3. Influence of Single-Tube Length on Operating Costs of a FT Reactor with Gas Recycle

The influence of the tube length L_t was until now not considered, i.e., we have assumed a typical value for FT reactors of 12 m, and a detailed analysis of the impact of L_t would go far beyond the scope of this work. Thus, **Table 6** only shows some selected data

for L_t in a range of 12–30 m for $d_t = 3$ cm and $u_s = 0.5$ m s⁻¹; details such as the number of tubes and diameter of the FT reactor for other values of L_t are given in SI 9.

A strong increase of L_t is needed to reach a conversion per pass, which is substantially higher than 63% reached for the “standard” case of $L_t = 12$ m: for example, for 20 m, $X_{CO,per\ pass}$ rises to 78%; this length was already technically realized

Table 6. Influence of L_t on performance data and opex for an electricity price of 0.06 € or 0.12 € kWh⁻¹ (100 000 tons of C₂₊-HCs/a (as carbon); $d_t = 3$ cm; $u_{s,z=0} = 0.5$ m s⁻¹; 95% ultimate conversion of CO and H₂).

L_t [m]	$X_{CO,per\ pass}$ [%]	γ_{CH_4} at inlet [%]	R	Δp_t [bar]	Partial and total production costs in € ton ⁻¹ carbon as C ₂₊ -HCs for two different prices of electricity					
					FT reactor	Recycle comp.	Electricity		Total (rounded)	
							0.06 € kWh ⁻¹	0.12 € kWh ⁻¹	0.06 € kWh ⁻¹	0.12 € kWh ⁻¹
12	63.2	46.7	1.10	1.20	27.1	3.4	29.8	59.6	60	90
15	69.9	39.8	0.79	1.35	28.3	2.9	24.1	48.2	55	79
18	75.0	28.4	0.58	1.51	29.5	2.4	20.1	40.2	52	72
20	77.8	23.9	0.49	1.61	30.3	2.1	17.8	35.6	50	68
30.2	85.0	20.0	0.26	2.11	35.9	1.6	12.4	24.8	50	62

Table 7. Performance characteristics of modeled multitubular FT reactor (this work), two commercial FT reactors (Sasol;^[25,26] Shell^[25]), and reactor design of Bechtel.^[26,27]

Reactor characteristic	Shell ^[25]	Sasol ^[25,26]	Bechtel ^[26,27]	This work
Catalyst	Cobalt	Iron	Cobalt ^{a)}	Cobalt
Pressure (inlet reactor) [bar]	40	27, ^[25] 25.4 ^[26]	28.3	30
Reaction temperature [°C]	237 ^{b)}	236 200 ^{b)} (in), 225 (out)	200 (in) 225 (out)	$T_{max} = 240$, $T_{cool} = 213$ 213 (in), 226 (out)
Reactor diameter ^{c)} [m]	6.2	3	4.8	4.8
Length of tubes	20	12	13.6	12
Number of tubes	8000	2050	9602	10 090
Internal tube diameter [cm]	5 ^{d)}	4.6	3.4	3
Volume reactor (catalyst) [m ³]	600 (310)	85 (48)	246 (110)	216 (86)
Catalyst charge [tons]	310	38, ^[25] 31 ^[26]	94	82
Catalyst particle size [mm]	2	2.5, ^[25] 3.7 ^[26]	3.7	3
Molar H ₂ -CO ratio (inlet)	–	–	1.9	2.2
Content of H ₂ /CO (inlet)	–	–	75% ^{e)}	72% ^{e)}
Total CO conversion	–	–(63%)	96%	95%
CO conversion per pass	–	–(26%)	37%	63%
Reactor productivity ^{f)} [tons] C ₂₊ -HCs (carbon) per year	250 000	55 000, ^[25] 17 000 ^{[26] g)}	84 200	100 000
Volumetric productivity ^{f)} , tons C ₂₊ -HCs per a and m ³ cat.	806	1145, ^[25] 345 ^{[26] h)}	765	1163
Superficial gas velocity [m s ⁻¹]	0.18	0.36, ^[25] 0.34 ^[26]	0.44	0.5
Pressure drop, bar	–	4, ^{[25] h)} 1.03 ^{[26] h)}	1.25	1.20
Recycle ratio	–	1.9, ^[25] 2.3 ^[26]	2.34	1.10
Electricity need for gas recycle relative to this work	–	8.33, ^[25] 2.16 ^[26]	1.62	Set to 1

^{a)}Co catalyst is not specified,^[26,27] and CO selectivities to CO₂ and CH₄ of 8% and 3% are assumed “as a compromise between Co and Fe catalysts”; ^{b)}Temperature is not specified,^[25] but probably refers to maximum; ^{c)}Ratio of cross-sectional area of tubes to area of reactor is 0.54 (Shell), 0.57 (Sasol), and 0.61 (Bechtel); ^{d)}The tubes are smaller for Co compared to Fe,^[28] which is in contradiction to 5 cm;^[25] ^{e)}Besides H₂ and CO, syngas at reactor entrance (fresh feed + recycle gas) contains 28% CH₄ (this work) and 13% CH₄, 1% CO₂, 5% N₂, and 5% C₂/C₃-HCs in the Bechtel design with syngas from coal gasification;^[25] ^{f)}Productivity data (for 8000 h a⁻¹) only related to carbon; values in tons C₂₊-HC are by factor 1.17 (17%) higher; ^{g)}Productivity data given in ref.[25] are much higher compared to ref. [26]. Lower values are probably more reliable, as similar values are given in the literature (17 200 tons a⁻¹,^[28] 14 300 tons a⁻¹^[29]). ^{h)} Δp_t given in ref. [25] is high compared to ref. [26] and own estimation (SI 10); ≈ 1 bar is more realistic.

(see Shell's reactor in Table 7). But a length of 30 m, needed to reach $X_{\text{CO,per pass}}$ of 85% (Table 6), is unrealistic. As shown in SI 9, the border case of $X_{\text{CO,per pass}} = X_{\text{CO,total}} = 95\%$, where a gas recycle is not needed anymore, is only reached by an enormous length of 89 m (!), currently far beyond any technical realization.

The influence of L_t on the operating costs is less pronounced compared to tube size or gas velocity, at least as long as L_t is sufficient to reach a high per pass CO conversion, e.g., 63% for $L_t = 12$ m, and the price of electricity is not too high. For a low price of 0.06 € kWh^{-1} , only an increase of L_t from 12 m to not more than 20 m leads to a reduction of the total operating expenditures by 17% (reduction from 60 to 50 € ton^{-1} carbon as $\text{C}_{2+}\text{-HCs}$), which might be worth to be considered (Table 6, second to last column). For a doubling of the price to 0.12 € kWh^{-1} , the reduction of the opex is 25% for $L_t = 20$ m and 31% for $L_t = 30$ m (Table 6, last column).

Hence, 12 m is still an appropriate tube length of a multitubular FT reactor as long as the price of electricity is not too high ($<0.1 \text{ € kWh}^{-1}$), and 20 m is an option if the price is even higher.

5. Comparison of Performance of Modeled Reactor with Data of Commercial FT Reactors

Table 7 shows performance data of the FT reactor modeled ($d_t = 3 \text{ cm}$, $u_s = 0.5 \text{ m s}^{-1}$, $L_t = 12 \text{ m}$), of two commercial FT multitubular reactors from Sasol and Shell, and of the reactor design of the engineering company Bechtel. The reaction temperature and total pressure of all four multitubular reactors, one with an iron catalyst (Sasol) and three with cobalt, are similar, but the total production rates differ by a factor of about 10 in a range of 17 000–250 000 tons $\text{C}_{2+}\text{-HCs}$ (only counting carbon) per year, largely because of difference of reactor size (length, tube number, etc.) and thus of the demand of the catalyst by mass and volume (48–310 m^3). Hence, the annual productivity per volume of catalyst varies in a much smaller range of 345–1163 tons $\text{C}_{2+}\text{-HCs per m}^3$; the highest productivity is achieved by the reactor modeled in this work, but the numbers of Shell, Bechtel, and Sasol are not much less (Table 7).

The good agreement between the data of our modeled "optimal" reactor design and the reactor designed by Bechtel is remarkable (Table 7). All dimensions such as tube diameter and length, number of tubes, catalyst particle size, and reactor diameter are very similar. The same is true for the temperature, pressure, molar H_2 -to-CO ratio, gas velocity, total CO conversion, and pressure drop. The total annual reactor productivity of $\text{C}_{2+}\text{-HCs}$ is also only 16% lower in Bechtel's design as in this work, 86 000 tons as compared to 100 000 tons.

To prove, whether the value of the reactor productivity given Bechtel is consistent with our model and the design data of Table 7, we successfully re-evaluated Bechtel's reactor design by our reactor model (details in SI 10). The main difference is the conversion per pass, only 37% (Bechtel) compared to 63% (this work). The recycle ratio R is therefore higher, 2.3 compared to 1.1, and also the associated electricity demand of the gas recycle, which is according to Equation (9) and the data of Table 7 by 62% higher. The activity (Co content) of the catalyst presumed in Bechtel's design, unfortunately not specified,^[25,26] is obviously lower than that of the catalyst in this work with 30 wt% Co.

The estimation by our model indicates an intrinsic activity, which is by 60% lower ($C_a = 1.3$ for Bechtel and 3 this work), which reduces the effective rate ($\approx C_a^{0.5}$) by 34% (see Equation (6)). This explains casually the lower per pass conversion and the 34% lower volumetric productivity, 765 tons $\text{C}_{2+}\text{-HCs per year and m}^3$ catalyst compared to 1163 in this work, and indicates that our model reflects reality well.

6. Conclusions

A cooled multitubular FT fixed-bed reactor with gas recycle and purge gas stream was simulated based on a complex and reliable reactor model. The technical design data presented in combination with a techno-economic assessment indicate that a single-tube diameter of 3 cm and a superficial gas velocity (at reaction conditions) of about 0.5 m s^{-1} are optimal design parameters, even if the price of the electricity to run the recycle compressor varies in a large range of $0.06\text{--}0.30 \text{ € kWh}^{-1}$. For an annual production of 100 000 tons of $\text{C}_{2+}\text{-HCs}$ (only related to carbon), a reactor with about 10 000 single tubes is needed.

Depending on the price of electricity, an increase in the length of the tubes from 12 m (standard case) to about 20 m is also an option with regard to the opex of the FT reactor with gas recycle.

The comparison of the performance data of the FT reactor modeled in this work with data of commercial multitubular reactors run by Sasol and Shell or designed by Bechtel indicates that our reactor model reflects reality well and is thus reliable.

List of symbols and abbreviations

A_t	heat transfer area of tube (s) [m^2]
c_i	concentration of i ($i = \text{CO}, \text{H}_2, \text{H}_2\text{O} \dots$) [mol m^{-3}]
C_a	coefficient of catalytic activity (= 1 for 10 wt% Co) [–]
c_i	concentration of i (gas phase; $i = \text{CO}, \text{CH}_4, \text{H}_2$) [mol m^{-3}]
c_g	total concentration (molar density) of gas phase [mol m^{-3}]
c_p	heat capacity of gas [$\text{J mol}^{-1} \text{K}^{-1}$]
C_ϕ	factor in Equation (6), valid for $d_p = 3 \text{ mm}$ [$\text{kg}^{0.5} \text{s}^{0.5} \text{m}^{-1.5}$]
d_p	particle diameter [m]
d_{reactor}	diameter of FT reactor [m]
$d_b, d_{t,\text{int}}$	(internal) tube diameter [m]
$D_{\text{eff,CO,liq}}$	effective diffusion coefficient of CO in liquid-filled pore system [$\text{m}^2 \text{s}^{-1}$]
E_{recycle}	energy demand (electricity) per time (power) for gas recycle [J s^{-1}]
$E_{\text{recycle, rel}}$	relative energy demand (electricity) per time [–]
H_{CO}	Henry coefficient for CO in liquid HCs [J mol^{-1}]
L_t	length of tube (fixed bed) [m]
m_{cat}	mass of catalyst [kg]
M	molar mass [kg mol^{-1}]
n_t	total number of single tubes of multitubular FT reactor [–]
\dot{n}_i	molar flux of component i ($i = \text{CO}, \text{CH}_4, \text{H}_2, \text{total gas}$) [mol s^{-1}]
p	pressure [Pa]
r	radial distance from center of tube [m]

$r_{m,CO}$	total intrinsic reaction rate of CO, see Equation (3) [mol _{CO} kg _{cat} ⁻¹ s ⁻¹]
r_{m,CO,H_2O}	total intrinsic rate of CO, if inhibition by steam is considered [mol _{CO} kg _{cat} ⁻¹ s ⁻¹]
r_{m,CO,CH_4}	intrinsic reaction rate of CO to methane [mol _{CO} kg _{cat} ⁻¹ s ⁻¹]
r_{m,CO,C_2+}	intrinsic reaction rate of CO to C ₂₊ -hydrocarbons [mol _{CO} kg _{cat} ⁻¹ s ⁻¹]
r_{m,CO,H_2O}	intrinsic rate of CO, if steam inhibition is considered [mol _{CO} kg _{cat} ⁻¹ s ⁻¹]
r_t	internal radius of tube [m]
R_{gas}	gas constant (8.314), J mol ⁻¹ K ⁻¹ (in Equation (6) and (9)) [J mol ⁻¹ K ⁻¹]
R	recycle ratio (ratio of recycle gas to fresh syngas) [-]
s_{wall}	thickness of tube wall [m]
S_{CH_4}	selectivity of CO to CH ₄ (mol of CH ₄ per mol CO converted) [-]
T	temperature [°C, K]
U_{bed}	thermal transmittance of fixed bed (see Figure 6, right) [W m ⁻² K ⁻¹]
$u_{s,z=0}$	superficial gas velocity; initial value at 30 bar and 230 °C [m s ⁻¹]
$u_{s,z=12m}$	superficial gas velocity; final value at actual mean T and p_{total} [m s ⁻¹]
X_{CO}	conversion of CO [-]
y_i	molar content of i ($i = CO, CH_4, H_2$) [-]
z	axial coordinate in fixed bed [m]
Greek letters	
α_w	heat transfer coefficient [W m ⁻² K ⁻¹]
$\Delta_R H_i$	enthalpy of reaction, $l =$ reaction of CO to methane or C ₂₊ -HCs [J mol _{CO} ⁻¹]
$\Delta p_{ti}, \Delta p_{bed}$	pressure drop of fixed bed (tube) [Pa]
ϕ	Thiele modulus, Equation (6) [-]
η_{comp}	efficiency of recycle compressor (here 90%) [-]
η_{pore}	pore effectiveness factor, Equation (5) [-]
λ	thermal conductivity [W m ⁻¹ K ⁻¹]
$V_{i,Rn}$	stoichiometric coefficient of i in reaction n ($n = 1$ for methane formation and 2 for formation of C ₂₊ -HCs) [-]
ρ_{bed}	bulk density of fixed bed [kg m ⁻³]
Subscripts	
C	carbon
cool	cooling
eff	effective (rate)
ex	external
g	gas mixture
ig	ignition (temperature)
in	inlet of reactor/tubes
int	internal
max	maximum (temperature)
w,int	related to the internal side of the tube wall
rad	radial
R1	related to reaction of CO to methane
R2	related to reaction of CO to C ₂₊ -HCs
single	single tube
t	tube

Abbreviations

C ₂₊	hydrocarbons with two and more carbon atoms (all HCs without CH ₄)
C ₂₊	hydrocarbons with two and more carbon atoms (all HCs without CH ₄)
capex	capital expenditures
(-CH ₂ -)	methylene group of a normal paraffin (in Equation (1))
FT(S)	Fischer–Tropsch (synthesis)
HCS	hydrocarbons
in	reactor inlet
opex	operational expenditures
PTL	power-to-liquid
RWGS	reverse water–gas shift (CO ₂ + H ₂ → CO + H ₂ O)
SG	synthesis gas
SI	supporting information

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors gratefully acknowledge the support of the Open Access Publishing Fund of the University of Bayreuth.

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cobalt catalysts, Fischer–Tropsch, multitubular reactors, technoeconomic analysis

Received: November 29, 2023

Revised: February 19, 2024

Published online: March 12, 2024

- [1] C. Kern, A. Jess, *Catal. Sci. Technol.* **2023**, *13*, 516.
- [2] C. Kern, A. Jess, *Catal. Sci. Technol.* **2023**, *13*, 2212.
- [3] C. Kern, A. Jess, *Processes* **2023**, *11*, 3281.
- [4] F. Pöhlmann, A. Jess, *Energy Technol.* **2016**, *4*, 55.
- [5] F. Pöhlmann, A. Jess, *Catal. Today* **2016**, *275*, 172.
- [6] F. Pöhlmann, S. Rössler, C. Kern, A. Jess, *Catal. Sci. Technol.* **2016**, *6*, 6593.
- [7] S. Rößler, C. Kern, A. Jess, *Chem. Ing. Technol.* **2018**, *90*, 634.
- [8] F. Pöhlmann, PhD thesis, University Bayreuth, Germany **2017**.

- [9] F. Sauerhöfer-Rodrigo, I. Diaz, M. Rodrigez, P. Perez, *Rev. Chem. Eng.* **2024**, *40*, 151.
- [10] J. R. G. Sanchez-Lopez, A. Martinez-Hernandez, A. Hernandez-Ramitez, *Rev. Chem. Eng.* **2017**, *33*, 109.
- [11] C. I. Mendez, J. Ancheyta, F. Trejo, *Energy Fuels* **2017**, *31*, 13011.
- [12] A. Jess, P. Wasserscheid, in *Chemical Technology: From Principles to Processes*, Wiley, Weinheim **2020**.
- [13] Verein Deutscher Ingenieure (ed.), in *VDI-Wärmeatlas: Berechnungsblätter Für Den Wärmeübergang*, Springer, Berlin, Germany **2002**.
- [14] E.-U. Schlünder, E. Tsotsas, in *Wärmeübertragung In Festbetten, Durchmischten Schüttgütern Und Wirbelschichten*, Georg Thieme, Stuttgart, Germany **1988**.
- [15] M. Nilles, PhD Thesis, University Karlsruhe, Germany, **1991**.
- [16] E.-U. Schlünder, in *Einführung In Die Wärmeübertragung*, Vieweg, Braunschweig, Wiesbaden, Germany **1986**.
- [17] K. Stephan, *Chem. Ing. Technol.* **1963**, *35*, 775.
- [18] K. Stephan, in *Wärmeübergang Beim Kondensieren Und Beim Sieden*, Springer, Berlin **1988**.
- [19] W. Fritz, *Chem. Ing. Technol.* **1963**, *35*, 811.
- [20] S. Ergun, *Chem. Eng. Prog.* **1952**, *48*, 89.
- [21] <https://de.statista.com/statistik/daten/studie/252029/umfrage/industriestrompreise-inkl-stromsteuer-in-deutschland/> (accessed: June 2023).
- [22] J. Collis, K. Duch, R. Schomäcker, *Front. Energy Res.* **2022**, *10*, 1049229.
- [23] A. Tremel, P. Wasserscheid, M. Baldauf, T. Hammer, *Int. J. Hydrog. Energy* **2015**, *40*, 11457.
- [24] O. Machhammer, I. Janisch, *Chem. Eng. Technol.* **2023**, *46*, 1935.
- [25] C. H. Bartholomew, R. J. Farrauto, in *Fundamentals of Industrial Catalytic Processes*, Wiley & Sons, Hoboken, USA **2006**.
- [26] J. M. Fox, B. D. Degen, G. Cady, F. D. Deslate, R. L. Summers, Slurry reactor design studies. Slurry vs. fixed-bed reactors for Fischer-Tropsch and methanol: Final report of Bechtel Group for US Department of Energy (DE91005752), Pittsburg, USA, **1990**, www.fischer-tropsch.org/DOE/DOE_reports/91005752/de91005752_sec2.pdf (accessed: June 2023).
- [27] J. M. Fox, *Catal. Lett.* **1990**, *7*, 281.
- [28] A. P. Steynberg, M. E. Dry, B. H. Davies, B. B. Breman, in *Fischer-Tropsch Technology, Studies in Surface Science and Catalysis* (Eds: A. P. Steynberg, M. Dry), vol. 152, Elsevier, Amsterdam **2004**.
- [29] J. Falbe, in *Chemierohstoffe Aus Kohle*, Georg Thieme, Stuttgart, Germany **1977**.